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# Lower Duwamish Waterway Source Control Brandon Combined Sewer Basin Study Sampling and Analysis Plan

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August 2011



**King County**

Department of Natural Resources and Parks  
Water and Land Resources Division

**Science and Technical Support Section**

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# **Lower Duwamish Waterway Source Control Brandon Combined Sewer Basin Study**

## **Sampling and Analysis Plan**

### **Prepared for:**

King County Department of Natural Resources and Parks  
Wastewater Treatment Division

### **Prepared by:**

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Water and Land Resources Division



**King County**

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

## Citation

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# ACRONYMS

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AXYS	AXYS Analytical Services Ltd.
COC	chain of custody
CSO	combined sewer overflow
CVAA	cold vapor atomic absorbance
DOC	dissolved organic carbon
DQOs	data quality objectives
Ecology	Washington Department of Ecology (Washington State)
EIM	environmental information management
EPA	Environmental Protection Agency (United States)
FSU	Field Science Unit (King County)
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectroscopy
KCEL	King County Environmental Laboratory
LCS	lab control samples
LDW	Lower Duwamish Waterway
LCS	laboratory control sample
LIMS	Laboratory Information Management System
LMCLs	lowest method calibration limits
LVI	large volume injection
MDL	method detection limit
ML	minimum level
OPR	ongoing precision and recovery
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyls
RDL	reporting detection limit
PQL	practical quantitation limit
QA/QC	quality assurance/quality control
SAP	sampling and analysis plan
SIM	selected ion monitoring
SVOC	semi-volatile organic compounds
TSS	total suspended solids
WTD	Wastewater Treatment Division (King County)



## 1.0. INTRODUCTION

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This sampling and analysis plan (SAP) documents project information and sampling and analytical methodologies for the Lower Duwamish Waterway (LDW) combined sewer overflow (CSO) Brandon Basin Study. The SAP outlines the collection and analytical methods for samples to better understand the relative loadings of select chemicals during storm and baseflow conditions within the Brandon combined sewer basin, which discharges to the Duwamish River. Combined sewer basins include inputs from domestic wastewater, industrial wastewater, groundwater infiltration into combined sewer lines (infiltration), and stormwater runoff (inflow). Stormwater runoff is collected from streets, parking lots, roof drains, and other impervious surfaces. The chemical loading differences will be used to better understand the general sources of chemicals within the combined system (i.e., stormwater versus wastewater).

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), splitting at the southern end of Harbor Island to form the East and West Waterways, prior to discharging into Elliott Bay in Puget Sound, Seattle, Washington. The LDW Superfund site is about 5 miles long encompassing 441 acres and consists of the downstream portion of the Duwamish River, excluding the East and West Waterways. Over 200 outfalls, including public and private storm drains and CSOs drain into the LDW (Windward 2010). Of these, King County Wastewater Treatment Division (WTD) has eight CSOs and two emergency overflows discharging into the LDW.

The LDW Remedial Investigation (Windward 2010) identified four human health risk drivers: polychlorinated biphenyls (PCBs), arsenic, carcinogenic polycyclic aromatic hydrocarbons, and dioxins/furans. Further, 41 of the 47 chemicals (including total PCBs and arsenic), for which Washington State Sediment Management Standards (SMS) criteria are available, are risk drivers for benthic invertebrates. PCBs were also identified as a risk driver for river otters, one of the wildlife receptors evaluated in the Ecological Risk Assessment.

King County is a member of the Source Control Work Group for the LDW Superfund site. Other members include Washington Department of Ecology (Ecology) (lead agency), U.S. Environmental Protection Agency (EPA), City of Seattle, and the Port of Seattle. The Source Control Work Group works to understand potential sources of chemicals to the LDW Superfund site and works to control and reduce sources that can contaminate sediments in the waterway. As such, King County WTD wants to better understand the potential sources of LDW chemicals of concern that flow into CSO basins in the LDW.

### 1.1 Scope of Work

King County recently completed sampling of CSO whole water at various CSOs in the Duwamish River Basin (King County 2009). These data give an indication of CSO outfall water quality under CSO or near-CSO conditions; however, information is lacking on apportionment between the contributions from wastewater (domestic and industrial), groundwater, and stormwater runoff to combined sewers within CSO basins. This study will involve collecting flow-proportioned samples of wastewater from the Brandon CSO basin. The Brandon CSO basin is being targeted for this study because it has more frequent CSO discharges when compared to other CSOs within the LDW basin (King County 2010) and the basin is mainly composed of

highly industrial areas which have potential to have contaminated soils that could contribute contaminants by infiltration and inflow into the combined system. The LDW Remedial Investigation indicated exceedances of the SMS for mercury in sediment in the vicinity of the Brandon CSO outfall and exceedances for PCBs in the navigation channel just north and south of the Brandon CSO outfall.

Autosamplers and flow monitoring equipment will be used to collect flow-weighted composite samples from the Brandon combined sewer basin during both baseflow and stormflow during the course of one dry season and one wet season to gain information during storm and both dry and wet weather baseflow conditions.

## 1.2 Schedule

Field reconnaissance was conducted in March and April 2011 to evaluate feasible sampling locations within the Brandon CSO collection system. Flow monitoring will begin in June 2011 and water quality sampling will begin in July 2011. Both flow and water quality sampling will continue through early 2012. Analysis of samples is expected to continue through mid 2012. It is anticipated that data from all sampling events will be validated, reviewed, and ready for release by the last quarter of 2012. Based on the data collected during this study, additional, or Phase 2 sampling will be conducted to fill any identified data gaps and could include additional sampling at existing or new locations within the Brandon Basin, or new location in an additional basin such as the Michigan CSO basin.

## 1.3 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.	
Dean Wilson, Basin Study Project Manager.....	206-296-8252
Responsible for basin study project execution and adherence to SAP and schedule.	
Debra Williston, Water and Land Resources Division Technical Lead .....	206-263-6540
Technical Support for all Lower Duwamish River studies including basin 1 study project.	
Bruce Tiffany, Industrial Waste Project Lead.....	206-263-3011
Provides technical advice on all aspects of the project; King County representative on the LDW Source Control Work Group.	
Marc Patten, Field Science Unit Field Lead .....	206-684-2345
Responsible for sample collection.	

Fritz Grothkopp, KC Environmental Lab Project Manager.....206-684-2327  
Manages sample analysis, sample shipment, and data delivery.

Scott Mickelson, Data Validation Lead .....206-296-8247  
Responsible for all data validation.

## 2.0. STUDY DESIGN

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The objective of this study is to collect whole water data and flow measurements to better understand the chemical loadings to the Brandon combined sewer system that can be attributed to wastewater (domestic and industrial) and the loadings that can be attributed to groundwater and infiltration and stormwater inflow. Understanding the relative contributions of wastewater, infiltration, and stormwater will allow source control efforts to be focused on reducing the greatest potential sources that can discharge to the LDW and potentially recontaminate sediments following cleanup actions.

### 2.1 Data Quality Objectives

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

#### 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 laboratory quality assurance/quality control (QA/QC) samples: method blanks, spiked blanks, matrix spikes, matrix spike duplicates, certified reference materials, laboratory control samples, and laboratory duplicates or triplicates.

Field replicates will not be collected due to the logistical constraints of placing flow monitoring and auto-sampling equipment into access ports that are located in street right-of-ways. Additionally, the study design includes collecting study samples in a way that will attempt to characterize variability, including sampling variability. Precision and bias will also be measured using in-lab sample duplicates and triplicates and/or matrix spike duplicates.

Equipment blanks were previously collected during the Duwamish River Basin CSO Survey (King County 2009). The type of equipment, sampling installations, and decontamination procedures will be the same for the Brandon Basin Study as for the Duwamish River CSO Survey. Equipment blanks from the Duwamish River CSO Survey showed PCBs were detected in all field blanks. Higher concentrations of PCBs were found in the field blanks collected from Hanford #2 and Lander II regulator station when compared with other field blank results (see Table 1) Tubing used to collect samples at these two locations had to be decontaminated in place whereas tubing at all other locations could be decontaminated at the laboratory. However, even with differences in field blanks for PCBs, no bias is expected for PCB CSO samples because PCBs concentrations in CSO samples were always greater than five times the concentration found in field blanks.

**Table 1. Field blank results of detected analytes for the Duwamish River Basin CSO Survey.**

Analyte	Sample Location					
	Duwamish Siphon	Michigan Regulator	Duwamish Siphon	Hanford #2 CSO	Lander II Regulator	Kingdome Regulator
<b>Metals (µg/L)</b>						
Cadmium, Total	ND	ND	0.39 J	ND	ND	ND
Chromium, Total	ND	ND	0.48 J	ND	ND	ND
Copper, Total	ND	ND	0.4 J	ND	ND	ND
Manganese, Total	ND	ND	1.26	ND	0.22 J	0.19 J
Zinc, Total	2.2 J	0.63 J	1.7 J	ND	ND	0.74 J
<b>SVOCs (µg/L)</b>						
Benzyl Butyl Phthalate	ND	ND	0.103	ND	ND	ND
Bis(2-Ethylhexyl)Phthalate	ND*	0.0502	ND*	ND*	7.91	ND*
Diethyl Phthalate	0.193	0.147	0.186	0.371	0.135	ND*
Dimethyl Phthalate	ND	ND	ND	ND	0.108	ND
Di-N-Butyl Phthalate	ND	0.0962	ND*	ND*	ND*	ND*
Naphthalene	ND	ND	ND	ND*	0.0269	ND
<b>PCBs (ng/L)</b>						
Total PCBs	0.012	0.151	0.199	0.664	1.13	0.059

ND = not detected

J = Estimated value – detected value is between the method detection limit and quantitation limit.

\* = Detected in both field blank and method blank; qualified as not detected based on validation findings.

With the exception of cadmium, no bias was expected in the CSO samples based on field blank metals results. The metal concentrations detected in the CSO samples were greater than five times those detected in the field blanks. Cadmium was detected in the Duwamish siphon CSO samples at concentrations less than five times the concentration detected in the field blank collected at this location. There was possible high bias to these sample results based on field blank results.

There was a possible high bias in the Duwamish siphon CSO samples for benzyl butyl phthalate and diethyl phthalate results, which were typically detected in CSO samples at concentrations less than five or ten times the concentrations detected in the field blanks. For CSO samples collected at the Michigan St. Regulator there was a possible high bias for the three phthalates detected in the field blank because concentrations were often within five times that found in the field blank. This same potential high bias exists for diethyl phthalate in Hanford #2 CSO samples. Finally, for CSO samples collected at Lander II Regulator Station, there was possible high bias for phthalate compounds detected as well as for naphthalene in all but one sample, which had concentrations greater than five times the field blank.

Based on these results, one field blank at each location will be collected for the Brandon CSO basin study to determine how sample collection procedures affect sample results.

### 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. Flow-weighted, composite water samples will be collected from locations within the Brandon combined basin to represent dry and wet season baseflow and storm conditions. Flow-weighted composites should better represent the average concentrations in the waste stream. Samples are to be collected in such a manner as to minimize potential contamination and other types of degradation in the chemical and physical composition of the water. 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 according to project sampling criteria, along with adherence to standardized sampling and testing protocols outlined in this SAP, will aid in providing a complete set of data for this project. The goal for completeness is 90%. The samples from each event should produce greater than 90% acceptable data under the QC conditions described elsewhere in this SAP.

### 2.1.4 Comparability

Comparability is addressed through use of standard techniques to collect and analyze representative samples, along with standardized data verification and reporting procedures described below in this SAP. Changes or updates to analytical methods and sampling techniques midway into the project must be tested, validated, and shown to be equivalent to existing methods. This validation must be approved by the project manager and laboratory QA Officer before being implemented.

### 2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The analytical method detection limits presented in this plan are sensitive enough to detect PCB congeners and other analytes at concentrations of interest to understand contaminant loadings in the combined sewer basin.

## 2.2 Sampling Strategy

The Brandon combined sewer basin was chosen for this study because it is a relatively small CSO basin with smaller number of municipal and industrial discharges to the system and is in a highly industrialized area with the potential for contaminated soils. In addition, the Brandon CSO has a higher frequency of CSO discharges representing the largest CSO volume discharged to the LDW when compared with other CSOs in the basin, thus making source control investigations an important priority for this basin. It is also targeted for CSO treatment as a control measure. This study will collect data to help narrow the focus of source control efforts by determining loadings during storm flow and dry and wet season baseflow conditions.

Depending on the results, these data may also be used to better understand loadings to the combined system from commercial and industrial land uses and be used to guide future investigations into contributions from stormwater and infiltration into the sewer system.

This study is designed to help answer the following questions about conditions within the combined system:

- What are the chemical loadings to the CSO basin during storm flow conditions (which represents the sewage and stormwater inflow components and low infiltration due to the hydrostatic pressure gradient)?
- What are the chemical loadings to the CSO basin during wet season baseflow conditions (which represents sewage and infiltration components)?
- What are the chemical loadings to the CSO basin during dry season baseflow conditions (which represents sewage components)?
- What are the chemical loadings to the CSO basin from stormwater inflow (which represents the storm flow condition minus the sewage [dry season baseflow] component)?
- What are the chemical loadings to the CSO basin from infiltration (which represents the wet season baseflow condition minus the sewage [wet season baseflow] component)?

To answer these questions, an autosampler and flow measuring equipment will be used to collect flow-weighted composite samples from the Brandon combined sewer basin during dry and wet season baseflow and stormflow conditions. All flow in the Brandon combined system is routed through the Brandon regulator and into the Elliott Bay Interceptor, which then flows to the West Point treatment plant. Under storm conditions, the regulator can divert flows to the CSO into the Duwamish River. The first sampling site is located at the Brandon regulator and will allow the collection of samples that represent flow from the entire basin. Comparing results from storm and baseflow conditions from samples collected at this site will help our understanding of the differences in loadings from wastewater, stormwater inflow, and infiltration in the combined system. This in turn will help to focus source control efforts in the basin and the broader combined system.

Additional sampling locations upstream of the Brandon regulator will allow a better understanding of where loadings originate spatially within the basin and if there are spatial differences to the component contributions. Autosamplers and flow measuring equipment will be installed in two additional locations upstream in the basin to isolate smaller areas on a sub-basin scale.

All three locations will be sampled during each sampling event. There will not be sufficient space in the location where autosamplers are installed to install a replicate autosampler to collect field replicate samples and therefore none will be collected.

Sampling conducted by King County Industrial Waste in 2009 showed that sampling variability in combined systems was much greater during storm events as compared to baseflow events. Therefore, this study design will incorporate this information and collect more samples during storm events and fewer during dry and wet season baseflow events. Baseflow is defined as the time when flow in the CSO system returns to pre-storm conditions, approximately 48 hours after any significant rainfall event that generates runoff. For this project the wet season is November

through March and the dry season is July through September. Pre-storm condition baseflow will be characterized by analyzing flow data collected prior to the beginning of sampling as described in Section 3, Sampling Procedures.

To characterize stormflow conditions within the combined sewer system, 15 sampling events will be conducted and a total of 45 samples will be collected from 3 locations during storms between November 2011 and March 2012 (see Table 2). To characterize dry season baseflow conditions, 6 sampling events will be conducted and 18 samples collected from 3 locations between July and September 2011 during dry conditions. To characterize wet season baseflow conditions, 6 sampling events and 18 samples will be collected from 3 locations between November and March 2011 during wet season baseflow conditions.

Each sample will be analyzed for conventional parameters, selected metals, polycyclic aromatic hydrocarbon (PAHs), and phthalates. PCB congener and dioxin/furan congener samples will be collected on a subset of the samples listed above to meet project budget goals in both 2011 and 2012. During baseflow in the dry season, PCB and dioxin/furan samples will be targeted for collection during 3 sampling events at each location for a total of 9 samples. During storms in the wet season, PCB and dioxin/furan samples will be targeted for collection during 5 storm events at each location for a total of 15 samples. During baseflow in the wet season, PCB and dioxin/furan samples will be collected during 3 events at each location for a total of 9 samples (Table 2).

A total of 15 PCB and dioxin/furan samples are targeted for analysis in 2011. If additional PCB/dioxin/furan samples can be collected in 2011 that meet study criteria (storm, wet baseflow, dry baseflow), then the samples will be stored so that analysis can be conducted in early fiscal 2012.

**Table 2. Number of Sampling Events and Samples**

Event Conditions	Sample Events		Number of Total Samples	
	Conventionals, Metals, SVOCs	PCBs and Dioxin/furans	Conventionals, Metals, SVOCs	PCB and Dioxin/furans
Dry Season Baseflow	6	3	18	9
Wet Season Baseflow	6	3	18	9
Storm	15	5	45	15
<b>Totals</b>	<b>27</b>	<b>11</b>	<b>81</b>	<b>33</b>

Note: Semi-volatile organic compounds (SVOCs) to be analyzed are polycyclic aromatic hydrocarbons and phthalates.

### 2.2.1 Study Area

Water samples will be collected from the Brandon combined sewer drainage basin (Figure 1). The Brandon drainage basin is bounded on the West by East Marginal Way, on the North by S. Dawson St., on the South by S. Fidalgo St., and on the East by 6<sup>th</sup> Ave. S. This combined system drains an industrial/commercial area approximately four and a half acres.

### 2.2.2 Sampling Station Locations and Sample Identification

Sample locations will be identified using a unique locator name. The locator name, the date of collection and the unique sample identification number generated by King County Environmental Laboratory (KCEL) will identify individual samples collected at each location. Locator names of the three sampling locations are BranReg (site nearest the Brandon Regulator), A01007 (on the sidewalk of East Marginal Way near the intersection of Brandon St.), and BrandUtah (near the intersection of Brandon St. and Utah St.) (see Figure 2). The corresponding locator numbers and sample coordinates are shown in Table 3. The locator BrandReg is near the regulator building and out of traffic lanes. Access should be possible during normal business hours. Location A01007 is located on E. Marginal Way S. (Highway 99) near the intersection with Brandon St. S. This access port is within the E. Marginal Way right-of-way, but it is on the East side of the road near the edge. Access to this site during normal business hours should be possible. Location BrandUtah is on Brandon St. near the intersection with Utah Ave. S. Traffic on both Brandon and Utah are minimal, so access to these locations should be possible. All three sites will be sampled during each sampling event, giving three discrete results which could aid in source tracking within the basin during data interpretation.

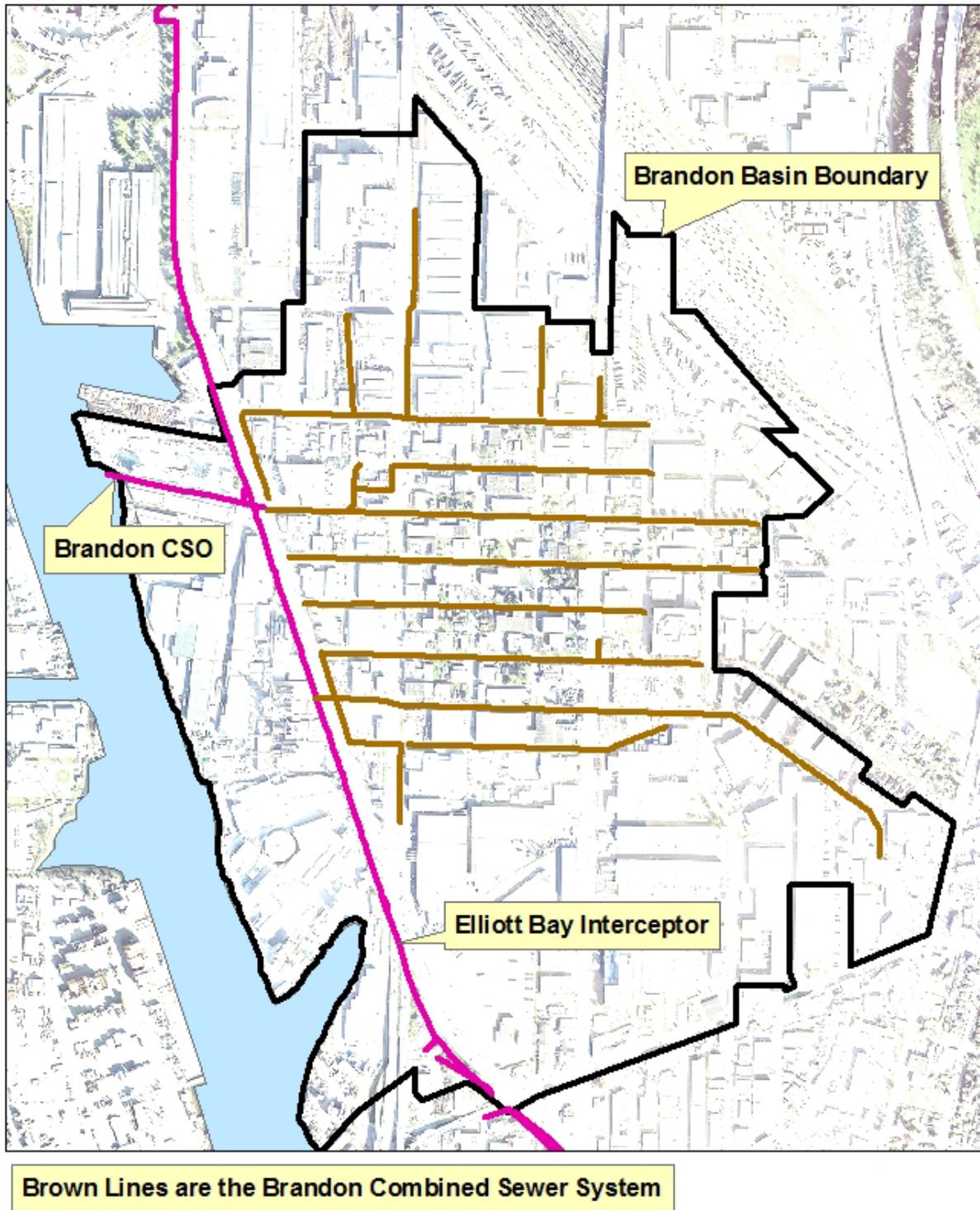
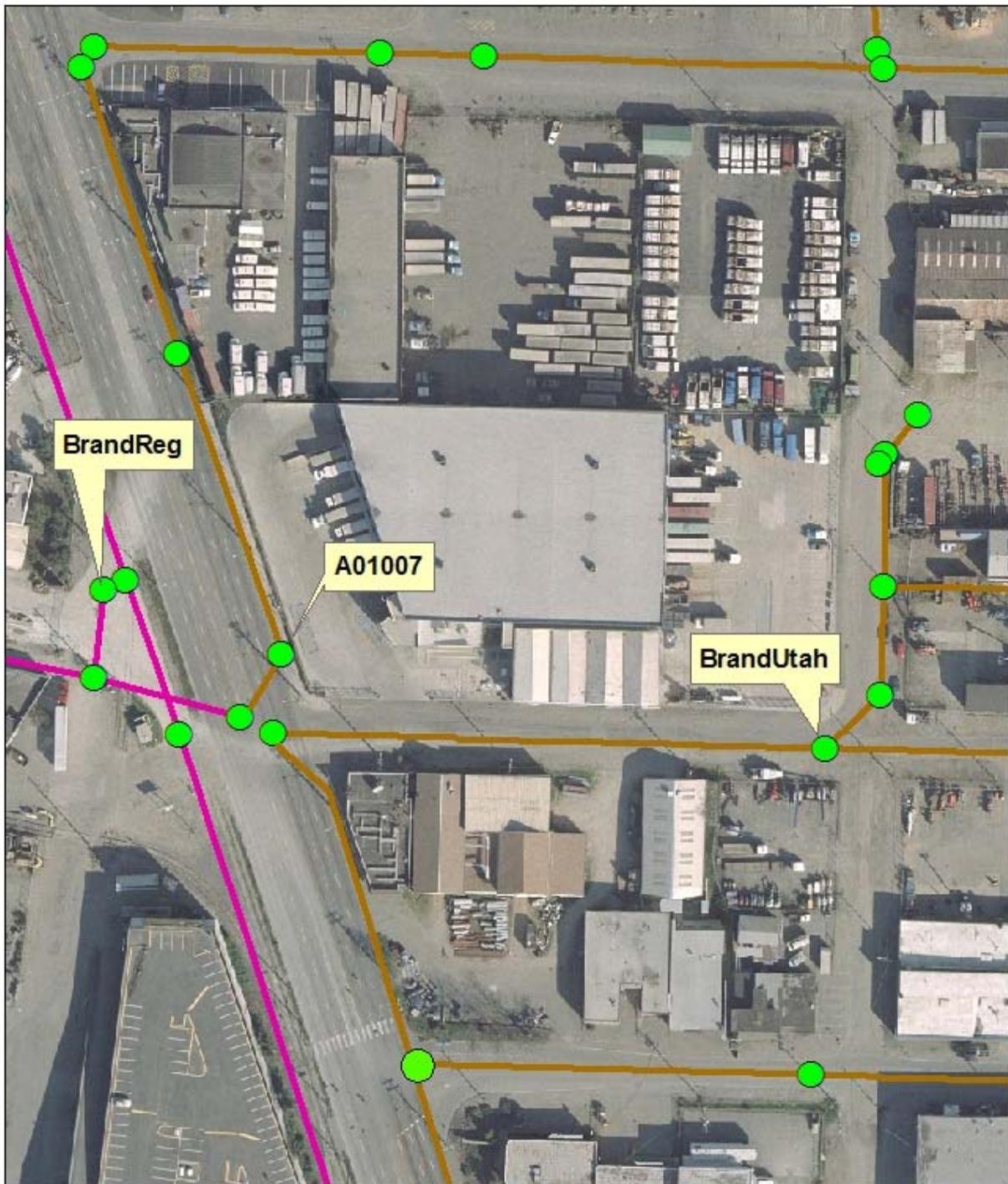


Figure 1. Brandon Combined Sewer Basin Area



Green Dots are Manholes

Figure 2. Sampling Locations

**Table 3. Brandon Basin Sampling Locations and Locator Names**

<b>Locator</b>	<b>Manhole Number</b>	<b>Locator Description</b>	<b>Northing<sup>a</sup></b>	<b>Easting<sup>a</sup></b>
BrandReg	063-050	Access Port at Brandon Regulator	205897	1268924
A01007	063-059	Access Port on E. Marginal Way S. near Brandon St. S.	205843	1269072
BrandUtah	063-073	Brandon St. S. near the intersection with Utah Ave. S.	205766	1269520

<sup>a</sup> State plane coordinates in North American Datum 1983 (NAD983) Washington State Plane North (4601)

### 2.2.3 Parameters

Each sample will be analyzed for conventional parameters, selected metals, PAHs and phthalates. A subset of samples (described above) will be analyzed for 209 PCB congeners and 17 dioxin/furan congeners. Conventional parameters to be analyzed include; dissolved organic carbon (DOC), total organic carbon (TOC), and total suspended solids (TSS). The specific metals, PAHs, and phthalates are listed in Section 4. The parameters being analyzed are generally based on contaminants of concern identified in the LDW Remedial Investigation (Windward 2010). PCB and dioxin/furan congener analysis will be conducted by AXYS Analytical Services, Ltd. in Sidney, British Columbia. All other chemical analyses and conventional analyses will be conducted by the KCEL Laboratory.

## 3.0. SAMPLING PROCEDURES

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This section describes field procedures that will be used to collect the samples. Procedures are described for collecting samples including equipment used, decontaminating sampling equipment, and recording field measurements and conditions. Requirements for sample containers and preservation, and sample custody procedures are also described. Samples will be collected by KCEL/FSU staff.

### 3.1 Auto Sampling Equipment

Composite water samples will be collected using ISCO autosamplers equipped with 10-liter glass (or suitable fluorinated plastic) sample carboys. Auto samplers will be installed inside access ports below street level using appropriate mounting hardware. Auto samplers will be fitted with new and pre-cleaned silicon tubing in the peristaltic pump for each sampling event. Teflon tubing and stainless steel fittings shall be used for all other tubing.

A flow meter will be installed and continuous flow data will be recorded for loading calculations and to trigger autosampler collection of sample aliquots. The flow meter proposed for use will be an ADS FlowShark, or similar, which is a device that WTD commonly uses for flow monitoring. The flow meter will allow the collection of a flow-weighted composite sample. After a pre-determined volume of water passes by the flow meter, a pulse trigger is sent to the autosampler to collect a predetermined aliquot ranging in volume from 100mL to 500mL, based on anticipated flow conditions in the particular combined sewer pipeline.

Autosamplers will be set up to collect flow-weight samples for 24 hour periods. The goal will be to establish the autosampler setpoints to collect a total of 10 liters per sampling event. If 10 liters are collected during a sampling event, 4 liters will be used for the PCB congener and dioxin/furan analyses. However, given the uncertainty and high peaking factors associated with the stormwater component of the combined sewers being sampled, a range of sample volumes is likely to be encountered. Per sampling event, a minimum of 4.5 liters will be collected for TOC, DOC, TSS, SVOC, metals, and mercury analyses. Any additional volume, with a minimum of 1 liter, will be used to create aqueous composite samples for PCB congener and dioxin/furan analyses. Based on sampling conditions, it also may be necessary to create an aqueous composite sample from two to four different sampling events. Compositing will be done in proportion to recorded flow and sample volumes will be measured to the nearest 10mL mark on a 1-L graduated cylinder.

Baseline flow information from the Brandon basin will be necessary to determine flow-weight aliquot collection pacing and to determine when the system is flowing at non-storm baseline. Sample pacing for base flow should be possible without much baseline flow data. However, sample pacing for storm flow will be more complicated as basin flow can react unpredictably to complex storm systems. It is proposed that flow meters be installed and flow data collected starting in June 2011 or as soon as possible to record as many storms as possible prior to collecting storm samples. This information will be used to understand dry season baseflow level, and system response to wet season infiltration and rain events.

## 3.2 Sample Collection

As soon as possible after an event ends, sampling staff will retrieve the carboys. Once at site, staff will review flow data to confirm that sample aliquots were collected over the twenty-four hour target sampling period. The composite sample will be stored on ice and transported back to KCEL where the sample will be split out into individual laboratory containers. This will be done by continuously agitating the sample in the carboy while transferring sample aliquots to the appropriate laboratory containers using a Teflon siphon tube. Each sample container will be filled to the appropriate level from the autosampler carboy. This procedure will ensure a representative sample from the carboy in each laboratory sample container. Once the sample has been split, the dissolved metals sample will be filtered. Dissolved metals samples will be drawn through a cleaned Nalgene 500mL filtration apparatus with 0.45 micron filters using a peristaltic pump.

Because the composite sample cannot be split out and filtered for dissolved metals within 15 minutes, appropriate hold-time violation flags will be added to the data.

## 3.3 Sampling Equipment

Entry into confined spaces for equipment installation or sample retrieval will be done by King County personnel who have the training and experience to safely enter these spaces. King County confined space entry requirements and safety protocols will be followed at all times. Field staff are confined-space entry certified through the WTD Permit-Required Confined Space Entry Program. All guidelines and requirements for confined space entry can be found in the WTD Permit-Required Confined Space Entry Program Manual (King County 1998). If traffic control is necessary for sample collection, FSU flagger-certified staff will be part of the sampling team. Additional field equipment is listed below.

- 1) Sampling supplies:
  - a) Ziploc® bags
  - b) Cooler with ice
  - c) Nitrile gloves
- 2) Safety equipment:
  - a) Hard hat
  - b) Safety vest
  - c) Safety shoes and glasses
  - d) Appropriate traffic control equipment and personnel where applicable (FSU supervisor will approve safety plan)
  - e) Documentation supplies:
    - f) Field notebook
    - g) Sample labels
    - h) Chain-of-custody forms
    - i) 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
- Weather conditions
- Number and type of samples collected
- Field measurements
- Log of photographs taken, if any taken
- 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)

### 3.4 Sample Delivery and Storage

All samples will be kept on ice until delivery to the KCEL, on the same day that they were collected. Because auto samplers will be setup to automatically initiate sampling, samples cannot be refrigerated during the compositing process. Additional sample preservation, if required, will be performed upon receipt of the samples at the KCEL. Samples will be split from the carboy into the appropriate analytical containers and preserved according to laboratory method specifications.

Containers for PCB congener and dioxin/furan congener analysis will be delivered to AXYS Analytical within 1 to 3 months of sample collection. Samples will be held at KCEL at the appropriate temperature until delivery date. Samples will be maintained on ice and/or ice packs during the delivery process. Samples will either be driven to AXYS Analytical or shipped via overnight express delivery service. Table 4 shows sample handling and storage requirements.

**Table 4. Sample Container, Preservation, Storage, and Hold Time Requirements**

Analyte	Container	Preservation	Storage	Hold Time
PCB Congeners/ Dioxin/furan congeners	3 x 1L amber glass	None	refrigerate at 4°C in the dark	1 year
Total Organic Carbon	2 x 40-mL amber glass VOA	H <sub>3</sub> PO <sub>4</sub> to pH<2 within 1 day	refrigerate at <6°C	28 days
Dissolved organic carbon	125 mL amber wide mouth HDPE	0.45 µm filtration, then H <sub>3</sub> PO <sub>4</sub> to pH<2 within 1 day	refrigerate at <6°C	28 days

Analyte	Container	Preservation	Storage	Hold Time
Total Suspended Solids	1-L clear wide mouth HDPE	None	refrigerate at <6°C	7 days
PAHs, Phthalates	2 x 1L amber glass	None	refrigerate at 4°C	7/40 <sup>2</sup>
Metals (Total & Dissolved)	500 mL Acid washed HDPE	ultra-pure HNO <sub>3</sub> to pH<2	n/a	180 days <sup>1</sup>
Mercury (Total & Dissolved) [CVAA-L]	Acid washed 500 mL fluoropolymer	ultra-pure HCl to pH<2	n/a	28 days <sup>1</sup>

<sup>1</sup> Within 15 minutes of collection, dissolved metals samples must be filtered (.45 µm).

<sup>2</sup> 7 days from sampling to extraction, 40 days from extraction to analysis

### 3.5 Chain of Custody

Chain of custody (COC) will commence at the time that each autosampler is deployed. The autosampler will be secured to ensure no tampering occurred. Thus, all samples will be under direct possession and control of King County field staff. For chain of custody purposes, closed/latched storm drains, autosamplers, and field vehicles will be considered “controlled areas.” 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 the laboratory. Upon arrival at the KCEL, the samples will be split and preserved and filtered as needed then logged into the laboratory data management system and stored in a secure refrigerator. The date and time of sample delivery will be recorded and the COC form will be signed off in the appropriate sections at this time. Once completed, original COC forms will be archived in the project file.

Samples delivered after regular business hours will be split and preserved and filtered as needed and stored in a secure refrigerator until the next day. Samples delivered to AXYS Analytical will be accompanied by a properly-completed KCEL COC form and custody seals will be placed on the shipping cooler. AXYS Analytical will be expected to provide a copy of the completed COC form as part of their analytical data package.

### 3.6 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. locator/station name
  3. in-pipe station water depth at initiation and termination of auto sampling.
  4. date and time of sample collection (start and end times of the compositing period)
  5. initials of all sampling personnel

- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.
- The field sheet will contain records of collection times, general weather, and the names of field crew.
- COC documentation will consist of the Lab's standard COC form, which is used to track release and receipt of each sample from collection to arrival at the lab.

### 3.7 Equipment Decontamination

Once samples are collected, all re-usable equipment should be decontaminated. Teflon tubing and autosampler containers shall be cleaned with: (1) alconox or other suitable laboratory detergent; (2) a H<sub>2</sub>SO<sub>4</sub> rinse; (3) a deionized water (ASTM I or II) rinse; and (4) an acetone rinse. All stainless steel fittings and connectors are cleaned in the same manner except they are not subjected to the acid rinse step. Composite autosampler bottles and autosampler tubing will be cleaned prior to each sampling event according to laboratory standard operating procedures (KCEL SOP # 234 and KCEL SOP #223) for collecting samples for low-level analysis using autosamplers. Acetone solvent rinses shall be used for carboys and tubing per EPA methods 1668a and 1613. Proofed clean PCB and dioxin/furan sampling containers will be supplied by the contract laboratory. One equipment blank per site will be analyzed to check for possible cross contamination between sampling events. The number of equipment blanks collected is based on data quality objectives and previously collected field blank noted earlier in this document. Proper personal protective equipment (new powder-free gloves) should be worn during sampling activities and during decontamination processes.

## 4.0. ANALYTICAL METHODS AND DETECTION LIMITS

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Analytical methods are presented in this section, along with analyte-specific detection limit goals. For PAHs and phthalates, metals and conventional analytes, the terms MDL and RDL, used in the following subsections, refer to method detection limit and reporting detection limit, respectively. KCEL reports both the Laboratory Information Management System (LIMS) reporting detection limit (LIMS RDL) and the LIMS method detection limit (LIMS MDL) for each sample and parameter, where applicable.

EPA's Office of Wastewater generally defines a PQL (practical quantitation limit) as the minimum concentration of a chemical constituent that can be reliably quantified while the MDL is defined as the minimum concentration of a chemical constituent that can be detected. The LIMS RDL is analogous to the PQL for all analyses. It 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.

For the majority of metals and conventionals analyses, 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 metals and conventionals tests, MDLs are evaluated by the procedure listed in this appendix 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, a standard analyzed near the MDL concentration during calibration must produce a valid mass spectra and this standard is used to define the MDL.

Actual LIMS MDLs and RDLs may differ from the target detection limit goals as a result of necessary analytical dilutions or a reduction of extracted sample amounts based upon available sample volumes. When sample extracts are diluted because the concentrations for one or more target analytes exceeded the upper end of the calibration curve or parameter-specific interferences, MDLs and RDLs from the original, undiluted extract will be reported for parameters other than the target analytes that required dilution. Every effort will be made to meet the MDL/RDL goals listed in the SAP. However there may be times when the MDL/RDL values rise because the sample must be run at a greater dilution. This may be due to the concentration of some target analytes exceeding the calibration range, interfering target or non-target compounds, or run QC not passing (ex. internal standard failures). Non-detected target analytes will be reported from the lowest dilution possible (no interferences and the run QC must pass). Target analytes that are detected must be reported from an appropriate dilution. The dilution chosen must have no interferences, the run QC must pass and wherever possible the value that is greater than the RDL will be chosen.

For PCB and 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 PCB congener and 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 MRL values.

The PCB congener and dioxin/furan congener data will be reported to LMCLs and flagged down to the SDL value. In many cases the SDL may be below the LMCL. EPA Method 1668A defines a Minimum Level (ML) value for each congener. The ML value is used to evaluate levels in the method blank. The ML is based on the lowest method calibration limit (LMCL) and any laboratory performing the method should be able to achieve at least that level. AXYS Analytical Services uses an additional lower calibration point lower than the calibration points specified in the method so is able to quantify congeners below the ML specified in the method.

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 or performance-based quality control limits. In the case of SVOCs and mercury a matrix spike duplicate 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 (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.
- The ongoing precision and recovery (OPR) samples must show acceptable recoveries, according to the respective methods for data to be reported without qualification. The OPR sample is typically called a Lab Control Sample (LCS) or Spiked Blank is LIMS.

## 4.1 PCB Congeners

PCB congener analysis will follow U.S. Environmental Protection Agency (EPA) Method 1668A Revision A (EPA 2003), which is a high-resolution gas chromatography/high-resolution

mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. AXYS Analytical Services may be switching to Revision C of Method 1668 sometime during this project depending on when EPA promulgates this revision. This method provides reliable analyte identification and very low detection limits. The principle differences between Method 1668A and 1668C are the replacement of individual laboratory acceptance criteria with interlaboratory developed acceptance criteria. This change is not anticipated to modify result values although there may be minor differences in data qualifiers not affecting usability. An extensive suite of labeled surrogate standards (Table 5) is added before samples are extracted. Data are “recovery-corrected” for losses in extraction and cleanup, and analytes are quantified against their labeled analogues.

AXYS Analytical will perform this analysis according to their Standard Operating Procedure MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668. A one-liter sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil and Alumina. Analysis is performed with an SPB Octyl column. An optional secondary DB1 column may be used to resolve the co-eluting congeners PCB156 and PCB157. Method 1668A requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted and analyzed separately.

**Table 5. Labeled Surrogates and Recovery Standards Used for EPA Method 1668A PCB Congener Analysis**

<sup>13</sup> C-labeled PCB Congener Surrogate Standards				
1	37	123	155	202
3	54	118	167	205
4	81	114	156/157	208
15	77	105	169	206
19	104	126	188	209
<sup>13</sup> C-labeled Cleanup Standards				
28	111	178		
<sup>13</sup> C-labeled Internal (Recovery) Standards				
9	52	101	138	194

Table 6 lists the 209 PCB congeners and their respective target MDL values. The reported MDLs for individual samples may differ from those in Table 5 since they are determined by signal to noise ratios and changes to final volumes. Note that several of the congeners co-elute and a single result or MDL value is provided for the congeners in aggregate.

**Table 6. PCB Congener water detection limit goals in pg/L and lower calibration limits by 1668A, AXYS Analytical Services method MLA 010.**

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
CL1-PCB-1	1.0	4.0
CL1-PCB-2	1.0	4.0
CL1-PCB-3	1.0	4.0
CL2-PCB-4	2.0	4.0
CL2-PCB-5	2.0	4.0
CL2-PCB-6	2.0	4.0
CL2-PCB-7	2.0	4.0
CL2-PCB-8	2.0	4.0
CL2-PCB-9	2.0	4.0
CL2-PCB-10	2.0	4.0
CL2-PCB-11	2.0	4.0
CL2-PCB-12/13	2.0	8.0
CL2-PCB-14	2.0	4.0
CL2-PCB-15	2.0	4.0
CL3-PCB-16	1.0	4.0
CL3-PCB-17	1.0	4.0
CL3-PCB-19	1.0	4.0
CL3-PCB-21/33	1.0	8.0
CL3-PCB-22	1.0	4.0
CL3-PCB-23	1.0	4.0
CL3-PCB-24	1.0	4.0
CL3-PCB-25	1.0	4.0
CL3-PCB-26/29	1.0	8.0
CL3-PCB-27	1.0	4.0
CL3-PCB-28/20	1.0	8.0
CL3-PCB-30/18	1.0	8.0
CL3-PCB-31	1.0	4.0
CL3-PCB-32	1.0	4.0
CL3-PCB-34	1.0	4.0
CL3-PCB-35	1.0	4.0
CL3-PCB-36	1.0	4.0
CL3-PCB-37	1.0	4.0
CL3-PCB-38	1.0	4.0
CL3-PCB-39	1.0	4.0
CL4-PCB-41/40/71	1.0	12.0
CL4-PCB-42	1.0	4.0
CL4-PCB-43	1.0	4.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
CL4-PCB-44/47/65	1.0	12.0
CL4-PCB-45/51	1.0	8.0
CL4-PCB-46	1.0	4.0
CL4-PCB-48	1.0	4.0
CL4-PCB-50/53	1.0	8.0
CL4-PCB-52	1.0	4.0
CL4-PCB-54	1.0	4.0
CL4-PCB-55	1.0	4.0
CL4-PCB-56	1.0	4.0
CL4-PCB-57	1.0	4.0
CL4-PCB-58	1.0	4.0
CL4-PCB-59/62/75	1.0	12.0
CL4-PCB-60	1.0	4.0
CL4-PCB-61/70/74/76	1.0	16.0
CL4-PCB-63	1.0	4.0
CL4-PCB-64	1.0	4.0
CL4-PCB-66	1.0	4.0
CL4-PCB-67	1.0	4.0
CL4-PCB-68	1.0	4.0
CL4-PCB-69/49	1.0	8.0
CL4-PCB-72	1.0	4.0
CL4-PCB-73	1.0	4.0
CL4-PCB-77	1.0	4.0
CL4-PCB-78	1.0	4.0
CL4-PCB-79	1.0	4.0
CL4-PCB-80	1.0	4.0
CL4-PCB-81	1.0	4.0
CL5-PCB-82	1.0	4.0
CL5-PCB-83/99	1.0	8.0
CL5-PCB-84	1.0	4.0
CL5-PCB-88/91	1.0	8.0
CL5-PCB-89	1.0	4.0
CL5-PCB-92	1.0	4.0
CL5-PCB-94	1.0	4.0
CL5-PCB-95/100/93/102/98	1.0	20.0
CL5-PCB-96	1.0	4.0
CL5-PCB-103	1.0	4.0
CL5-PCB-104	1.0	4.0
CL5-PCB-105	1.0	4.0

<b>PCB Congener</b>	<b>Typical Detection Limit/SDL</b>	<b>LMCL based on Low Cal./RDL</b>
CL5-PCB-106	1.0	4.0
CL5-PCB-107/124	1.0	8.0
CL5-PCB-108/119/86/97/125/87	1.0	24.0
CL5-PCB-109	1.0	4.0
CL5-PCB-110/115	1.0	8.0
CL5-PCB-111	1.0	4.0
CL5-PCB-112	1.0	4.0
CL5-PCB-113/90/101	1.0	12.0
CL5-PCB-114	1.0	4.0
CL5-PCB-117/116/85	1.0	12.0
CL5-PCB-118	1.0	4.0
CL5-PCB-120	1.0	4.0
CL5-PCB-121	1.0	4.0
CL5-PCB-122	1.0	4.0
CL5-PCB-123	1.0	4.0
CL5-PCB-126	1.0	4.0
CL5-PCB-127	1.0	4.0
CL6-PCB-128/166	1.0	8.0
CL6-PCB-130	1.0	4.0
CL6-PCB-131	1.0	4.0
CL6-PCB-132	1.0	4.0
CL6-PCB-133	1.0	4.0
CL6-PCB-134/143	1.0	8.0
CL6-PCB-136	1.0	4.0
CL6-PCB-137	1.0	4.0
CL6-PCB-138/163/129/160	1.0	16.0
CL6-PCB-139/140	1.0	8.0
CL6-PCB-141	1.0	4.0
CL6-PCB-142	1.0	4.0
CL6-PCB-144	1.0	4.0
CL6-PCB-145	1.0	4.0
CL6-PCB-146	1.0	4.0
CL6-PCB-147/149	1.0	8.0
CL6-PCB-148	1.0	4.0
CL6-PCB-150	1.0	4.0
CL6-PCB-151/135/154	1.0	12.0
CL6-PCB-152	1.0	4.0
CL6-PCB-153/168	1.0	8.0
CL6-PCB-155	1.0	4.0

<b>PCB Congener</b>	<b>Typical Detection Limit/SDL</b>	<b>LMCL based on Low Cal./RDL</b>
CL6-PCB-156/157	1.0	8.0
CL6-PCB-158	1.0	4.0
CL6-PCB-159	1.0	4.0
CL6-PCB-161	1.0	4.0
CL6-PCB-162	1.0	4.0
CL6-PCB-164	1.0	4.0
CL6-PCB-165	1.0	4.0
CL6-PCB-167	1.0	4.0
CL6-PCB-169	1.0	4.0
CL7-PCB-170	1.0	4.0
CL7-PCB-171/173	1.0	8.0
CL7-PCB-172	1.0	4.0
CL7-PCB-174	1.0	4.0
CL7-PCB-175	1.0	4.0
CL7-PCB-176	1.0	4.0
CL7-PCB-177	1.0	4.0
CL7-PCB-178	1.0	4.0
CL7-PCB-179	1.0	4.0
CL7-PCB-180/193	1.0	8.0
CL7-PCB-181	1.0	4.0
CL7-PCB-182	1.0	4.0
CL7-PCB-183/185	1.0	8.0
CL7-PCB-184	1.0	4.0
CL7-PCB-186	1.0	4.0
CL7-PCB-187	1.0	4.0
CL7-PCB-188	1.0	4.0
CL7-PCB-189	1.0	4.0
CL7-PCB-190	1.0	4.0
CL7-PCB-191	1.0	4.0
CL7-PCB-192	1.0	4.0
CL8-PCB-194	1.0	4.0
CL8-PCB-195	1.0	4.0
CL8-PCB-196	1.0	4.0
CL8-PCB-197/200	1.0	8.0
CL8-PCB-198/199	1.0	8.0
CL8-PCB-201	1.0	4.0
CL8-PCB-202	1.0	4.0
CL8-PCB-203	1.0	4.0
CL8-PCB-204	1.0	4.0

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
CL8-PCB-205	1.0	4.0
CL9-PCB-206	1.0	4.0
CL9-PCB-207	1.0	4.0
CL9-PCB-208	1.0	4.0
CL10-PCB-209	1.0	4.0

SDL = sample detection limit

LMCL = lower method calibration limit

pg/L = picograms per liter

Quality control samples include method blank, OPR sample, and surrogate spikes. Method blanks and OPR (equivalent to spike blanks), 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 1668A. Method 1668A has specific requirements for method blanks that must be met before sample data can be reported (see section 9.5.2 of Method 1668A). The OPR samples must show acceptable recoveries, according to Method 1668A, in order to samples to be analyzed and data to be reported. A summary of the quality control samples are shown in Table 7.

**Table 7. PCBs QA/QC Frequency and Acceptance**

	Method Blank	Lab Duplicate (RSD)	OPR (% Recovery)	Surrogate Spikes
<b>Frequency</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>Each sample</b>
PCB Congeners	<LMCL <sup>a</sup>	RPD <50%	laboratory QC limits <sub>b</sub>	laboratory QC limits <sub>b</sub>

batch = 20 samples or less prepared as a set

<sup>a</sup>EPA Method 1668A blank criteria (see Table 2 of the published method) is to be below the Minimum Levels: 2, 10, 50 pg/congener depending on the congener with the sum of all congeners below 300 pg/sample. Higher levels are acceptable when sample concentrations exceed 10x the blank levels.

<sup>b</sup>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

## 4.2 Dioxin/furan Congeners

Dioxin/furan congener analysis will be performed according to EPA Method 1613B (EPA 2003), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification similar to Method 1613B for dioxins/furans. This method provides reliable analyte identification and very low detection limits. Labeled native and surrogate standards (Table 8) 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 Analytical Services will perform this analysis according to their Standard Operating Procedure MLA-017 which is based on EPA Method 1613b Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. A one-liter sample will be extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil, and Alumina.

**Table 8. Labeled Surrogates and Recovery Standards Used for EPA Method 1613b Dioxins/Furans Congener Analysis.**

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

Table 9 lists the 17 dioxin/furan congeners and their respective target SDL values. The reported SDLs for individual samples may differ from those in Table 8 since they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown.

**Table 9. Dioxin/furan water sample detection limit goals in pg/L and lower calibration limit goals by EPA method 1613b, AXYS Analytical Services method MLA 017**

Dioxin	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
2,3,7,8 TCDD	0.5	2.0
1,2,3,7,8 PeCDD	1.0	10.0
1,2,3,4,7,8 HxCDD	1.0	10.0
1,2,3,6,7,8 HxCDD	1.0	10.0
1,2,3,7,8,9 HxCDD	1.0	10.0
1,2,3,4,6,7,8 HpCDD	1.0	10.0
OCDD	5.0	20.0
Furan		
2,3,7,8 TCDF	0.5	2.0
1,2,3,7,8 PeCDF	1.0	10.0
2,3,4,7,8 HxCDF	1.0	10.0

Dioxin	Typical Detection Limit/SDL	LMCL based on Low Cal./RDL
1,2,3,4,7,8 HxCDF	1.0	10.0
1,2,3,6,7,8 HxCDF	1.0	10.0
1,2,3,7,8,9 HxCDF	1.0	10.0
2,3,4,6,7,8 HxCDF	1.0	10.0
1,2,3,4,6,7,8 HpCDF	1.0	10.0
1,2,3,4,7,8,9 HpCDF	1.0	10.0
OCDF	5.0	20.0

SDL = sample detection limit

LMCL = lower method calibration 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 1668A, in order to samples to be analyzed and data to be reported. A summary of the quality control samples are shown in Table 10.

**Table 10. Dioxins/furans QA/QC Frequency and Acceptance Criteria**

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

batch = 20 samples or less prepared as a set

<sup>a</sup>EPA Method 1613B blank criteria (see Table 2 of the published method) is to be below the Minimum Levels: 1, 5, 10 pg/g for the tetra, penta through hepta, and octa respectively

<sup>b</sup>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

### 4.3 PAHs and Phthalates

Samples will be analyzed for PAHs and phthalates (see Table 11). The samples will be prepared by liquid-liquid extraction as detailed in method EPA method 3520C, KCEL SOP 701. This extraction will be modified by breaking down the liquid-liquid extractors without decanting the remaining solvent in the extractor body into the round bottomed flask. Leaving this step out will

remove the need for sodium sulfate use as a drying agent. Sodium sulfate is a significant contributor to PAH and Phthalate contamination at these levels. Samples will be analyzed by a modified EPA Method 625 Gas Chromatography/Mass Spectrometry – Selected Ion Monitoring Large Volume Injection method (GC/MS-SIM LVI), being developed for this project. MDL and RDL goals will be determined following completion of an MDL study and will be based upon extraction of one-liter of sample concentrated to 1 ml final volume. Both the SOP and MDL study will be completed prior to sample analyses.

Every effort will be made to meet the target MDL and RDL goals. Due to the challenges of reporting as many detectable compounds as possible, there may be a need to change the sample volumes, concentration factors or employ additional cleanups if the analytical protocols in the SOP do not yield enough detectable analytes to meet the project DQOs. Conversely if the samples are sufficiently contaminated with the SVOCs in question, it may be analytically preferable to analyze the samples without an LVI or SIM mode rather than greatly dilute them for the GCMS-SIM LVI system. Prior to implementing a method changes, the project manager will be consulted and method change will undergo a project level review.

In addition to reporting individual polycyclic aromatic hydrocarbon (PAH) results, 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<sup>1</sup>. 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 11. PAH and Phthalate Target Compounds and Detection Limit Goals in µg/L.**

Analyte	MDL	RDL	Analyte	MDL	RDL
2-Methylnaphthalene	0.00061	0.00610	Dibenzo(a,h)anthracene	0.00070	0.00700
Acenaphthene	0.00030	0.00300	Diethyl phthalate	0.00050	0.0250
Acenaphthylene	0.00050	0.00410	Dimethyl phthalate	0.00050	0.0500
Anthracene	0.00050	0.00500	Di-n-butyl phthalate	0.00050	0.0500
Benzo(a)anthracene	0.00050	0.00500	Di-n-octyl phthalate	0.00050	0.0250
Benzo(a)pyrene	0.0010	0.0100	Fluoranthene	0.00033	0.00330
Benzo(b,j,k)fluoranthene	0.0010	0.0100	Fluorene	0.00030	0.0030

<sup>1</sup> 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	RDL	Analyte	MDL	RDL
Benzo(g,h,i)perylene	0.00060	0.00600	Indeno(1,2,3-cd)pyrene	0.00050	0.0050
Benzyl butyl phthalate	0.00050	0.0250	Naphthalene	0.00100	0.0100
Bis(2-ethylhexyl)phthalate	0.0010	10.0	Phenanthrene	0.00031	0.00310
Chrysene	0.00050	0.00500	Pyrene	0.00035	0.00350

NOTE: The MDL/RDL limits are based on extracting 1 liter of sample to a final volume of 1 ml. They are subject to change based upon the amount analyzed, dilutions and a GPC cleanup. A new MDL study may be performed for Bis(2-ethylhexyl)phthalate in the future if continuing method development reduces the level of lab contamination seen for this compound. Any change to the MDL/RDL for this compound would be noted in the data report as a SAP deviation.

In addition to the surrogates and internal standards, which assess sample accuracy and bias, a method blank, spike blank, matrix spike, and matrix spike duplicate or laboratory duplicate 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 12.

**Table 12. PAH and Phthalate QA/QC Frequency and Acceptance Criteria**

	Method Blank	Spike Blank (% Recovery)**	Matrix Spike (% Recovery)**	Matrix Spike Duplicate or Lab Duplicate (RPD)
Analyte / Frequency	1 per Extraction batch*	1 per Extraction batch*	1 per QC batch	1 per QC batch
PAHs and Phthalates	<MDL	40-160	40-160	40

	Surrogate (% Recovery)**
Surrogate / Frequency	Added to all samples and QC
2-Fluorobiphenyl	40-160
D14-Terphenyl	40-160

\* QC Extraction batch = 20 samples or less prepared within a 12 hour shift

\*\* These generic control limits are due to the fact that there are currently no data points to empirically derive QC Limits.

Empirically derived performance-based control limits may be updated once per calendar year and the limits in effect at the time of analysis will be used as QC limits for all ongoing precision and accuracy QC samples and surrogates. Changes to QC Limits due to annual updates should be noted in a SAP addendum.

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

RPD = Relative Percent Difference

## 4.4 Metals and Mercury

Metals samples will be analyzed and reported by EPA Method 200.8 (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL SOP 624. Mercury will be analyzed by EPA Method 245.1 (Cold Vapor Atomic Absorbance [CVAA]), KCEL SOP 604. Total and dissolved metals samples will be preserved to a pH less than 2 with ultrapure nitric acid for ICP-MS analysis and ultrapure hydrochloric acid for CVAA analyses. The detection limit goals shown in Tables 13 and 14 are targets for metals and mercury. 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 13. Trace Metals Target Analytes and Detection Limit Goals (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

**Table 14. Mercury Detection Limit Goals (ug/L)**

Analyte / Range	MDL	RDL
Mercury / Low Range	0.005	0.015

Sample accuracy and bias will be evaluated by method blanks, laboratory duplicates, spike blanks, and matrix spikes/matrix spike duplicates, which 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 15.

**Table 15. Trace Metals and Mercury QA/QC Frequency and Acceptance Criteria**

	Method Blank	Spike Blank (% Recovery)	Lab Duplicate (RPD)	Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike Duplicate (RPD)
<b>Analyte / Frequency</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>	<b>1 per batch</b>
Metals by ICP-MS	< MDL	85 – 115%	≤ 20%	75 - 125%	NA
Mercury (CVAA-L)	< MDL	85 – 115%	NA	75 - 125%	≤ 20%

batch = 20 samples or less

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

RPD = Relative Percent Difference

NA = Not Applicable

## 4.5 Conventionals

All conventional analyses will follow Standard Methods (SM) protocols (American Public Health Association [APHA] 1998). Table 16 presents the analytical methods, detection limits and units for conventional analyses. Detection limits will vary slightly from sample to sample, depending on the exact amount of sample volume used for analysis.

**Table 16. Conventionals Analytical Methods and Detection Limit Goals in mg/L**

Analyte	Method	KCEL SOP	MDL	RDL
Dissolved Organic Carbon	SM5310-B	336	0.5	1.0
Total Organic Carbon	SM5310-B	336	0.5	1.0
Total Suspended Solids	SM2540-D	309	0.5	1.0

Table 17 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 17. Conventional QA/QC Frequency and Acceptance Criteria**

	<b>Method Blank</b>	<b>Lab Duplicate (RPD)</b>	<b>Spike Blank (% Recovery)</b>	<b>Matrix Spike (% Recovery)</b>	<b>LCS (% Recovery)</b>
<b>Analyte / Frequency</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>1 per batch*</b>	<b>1 per batch*</b>
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%
Total Suspended Solids	<MDL	25%	N/A	N/A	80-120%

\*batch = 20 samples or less prepared as a set  
 < MDL = less than the Method Detection Limit.  
 RPD = Relative Percent Difference  
 LCS = Lab Control Sample  
 N/A = not applicable

## 5.0. DATA VALIDATION, REPORTING AND RECORD KEEPING

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This section presents the data validation, reporting and record keeping for the samples collected under this SAP. Chemical data generated during this survey study will be validated according to accepted Environmental Protection Agency (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. All necessary data needed for independent review of PCB congener and 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 Water and Land Resources Division (WLRD) for all data generated by KCEL. Data validation for PCB congener and dioxin/furan congener data maybe conducted by either an outside party for this study or by WLRD. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

### 5.1 Reporting

All data and supporting information will be documented in a data report for data collected in 2011 and 2012 from the Brandon CSO Basin. Data validation memoranda and copies of COC forms will be included in the data report. If appropriate data fields can be generated in Ecology’s Environmental Information Management (EIM) database, data will be submitted for loading into the EIM database.

### 5.2 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 Analytical will provide electronic data deliverables and associated quality control results to King County. While KCEL will maintain a copy of deliverables from AXYS Analytical, copies of full data packages pertaining to King County samples analyzed by AXYS Analytical will be maintained by AXYS Analytical for 10 years from the analysis date.

## 6.0. REFERENCES

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# APPENDIX A: CHAIN-OF-CUSTODY FORM

KING COUNTY DNR ENVIRONMENTAL LABORATORY

322 West Ewing Street Seattle, WA 98119

**LABORATORY WORK ORDER**

Project Name: East Waterway Inline Sediments  
 Project Number: 423368-110-4 (T\_IW\_EW.SEDS)

Laboratory Project Manager: Fritz Grothkopp

Sampler: \_\_\_\_\_

684-2327

Lab SAMPLE #	LOCATOR	MATRIX	COLLECT DATE	COLLECT TIME	Parameters							No. of Containers	Comments
					BNALL	PCBLL	ICP Metals	Mercury	Total Solids	TOC	PSD		
Additional Comments:										Total # of Containers:			
RELINQUISHED BY					RECEIVED BY					Date			
Signature					Signature								
Printed Name					Printed Name					Time			
Organization					Organization								