Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan

August 2011

Final

King County

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Seattle, WA 98104

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Citation

King County. 2011. Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan. Prepared by Richard Jack and Jenée Colton, King County Water and Land Resources Division. Seattle, Washington.

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ACRONYMS

AXYS	AXYS Analytical Services
COC	contaminant of concern
DI	deionized water
DQO	data quality objective
Ecology	Washington Department of Ecology
EIM	Environmental Information Management
EPA	U.S. Environmental Protection Agency
FSU	Field Science Unit
HDPE	high density polypropylene
ICP-MS	inductively coupled plasma-mass spectrometry
KCEL	King County Environmental Lab
LCS	laboratory control sample
LDW	Lower Duwamish Waterway
LMCL	lowest method calibration limits
LIMS	Laboratory Information Management System
LVI	large volume injection
MDL	method detection limit
ML	minimum level
MRL	minimum reporting level
OPR	ongoing precision and recovery
PAHs	polycyclic aromatic hydrocarbons
PBDEs	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
PCDDs	polychlorinated dibenzo-dioxins
PCDFs	polychlorinated dibenzo-furans
PSCAA	Puget Sound Clean Air Agency
QA	quality assurance
QC	quality control
RDL	reporting detection limit
RO	reverse osmosis

SAP	sampling and analysis plan
SDL	sample detection limit
SOP	standard operating procedure
SRM	standard reference material
WLRD	Water and Land Resources Division (of King County)

1.0 INTRODUCTION

This sampling and analysis plan (SAP) presents project information along with sampling and analytical methodologies for a year-long study of atmospheric deposition in the Green/Duwamish River Basin. The objective of this study is to compare the measurements of bulk deposition (dry particulate and rainfall) at a small number of stations in areas of different land use within the Green/Duwamish River Basin and to provide information to assist in understanding atmospheric sources to the Lower Duwamish Waterway (LDW). Samples will be analyzed for select metals, mercury, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), seven polychlorinated dibenzo-dioxins (PCDDs), and ten polychlorinated dibenzo-furans (PCDFs). These chemicals have been identified as contaminants of concern (COCs) for the LDW Superfund site. The sample collection method applied in this study is not accurate enough to enable high quality absolute estimates of contaminant loading from atmospheric sources. However, the sampling method is consistent with that used in previous King County (King County 2008) and Puget Sound Partnership (Brandenberger et al. 2010) air deposition studies providing comparable data, and will enable relative comparison of deposition estimates between sites. Also, a U.S. Environmental Protection Agency (EPA) funded air deposition study was initiated in April 2011 by King County as part of an investigation into the major input pathways of PCBs and polybrominated diphenyl ethers (PBDEs) into Lake Washington (King County 2011). The Lake Washington study is sampling bulk air deposition at the Beacon Hill location using the same sampling methods[1] which will complement the data collected for this LDW study.

This SAP documents the field and laboratory activities associated with planned bulk deposition sampling to occur within the Duwamish River Basin, and in the middle and upper portions of the Green River Valley, which drain to the LDW and Elliott Bay. Data collected from this study will enhance the understanding of how atmospheric deposition may contribute COCs to the combined sewer system leading to the LDW in Seattle, Washington. These values will be compared with bulk deposition from other areas within the Duwamish/Green River Basin which contribute COCs to the Green River, flowing into the LDW and Elliott Bay.

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), 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 is about 5 miles long and consists of the downstream portion of the Duwamish River, excluding the East and West Waterways.

The study area encompasses the LDW, Lower Green and Middle Green River portions of the Green/Duwamish Basin. The land use within the Basin includes industrial, commercial, residential, and transportation corridors. The study area also includes parks and relatively

[1] The sampling frequency is two collection periods or approximately one month per quarter.

undeveloped locations, consisting of evergreen and deciduous forests, riparian shorelines, and wetlands. The amount of developed land varies greatly between sub-basins, ranging from heavily urbanized to almost entirely undeveloped. The study area has been expanded beyond LDW to evaluate the degree to which urban residential, suburban, and rural bulk deposition differs from the LDW.

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), EPA, City of Seattle, and the Port of Seattle. The Source Control Work Group collaborates to understand potential sources of contaminants to the LDW Superfund site and works to control and reduce sources that can contaminate sediments in the waterway. Thus, King County Wastewater Treatment Division (WTD) wants to better understand the potential sources of COCs into combined sewer overflow (CSO) basins[2] in the LDW relative to other inputs to the LDW. King County has eight CSOs and two emergency overflows that discharge into the LDW. King County has recently completed sampling of whole waters at various CSOs in the Duwamish River Basin (King County 2009). King County has also begun sampling solids within two Duwamish River CSO Basins. To complement these data, King County would like to better understand atmospheric loadings of sources to CSO basins. Bulk atmospheric deposition was previously estimated for some COCs by King County (2008). The bulk deposition data collected under this SAP will be used to fill gaps for other COCs in those data and to provide additional understanding of the spatial variability of bulk deposition across the range of land uses within the Green/Duwamish Basin.

The bulk deposition data collected under this SAP will assist in understanding atmospheric loadings to the combined sewer systems and the degree to which these create a baseline load in these conveyance systems. These data will also be helpful for evaluating atmospheric sources to separated stormwater basins and less developed basins upstream which contribute loadings to the Green River.

Specifically, King County will perform this work to help identify the significance of COCs in this pathway and as a line of evidence to be used in evaluating whether these chemicals are present in sufficient amounts to potentially recontaminate sediments in the LDW.

1.2 Survey Schedule

Collection of bulk deposition samples will begin in summer and fall of 2011 and continue through the winter and spring of 2012. Bulk deposition will be collected approximately monthly during the July through September dry season and biweekly during the October through May wet season. It is anticipated that all data analysis will be completed by summer 2012 and data from all sampling events will be validated and reviewed by the last quarter of 2012 and documented in a report by December 2012.

[2] CSOs include discharges of both sanitary sewer and stormwater.

1.3 Project Staff

The following King County 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.

—Jenée Colton, Bulk Deposition Project Manager.....206-296-1970

Responsible for bulk deposition project execution and adherence to SAP and schedule.

—Debra Williston, Water and Land Resources Technical Lead.....206-263-6540

Technical Support for all Lower Duwamish River studies including bulk deposition project.

—Bruce Tiffany, Industrial Waste Project Lead.....206-263-3011

Provides technical advice on all aspects of the project; King County representative on LDW Source Control Workgroup.

—Bob Kruger, Field Science Unit Field Lead.....206-684-2323

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

Atmospheric deposition sampling presents multiple challenges due to factors such as high spatial variability, non-standardized sampling methods, a lack of local air flow pattern information, and a wide range of sampling costs. This study implements a simple, cost-effective method for sampling bulk deposition (i.e., rainfall and dry particulate deposition) for the purpose of comparing measurements across stations located in areas representing urban, suburban and rural land uses. To contain analytical costs, a limited number of stations was selected. All of the stations selected are part of the Puget Sound Clean Air Agency's (PSCAA) regional network of air quality monitoring stations. This consistency provides not only complementary meteorological data where possible, but also congruence with the concept of these locations supplying locally representative air quality data. For the purposes of this study, the land uses attributed to each sampling location are based on PSCAA nomenclature. Sampling locations are therefore attributed to one or more of six broad land use categories.

- Urban center
- Suburban
- Rural
- Commercial
- Industrial
- Residential

Five stations were selected for sampling (see Figure 1). Two stations were selected within the LDW corridor to supply some spatial variability in the main area of interest. The "Duwamish" station represents industrial and urban land uses and the South Park location represents a mix of suburban, industrial and residential land uses. A station was selected in each of two areas upstream in the Green River. The Kent station represents suburban and commercial while the Enumclaw station represents rural land uses. The Enumclaw station may be dropped from the sampling after two quarters if parameters of interest are consistently not detected. Lastly, a fifth station at Beacon Hill was selected as representative of regional urban atmospheric deposition in the south Seattle metropolitan area. PSCAA categorizes the major land uses around their stations. For example, the Beacon Hill location is categorized as suburban, industrial, and residential. There are other land uses near all of the selected air deposition stations, but the PSCAA designations are used herein to provide consistent terminology with other air sampling efforts.

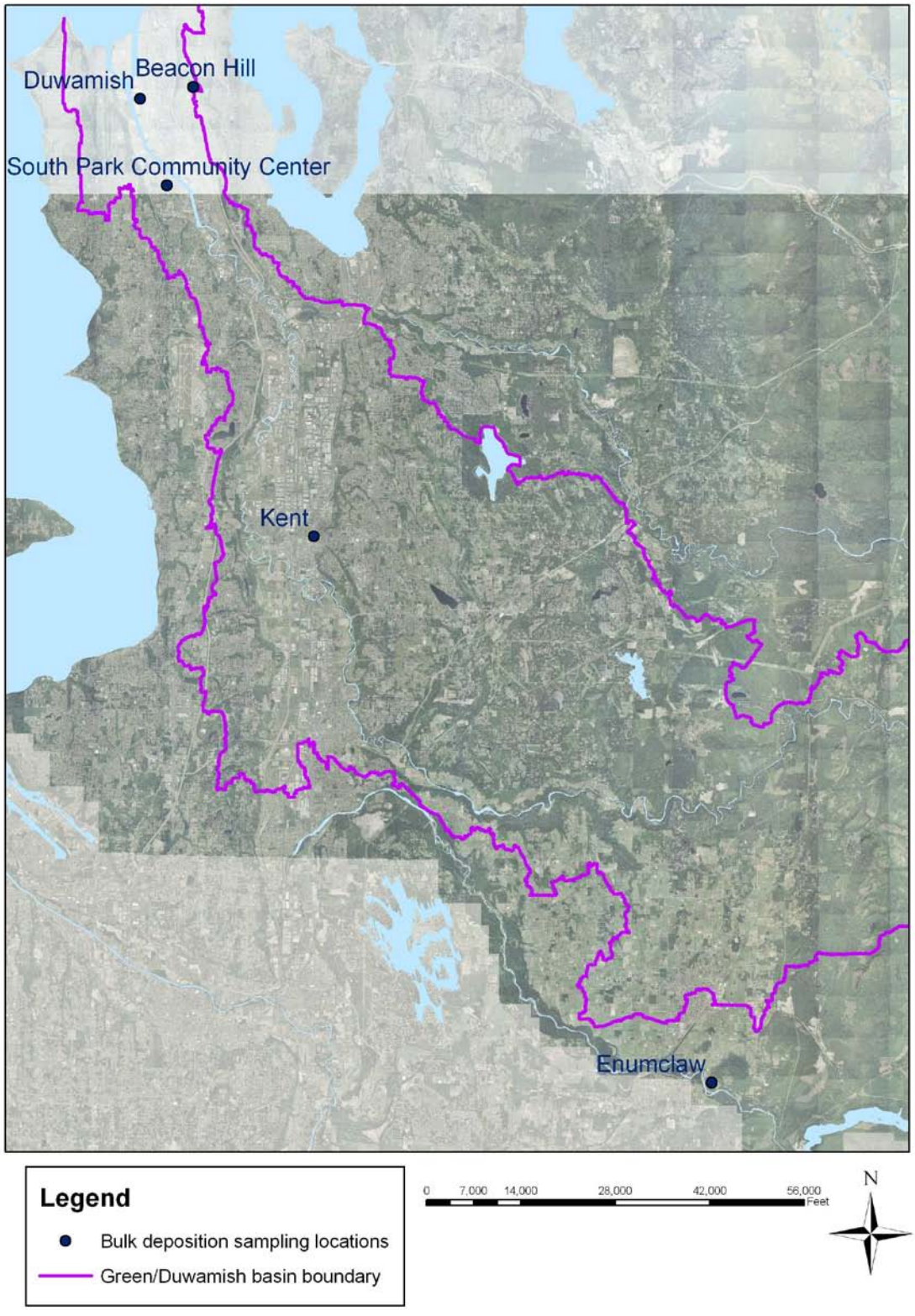

Figure 1. PSCAA air stations selected for bulk deposition sampling

Passive bulk samplers will be deployed for approximately 4-week periods during the dry season and for 2-week periods during the wet season for one year. Twenty sampler deployments over the one year duration are planned to capture seasonal differences in emissions and deposition. Samples collected will be analyzed by King County Environmental Lab (KCEL) for select metals, mercury, and PAHs, while 25% of the samples will also be analyzed for PCB congeners and 17 dioxin/furan congeners at AXYS Analytical Services (AXYS).

2.1 Data Quality Objectives

The data quality objectives (DQOs) are to collect data of known and sufficient quality to meet the project goals. Validation of project data will assess whether the data collected are of sufficient quality to meet the project 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 quality control (QC) procedures:

- analysis of various laboratory QC samples such as blanks, surrogates, and replicates; and
- collection and analysis of field replicate and duplicate samples.

Because contaminant concentrations in air and rainfall are known to be highly variable, precision is expected to be relatively low. Accuracy, for metals, mercury, polycyclic aromatic hydrocarbon (PAHs), dioxins/furans, and PCB congener data is not directly quantifiable since certified reference materials do not exist for bulk deposition. The ongoing precision and recovery sample control charts used by the analytical laboratories, however, provide some indication of overall accuracy. Additionally, the isotopic dilution method chosen for this study is the most rigorous method for dioxins/furans and PCB congener analysis. This method uses isotopically labeled congeners, to track the recovery performance of the range of congener homologs. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample.

Analytical bias from this study cannot be quantified because samples in this study represent ambient dry air and rainfall deposition, which lack certified reference materials.

2.1.2 Representativeness

Representativeness expresses the degree to which sample data represent a population, parameter variations at the sampling point, or an environmental condition. Atmospheric deposition samples collected in this study are intended to represent the average wet and dry deposition to the general urban area, and specifically the Duwamish Valley, suburban areas of the Lower Green Valley

and rural areas of the Middle Green Valley. The Upper Green River is predominantly National Forest and National Park and these areas are not included in this bulk deposition study.

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 with adherence to standardized sampling and testing protocols will aid in providing a complete set of data for this study. The goal for completeness is 90% for these bulk/air deposition samples. Samplers and rainfall will be checked frequently, however, it is still possible for sample jars to overflow with rainwater. Overtopped samplers will be discarded as invalid because documentation of deposition lost is not possible. If completeness is not achieved, the project team will evaluate if the DQOs can still be met or if additional samples may be needed.

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 use of standard techniques to collect and analyze representative samples, along with standardized data validation and reporting procedures. King County has collected bulk deposition data via these field methods before and these data should be comparable with previous methods. By following the guidance of this SAP, the goal of field comparability between this and future sampling events will be achieved. Because these bulk deposition samples will be analyzed by various methods, future result comparability will require use of similar methods as those chosen here.

2.1.5 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The concentrations of PAHs, metals, mercury, dioxins/furans and PCB congeners in bulk deposition water samples are anticipated to be in the pg/L to µg/L range depending on the analyte. The analytical method detection limit goals presented in Section 4 are adequately sensitive to detect selected metals, mercury, PAHs, dioxins/furans, and PCB congeners at concentrations of interest to understand contaminant fluxes per unit area. Based on historical data, PAHs, metals, and mercury will likely be detected at the Duwamish, South Park, and Beacon Hill stations. Urban locations such as these are expected to exceed the lower calibration limits for at least some of the 17 dioxin/furan and 209 PCB congeners.

2.2 Sampling and Analytical Strategy

This study is designed to collect metals, mercury, PAHs, dioxins/furans, and PCB concentration data which will be used to estimate average annual bulk deposition loadings from the stations sampled in the Seattle urban area, LDW, and upstream suburban and rural areas in the greater Green/Duwamish Basin.

2.2.1 Sampling Station Locations and Sample Identification

The Laboratory Information Management System (LIMS) is used to track samples at KCEL. This system creates "locators" or unique codes for each sampling location (i.e. station). Some of the stations being sampled for this study have been previously sampled by KCEL. The locators that have previously been used will also be used for this study. Where stations have never been sampled by KCEL, a new unique locator will be created incorporating the PSCAA station ID.

A location code (locator), the date of collection and the unique sample identification number generated by KCEL will identify individual samples collected at each location. Samples will be identified using a location code, a unique laboratory assigned sample number per collection vessel and the date of collection. This study will employ the KCEL sample tracking system which has sample labeling and identification conventions. Table 1 presents the locator names and state plane north coordinates for each sampling location.

Table 1. Air Sampling Locations and Locator Names

Station Location	KC Locator	PSCAA ID	Location	State Plane Easting	State Plane Northing
Beacon Hill, relocated[1]	BWR	BW	15th S. and Charlestown	1276200	210777
Duwamish relocated [2]	CER	CE	4401 E. Marginal Wy. S.	1268326	209111
South Park	SPCC-R	DD	8201 10th Ave S. Seattle	1273043	196688
Kent	PSCAA-CW	CW	James St. & Central Ave., Kent	1293960	144039
Enumclaw	PSCAA-DF	DF	30525 SE Mud Mountain Rd, Enumclaw	1365590	53337

[1]The PSCAA Beacon Hill sampling station was historically located approximately 300 meters to the northwest of the current location. It was moved to accommodate changes in the covered reservoir/park which is nearby.

[2]The PSCAA Duwamish station was historically located 600m to the south-southeast.

2.2.2 Sample Acquisition and Analytical Parameters

King County Field Science Unit (FSU) staff will primarily conduct sampling; however, other King County Water and Land Resources (WLRD) staff may provide assistance as needed. Sampling techniques are discussed in Section 3. Each sample will be analyzed for select metals and PAHs. A subset of samples will be analyzed for 209 PCB congeners and 17 dioxins/furan congeners. Table 2 summarizes the number of samples to be collected at each station, sample replicates and quality control samples (see Sections 3.6 and 3.7 for further discussions of these samples). The specific metals and PAHs are listed in Section 4. The parameters being analyzed are generally based on contaminants of concern identified in the LDW Remedial Investigation (Windward 2009). PCB and dioxin/furan congener analysis will be conducted by AXYS in Sidney, British Columbia. All other chemical analyses and conventional analyses will be conducted by KCEL, a Washington State Department of Ecology Certified Laboratory.

Table 2. Sample counts for each analytical parameter by station location

		PAH, Metals, Mercury				PCB, dioxins/furans congeners				
Station Location	**PSCAA ID**	**Sample Count**	**Field Replicates**	**QC wipes**	**Equipment Blanks**	**Sample Count**	**Field Replicates**	**QC wipes**	**Equipment Blanks**	**Field Spikes**
Beacon Hill	BW	20	2	1	1	5	1	1	1	1
Duwamish	CE	20	2	1	0	5	1	1	0	1
South Park	DD	20	2	0	0	5	0	0	0	0
Kent	CW	20	2	0	0	5	0	0	0	0
Enumclaw	DF	20	2	0	0	5	0	0	0	0
Total		**100**	**10**	**2**	**1**	**25**	**2**	**2**	**1**	**2**

3.0 SAMPLING PROCEDURES

This section describes the sampling procedures that will be followed over the course of all sampling events to meet the study DQOs. 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. Air deposition will be sampled as bulk deposition using modifications of the method used by Brandenberger et al. (2010) to collect bulk air deposition samples for their Puget Sound air deposition study. Samplers were fabricated at KCEL.

3.1 Sample Collection and Sampler Decontamination

Sampling systems will include a wood-framed structure supporting four collection funnels that each drain directly into a sample bottle (Appendix A). The framing will be constructed to hold the collection system about 6 feet off the ground. One sampling system will be constructed for each sampling site (5 locations) and an additional sampling system will be constructed to serve as a rotating field duplicate. A total of 6 systems will be constructed.

Each organics deposition sampler consists of the following components:

- A large stainless steel collection bowl (23 or 45 cm diameter) with a hole in the middle and stainless steel funnel welded to the bottom.
- An amber glass collection vessel, protected from light, with a minimum capacity of 4 L and a Teflon®-lined cap.
- A series of Teflon® tubing secured from the bottom of the funnel into the collection vessel through the Teflon® cap.
- A Teflon® vent tube from the cap draining downwards.

Each metals and mercury deposition sampler consists of the following components:

- A precleaned 6-inch-diameter High DensityPolypropylEne (HDPE) funnel with a side vent.
- A precleaned fluoropolymer sample bottle that accepts a screw cap.

Two organics samplers will be grouped with a metals sampler and a mercury sampler to comprise a sampling system. Samples for metals and mercury will be collected from two separate samplers using the setup described above such that two separate, 500 mL, sample bottles will be filled during the collection process. One organics sampler will collect samples for PCB congener and dioxins/furans analysis and the second organics sampler will collect samples for PAHs analysis. Larger diameter (45 cm) bowls will be used with the organics samplers during the dry season while smaller diameter (23 cm) bowls will be deployed during the wet season. These changes are necessary to collect sufficient mass in the dry season without overflowing the collection vessels in the wet season.

Glass, HDPE, Teflon® or stainless steel equipment will be used for sample collection wherever possible. Carboys, funnels, and other components will be cleaned using: (1) Alconox or other

suitable laboratory detergent; (2) a deionized water rinse; (3) an acetone rinse. Teflon® and silicon tubing will receive this same general cleaning protocol. Equipment will incorporate as little silicon tubing as possible to minimize loss of target compounds to adhesion.

The collection bowl and attached tubing will be cleaned at KCEL prior to deployment. The 4 L amber glass proofed sample bottles for PCB congener and dioxins/furans samples will be provided by AXYS Analytical Services. KCEL will pre-clean similar 4 L amber glass bottles for PAH samples.

Samples will be collected consecutively over 2–4 week collection periods. Shorter collection periods will occur during the wet season (October–May) to reduce risk of sampler container overflow. Longer collection periods will be employed during the dry season (June–September) to maximize atmospheric deposition collection. There is no minimum rainfall requirement for a successful sample in the dry season, as it may be composed of particulate alone. However, during the wet season, a sampling period will be targeted that includes at least one rain event but avoiding sampler overflow due to excess rain.

At the time of retrieval, but before dry particulates are rinsed into the sample, the depth of rainfall in each collection vessel will be recorded on the sample container using lab tape and a marking pen (deposition volume). Deposition volume will be measured by comparing the rainfall depth mark to a calibrated bottle. After the depth is marked in the field, a known quantity of reverse osmosis (RO) water up to 400 mL will be used in a Teflon® squirt bottle to rinse dry particulates into each of the three collection vessels (rinse volume). The rinse volume and pan area will be recorded on fieldsheets and entered into LIMS by FSU. The deposition volume will be determined by the laboratory and FSU will enter this into LIMS. During the dry season, when little or no water may be present, volume will only be measured after the known volume of RO water is added.

Removal of particulates will be enhanced by brushing the funnel during rinsing with a natural hair, acetone-cleaned paintbrush (2-3 inch width). The brush will be rinsed before a final rinse of the funnel occurs. Then, the funnel will be disconnected, the collection vessel capped, and stored on ice during the return to the lab. Sample collection procedures may be modified to increase deposition mass collection if detections are not observed in early analytical results for PAHs, mercury and metals.

The organics sampler for PCBs and dioxins/furans will be removed from the field between sampling periods and re-cleaned and stored at KCEL before redeployment[3]. Organics sampler units for PCBs and dioxins/furans will be assigned for each station and remain with their assignments throughout the study. The other samplers will remain in the field continuously and only be rinsed as per the sample collection protocol between sampling periods.

[3] Samples for PCB and dioxin/furan congeners will be collected and analyzed at a lower frequency; samples for all other parameters will be collected and analyzed for each sampling event.

3.2 Sample Delivery and Storage

Samples will be collected directly into the appropriate analytical containers and preserved according to laboratory method specifications. These samples will be kept in ice-filled coolers until delivery to KCEL on the same day that they were collected. Sample preservation for metals and mercury will be performed upon receipt of the samples at the KCEL. PCB and dioxins/furans congener samples will be delivered to AXYS within 1–3 months of sample collection. Samples will be held at KCEL at the appropriate temperature until delivery date. Samples will be maintained in cooler with ice and/or ice packs during the delivery process. Samples will either be driven to AXYS or shipped via overnight express delivery service. Actual delivery dates to AXYS may vary depending on whether additional samples are expected and packaging limitations. The holding times are more than adequate to allow shipment to be delayed for delivery efficiencies and convenience. Table 3 shows sample handling and storage requirements.

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

Analyte	Container	Preservation Holding Time	Preservation Technique	Acceptable Storage Conditions	Hold Time
Metals	Acid washed 500 mL FP[1,2]	Preserve with acid at least 24 hours before digestion	Ultra pure HNO3 to pH <2	store at room temperature	6 months to analyze
Mercury	Acid washed 500 mL FP[1]	48 hrs	Ultrapure HCl to pH <2	Store at room temperature	90 days to analyze
PAHs	4L amber glass	n/ap	None	refrigerate at 4°C	14 days to extract 40 days to analyze
PCB Congeners, Dioxins/ furans	4L amber glass	n/ap	None	refrigerate at 4°C in the dark	1 year

[1]Transport on ice
[2] Flouropolymer
n/ap = not applicable.
Holding times based on the date of collection not the date of deployment of the samplers.

3.3 Chain of Custody

Chain of custody (COC) will commence at the time that samplers are deployed. For chain of custody purposes, locked vehicles, and access controlled properties will be considered "controlled areas." The PSCAA/Ecology air monitoring stations selected for sampling are access controlled with fences and locked gates.

All sample information will be recorded on a COC form (Figure 2, Appendix B). This form will be completed in the field and will accompany all samples during transport and delivery to the laboratory. The date and time of sample delivery will be recorded and both parties will sign off in the appropriate sections on the COC form at this time. Once completed, original COC forms

will be archived in the project file. COC documentation will track release and receipt of each sample from collection to arrival at the lab.

Samples delivered to AXYS will be accompanied by a properly-completed KCEL COC form and custody seals will be placed on the shipping cooler. AXYS will provide a copy of the completed COC form as part of their analytical data package.

3.4 Sampling Equipment

Besides the samplers discussed in Section 3.1, the following additional field equipment will be available for the field sampling crew.

1) Sampling supplies:
   a) Pre-cleaned sampling containers
   b) Ziploc® bags
   c) Cooler with ice
   d) Nitrile gloves
   e) Natural bristle brushes
   f) RO Water
2) Safety equipment:
   a) Safety shoes and glasses
3) Documentation supplies:
   a) Field notebook
   b) Fieldsheets
   c) Sample labels
   d) Chain-of-custody forms
   e) Camera
   f) Ladder for South Park Community Center roof access

When visiting the sampling station, field personnel will record the following information (if applicable) on field forms that are maintained on fieldsheets, COC forms, and Field Observation forms. All of these are loaded into LIMS and stored with the final LIMS data.

- 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

3.5 Sample Documentation

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

- Field sheets generated by King County's LIMS will be used at all stations and will include the following information:
  - Sample ID number
  - Locator name
  - Date and time of sample collection (start and end times/dates of the sampling period)
  - Initials of all sampling personnel
  - Water volume in containers (deposition volume)
  - Funnel RO rinse volume
  - Funnel diameter
- LIMS-generated container labels will identify each container with a unique sample number, locator/station and site names, collect date, analyses required, and preservation method.
- The field sheet will contain records of rainfall, collection times, general weather, and the names of field crew.

3.6 Field Replicates

For bulk atmospheric deposition sampling, replicates will be collected using a completely separate bulk deposition sampler rotated between the 5 sampling stations with each station having 2 replicates collected over the course of the year-long sampling design. Therefore, for PAHs, metals and mercury, 10 replicates will be collected. However, replicates will be collected from only two locations for PCB and dioxins/furans analysis for a total of two replicates. This is because of budget limitations of the project. The frequency of sample replication is summarized in Section 2.2.2, Table 2.

3.7 Equipment Blanks and Field QC

Collection and analysis of equipment/field blanks will be required for one sampling event. The analysis of field blanks is used to evaluate the levels of contamination that might be associated with the collection of samples and introduce bias into the sample result. Blanks will be collected once at the beginning of the sampling year for PCB congeners, dioxins and furans, PAHs, metals, and mercury analysis. Field blank results for PCB and dioxin/furan congeners should be consistent with the blank criteria in sections 4.1 and 4.2. For PAHs, metals and mercury, field blank results should be less than the method detection limits (MDL).

An aliquot of a clean reference matrix (reverse osmosis water) will be processed through the sampling equipment as a blank. One blank will be collected and analyzed per sampler funnel for a total of four equipment blanks: one for PCB and dioxin/furan congeners, one for PAHs, a third for metals and a fourth for mercury analysis.

Because standard methods for bulk deposition are not available, additional QC samples will be collected for this matrix to evaluate their capabilities. These procedures involve wipe tests after the reverse osmosis water flush is conducted to evaluate the efficiency of the brushing and flushing at removing dry deposition from the funnel walls. A spiked blank sample (field spike) will also be deployed as described below to measure potential loss of analytes from the sampler. These are discussed below and will be used to qualitatively describe sampling efficiency.

3.7.1 Wet Deposition QC Samples

Because bulk samplers will be field deployed for approximately two weeks and analytes of interest may be lost during deployment, field loss QC samples (field spikes) will be collected. For the PCB and dioxin/furan congeners field spike, a 2 L aliquot of reverse osmosis (RO) water will be spiked with 1 mL of PCB standard solution, and 1 mL of native, 0.02 mL of labeled surrogate dioxins/furans.

For the PAH field spike, a 1 L aliquot of RO water will be spiked with approximately 750 ng. (see Appendix C for analyte concentrations in the deployed field spikes). Metals and mercury will be spiked into two 200 mL aliquots of reverse osmosis water. In the third calendar quarter, field spikes will be deployed with the collection vessel in the same manner as the bulk deposition samplers, but with the inlet tubing disconnected. The vent tubing will remain open to allow the spike to remain exposed and equilibrate in the field for the two week deployment period. Expected volatilization loss rates from the collection vessel are unknown. Because low molecular weight PAHs and mercury are known to be much more volatile, loss rates for these parameters are expected to be higher. These QC samples will be the first known attempt to quantify possible bulk deposition sampler loss for these parameters.

3.7.2 Dry Deposition QC Samples

While wet deposition collection efficiency is assumed to be 100%, dry deposition collection efficiency for the bulk samplers is currently unknown. To understand the potential loss or selective sampling of dry particulates with the bulk samplers, wipe tests will be conducted twice during the sampling period on PAH and PCB/dioxins/furans funnels after the dry particulates are brushed and flushed into the collection vessel. Wipe tests will occur once during the second quarter and again in the third quarter for a total of two (2) PAH funnel wipes and two (2) PCB/dioxins/furans funnel wipes.

Wipes are saturated with methanol. For PCBs and dioxins/furans wipes are proofed and supplied by AXYS Analytical Services. KCEL will proof the PAH wipes. Loss rates of individual PAHs, and PCB and dioxin/furan congeners due to inadequate flushing and/or brushing (such as adhering to the funnel and collection tubing), are unknown for this method. Thus, this analysis will investigate this study's measured loss rate.

KCEL will test a proofing process of wipes for metals and mercury analysis. Many wipe materials are likely to be contaminated with multiple metals. If the proofing process is successful, QC wipe tests will be conducted twice on the bulk samplers and analyzed for metals and mercury. If the proofing process is unsuccessful, a second equipment rinse blank will be conducted after brushing and rinsing.

4.0 ANALYTICAL METHODS AND DETECTION LIMITS

Analytical methods for PCB congeners, dioxins/furans, PAHs, metals and mercury analyses are presented in this section, along with analyte-specific detection limits. For the PAHs, metals and mercury, the terms MDL and reporting detection limit (RDL), used in the following subsections, refer to method detection limit and reporting detection limit, respectively. The KC Laboratory reports both the reporting detection limit (KCEL RDL) and the method detection limit (KCEL MDL) for each sample and parameter, where applicable.

EPA's Office of Wastewater generally defines the 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 KCEL 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 trace metals and mercury analyses, KCEL 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. In the case of some Trace Metals and Conventionals tests, MDLs are evaluated by the procedure listed in Appendix D: 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*. 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 Trace Organic mass spectral analyses, a standard analyzed near the KCEL MDL concentration during calibration must produce a valid mass spectra and this standard is used to define the KCELMDL.

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 amounts based upon available sample volumes. Every effort will be made to meet the MDL/RDL goals listed in the SAP.

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 minimum reporting level (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. 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 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. Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result.
- 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 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. No laboratory sample or matrix spike duplicates will be performed for PAHs because the entire bottle contents must be used for each sample. The field replicate will be used to assess precision in the matrix.
- 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 or 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. Spiked blank duplicates will be included for the PAH analyses.
- 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 in LIMS.

4.1 PCB Congeners in Waters and QC Wipe Samples[4]

PCB congener analysis will follow 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 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. An extensive suite of labeled surrogate standards (Table 4) is added before samples are extracted (Concentrations are in Table C-1). Data are "recovery-corrected" for losses in extraction and clean-up, and analytes are quantified against their labeled analogues. 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 which will not affect data usability.

AXYS 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. Method 1668A requires that if an aqueous sample contains more than 1% total solids (measured by mass at AXYS), the solids and liquid will be extracted separately and extracts combined for analysis. Because these bulk deposition samples are expected to be very low in solids (dust) this procedure is not expected to be applicable. If filtration is required, additional laboratory filter blanks (1 per batch of 20) are conducted.

Table 4. Labeled Surrogates and Recovery Standards Used for EPA Method 1668A PCB Congener Analysis

^{13}C-labeled PCB 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
^{13}C-labeled Cleanup Standards				
28	111	178		
^{13}C-labeled Internal (Recovery) Standards				
9	52	101	138	194

[4] QC wipe samples are analogous to solid sample matrix.

Table 5 lists the 209 PCB congeners and their respective target SDL and LMCL values. The reporting limits for individual samples may differ from those in Table 5 since they are determined by signal to noise ratios and changes to final volumes. Typical sample detection limits are shown. Note that several of the congeners co-elute and a single SDL or LMCL value is provided for the congeners in aggregate.

Table 5. PCB Congener water detection limit goals and lower calibration limits by1668A, AXYS Analytical Services method MLA 010 (in pg/L).

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
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

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
CL4-PCB-42	1.0	4.0
CL4-PCB-43	1.0	4.0
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

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
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
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

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
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
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

PCB Congener	Typical Detection Limit/SDL	LMCL based on Low Cal.
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
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 assurance/quality control (QA/QC) samples include method blank, ongoing precision and recovery (OPR) sample, and surrogate spikes. Method blanks and OPR, which are the same as 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 6.

Table 6. PCBs QA/QC Frequency and Acceptance Criteria for Bulk Deposition Samples

	Method Blank	Lab Duplicate (RPD)	OPR (% Recovery)	Surrogate Spikes
Frequency	**1 per batch[a]**	**1 per batch[a]**	**1 per batch[a]**	**Each sample**
PCB Congeners	<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 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.
[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
RPD = Relative Percent Difference
OPR = ongoing precision and recovery

4.2 Dioxins/furans Congeners in Waters and QC Wipe Samples

Dioxins/furans congener analysis will be determined by 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 similar to Method 1668A for PCBs. This method provides reliable analyte identification and very low detection limits. Labeled native and surrogate standards (Table 7, Table C-2) 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.

Table 7. 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	
$^{37}Cl_4$-labeled Cleanup Standards	
1,2,3,4 TCDD	
^{13}C-labeled Internal (Recovery) Standards	
1,2,3,4 TCDD	1,2,3,7,8,9 HxCDD

Table 8 lists the 17 Dioxins/furans congeners and their respective target MRL 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 8. Dioxins/furans water sample detection limit goals and lower calibration limits by EPA method 1613b, AXYS Analytical Services method MLA 017(in pg/L).

Dioxin	Typical Detection Limit/SDL	LMCL based on Low Cal.
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
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 blank, ongoing precision and recovery (OPR) sample, and surrogate spikes. Method blanks and OPR, which are the same as 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 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 9.

Table 9. Dioxins/furans QA/QC Frequency and Acceptance Criteria for Bulk Deposition Samples

	Method Blank	Lab Duplicate (RPD)	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: 1, 5, 10 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
RPD = Relative Percent Difference
OPR = ongoing precision and recovery

4.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Semivolatile organics analyzed for this survey will consist of the PAHs listed in Table 10. The samples will be prepared by solid-phase extraction (SPE) in general agreement with EPA method 3535A. The entire sample container volume is used. The PAHs retained on the SPE disks are eluted with methylene chloride and acetone. The elution solvent is then concentrated via TurboVap/NEvap apparatus to a final volume of 1 mL. Additional cleanups may be performed to ensure adequate instrument performance.

Samples will be analyzed by a modified EPA Method 8270 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 Standard Operating Procedures and MDL study will be completed prior to sample analysis.

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, changes may need to occur to the sample volumes, concentration factors or additional cleanups may be required 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 PAHs in question, it may be analytically preferable to analyze the samples without an LVI or SIM mode rather than greatly dilute them for the GC/MS-SIM LVI system. Prior to implementing a method changes, the project manager will be consulted and method change will undergo a project level review.

KCEL will report each individual polycyclic aromatic hydrocarbon (PAH) result and calculate total high molecular weight PAHs (HPAHs) and total low molecular weight PAHs (LPAHs) as the sum of detected HPAHs or LPAHs, respectively[5].

[5] When no PAHs are detected, the reported MDL/RDL for the total LPAH or total HPAH parameter will be highest MDL/RDL of the individual LPAHs or HPAHs, respectively

Table 10. PAH Target Compounds and Detection Limit Goals in µg/L

Analyte	MDL	RDL	Analyte	MDL	RDL
2-Methylnaphthalene	0.001	0.02	Chrysene	0.00025	0.00125
Acenaphthene	0.001	0.005	Dibenzo(a,h)anthracene	0.0005	0.0025
Acenaphthylene	0.001	0.005	Fluoranthene	0.00065	0.0065
Anthracene	0.0005	0.0025	Fluorene	0.0011	0.0055
Benzo(a)anthracene	0.0005	0.0025	Indeno(1,2,3-cd)Pyrene	0.00025	0.00125
Benzo(a)pyrene	0.00025	0.00125	Naphthalene	0.001	0.04
Benzo(b,j,k)fluoranthene	0.0005	0.005	Phenanthrene	0.001	0.01
Benzo(g,h,i)perylene	0.00025	0.00125	Pyrene	0.0005	0.005

NOTE: The MDL/RDL limits are calculated on a 1 liter extraction to a final volume of 1 ml. MDL/RDL limits will vary depending on amount extracted and final volume.

TBD (to be determined) MDL/RDLs are currently being evaluated and will be updated in a SAP addendum prior to sample analysis. The MDL/RDL limits will be based on extraction of 1 liter of sample to a final volume of 1 ml final extract volume. Final MDL/RDL limits will vary depending on amount extracted and final volume.

In addition to the surrogates and internal standards, which assess sample accuracy and bias, a method blank, spike blank and spike blank duplicate will be analyzed with each QC Batch. PAH spike surrogate concentrations can be found in Table C-3. Field replicates will be analyzed according to the schedule described above. True lab duplicates will not be included in this study. QA/QC frequencies and acceptance criteria are shown in Table 11 for PAH analysis.

Table 11. PAH QA/QC Frequency and Acceptance Criteria

	Method Blank	Spike Blank/Spike Blank Duplicate (% Recovery)
Frequency	**1 per Extraction batch[a]**	**1 per Extraction batch[a]**
PAHs	<MDL	40-160

	Surrogates (% Recovery)
Frequency	**Added to all samples**
2-Fluorobiphenyl	40-160
D14-Terphenyl	40-160

[a] QC Extraction batch = 20 samples or less prepared within a 12 hour shift
< MDL = Method Blank result should be less than the KCEL *method detection limit*.
RPD = Relative Percent Difference
NA = Not Applicable
These control limits are generic because 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.

4.4 Metals

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 1631, Revision E (Cold Vapor Atomic Fluorescence [CVAF]), KCEL SOP 606, ultra-low range. The following detection limit goals are targets for metals and mercury (Tables 12 and 13). Every effort will be made to meet these limits; however, they may increase based on sample results and the need to perform corrective actions due to matrix interferences or analyte concentrations exceeding the linear dynamic range of the instrument. MDL and RDL values will be reported to 2 and 3 significant figures, respectively.

Table 12. Trace Metals Target Analytes and Detection Limits (µg/L)

Analyte	MDL	RDL
Arsenic	0.01	0.05
Cadmium	0.01	0.05
Chromium	0.05	0.25
Copper	0.1	0.5
Lead	0.025	1.25
Nickel	0.05	0.25
Silver	0.01	0.05
Vanadium	0.025	0.125
Zinc	0.5	2.5

Table 13. Mercury Detection Limits (µg/L)

Analyte / Range	MDL	RDL
Mercury / Ultra-Low Range	0.0002	0.0005

Sample accuracy and bias will be evaluated by a laboratory duplicates, spike blanks and matrix spike/matrix spike duplicate samples. QA/QC frequency and acceptance criteria for metals and mercury analysis are as shown in Table 14. Concentrations of metals and mercury in field spike surrogates are presented in Tables C-4 and C-5. Matrix spikes, matrix spike duplicates, and lab duplicates may not be analyzed if sufficient sample volume is not available.

Table 14. Trace Metals and Mercury QA/QC Frequency and Acceptance Criteria

Method	Method Blank	Lab Duplicate	Matrix Spike Duplicate	Spike Blank (% Recovery)	Matrix Spike (% Recovery)
Frequency	1 per batch [a]	1 per batch	1 per batch	1 per batch	1 per batch
Total Metals by ICP-MS	< MDL	RPD $\leq$ 20%	NA	85 – 115%	75 - 125%
Total Mercury by CVAF[b]	< MDL	NA	RPD $\leq$ 24%	77 – 123%	71 - 125%

[a] Batch = 20 samples or less prepared as a set
[b]Total mercury by CVAF requires 3 method blanks.
< MDL = Method Blank result should be less than the KCEL *method detection limit*.
RPD = Relative Percent Difference
NA = Not Applicable

5.0 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 survey study will be validated according to accepted Environmental Protection Agency (EPA) guidelines (EPA 2001, 2004, 2005 and 2010), 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 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 PCB congener and dioxin/furan congener data maybe conducted by either an outside party for this study or by King County WLRD. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

5.2 Reporting

All data and supporting information will be documented in a data report for data collected in 2011and 2012 from the Bulk Deposition Study. Data validation memoranda will be included in the data report, as will copies of COC forms. It is anticipated that data from all sampling events will be validated, reviewed, and ready for release by late-summer or early fall 2012. The data report is expected to be completed by December 2012. 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.

5.3 Record Keeping and Data Management

All hardcopy field sampling records, custody documents, raw lab data, and laboratory summaries and narratives will be archived according to KCEL policy for the Lower Duwamish Waterway Superfund site. A unique matrix code, "Air_Dep" will be used for these samples and sampler deployment duration, funnel area, and sample volume will also be maintained on a per sample basis. Records will include both hard copy and electronic data received from AXYS. Metals, mercury and PAH analytical data produced by the KCEL will be maintained on its LIMS database in perpetuity. AXYS will provide electronic data deliverables 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.

6.0 REFERENCES

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APPENDIX A. BULK DEPOSITION SAMPLER DESIGN

Drainage tubing from funnel to sample bottle,and air vent.

Organics samplers in the field.

Large and small stainless steel funnels for organics and HDPE funnel for metals and mercury sample collection.

APPENDIX B. 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: 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 C. FIELD SPIKE BLANK SOLUTION CONCENTRATIONS

Table C-1 PCB Congener Field Spike Concentrations

PCB Congeners	Congener No.	Concentration of Field Spike Blank (ng/mL)
2-MoCB	1	1
4-MoCB	3	1
2,2'-DiCB	4	1
4,4'-DiCB	15	1
2,2',6-TriCB	19	1
2,3,5-TriCB	23	1
2',3,5-TriCB	34	1
3,4,4'-TriCB	37	1
2,2',6,6'-TeCB	54	1
3,3',4,4'-TeCB	77	1
3,4,4',5-TeCB	81	1
2,2',4,6,6'-PeCB	104	1
2,3,3',4,4'-PeCB	105	1
2,3,4,4',5-PeCB	114	1
2,3',4,4',5-PeCB	118	1
2',3,4,4',5-PeCB	123	1
3,3',4,4',5-PeCB	126	1
2,2',4,4',6,6'-HxCB	155	1
2,3,3',4,4',5-HxCB	156	1
2,3,3',4,4',5'-HxCB	157	1
2,3',4,4',5,5'-HxCB	167	1
2-3,3',4,4',5,5'-HxCB	169	1
2,2',3,3',4,4',5-HpCB	170	1
2,2',3,4,4',5,5'-HpCB	180	1
2,2',3,4,4',5,6'-HpCB	182	1
2,2',3,4',5,5',6-HpCB	187	1
2,2',3,4',5,6,6'-HpCB	188	1
2,3,3',4,4',5,5'-HpCB	189	1
2,2',3,3',5,5',6,6'-OcCB	202	1
2,3,3',4,4',5,5',6-OcCB	205	1
2,2',3,3',4,4',5,5',6-NoCB	206	1
2,2',3,3',4,5,5',6,6'-NoCB	208	1
2,2',3,3',4,4',5,5',6,6'-DeCB	209	1

Table C-2 Dioxins/furans Congener Field Spike Concentrations

Dioxin	Concentrations of Native Congeners (pg/L)	Concentrations of 13C-Labeled Surrogate Congeners (ng/mL)
2,3,7,8 TCDD[1]	200	100
1,2,3,7,8 PeCDD[1]	1040	100
1,2,3,4,7,8 HxCDD[1]	1130	100
1,2,3,6,7,8 HxCDD	1110	100
1,2,3,7,8,9 HxCDD[1]	1080	None
1,2,3,4,6,7,8 HpCDD	950	100
OCDD	2000	200
2,3,7,8 TCDF[1]	214	100
1,2,3,7,8 PeCDF[1]	920	100
2,3,4,7,8 PeCDF	940	100
1,2,3,4,7,8 HxCDF[1]	1000	100
1,2,3,6,7,8 HxCDF	950	100
1,2,3,7,8,9 HxCDF[1]	1050	100
2,3,4,6,7,8 HxCDF	1060	100
1,2,3,4,6,7,8 HpCDF	1000	100
1,2,3,4,7,8,9 HpCDF	1000	100
OCDF	2080	None

1 This congener is labeled $^{13}C_{12}$ in the surrogate solution.

Table C-3 PAH Field Spike Compounds and Concentrations.

PAH Analyte	Concentration of Field Spike Blank (ug/L) assuming 1 L
2-Methylnaphthalene	0.750
Acenaphthene	0.750
Acenaphthylene	0.750
Anthracene	0.750
Benzo(a)anthracene	0.750
Benzo(a)pyrene	0.750
Benzo(b,j,k)fluoranthene	1.5
Benzo(g,h,i)perylene	0.750
Chrysene	0.750
Dibenzo(a,h)anthracene	0.750
Fluoranthene	0.750
Fluorene	0.750
Indeno(1,2,3-cd)Pyrene	0.750
Naphthalene	0.750
Phenanthrene	0.750
Pyrene	0.750

Table C-4 Metals Field Spike Compounds and Concentrations.

Metal Analyte	Concentration of Field Spike Blank (µg/L)
Arsenic	10
Cadmium	10
Chromium	10
Copper	10
Lead	10
Nickel	10
Silver	10
Vanadium	10
Zinc	10

Table C-5 Mercury Field Spike Concentrations.

Mercury	Concentration of Field Spike Blank (µg/L)
Mercury	0.02