
Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan – 2013 Addendum

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King County

Department of Natural Resources and Parks
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Science and Technical Support Section

King Street Center, KSC-NR-0600
201 South Jackson Street, Suite 600
Seattle, WA 98104

206-296-6519 TTY Relay: 711

www.kingcounty.gov/environment/wlr/science-section.aspx

Alternate Formats Available

206-296-7380 TTY Relay: 711

Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan: 2013 Addendum

Prepared for:

King County Department of Natural Resources and Parks
Wastewater Treatment Division
Seattle, WA 98104

Submitted by:

Jenée Colton
King County Water and Land Resources Division
Department of Natural Resources and Parks



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Department of
Natural Resources and Parks

Water and Land Resources Division

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1.0. INTRODUCTION

This sampling and analysis plan (SAP) Addendum describes the 2013 study design and identifies any sampling, analytical, validation or reporting methods or procedures that differ from the 2011 study SAP - Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan (King County 2011).

King County is conducting a study (King County, in progress) comparing the measurements of bulk deposition (dry particulate and rainfall) in areas of different land use within the Green/Duwamish River Basin. The study will provide information to assist in understanding chemical contributions from the air pathway to combined sewer systems in the Lower Duwamish Waterway as well as to assist in general understanding of atmospheric sources to the Lower Duwamish Waterway. The study collected samples from July 2011 to October 2012 at the following sampling locations: Beacon Hill, Duwamish, South Park Community Center, Kent, Kent Senior Activity Center, and Enumclaw. Except for the Kent Senior Activity Center, all these sampling stations are co-located with Puget Sound Clean Air Agency sampling sites.

The bulk deposition data collected under this Sampling and Analysis Plan (SAP) addendum will be used to fill a spatial gap in Georgetown and to collect supplementary data for polychlorinated biphenyls (PCBs) and dioxins/furans in the Lower Duwamish Valley. These data will further assist in understanding atmospheric loadings to the combined sewer systems and provide greater spatial coverage to the drainage area along the Lower Duwamish Waterway.

2.0. STUDY DESIGN

The data quality objectives for this study remain the same as those found in the original SAP (King County 2011). Sampling will be conducted beginning in April, 2013 and concluding in December of the same year. Two stations will be sampled continuously during this period for metals, mercury and polycyclic aromatic hydrocarbon (PAHs) analyses. One of the two stations will be Beacon Hill, which was also sampled in 2011 and 2012. The second station will be at the South Seattle Community College, Georgetown campus. The latter station was selected to represent deposition in the Georgetown neighborhood of the Duwamish Valley and sampling at the Beacon Hill station is intended to provide a reference point to gauge whether observed changes are local or regional in nature. In addition to sampling Georgetown for metals, mercury and PAHs, the Duwamish, South Park and Georgetown stations will be sampled for PCB and dioxins/furan congeners. The Duwamish and South Park stations are being sampled for PCBs and dioxins/furans to increase the amount of data for these analytes; PCBs and dioxins/furans were sampled at a lower frequency compared to other analytes in 2011 and 2012. PCB and dioxin/furan samples will be collected intermittently during the study period. The address, coordinates, and the relative location of all stations are listed in Table 1 and shown in Figure 1.

Table 1. Station Locations and Coordinates

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 ¹	CER	CE	4401 E. Marginal Wy. S.	1268326	209111
South Park ¹	SPCC-R	DD	8201 10th Ave S.	1273043	196688
Georgetown	SSCC	None	6737 Corson Ave S.	1271653	201564

¹ This station was also sampled in 2011 and 2012.

All samplers will be deployed for approximately two weeks during the wet season (April through June and October through December) and for approximately four weeks during the dry season (July – September). Best professional judgment will be used to conclude wet period deployments before sample bottles overflow. Georgetown and Beacon Hill samples for metals, mercury and PAH analyses will be sampled consecutively during the study period. Assuming the first deployment starts on April 9th, 2013, the first samples will be collected and a new deployment will begin on April 23rd, 2013. This deployment will be sustained two weeks before sample collection and the third deployment begins, etc. During the dry season, the deployments will be extended to approximately four weeks duration until the wet season begins again. The sample total for nine months duration in 2013 is estimated to be 16 per station or 32 samples for each analysis (Table 2).

Table 2. Sample Totals for Each Analytical group by Station

Station	Metals	Mercury	PAHs	PCBs & Dioxins/Furans
Beacon Hill	16	16	16	None
Duwamish	None	None	None	5
Georgetown	16	16	16	5
South Park	None	None	None	5
TOTALS	32	32	32	15

Samplers for PCBs and dioxins/furans will be deployed with a frequency of one month per quarter for three quarters with April through June being the first quarter. Therefore, during a wet season quarter, samples will be deployed for two consecutive sampling periods of two weeks each. With a total of two wet season quarters in the study period, the per station sample count is estimated to be four samples. Only one dry season quarter will occur in the study period in which there will be one deployment of one month duration. Thus, one dry season sample per station is anticipated. Cumulatively, there will be a wet and dry season total of five samples per station or 15 samples for PCBs and dioxins/furans analyses (Table 2). If rainfall during the dry season quarter sampling requires cessation of the deployment earlier than 21 days, a second sample will be deployed to cover the remainder of the month.

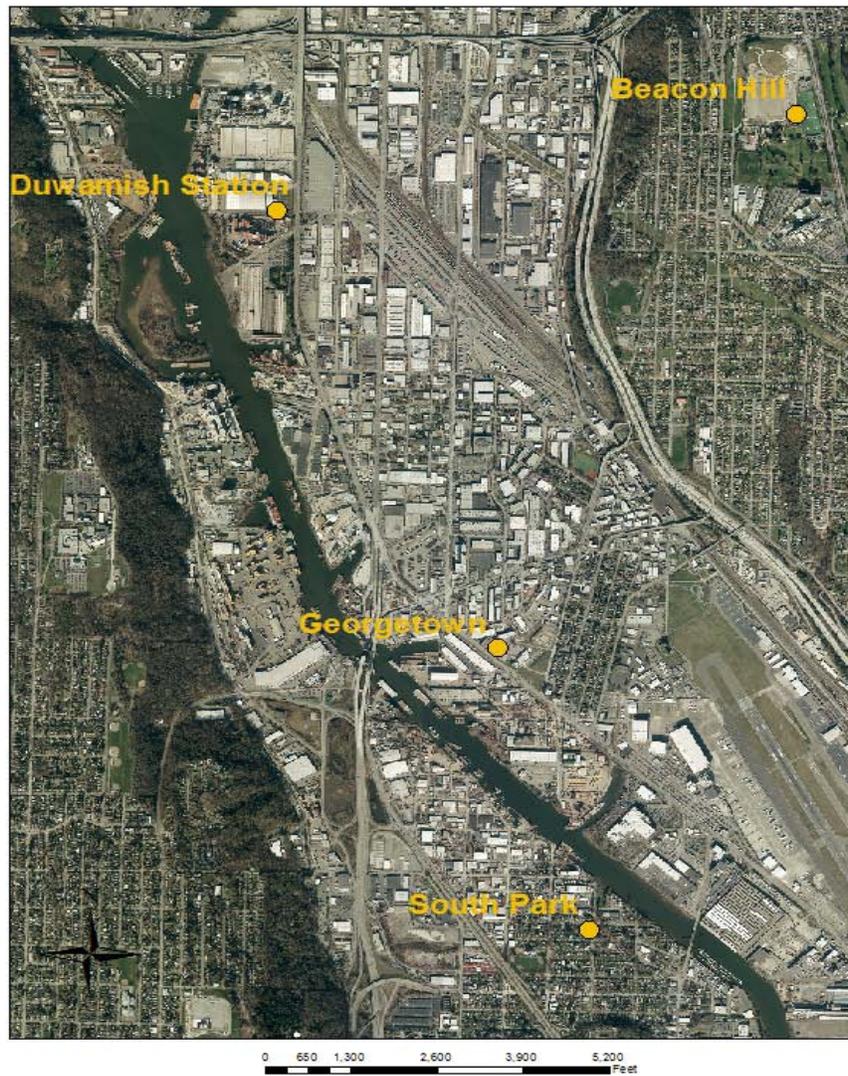


Figure 1. 2013 Bulk Air Deposition Sampling Stations

An anticipated sampling schedule for all locations and analyte types is provided in Table 3. This schedule may be adapted as necessary to accommodate rainfall, replacements for overflow events, and/or staffing schedule conflicts. The primary goals of sampling are to sample continuously for metals, mercury and PAHs analyses and to stay within the total number of samples in the budget: 32 samples each for metals, mercury and PAHs analysis

(96 samples total) and 16 samples for PCBs and dioxins/furans analysis. Therefore, sampling for metals, mercury and PAHs analysis should occur consecutively, without temporal gaps, and cease when these sample totals are met, regardless of the calendar date.

Table 3. Anticipated Sampling Schedule

Event #	Deployment Date	Collection Date	Analysis by Station			
			Beacon Hill	Duwamish	Georgetown	South Park
1	4/9/2013	4/23/2013	Metals, Mercury, PAHs	PCBs & Dioxins/Furans	Metals, Mercury, PAHs, PCBs & Dioxins/Furans	PCBs & Dioxins/Furans
2	4/23/2013	5/7/2013	Metals, Mercury, PAHs	PCBs & Dioxins/Furans	Metals, Mercury, PAHs, PCBs & Dioxins/Furans	PCBs & Dioxins/Furans
3	5/7/2013	5/21/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
4	5/21/2013	6/4/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
5	6/4/2013	6/18/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
6	6/18/2013	7/2/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
7	7/2/2013	7/30/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs,	None
8	7/30/2013	8/27/2013	Metals, Mercury, PAHs	PCBs & Dioxins/Furans	Metals, Mercury, PAHs, PCBs & Dioxins/Furans	PCBs & Dioxins/Furans
9	8/27/2013	9/24/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
10	9/24/2013	10/8/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
11	10/8/2013	10/22/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs,	None
12	10/22/2013	11/5/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs,	None

Event #	Deployment Date	Collection Date	Analysis by Station			
			Beacon Hill	Duwamish	Georgetown	South Park
13	11/5/2013	11/19/2013	Metals, Mercury, PAHs	PCBs & Dioxins/Furans	Metals, Mercury, PAHs, PCBs & Dioxins/Furans	PCBs & Dioxins/Furans
14	11/19/2013	12/3/2013	Metals, Mercury, PAHs	PCBs & Dioxins/Furans	Metals, Mercury, PAHs, PCBs & Dioxins/Furans	PCBs & Dioxins/Furans
15	12/3/2013	12/17/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None
16	12/17/2013	12/31/2013	Metals, Mercury, PAHs	None	Metals, Mercury, PAHs	None

3.0. SAMPLING PROCEDURES

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 will be fabricated at King County Environmental Laboratory (KCEL).

King County Field Science Unit (FSU) staff will conduct all sampling following the procedures described in the original SAP (King County 2011) with one exception: 2-L bottles will be used for metals and mercury sample collection instead of 500 mL bottles. In summary, sampling systems will include a wood-framed structure supporting up to four collection funnels that each drain directly into a sample bottle (see Appendix A of original SAP). The framing will be constructed to hold the collection system about 6 feet off the ground or roof, depending on the station. One sampling system will be constructed for each sampling site (4 locations) and catered to the analyte requirements.

Each organics (i.e., PAHs or PCBs/dioxins/furans) 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 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 full sampling system for all analytes. Samples for metals and mercury will be collected in two separate 2-L sample bottles. One organics sampler will collect samples for PCB and dioxins/furan congener analysis by AXYS Analytical Laboratories, and a separate organics sampler will collect samples for PAHs analysis by King County Environmental Laboratory (KCEL). The metals and mercury samples will also be analyzed by KCEL.

All sample handling, sampling equipment, decontamination procedures, chain of custody and sample documentation will be the same as that listed in the original SAP. Quality control samples will include one equipment blank to be collected using the same procedures described in the original SAP. Field replicates will not be collected because of budget constraints and because field replicate data is available from the 2011 and 2012 sampling period.

4.0. ANALYTICAL METHODS

Samples will be analyzed using the same methods described in the original SAP. Metals samples will be analyzed and reported by EPA Method 200.8 (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL SOP 624, ultra low range. The specific metals to be analyzed include: arsenic, cadmium, chromium, copper, lead, nickel, silver, vanadium and zinc. Mercury will be analyzed by EPA Method 1631, Revision E (Cold Vapor Atomic Fluorescence [CVAF]), KCEL SOP 606, ultra-low range. PAH 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) (KCEL SOP 772v0). The specific PAHs to be analyzed and their detection limits are listed in Table 4.

Table 4 PAH Target Compounds and Detection Limits in µg/L

Analyte	MDL	RDL	Analyte	MDL	RDL
2-Methylnaphthalene	0.0010	0.0100	Chrysene	0.00025	0.00100
Acenaphthene	0.0010	0.00250	Dibenzo(a,h)anthracene	0.00050	0.00100
Acenaphthylene	0.0010	0.00250	Fluoranthene	0.00065	0.00400
Anthracene	0.00050	0.00100	Fluorene	0.0011	0.00250
Benzo(a)anthracene	0.00050	0.00100	Indeno(1,2,3-cd)Pyrene	0.00025	0.00100
Benzo(a)pyrene	0.00025	0.00100	Naphthalene	0.0010	0.0200
Benzo(b,j,k)fluoranthene	0.00050	0.00200	Phenanthrene	0.0010	0.0100
Benzo(g,h,i)perylene	0.00025	0.00100	Pyrene	0.00050	0.00400

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. When there is no rainfall, it is possible that the volume may be as low as 400 ml which would increase the MDLs and RDLs.

PCB congener analysis for all 209 congeners will follow EPA Method 1668A Revision C (EPA 2010a), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. Lastly, dioxins/furans congener analysis for 7 dioxin and 10 furan congeners 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.

For the PAH analyses, the spike blank, spike blank duplicate and surrogate recovery limits will be based on laboratory QC limits; these are empirically derived performance-based laboratory control limits. These limits may be updated once per calendar year and the limits in effect at the time of analysis will be used. For the metals and mercury, QA/QC requirements for the laboratory control samples will also be based on laboratory QC limits; all other requirements are the same as in the original SAP.

The deposition volume of the samples will be measured by mass for metals and mercury sample bottles. Because of the heavy weight of the 4-L glass organics sample bottles and lack of an appropriate scale for such a mass, deposition volume for organics will be measured by volume.

5.0. DATA VALIDATION, REPORTING AND RECORD KEEPING

This section summarizes the data validation, reporting, and record keeping for the samples collected under this SAP Addendum which remain the same as described in the original SAP.

5.1 Data Validation

Chemical data generated during this survey study will be validated according to accepted Environmental Protection Agency (EPA) guidelines (EPA 2008 and 2010b), 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. For analyses performed by KCEL, the validator will also review data anomaly forms (DAFs) generated by the laboratory. These forms include any issues related to 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. PCB and dioxin/furan data will undergo a Level III data validation. 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 will be conducted by an outside party for this study. Data validation memoranda will be produced and maintained along with the analytical data as part of the project records.

5.2 Reporting

All data and supporting information will be documented in a data report for data collected in 2013 from the Lower Duwamish Waterway Bulk Atmospheric 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 and reviewed by second quarter of 2014. The data report is expected to be completed by third quarter of 2014. 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_DepBulk" 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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