Lower Duwamish Waterway Source Control: Supplemental Bulk Atmospheric Deposition Study Final Data Report

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King County

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Acronyms

µg/L	micrograms per liter
µg/m^2	micrograms per meter squared
ANOVA	analysis of variance
AXYS	AXYS Analytical Services Laboratory
cm	centimeters
COCs	chemicals of concern
CSO	combined sewer overflow
CVAF	cold vapor atomic fluorescence
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
FP	fine particles

HPAH	high-molecular weight polychlorinated biphenyls
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
KCEL	King County Environmental Laboratory
Kent SC	Kent Senior Activity Center
L	liter
LDW	Lower Duwamish Waterway
LIMS	King County Laboratory Information Management System
LMCLs	lowest method calibration limits
LPAHs	low-molecular weight polychlorinated biphenyls
MDL	method detection limit
mL	milliliter
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
pg/L	picograms per liter
ppm	parts per million
PM	particulate matter
PSCAA	Puget Sound Clean Air Agency
QC	quality control
RDL	reporting detection limit
RO	reverse osmosis
SAP	sampling and analysis plan
SDL	specific detection limit
SOP	standard operating procedure
SPE	solid-phase extraction
TEFs	toxicity equivalency factors
TEQs	toxicity equivalents
WTD	King County Wastewater Treatment Division

EXECUTIVE SUMMARY

King County is currently conducting several studies to characterize potential sources of contaminants of concern identified in the Lower Duwamish Waterway (LDW) Superfund site. These studies evaluate chemical concentrations in water, sediment and suspended solids in the Green River Watershed and in atmospheric deposition within the Green/Duwamish River Watershed that may contribute chemical inputs to the LDW.

This study supplements a previous atmospheric deposition study conducted in 2011/2012. This report, like the previous one, presents study results examining how atmospheric deposition of pollutants in the Green/Duwamish River Watershed varies with land use type and degree of urbanization. The amount of information previously available on air deposition as a source pathway to the Lower Duwamish Waterway was limited; these studies strengthen existing local knowledge and will provide more information to Ecology and other entities for use in source control investigations. The objectives of these studies were to compare measurements of bulk deposition (dry particulates and precipitation) at a small number of stations in areas with different land uses and development density within the Green/Duwamish River Watershed and provide information to assist in understanding of atmospheric contaminant sources to the Lower Duwamish Waterway (LDW). The results of the 2011/2012 study were previously presented in a separate report (King County 2013a). That report recommended that additional PCB and dioxin/furan congener data be collected to increase the ability to detect temporal trends and relationships with weather parameters and air concentrations of fine particulate matter. The report also suggested adding a third sampling location in the Duwamish River Valley to evaluate variability between stations. Thus, a supplemental study was designed and implemented in 2013 to pursue these recommendations. This data report presents the results of the 2013 sampling program and discusses the combined results of both studies with respect to spatial and temporal observations of deposition and relationships with environmental parameters (e.g., temperature, wind).

Four stations were monitored in 2013; three of which were previously monitored in the 2011/2012 study and one station that was new in 2013. Three stations are located in the LDW Valley: Duwamish, South Park, and Georgetown. The Duwamish station represents industrial land use in an urban area and the South Park and Georgetown stations represent a mix of commercial, industrial, and residential land uses in urban areas. These three sites are centrally positioned in the LDW Valley. A fourth station at Beacon Hill was selected to represent urban residential land use outside the Valley. Samples from Beacon Hill and Georgetown were analyzed for metals, mercury, and polycyclic aromatic hydrocarbons (PAHs). Samples from the three LDW stations were analyzed for polychlorinated biphenyl (PCB) and dioxin/furan congeners. The sampling design was intended to increase sample sizes for congener data at 2011/2012 LDW stations and add a full chemical suite of data for the Georgetown location with Beacon Hill sampled in parallel for comparison. Samples for the analysis of metals, mercury, and PAHs were continuously collected at each station over the study period, while samples for PCB and dioxin/furan congener analysis were collected intermittently.

Stations monitored only in 2011/2012 included Kent, Kent Senior Activity Center (Kent SC) and Enumclaw. The Kent stations are located in a suburban area of primarily commercial land use while the Enumclaw site is located in a rural area with primarily forested land use.

Contaminant deposition data from both studies were combined and analyzed to evaluate spatial and temporal differences in daily deposition rate. Deposition rates for metals (including mercury) and organic compounds (i.e. PAHs, PCBs, dioxins/furans) were generally higher at stations with greater urbanization. Enumclaw (representing forested land use in a rural area) usually experienced the lowest atmospheric deposition rates of the measured chemicals, while the Duwamish, Georgetown, or South Park locations often experienced the highest contaminant atmospheric deposition rates. Georgetown station often exhibited the highest median deposition rates for metals compared to all other stations. Average PCBs deposition rates at this location were significantly higher than any other station. Major transportation activity located within the Georgetown area may influence contaminant deposition at this station; however, the particular cause of elevated deposition of organic compounds and metals in this area is unknown. It should be noted that only one station was sampled in each LDW Valley neighborhood. The inherent spatial variability of air deposition means that the measured deposition rates do not likely represent an average deposition rate for that neighborhood.

PCB congener contributions to Duwamish and Beacon Hill samples appear similar to each other as do those at South Park and Georgetown. Congener patterns at Enumclaw appear different than at other stations. This preliminary PCB congener analysis indicates that local sources vary by location. Average dioxin/furan congener contributions to atmospheric deposition were generally consistent between Beacon Hill, Duwamish, Georgetown, South Park and Kent SC stations; Kent and Enumclaw each differ from the others.

The washout of particulate matter from the air by rainfall may influence metals and mercury deposition rates and help to explain temporal deposition patterns observed during the late dry- and early wet seasons of both 2011 and 2013. Further study and analysis is needed to investigate the temporal trends in metals deposition observed in the dry to wet period transition.

Of the environmental drivers evaluated (i.e., wind speed, temperature, rainfall, fine particulate concentrations), average wind speed and fine particulate concentrations in the air were found to be the most important environmental drivers of metals deposition. Average temperature and total rainfall were not as important for metals deposition. Average fine particulate concentration was found to be a significant driver for high molecular weight PAHs and total PCB deposition but not for dioxin/furan deposition. Average temperature was also found to be a significant driver for total PCB deposition. Fine particulate matter concentrations and average temperature are moderately useful for predicting total PCB deposition, but relatively poor for predicting high molecular weight PAHs deposition.

Air deposition is highly variable over time and space; however, urbanization does appear to result in higher local air deposition of the metals and organic compounds measured in this study. Additional PCB and dioxin/furan congener data analysis (e.g., fingerprinting) and collection of additional particulate data may provide more insight regarding the types of sources contributing to contaminant air deposition in the Lower Duwamish Waterway.

1.0 INTRODUCTION

This report presents an analysis of how atmospheric deposition of pollutants in the Green/Duwamish River Watershed varies with land use type and proximity to various levels of urbanization. Two studies have been conducted: one in 2011/2012 and a supplemental study in 2013. The objectives of these studies were to (1) compare the measurements of contaminant bulk deposition (dry particulates and precipitation) stations in areas of different land use and urbanization within the Green/Duwamish River Watershed, and (2) to provide information to assist in understanding atmospheric sources of contaminants to the Lower Duwamish Waterway (LDW). The results of the 2011/2012 study were previously presented in a separate report (King County 2013a). That report recommended that additional polychlorinated biphenyl (PCB) and dioxin/furan congener data be collected to increase the ability to detect temporal trends and relationships with weather parameters and fine particulate matter (PM) 2.5[1] concentrations. The report also suggested adding a third sampling location in the Duwamish River Valley to look at variability between stations in the Valley. A supplemental study was designed to pursue these recommendations.

This data report presents the results of the 2013 supplemental sampling program and discusses the combined results of both studies with respect to spatial and temporal observations and relationships with environmental parameters (e.g., temperature, wind). This report describes the project background and geographic study area (Section 1.0), the sample collection and processing methods (Section 2.0), the laboratory analytical methods (Section 3.0), data analysis (Section 4.0), and the results (Section 5.0). Section 5.0 summarizes the results of the 2013 study as well as the combined 2011/2012 and 2013 datasets. The end of Section 5.0 includes presentation of multivariate analyses investigating spatial patterns and relationships between chemical flux and environmental parameters. A discussion of the findings and conclusions of this study are in Section 6.0. Supporting appendices include chain of custody forms, laboratory data results, chemistry flux[2] data, chemistry data validation reports and a summary of LPAH data[3].

1.1 Project Background

King County is a member of the Source Control Work Group for the Lower Duwamish Waterway (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 collaborates to understand

[1] PM 2.5 is a measurement of atmospheric concentrations of particles < 2.5 microns in size.
[2] "Flux" is used in this report to refer to the mass of a chemical deposited on one square meter of land surface per day.
[3] LPAH data were excluded from the main report because of low bias associated with the sampling methods applied. These data were deemed meaningful for indications of relative spatial differences in flux because the bias is expected to be similar across stations. However, LPAH flux data should not be used for quantitative estimates (e.g., loadings calculations).

potential sources of contaminants to the LDW Superfund site and works to control and reduce sources that can contaminate sediments and resident fish and shellfish in the waterway. King County wants to better understand the potential sources and pathways of contaminants of concern (COCs) identified in the LDW Superfund site that contribute chemical inputs and is currently conducting several studies to evaluate chemical concentrations in various media in the Green/Duwamish Watershed.

King County previously completed chemical analysis of whole water samples at a number of combined sewer overflows (CSOs) [4] in the LDW Basin (King County 2011a) and has been characterizing solids within the combined sewer structures and lines that discharge to the LDW (King County 2011b). King County has also completed studies of sediment and water quality in the Green River Watershed (King County 2011c, 2014a, 2014b, 2015) and is currently conducting a study to evaluate chemical concentrations in suspended solids in the Green River Basin (King County 2013b). As previously discussed, the County has also recently completed studies of chemical mass flux in atmospheric deposition within the Green/Duwamish River Watershed (King County 2011d, 2013a). The bulk atmospheric deposition study presented here is intended to complement data from these additional studies and to supplement the previous 2011/2012 bulk atmospheric deposition investigations.

King County conducted atmospheric deposition sampling in the LDW basin from 2005 to 2007 (King County 2008). This sampling focused on phthalates, but data were also collected for polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyl (PCB) Aroclors®. Additional bulk atmospheric deposition data were collected in 2011 and 2012 to fill data gaps for other COCs and to provide additional understanding of the spatial variability of bulk atmospheric deposition across the range of land uses within the Green/Duwamish River Watershed (King County 2013a). The COCs were metals, including mercury, PAHs, and dioxin/furan and PCB congeners. The study focused on these contaminants because the LDW Remedial Investigation (RI) identified these chemicals as COCs for human health and/or ecological receptors within the LDW.

Additional bulk atmospheric deposition data were collected in 2013 to increase the sample size for PCB and dioxin/furan congener data, and provide data for the Georgetown area within the LDW. The bulk atmospheric deposition data collected in the 2011/2012 and 2013 studies assists in understanding atmospheric sources across the watershed, including areas with combined sewer systems (CSOs), separated stormwater basins, and less developed upstream basins which drain to the Green River. Specifically, King County conducted this work to help identify the significance of COCs in this pathway, better understand any spatial differences, and as a line of evidence in evaluating sources to the LDW.

[4] CSOs include discharges of both industrial and municipal wastewater and stormwater.

1.2 Study Area

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 overall study area for the bulk atmospheric deposition study remains as described in the 2011/2012 Data Report (King County 2013a) and includes the LDW, Lower Green, and Middle Green portions of the Green/Duwamish Watershed. This study area spans a gradient of development density and land use designed to allow detection of differences in bulk atmospheric deposition rates. The scope of the study area for this supplemental bulk atmospheric deposition study (supplemental study) was limited to the LDW and the urban reference station at Beacon Hill. The land use within the LDW includes urban industrial, commercial, residential, and transportation corridors, while Beacon Hill is mainly urban residential in nature.

2.0 FIELD SAMPLING METHODS

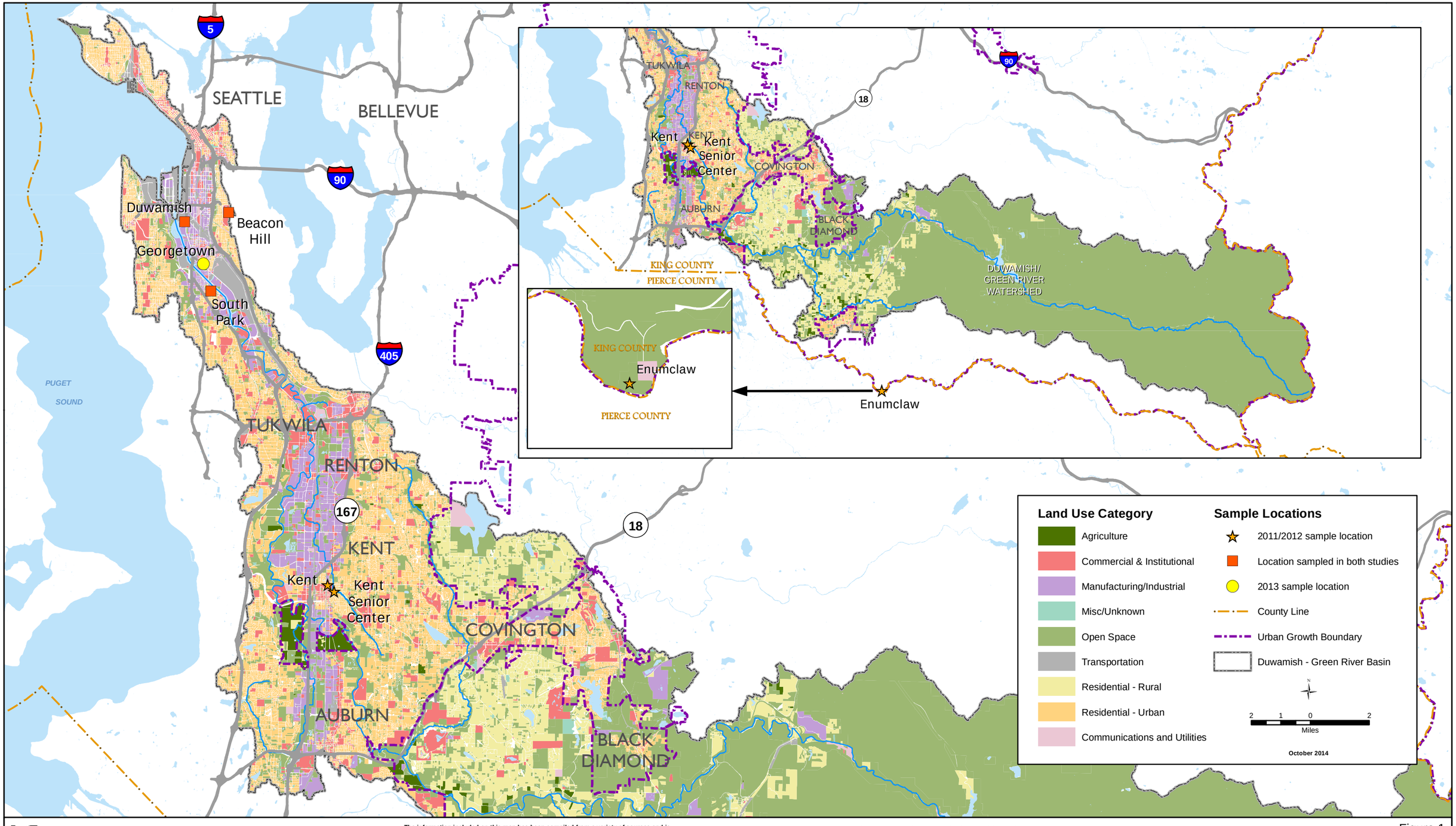
This section reviews the field sampling methods used in this supplemental study. The field procedures are described in greater detail in the project Sampling and Analysis Plan (SAP) Addendum (King County 2013c). The locations where atmospheric deposition samples were collected are described in Section 2.1. The methods for field sample collection and processing are summarized in Section 2.2. Section 2.3 summarizes the sampling schedule for the study and Section 2.4 notes deviations from the project SAP that occurred during field sampling (King County 2013c). Copies of completed chain-of-custody forms used to track sample custody are presented in Appendix A.

2.1 Sample Locations and Analytes

Four stations were selected for sampling in the supplemental study (see Figure 1, Table 1). With the exception of the Georgetown location, all of these stations were also included in the previous study and are also part of the Puget Sound Clean Air Agency Monitoring (PSCAA) regional network of air monitoring stations. This allows for co-location with other monitored parameters such as air temperature and rainfall which can co-vary with bulk atmospheric deposition. The Georgetown station was located at the South Seattle Community College – Georgetown Campus, on the roof of a campus building. No other air monitoring occurs at this location by King County, Ecology, or PSCAA.

Three of the four stations are located in the LDW: the Duwamish, South Park, and Georgetown. The Duwamish station represents industrial land use in an urban area and the South Park and Georgetown locations represent a mix of commercial, industrial, and residential land uses in an urban area. These three sites are centrally positioned in the LDW corridor. Lastly, a fourth station at Beacon Hill was selected to represent urban residential land use. This site, which also represents an EPA Pacific Northwest urban scale air toxics station (Ecology 2012a), was retained in the supplemental study to serve as an urban reference location for comparison with the Georgetown station. The Beacon Hill station is owned and operated by Ecology. The Duwamish and South Park stations are owned and operated by PSCAA.

Target analytes varied by station. The Georgetown and Beacon Hill stations were sampled for metals, mercury, and PAHs. The three LDW stations were sampled for PCB and dioxin/furan congeners. Georgetown station was the only one sampled for all analytes. See Section 3.0 for the specific chemicals included in each analyte group.



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**Land use categories were designated based on King County Assessor data from May, 2013. Residential land was split into urban and rural based on the Urban Growth Area Line for 2013. Parcels with over 50% cultivated land cover, based on the 2007 Landsat Landcover classification, were designated as agricultural land.*

Figure 1

All Bulk Atmospheric Deposition Sampling Stations and Associated Land Use in the Green/Duwamish River Basin

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Table 1. Supplemental Air Sampling Locations and Locator Names

Station Location	KC Locator	PSCAA ID	Location	State Plane Easting[3]	State Plane Northing[3]
Beacon Hill, relocated[1]	BWR	BW	15th S. and Charlestown, Seattle	1276200	210777
Duwamish relocated [2]	CER	CE	4401 E. Marginal Way S., Seattle	1268326	209111
South Park	SPCC-R	DD	8201 10th Ave S. Seattle	1273043	196688
Georgetown	SSCC	None	6737 Corson Ave. S, Seattle	1271653	201564

[1]The PSCAA Beacon Hill sampling station was historically located approximately 300 meters to the northwest of the current location. It was moved in 2006 to accommodate changes in the covered reservoir/park which is nearby.
[2]The PSCAA Duwamish station was historically located 600m to the south-southeast of the current location.
[3]Coordinates are in North American Datum 1983 (NAD83) Washington State Plane North (4601)

2.2 Sample Collection and Processing

Sampling systems were constructed based on the design described in the project SAP (King County 2011d) and consisted of a wood-framed structure supporting up to four collection funnels that each drain directly into a sample bottle. Collection funnels sat approximately six feet above the ground or roof, depending on the station. Each sampling system was comprised of one or two organics samplers, and if identified in study design, a metals sampler and a mercury sampler. Organics samplers collected dry and wet deposition with a stainless steel funnel connected to a 4L amber glass sample bottle by Teflon® tubing. The sample bottle was protected from light by a wooden enclosure. One organics sampler collected samples for PCB and dioxin/furan congener analyses and a second organics sampler collected samples for PAHs analysis. Mercury and metals samplers collected wet and dry deposition with a plastic funnel (high-density polyethylene) connected to a 2 L fluoropolymer sample bottle.

Larger diameter (45 cm) funnels were deployed with the organics samplers during the dry season (July 2 through September 5) while smaller diameter (23 cm) funnels were deployed during the wet season. Differences in funnel size were necessary to collect sufficient mass for analysis in the dry season yet prevent overflow in the collection vessels during the wet season.

Carboys, funnels, and other sampler components were cleaned using: (1) laboratory detergent; (2) a deionized water rinse; and (3) an acetone rinse. The collection bowl and attached tubing were cleaned at King County Environmental Laboratory (KCEL) prior to deployment. The 4 L amber glass sample bottles for PCB and dioxin/furan congener samples were proofed and provided by AXYS Analytical Services (AXYS). KCEL pre-cleaned similar 4 L amber glass bottles for PAH samples. Sample bottles for metals and mercury analysis were cleaned prior to use by KCEL using the following steps: fill each bottle with 1:1 nitric acid and soak in a hot water bath for 24 hours, rinse with reagent water, then repeat these two steps and fill the bottle with 1% hydrochloric acid instead of nitric acid.

Samples were collected by consecutively targeting 2- to 4-week collection periods for PAHs, metals and mercury. Because a limited number of samples were collected for PCB and dioxin/furan analyses, the collection periods for these samples were not necessarily consecutive. Shorter collection periods occurred during the wet season for all samples (i.e. October–May) to reduce risk of sample overflow. Longer collection periods were employed during the dry season (i.e. June–September) to maximize atmospheric deposition collection.

At the time of retrieval, the rainfall level or "deposition volume" in each collection vessel was recorded on the sample container using lab tape and a marking pen. After marking the water level on the sample container, a known quantity of reverse osmosis (RO) water was used to rinse dry particulates from the funnel into each collection vessel (i.e. rinse volume). Removal of particulates was enhanced by brushing the funnel during rinsing with a natural hair, acetone-cleaned paintbrush. Following this step, the funnel was disconnected, and the collection vessel was capped and stored on ice during return to KCEL. The rinse volume and funnel surface area were recorded on field sheets and entered along with deposition volume into the King County Laboratory Information Management System (LIMS).

The organics sampler for PCBs and dioxins/furans was removed from the field between sampling periods and re-cleaned and stored at KCEL before redeployment[5]. Organics sampler units for PCBs and dioxins/furans were dedicated to each station and remained with their assignments throughout the study. The other samplers (for metals and PAHs) remained in the field continuously and were only rinsed with RO water as per the sample collection protocol between sampling periods. A total of three field replicates were collected for PAHs analyses.

2.3 Sampling Schedule

Bulk atmospheric deposition sampling began on April 10, 2013 and the last sample was collected on December 24, 2013. Samples for PAHs, metals and mercury analyses were collected continuously at all stations (Table 2). Exceptions occurred when high wind conditions caused blow-over of collection funnels. When samplers were blown over by wind, the samples were discarded. The deployment period ranged from 7 to 30 days for metals, mercury, and PAHs samples.

Samples for PCBs and dioxin/furan analyses were collected intermittently due to budget limitations (Table 3). The number of stations sampled and the locations varied with deployment date. The deployment period to collect samples for PCBs and dioxin/furan analysis ranged from 7 to 29 days.

[5] Samples for PCB and dioxin/furan congeners were collected at a lower frequency; samples for all other parameters were collected continuously.

Table 2. Sample Collection Dates at Each Station for Metals, Mercury and PAHs Analyses

Deployment End Date	Days Deployed	Beacon Hill	Georgetown
4/25/2013	15	X	X
5/9/2013	14	X	X
5/23/2013	14	X	X
6/6/2013	13	X^R	X
6/19/2013	13	X^R	X
7/2/2013	13	X	X
8/1/2013	30	X^R	X
8/29/2013	28	X	X
9/5/2013	7	X	X
9/25/2013	20	X	X
10/2/2013	7	X	X
10/17/2013	15	X	X
10/31/2013	14	X	X
11/14/2013	14	X	X
11/26/2013	12	X	X
12/11/2013	16	X	X
12/24/2013	13	X	X

X^R = Field replicate collected for PAH analysis

Table 3. Sample Collection Dates at Each Station for PCBs and Dioxin/Furan Analyses

Deployment End Date	Days Deployed	Duwamish	South Park	Georgetown
4/25/2013	15	X	X	X
5/9/2013	14	X	X	X
8/1/2013	30	X	X	X
10/31/2013	14	X	X	X
11/14/2013	14	--	X	X

-- = Sample lost due to wind blowing sampler over.

The total number of samples, including field replicates, collected at each station ranged from 8 at the Duwamish station to 61 at the Georgetown station (Table 4). At the Beacon Hill and Georgetown stations, 17 or more samples were collected each for PAHs, metals and mercury analyses. Four to five samples were collected for PCBs and dioxin/furan analyses at each station with the exception of Beacon Hill where these parameters were not analyzed.

Table 4. Sample Totals for Each Analyte Group by Station

Analyte Group/Station	Beacon Hill	Duwamish	South Park	Georgetown
PAHs	20	0	0	17
Metals	17	0	0	17
Mercury	17	0	0	17
PCBs	0	4	5	5
Dioxins/Furans	0	4	5	5
Totals	**54**	**8**	**10**	**61**

2.4 Deviations from the SAP

Sampling methods that deviated from the project SAP and Addendum are summarized here:

- Field replication was not included in the SAP. Three PAH field replicates were collected, but this deviation to the SAP does not impact data quality or data analyses. During the 2011/2012 study, an inconsistently low spike blank recovery of benzo(a)pyrene (BaP) was observed which led to qualification of the results due to low bias (King County 2013a). Blank spike recovery was used as a quality control metric for accuracy because the volume collected for atmospheric deposition samples was too low to allow for matrix spike analyses. Two causes of the highly variable BaP spike blank recoveries were suspected: variability related to the extraction method and variability related to use of laboratory reverse-osmosis (RO) water as a matrix substitute for atmospheric deposition samples. After the SAP addendum was completed, three PAH field replicates were added to the study plan to investigate the lab RO matrix substitution issue through further measurement of BaP variability in the sample matrix. Improvements made to the extraction method before the 2013 sampling began resulted in BaP spike blank recoveries all within control limits in 2013. Thus, it was concluded that no further corrective action was necessary to address this issue in the 2013 sampling and analysis.

3.0 LABORATORY METHODS

A summary of analytical methods for PAHs, metals, mercury, and PCB and dioxin/furan congener analyses is presented in this section. KCEL reports both the reporting detection limit (RDL) and the method detection limit (MDL) for each sample and parameter, where applicable. 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. Therefore, PCB congener and dioxin/furan congener data are reported to lowest method calibration limits (LMCLs) and flagged down to the sample specific detection limit (SDL) value. In many cases the congener-specific SDL is below the LMCL. KCEL conducted analyses for all parameters, except for PCB and dioxin/furan congeners which were analyzed by AXYS Analytical.

3.1 Metals and Mercury

With the exception of mercury, all metals samples were analyzed by EPA Method 200.8 (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL Standard Operating Procedure (SOP) 624, ultra-low range. The specific metals analyzed included: arsenic, cadmium, chromium, copper, lead, nickel, silver, vanadium, and zinc. Mercury was analyzed by EPA Method 1631, Revision E (Cold Vapor Atomic Fluorescence [CVAF]), KCEL SOP 606, ultra-low range.

3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs samples were prepared by solid-phase extraction (SPE) in general agreement with EPA method 3535A. Samples were analyzed by a modified EPA Method 8270 Gas Chromatography/Mass Spectrometry – Selected Ion Monitoring Large Volume Injection method (GC/MS-SIM LVI), developed for this project (see KCEL SOP 772v0). The specific PAHs analyzed included: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, benzo(b,j,k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluorene, fluoranthene, indeno (1,2,3-cd)perylene, naphthalene, phenanthrene, and pyrene.

3.3 PCB Congeners

PCB congener analysis followed EPA Method 1668A Revision C (EPA 2010), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. The analysis included all 209 PCB congeners. This method provides reliable analyte identification and very low detection limits.

AXYS performed the analysis according to their SOP MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668. Whenever possible, one liter samples were extracted followed by standard method clean-up, which included layered Acid/Base Silica, Florisil, and Alumina. Analysis was performed with an SPB Octyl column

and a secondary DB1 column used to resolve the co-eluting congeners PCB156 and PCB157.

3.4 Dioxin/Furan Congeners

Dioxin/furan congeners were analyzed 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. The analysis included 7 dioxin and 10 furan congeners. This method provides reliable analyte identification and very low detection limits. AXYS performed this analysis according to their SOP MLA-017 which is based on EPA Method 1613B Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.

3.5 Deviations from the SAP

The extraction process for PAH samples was adjusted prior to the 2013 supplemental study to improve the benzo(a)pyrene recoveries measured in blank spike samples in the main study. The key change included increasing the number of times the acetone wash step was implemented from once to twice. This change reduced the amount of water retained on the speedisk and increased the extraction efficiency of the methylene chloride elution for benzo(a)pyrene. These changes were not reflected in the project SAP. This change resulted in improved data quality control measurements for the samples.

4.0 DATA ANALYSIS

The analytical concentration data were prepared for data analysis by conversion to flux and by applying rules for managing laboratory and field replicates, PAH, PCB and dioxin/furan sums, and dioxin Toxicity Equivalents or TEQs. Various statistical methods were also employed to analyze the results. The methods for these calculations are described in this section.

4.1 Conversion to Flux

Concentration data must be standardized before results can be compared due to differences in deployment duration, sample rinse volume, rainfall volume and the funnel size used for collection of atmospheric deposition samples. Thus, concentrations as mass per volume were converted to flux as mass deposited per unit area per day. Flux refers to the rate of flow of particles and rainfall (i.e. bulk air) from air to the land surface; it is a way to express deposition rate. The algorithm used to convert concentration to flux is:

Concentration (µg/L) x (Rainfall volume (L) + Sample rinse volume (L)) / Funnel area (m^2)/Deployment duration (days) = Flux (µg/m^2-day)

All data analyses were conducted using flux values.

4.2 Summation for PAHs, PCB and Dioxin/Furan Congeners

Chemical group fluxes were based on total concentrations to simplify data analysis and interpretation. PAHs were summed as low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs) following the definitions set under the Washington State Sediment Management Standards (Ecology 2013): LPAHs included acenaphthene, acenaphthylene, anthracene, fluoranthene, naphthalene, and phenanthrene. HPAHs included benzo(a)anthracene, benzo (g,h,i)perylene, benzo(a)pyrene, benzo(b,j,k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluorene, indeno (1,2,3-cd)perylene, and pyrene. The following rules were applied for handling of nondetect compounds:

- The sum includes only detected compounds.
- When all results are nondetect, the flux based on the single highest nondetect value (U-flagged) represents the sum.

The PCB and dioxin/furan congener results were summed by including only detected congeners.

4.3 Laboratory and Field Replicates

Laboratory replicates were considered laboratory quality control values and were not used in data analysis but rather as part of the data validation process. Field replicate results

were considered a second estimate of the sample and were combined with their primary sample result using the following rules:

- All concentrations were converted to fluxes[6].
- When sample results were nondetect (U-flagged) in both samples, the highest of two fluxes based on U-flagged data was used. This was often the MDL value.
- When one result was a detect and one a nondetect, the combined value was the average of the detected value flux and ½ the U-flagged flux.
- When both results were detected, the two fluxes were simply averaged.

The total LPAHs, HPAHs and PCBs were summed prior to applying these rules for field replicates.

4.4 Dioxin Toxic Equivalents (TEQs)

Dioxin and furan congener data were evaluated on a concentration basis and on a TEQ basis because the cleanup targets for the LDW are based on dioxin TEQs. TEQs provide a toxicity-based approach to interpret the dioxin and furan congener data. Dioxin and furan congener concentrations were converted to TEQs based on 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) toxicity by first converting concentration to flux, then multiplying by toxicity equivalency factors (TEFs) for mammals from Van den Berg et al. (2006) (Table 5) to result in a TEQ flux. The dioxin TEQ flux was based on summing the 17 TEQ values. Whenever a dioxin or furan congener was not detected, the TEF was applied to the flux based on the full non-detect value (or U qualified value)[7].

Table 5. TEFs Applied in Calculation of Dioxin TEQs

COMPOUND	TEF
Dioxins	
2,3,7,8-TCDD	1
OCDD	0.0003
1,2,3,4,6,7,8-HPCDD	0.01
1,2,3,4,7,8-HXCDD	0.1
1,2,3,6,7,8-HXCDD	0.1
1,2,3,7,8,9-HXCDD	0.1
1,2,3,7,8-PECDD	1
Furans	
2,3,7,8-TCDF	0.1

[6] The funnel area and deployment duration of the primary sample and its replicate were the same but the total sample volume was sometimes different. Thus, the sample concentrations were converted to flux using their respective areas, deployment durations and sample volumes before averaging.

[7] For laboratory results qualified as "K" by AXYS, which were re-qualified as U by data validation, the dioxin and furan congener flux based on the result value (rather than sample specific detection limit) was multiplied by the respective TEF.

COMPOUND	TEF
1,2,3,4,6,7,8-HPCDF	0.01
1,2,3,4,7,8,9-HPCDF	0.01
1,2,3,4,7,8-HXCDF	0.1
1,2,3,6,7,8-HXCDF	0.1
1,2,3,7,8,9-HXCDF	0.1
1,2,3,7,8-PECDF	0.03
2,3,4,6,7,8-HXCDF	0.1
2,3,4,7,8-PECDF	0.3
OCDF	0.0003

4.5 Data Analysis Methods

To illustrate how fluxes differed by location and time, scatterplots were created of individual 2013 results. One plot was made for each analyte (i.e. metals and mercury) or analyte group (i.e. LPAHs, HPAHs, PCBs, dioxins/furans). Analysis of temporal differences was limited to only visual observations given the length of the study periods. To examine spatial differences across all stations, boxplots of all collected flux data (i.e. 2011–2013 sampling events) were also created. In preparation for testing significant differences in flux between locations, the assumption of normality was tested for each analyte or analyte group using the Shapiro-Wilk test. The assumption that the data groups had equal variances was also tested. The tests were run with and without log-normalization of data. All analytes and analyte groups failed the normality and/or equal variance assumptions except mercury, silver, and PCBs. Thus, the majority of the flux data grouped by station were then tested using a non-parametric one-way analysis-of-variance (ANOVA) by ranks (i.e. Kruskal-Wallis) test for significant differences. The flux data for the three chemicals that passed the normality and equal variance assumptions were tested using a parametric one-way ANOVA for significant differences. Differences were considered statistically significant when the p value was less than 0.05. Post-hoc testing to identify which stations were significantly different included Dunn's (for non-parametric distributions), also known as Bonferroni, or Holm-Sidak (for parametric distributions). The ANOVA and post-hoc testing on individual chemistry flux data across sites was completed using the software program SigmaPlot® 12.5.

Two analyses were conducted to examine spatial differences across metals fluxes between stations. A principal component analysis (PCA) correlation matrix was employed to summarize patterns of metals flux at the Beacon Hill, Duwamish, Georgetown, South Park, Kent, and Enumclaw sites. Permutation multivariate analysis of variance (perMANOVA) using Euclidian distance was also performed to examine pooled metals flux differences among all stations except Kent SC. Kent SC data were excluded because of the small sample sizes for this station.

Multiple analyses were conducted to examine the influence of environmental factors on pooled and individual chemical flux. The environmental variables included were average

temperature, average wind speed, total rainfall, and average PM 2.5 concentration (PM 2.5)[8]. A redundancy analysis (RDA) was conducted to explore common structure between metals deposition and environmental variables at four sites with the most complete[9] environmental data: Beacon Hill, Duwamish, Georgetown, and Kent. The first two ordination axes were used for interpretation because they explained the majority of the variance within the dataset. As a direct extension of multiple regression analysis, RDA provides a useful method to explicitly test whether environmental variables significantly explain the variation observed in chemical flux. RDA was not conducted on PCBs and dioxin/furan flux data because the method is sensitive to unequal sample sizes requiring constraint to the smallest sample size and PCBs and dioxin/furan sample sizes were much smaller than metals. Stepwise regression was employed to determine which specific environmental variable(s) influence metals, HPAH, PCB and dioxin/furan flux. Stepwise regression was also used to verify ordination results for metals. Metal flux data were log-transformed prior to analysis to linearize data. In addition, environmental variables were standardized to unitless values by z-score prior to analysis due to the different measurement units for each variable. Any missing metal flux values were replaced with the median value for that metal. All multivariate analyses were performed with R statistical programming version 3.1.1 (R Development Core Team 2014) using the "vegan" package.

[8] PM 2.5 was included as a variable because some contaminants adsorb to particles and are transported through the atmosphere. Particulate concentrations are measured at some of the sampling stations by Ecology as PM 2.5 but not any other particulate size class.

[9] Not all environmental variables are monitored at all stations. To eliminate gaps, the analysis was limited to the stations for which there were data for all four environmental variables.

5.0 RESULTS

Summary results for 2013 chemistry (presented as flux measurements) and associated measurements of temperature, rainfall, fine particulates (PM2.5) and wind are presented in this section, as well as the chemistry results for the combined main (2011/2012) and supplemental (2013) studies. All analytical data as reported by the laboratories can be found in Appendix B, while chemistry results presented as calculated flux are included in Appendix C. Finally, a summary of data validation findings for all chemistry analyses is included in Section 5.9. The complete data validation reports are included in Appendices D and E. Some figures in this section are presented in a boxplot format following a consistent symbology. Figure 2 presents the symbology used for all boxplots in this report. All field replicates were averaged before calculation of boxplot statistics.

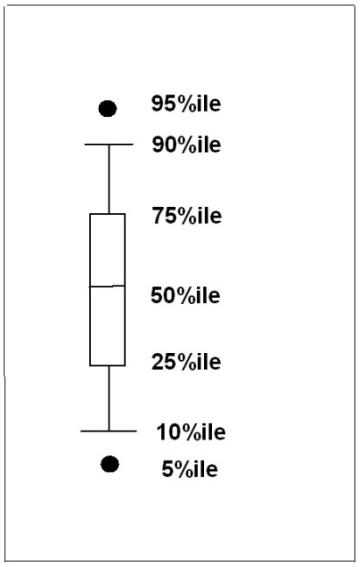


Figure 2. Box Plot Legend

5.1 Metals and Mercury

Seventeen metals and mercury samples were collected at both the Beacon Hill and Georgetown stations in 2013. The 2013 results are presented in this section followed by a review of the combined 2011/2012 and 2013 data and summary of overall spatial differences. Summary statistics are based on detected and undetected results using the MDL value to represent undetected results. When any analyte was not detected, the number of detects and number of non-detects are included in the summary table.

5.1.1 Arsenic

This section presents the 2013 arsenic flux data and a summary of all the arsenic flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.1.1 Arsenic Flux – 2013 Data

In paired measurements, arsenic fluxes were always higher at Georgetown than at the Beacon Hill station with the exception of one sampling period in September (Figure 3). Arsenic fluxes at the Beacon Hill station were consistently below 0.6 µg/m^2-day except for this September sampling period when arsenic flux reached approximately 1.3 µg/m^2-day (Table 6). The mean arsenic flux at Beacon Hill station was 0.4 µg/m^2-day. In comparison, arsenic flux at the Georgetown station varied from 0.4 up to 1.9 µg/m^2-day with a mean of 1.0 µg/m^2-day.

Over time, arsenic flux at Beacon Hill station varied little from April through December except for the peak flux in September (Figure 3). Relative to the Beacon Hill location, variability in arsenic flux at Georgetown station was greater between sampling periods. However, the direction of change appears to be similar as that observed at Beacon Hill during most of the study period. A temporal pattern is not apparent, but increases occur over approximately month long periods that are followed by rapid and substantial decreases; this pattern is most evident at Georgetown during May, June, and December.

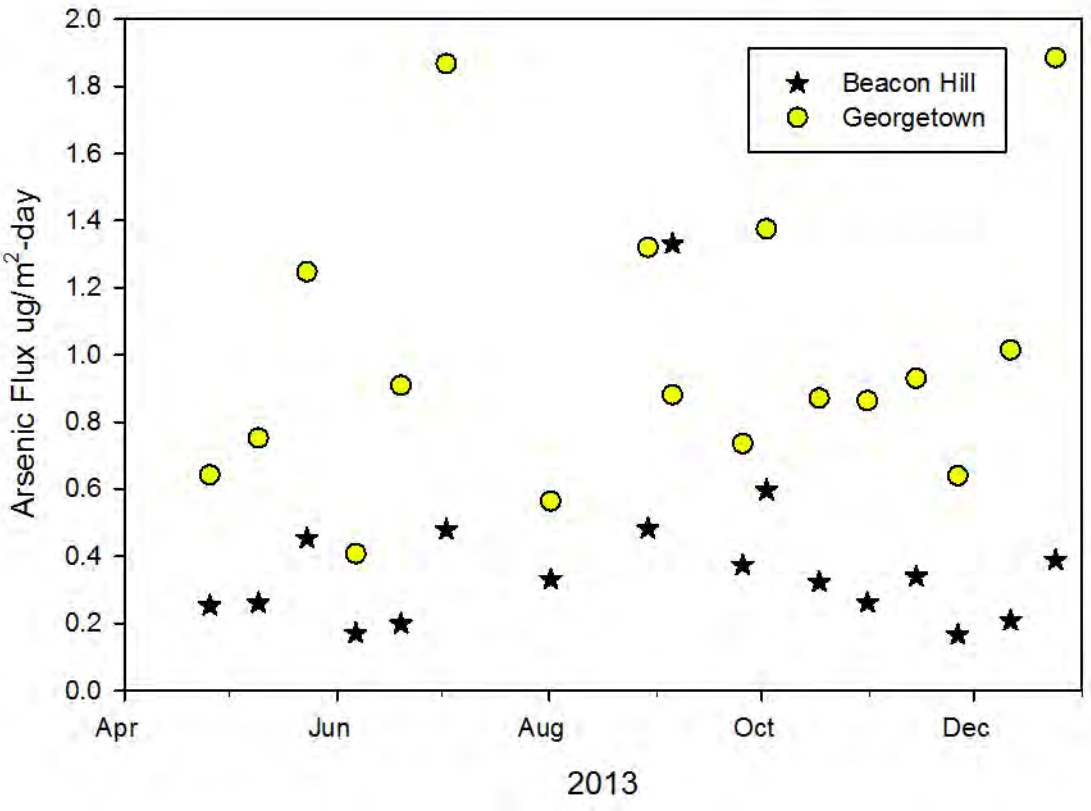


Figure 3. Arsenic Flux for each Collection Period by Collection Date and Station

Table 6. Summary of 2013 Arsenic Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.17	0.41
Maximum	1.33	1.88
Median	0.33	0.88
Mean	0.39	0.99

5.1.1.2 Arsenic Flux – All Data

The arsenic flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured arsenic fluxes ranged from 0.13 µg/m^2-day at Enumclaw station to a maximum of 2.67 µg/m^2-day at the Duwamish station (Table 7).

Table 7. Summary of All Arsenic Flux Data by Station (µg/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	0.17	0.49	0.41	0.28	0.14	0.33	0.13
Maximum	1.33	2.67	1.88	1.19	0.64	1.12	1.67
Median	0.34	0.93	0.88	0.63	0.44	0.46	0.41
Mean	0.38	1.10	0.99	0.67	0.44	0.54	0.56

Figure 4 displays boxplots of arsenic flux distributions by station including results of significant differences testing. Variability in arsenic flux as indicated by the 5th and 95th percentiles was largest at Duwamish and Enumclaw stations and smallest at the Beacon Hill and Kent stations. ANOVA by ranks and post-hoc testing results indicate that median arsenic fluxes at Duwamish and Georgetown are significantly higher than at Beacon Hill, Kent and Enumclaw stations. Median arsenic fluxes at the South Park and Kent SC stations were not significantly lower than either Duwamish or Georgetown stations. However, median arsenic flux at the South Park station was significantly higher than at Beacon Hill station. Median arsenic fluxes at Beacon Hill, Kent, Kent SC and Enumclaw were not significantly different from each other.

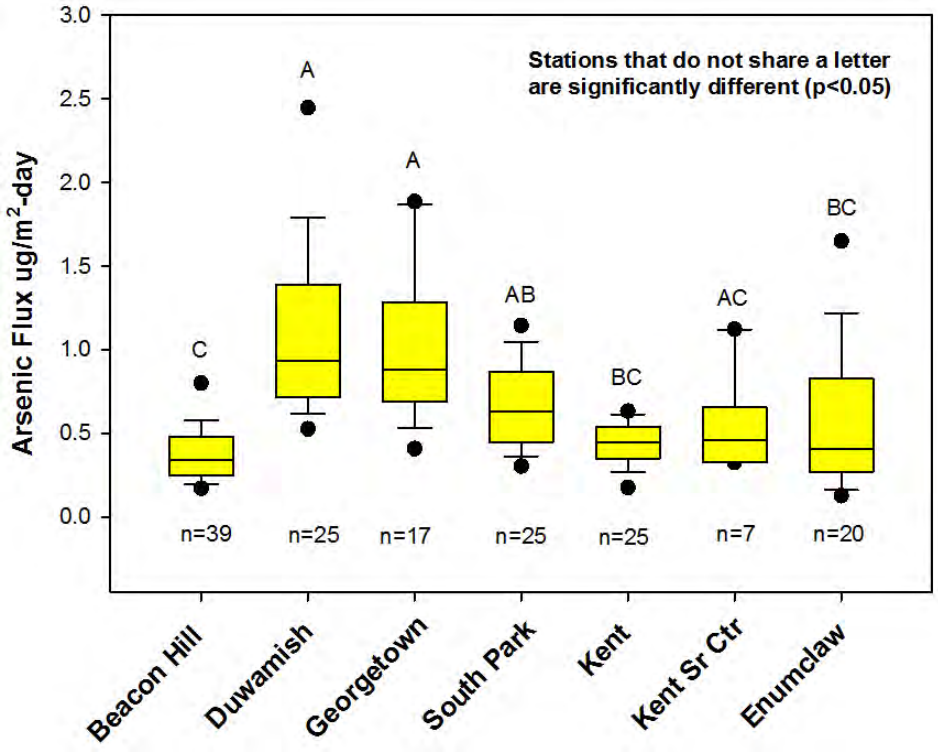


Figure 4. Boxplots of Arsenic Flux by Station

5.1.2 Cadmium

This section presents the 2013 cadmium flux data and a summary of all the cadmium flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.2.1 Cadmium Flux – 2013 Data

In paired measurements, cadmium fluxes were always higher at Georgetown relative to the Beacon Hill station (Figure 5). Cadmium fluxes at Beacon Hill station were consistently below 0.3 µg/m^2-day with a mean of 0.09 µg/m^2-day (Table 8). In comparison, cadmium fluxes at Georgetown station ranged from 0.2 up to 0.9 µg/m^2-day with a mean of 0.5 µg/m^2-day.

Unlike arsenic fluxes, cadmium fluxes at Beacon Hill and Georgetown do not appear to follow the same direction of change with time (Figure 5). Cadmium fluxes at Beacon Hill were relatively stable from April through June and again from October through December. The highest fluxes were observed from July through September. Cadmium fluxes at Georgetown were more variable over time with no apparent temporal trend. However, increases occur over approximately month long periods that are followed by rapid and substantial decreases; this pattern is most evident at Georgetown during May, June and September.

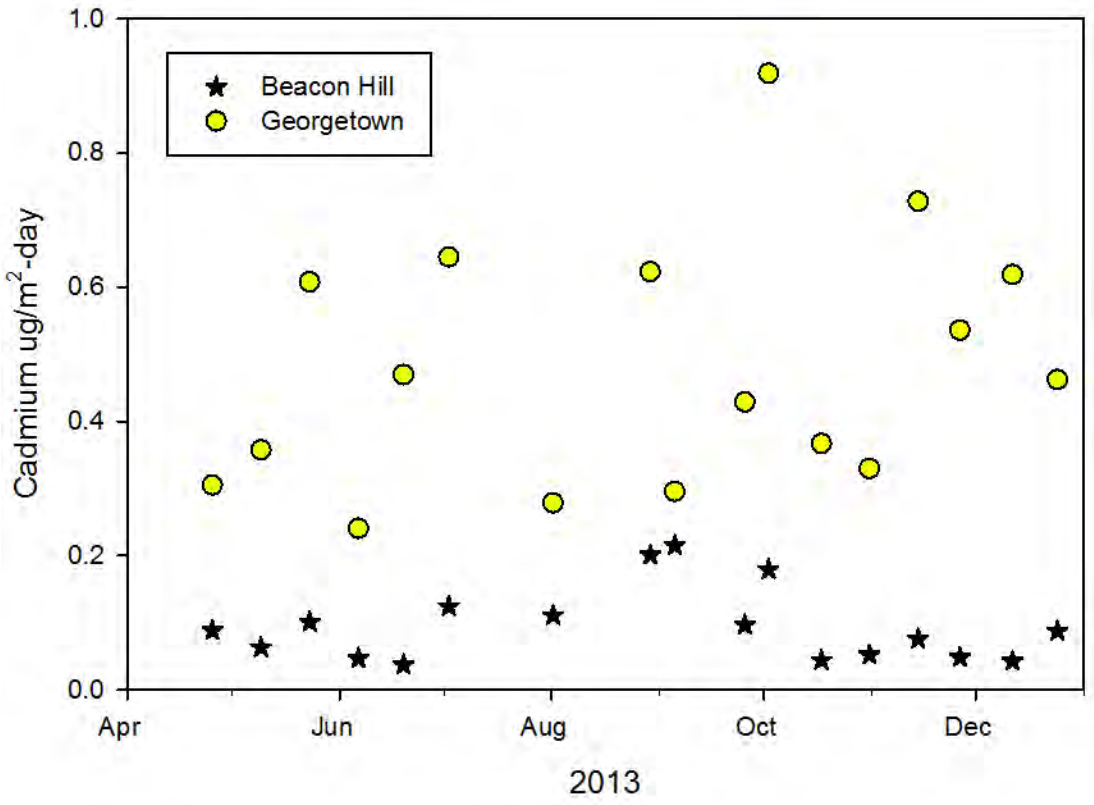


Figure 5. Cadmium Flux for each Collection Period by Collection Date and Station

Table 8. Summary of 2013 Cadmium Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.04	0.24
Maximum	0.21	0.92
Median	0.09	0.46
Mean	0.09	0.48

5.1.2.2 Cadmium Flux – All Data

The cadmium flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured cadmium fluxes ranged from 0.010 µg/m^2-day at Enumclaw station to a maximum of 1.57 µg/m^2-day at the Beacon Hill station (Table 9).

Table 9. Summary of All Cadmium Flux Data by Station (µg/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	0.037	0.13	0.24	0.048	0.046	0.050	0.010
Maximum	1.57	0.79	0.92	0.73	0.71	0.13	0.20
Median	0.085	0.34	0.46	0.24	0.11	0.099	0.080
Mean	0.13	0.38	0.48	0.27	0.16	0.095	0.080

Figure 6 displays boxplots of cadmium flux distributions by station with results of significant differences testing. Variability in cadmium flux as indicated by the 5th and 95th percentiles was largest at the Duwamish, Georgetown, South Park and Kent stations and smallest at the Kent SC station. ANOVA by ranks and post-hoc testing results indicate that median cadmium fluxes at Duwamish and Georgetown are significantly higher than at all other stations except South Park. Median cadmium fluxes at South Park, Kent and Kent SC stations were not significantly different from each other. Median cadmium fluxes at Beacon Hill, Kent SC and Enumclaw were also not significantly different from each other.

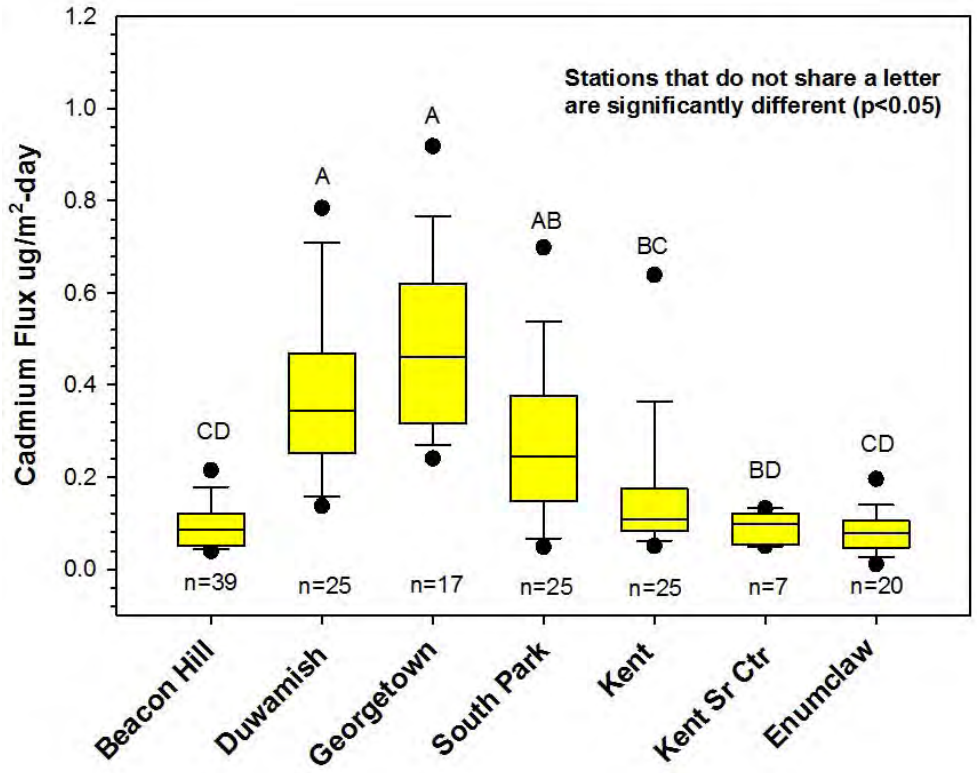


Figure 6. Boxplots of Cadmium Flux by Station

5.1.3 Chromium

This section presents the 2013 chromium flux data and a summary of all the chromium flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.3.1 Chromium Flux – 2013 Data

In paired measurements, chromium fluxes were always higher at Georgetown than at the Beacon Hill station (Figure 7). Chromium fluxes at the Beacon Hill station were consistently below 2.8 µg/m^2-day with a mean flux of 1.3 µg/m^2-day (Table 10). In comparison, chromium fluxes at the Georgetown station varied from 2.5 up to 6.2 µg/m^2-day with a mean of 4.0 µg/m^2-day.

Similar to arsenic fluxes, chromium fluxes appear to show changes in the same direction at both Beacon Hill and Georgetown during most of the study (Figure 7). A temporal pattern is not apparent but flux increases occur over approximately month long periods that are followed by substantial decreases; this pattern is most evident at Georgetown during May and June.

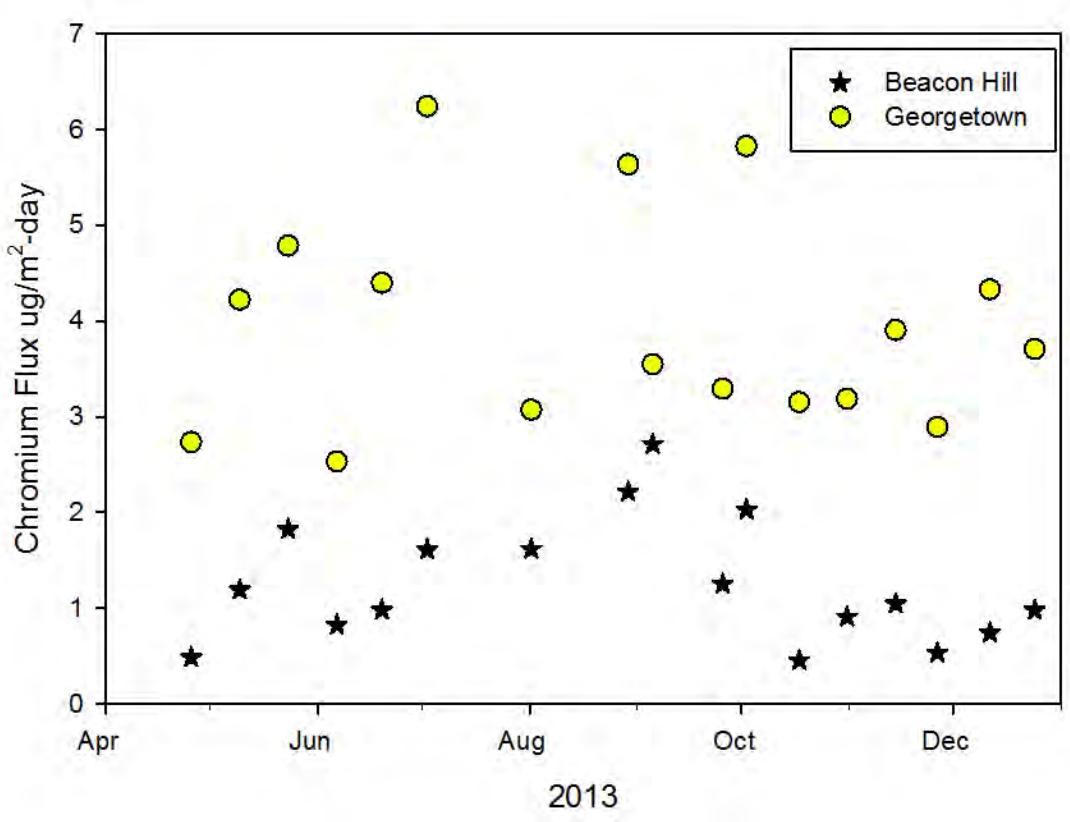


Figure 7. Chromium Flux for each Collection Period by Collection Date and Station

Table 10. Summary of 2013 Chromium Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.45	2.53
Maximum	2.71	6.24
Median	1.0	3.71
Mean	1.3	3.97

5.1.3.2 Chromium Flux – All Data

The chromium flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured chromium fluxes ranged from 0.14 µg/m^2-day at Enumclaw station to a maximum of 8.78 µg/m^2-day at the Duwamish station (Table 11).

Table 11. Summary of All Chromium Flux Data by Station (µg/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	0.45	1.97	2.53	0.76	1.07	0.96	0.14
Maximum	2.71	8.78	6.24	5.69	4.59	3.86	5.48
Median	1.19	3.94	3.71	2.57	2.61	2.53	0.89
Mean	1.30	4.15	3.97	2.62	2.61	2.49	1.28

Figure 8 displays boxplots of chromium flux distributions by station with results of testing for significant differences between rank means. Variability in chromium flux as indicated by the 5th and 95th percentiles was largest at the Duwamish station and smallest at the Beacon Hill station. ANOVA by ranks and post-hoc testing results indicate that median chromium fluxes at Enumclaw are significantly lower than at all other stations except Beacon Hill. Median chromium fluxes at the Beacon Hill and Kent SC stations were not significantly different from each other. Median chromium fluxes at the .Duwamish, Georgetown, South Park, Kent, and Kent SC stations were not significantly different from each other.

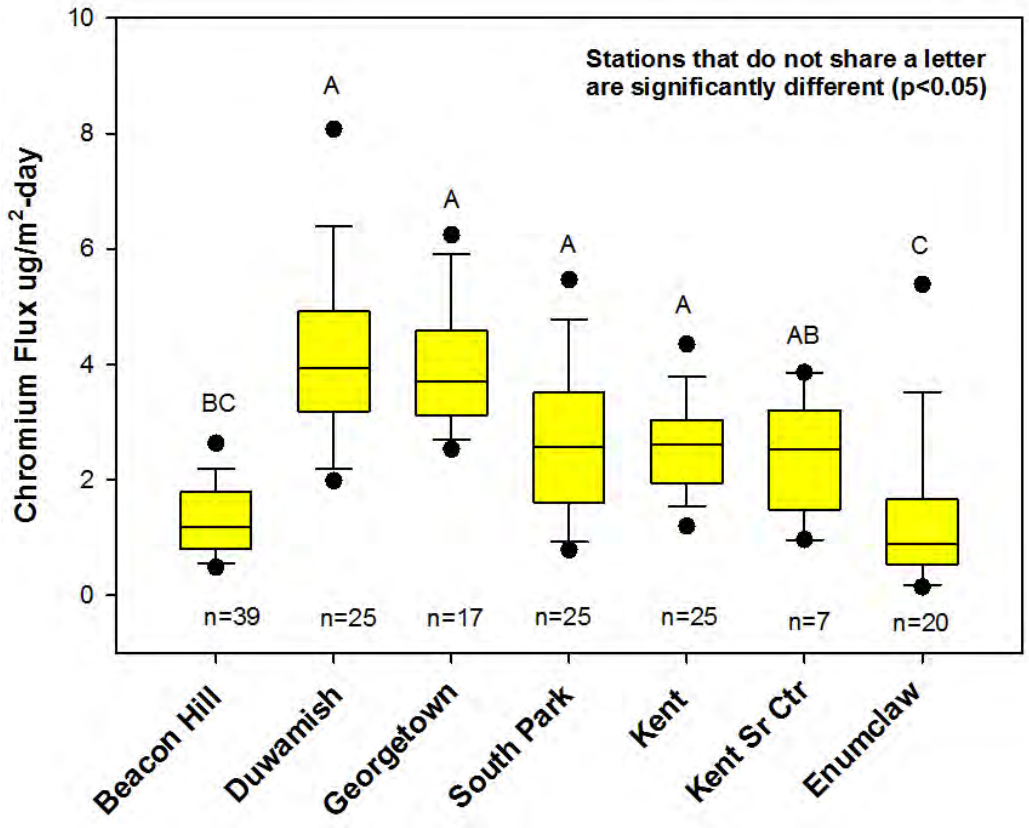


Figure 8. Boxplots of Chromium Flux by Station

5.1.4 Copper

This section presents the 2013 copper flux data and a summary of all the copper flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.4.1 Copper Flux – 2013 Data

In paired measurements, copper fluxes were always higher at Georgetown relative to the Beacon Hill station except during one sampling period in September where they were similar (Figure 9). Copper fluxes at the Beacon Hill station ranged from 5.9 to 25 µg/m^2-day with a mean of 11 µg/m^2-day (Table 12). In comparison, copper fluxes at the Georgetown station varied from 12 up to 42 µg/m^2-day with a mean of 25 µg/m^2-day.

A temporal pattern is not apparent in copper fluxes but increases occur over approximately month long periods that are followed by substantial decreases (Figure 9).

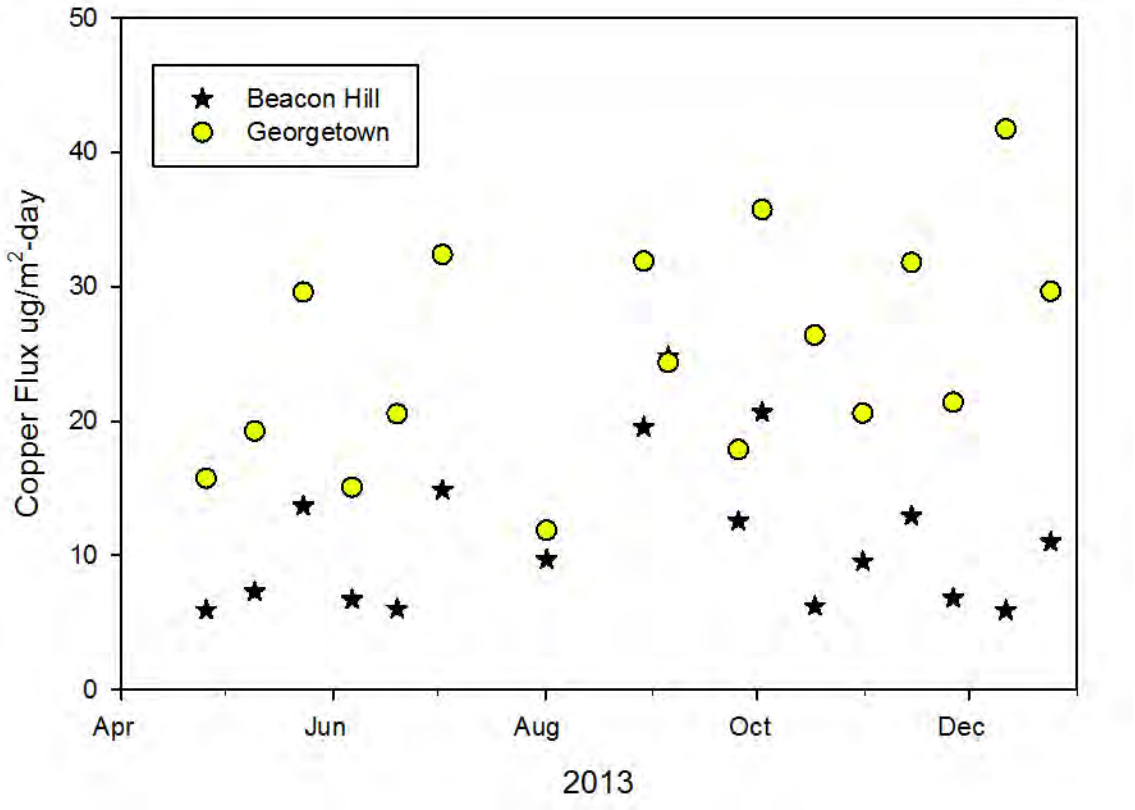


Figure 9. Copper Flux for each Collection Period by Collection Date and Station

Table 12. Summary of 2013 Copper Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	5.9	12
Maximum	25	42
Median	9.7	24
Mean	11	25

5.1.4.2 Copper Flux – All Data

The copper flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured copper fluxes ranged from 0.63 µg/m^2-day at the Enumclaw station to a maximum of 43.8 µg/m^2-day at the Duwamish station (Table 13).

Table 13. Summary of All Copper Flux Data by Station (µg/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	5.36	13.1	11.9	7.60	5.92	8.30	0.63
Maximum	24.8	43.8	41.7	38.4	26.5	29.0	6.41
Median	10.8	23.7	24.4	18.3	11.7	14.2	1.75
Mean	11.3	23.5	25.0	18.8	13.3	15.8	2.46

Figure 10 displays boxplots of copper flux distributions by station with results of testing for significant differences between means. . Variability in copper flux as indicated by the 5th and 95th percentiles was largest at the Duwamish, Georgetown and South Park stations and lowest at the Enumclaw station. ANOVA by ranks and post-hoc testing results indicate that median copper fluxes at Enumclaw are significantly lower than at all other stations. Median copper fluxes at Beacon Hill were higher than Enumclaw and lower than Duwamish, Georgetown and South Park stations ($p<0.05$). Median copper fluxes at the Duwamish, Georgetown, South Park, and Kent SC stations were not significantly different from each other. Median copper fluxes at South Park, Kent and Kent SC were also not significantly different from each other.

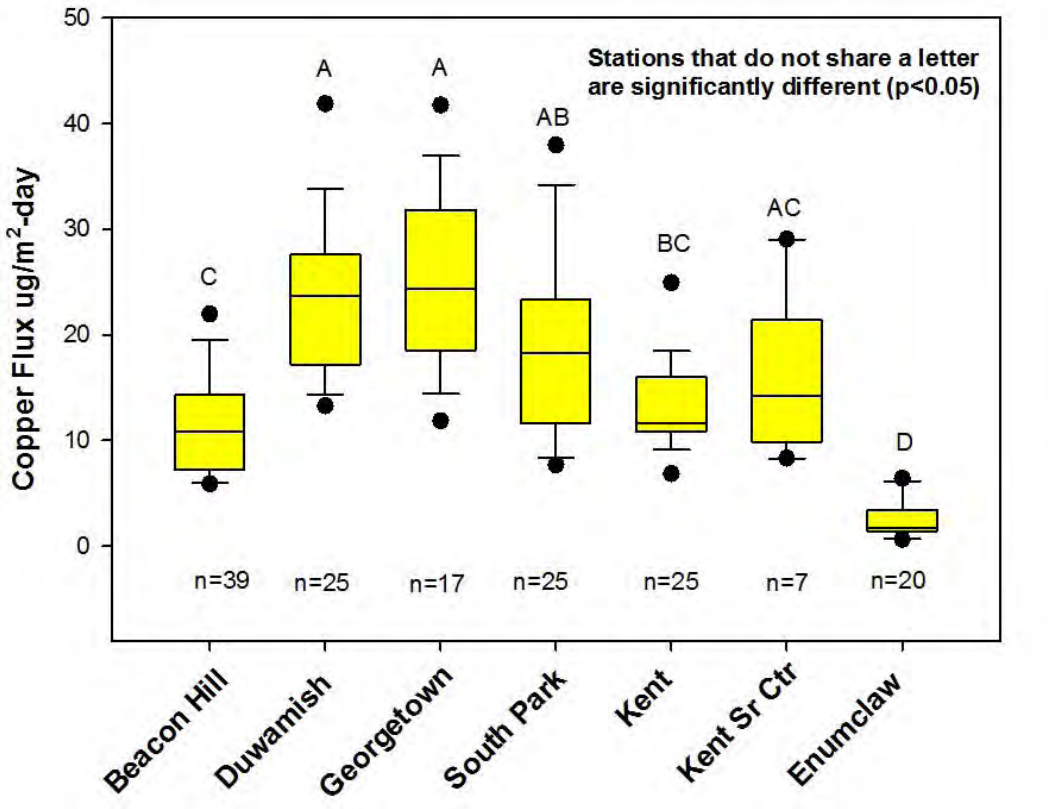


Figure 10. Boxplots of Copper Flux by Station

5.1.5 Lead

This section presents the 2013 lead flux data and a summary of all the lead flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.5.1 Lead Flux – 2013 Data

In paired measurements, lead fluxes were always higher at Georgetown than at the Beacon Hill station (Figure 11). Lead fluxes at the Beacon Hill station ranged from 1.3 to 9.7 µg/m^2-day and the mean was 4.5 µg/m^2-day (Table 14). In comparison, lead fluxes at the Georgetown station ranged from 14 to 78 µg/m^2-day with a mean of 26 µg/m^2-day.

Lead fluxes appear to show changes in the same direction at both Beacon Hill and Georgetown during most of the study (Figure 11). A temporal pattern is not apparent in lead fluxes but increases occur over approximately month-long periods that are followed by substantial decreases. This pattern is similar to that observed for other metals and most evident at the Georgetown station during May and June.

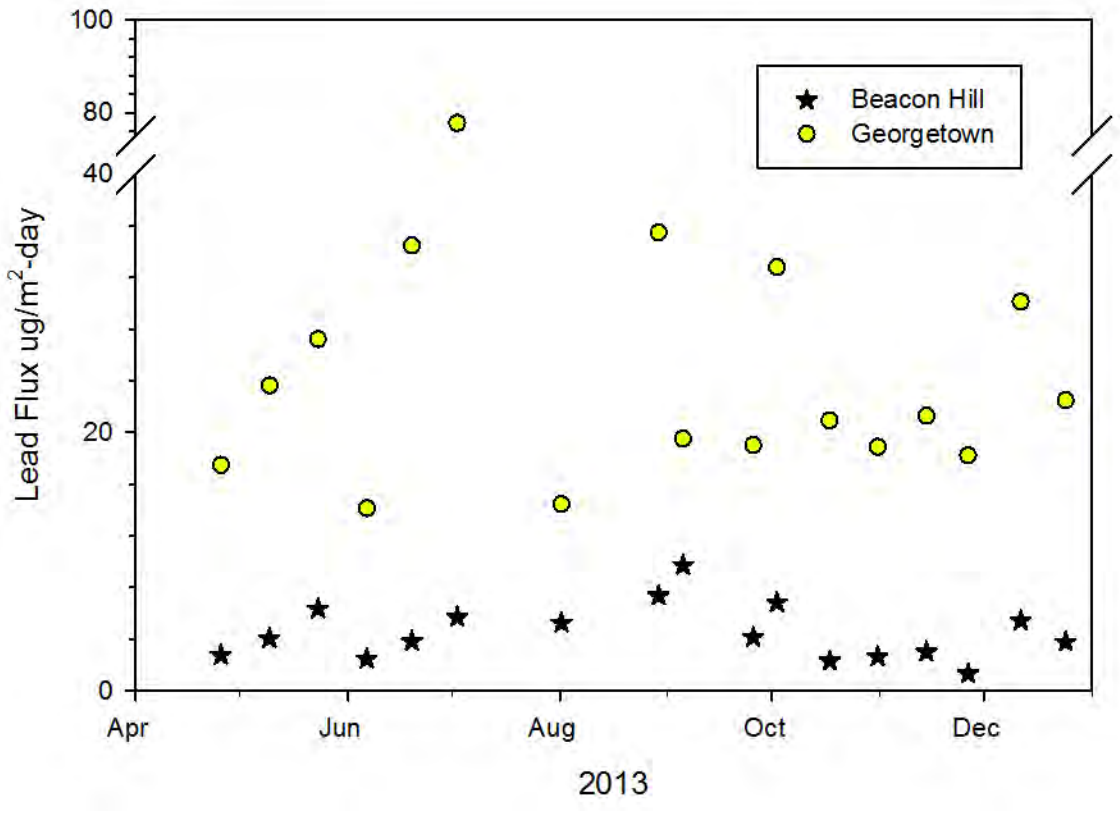


Figure 11. Lead Flux for each Collection Period by Collection Date and Station

Table 14. Summary of 2013 Lead Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	1.3	14
Maximum	9.7	78
Median	4.0	21
Mean	4.5	26

5.1.5.2 Lead Flux – All Data

The lead flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured lead fluxes ranged from 1.32 µg/m^2-day at the Beacon Hill station to a maximum of 275 µg/m^2-day at the Enumclaw station (Table 15). The relatively large difference between the mean (26.7 µg/m^2-day) and median (6.8 µg/m^2-day) lead flux at Enumclaw is indicative of a skewed distribution with the mean raised more than a factor of four times the median by a small number of high measurements.

Table 15. Summary of All Lead Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	1.32	3.68	14.1	3.00	1.75	3.25	1.51
Maximum	9.71	24.1	77.7	42.3	11.0	10.1	275
Median	4.04	11.1	21.3	13.1	5.54	7.87	6.85
Mean	4.47	11.8	26.3	16.3	5.96	7.15	26.7

Figure 12 displays boxplots of lead flux distributions by station with results of testing for significant differences between means. Variability in lead flux as indicated by the 5th and 95th percentiles was largest at the Enumclaw station and lowest at the Beacon Hill station. ANOVA by ranks and post-hoc testing results indicate that median lead flux at Georgetown is significantly higher than all other stations except Duwamish and South Park. Although median lead fluxes at Kent SC and Enumclaw were significantly lower than Georgetown, they were not significantly different than those measured at the Duwamish or South Park stations. Median lead fluxes at Beacon Hill, Kent, Kent SC and Enumclaw were not significantly different from each other.

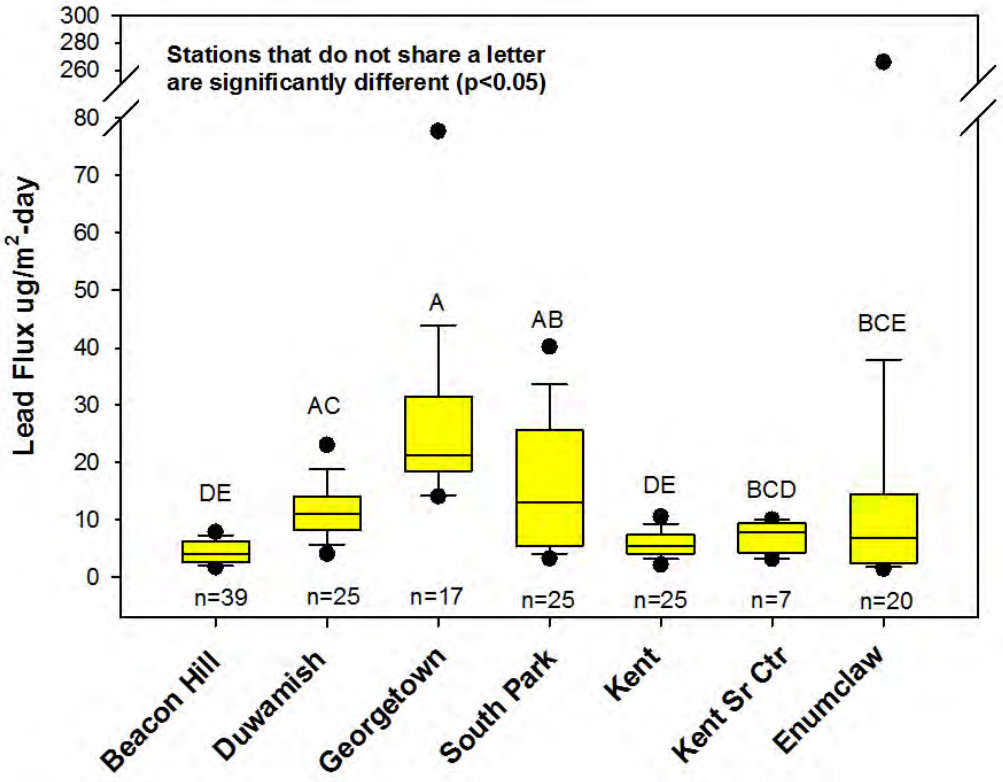


Figure 12. Boxplots of Lead Flux by Station

5.1.6 Mercury

This section presents the 2013 mercury flux data and a summary of all the mercury flux data collected in both the 2011/2012 and 2013 studies. The results of the parametric ANOVA testing for significant differences are also presented.

5.1.6.1 Mercury Flux – 2013 Data

In paired measurements, mercury fluxes were always higher at Georgetown than at the Beacon Hill station with one exception in September (Figure 13). Mercury fluxes at the Beacon Hill station ranged from 0.002 to 0.04 µg/m^2-day with a mean of 0.01 µg/m^2-day (Table 16). In comparison, mercury fluxes at the Georgetown station ranged from 0.01 up to 0.09 µg/m^2-day with a mean of 0.03 µg/m^2-day.

Mercury fluxes appear to show changes in the same direction at the Beacon Hill sites relative to Georgetown during most of the study period (Figure 13). A temporal pattern is not apparent in mercury fluxes.

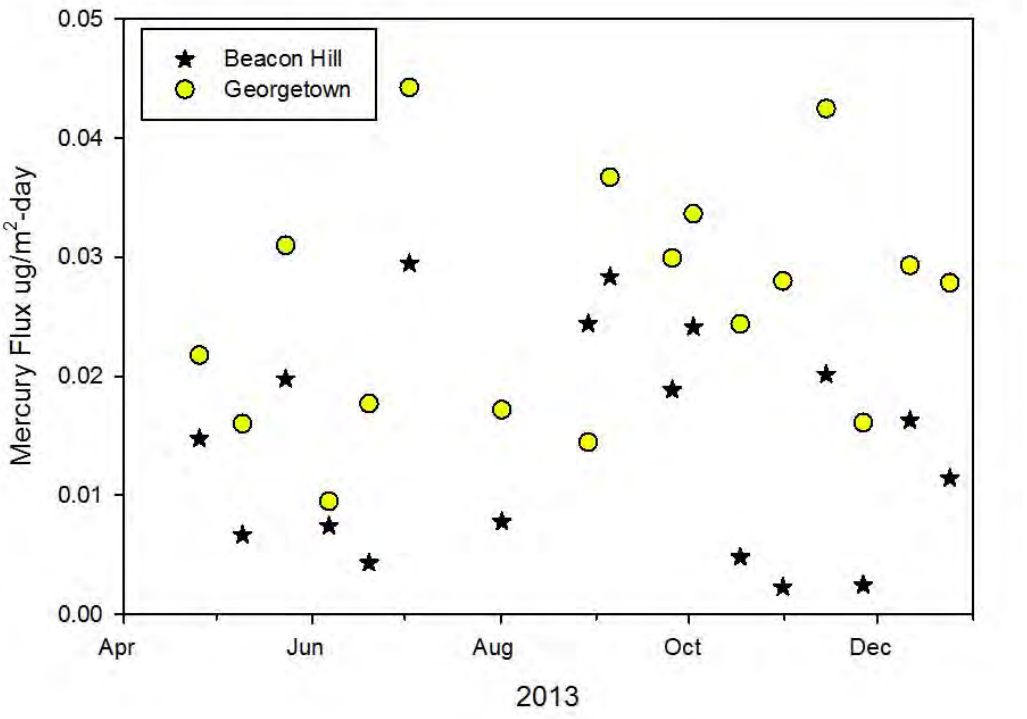


Figure 13. Mercury Flux for each Collection Period by Collection Date and Station

Table 16. Summary of 2013 Mercury Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.002	0.009
Maximum	0.039	0.094
Median	0.011	0.022
Mean	0.015	0.027

5.1.6.2 Mercury Flux – All Data

The mercury flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured mercury fluxes ranged from 0.0023 µg/m^2-day at the Beacon Hill station to a maximum of 0.15 µg/m^2-day at the Duwamish station (Table 17).

Table 17. Summary of All Mercury Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	19
Minimum	0.0023	0.0049	0.0095	0.0055	0.0040	0.0043	0.0035
Maximum	0.029	0.15	0.044	0.063	0.041	0.043	0.025
Median	0.0095	0.014	0.028	0.018	0.0076	0.012	0.0061
Mean	0.012	0.023	0.026	0.0221	0.010	0.015	0.0089

Figure 14 displays boxplots of log normalized mercury flux distributions by station with results of testing for significant differences between means. Variability in mercury flux as indicated by the 5th and 95th percentiles was largest at the Duwamish station and lowest at the Georgetown station. ANOVA and post-hoc testing results indicate that mean mercury fluxes at Georgetown and South Park were significantly higher than at all other stations except Duwamish and Kent SC. Mean mercury fluxes at Beacon Hill and Duwamish were not significantly different from each other. Mean mercury fluxes at Beacon Hill, Kent and Enumclaw were also not significantly different from each other.

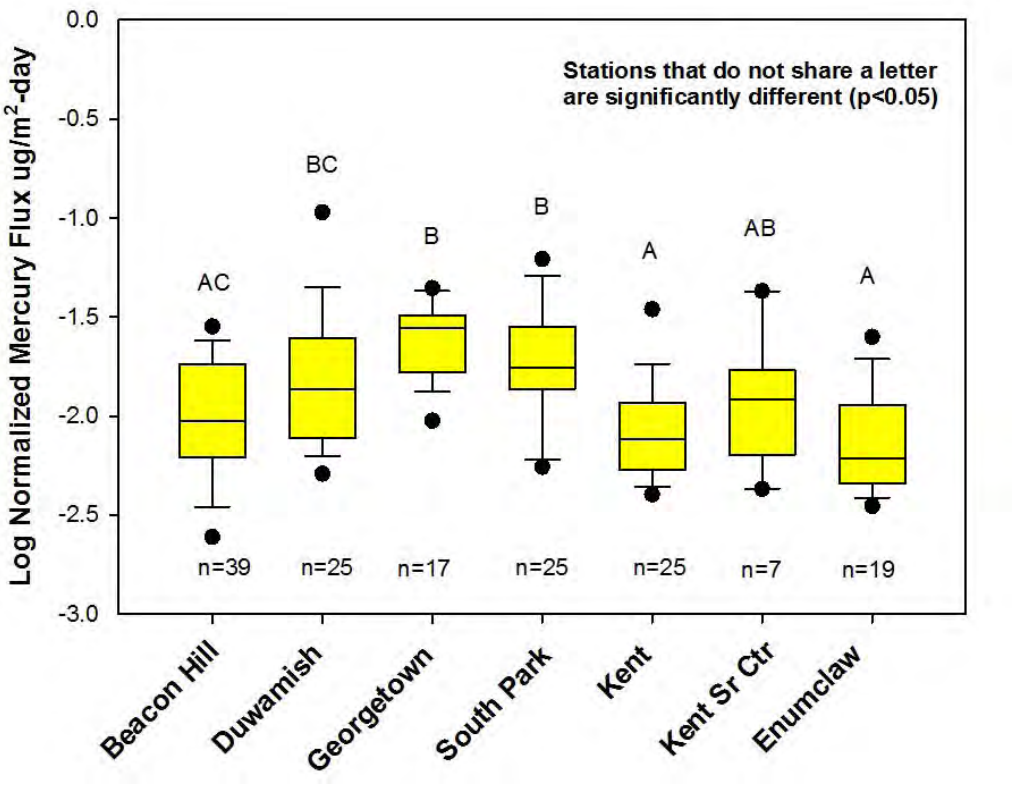


Figure 14. Boxplots of Log Normalized Mercury Flux by Station

5.1.7 Nickel

This section presents the 2013 nickel flux data and a summary of all the nickel flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.7.1 Nickel Flux – 2013 Data

In paired measurements, nickel fluxes were always higher at Georgetown relative to the Beacon Hill station except for the first sampling event in April (Figure 15). Nickel fluxes at Beacon Hill station ranged from 0.76 to 6.9 µg/m^2-day with a mean of 2.2 µg/m^2-day (Table 17). In comparison, nickel fluxes at the Georgetown station ranged from 2.9 to 14 µg/m^2-day with a mean of 5.7 µg/m^2-day.

A temporal pattern is not apparent in nickel fluxes but some of the increases followed by substantial decreases seen for other metals can be seen, particularly in May and June at Georgetown (Figure 15).

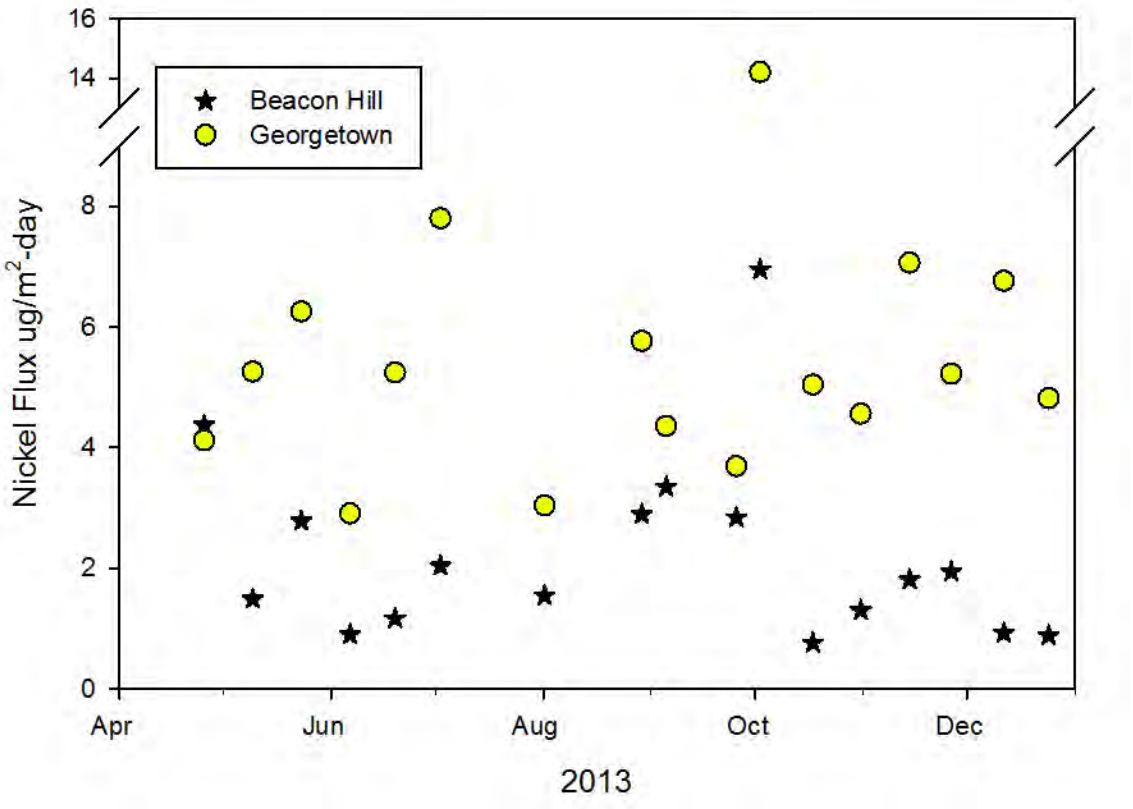


Figure 15. Nickel Flux for each Collection Period by Collection Date and Station

Table 18. Summary of 2013 Nickel Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.76	2.9
Maximum	6.9	14
Median	1.8	5.2
Mean	2.2	5.7

5.1.7.2 Nickel Flux – All Data

The nickel flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured nickel fluxes ranged from 0.22 µg/m^2-day at the Enumclaw station to a maximum of 14 µg/m^2-day at the Georgetown station (Table 19).

Table 19. Summary of All Nickel Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	38	25	17	25	25	7	20
Minimum	0.71	1.83	2.90	1.03	0.92	0.75	0.22
Maximum	6.95	6.05	14.2	6.16	2.69	3.68	1.81
Median	1.76	3.48	5.23	3.33	1.70	1.78	0.45
Mean	1.97	3.68	5.65	3.22	1.70	1.89	0.69

Figure 16 displays boxplots of nickel flux distributions by station with results of testing for significant differences between means. Variability in nickel flux as indicated by the 5th and 95th percentiles was largest at the Georgetown station and lowest at the Kent and Enumclaw stations. ANOVA by ranks and post-hoc testing results indicate that the median nickel flux at Georgetown is significantly higher than at all other stations except Duwamish and South Park. Median nickel flux at Enumclaw was significantly lower than at all other stations except Kent. Neither Duwamish nor South Park median fluxes were significantly different than Beacon Hill or Kent SC. Median lead fluxes at Beacon Hill, Kent, and Kent SC were not significantly different from each other.

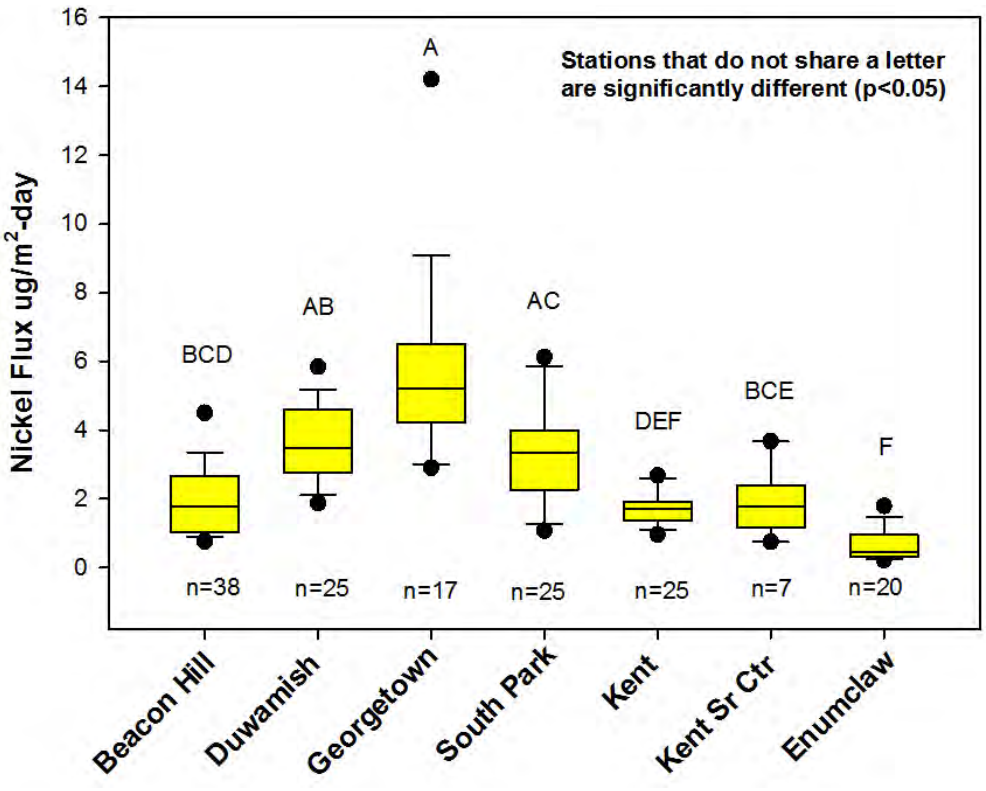


Figure 16. Boxplots of Nickel Flux by Station

5.1.8 Silver

This section presents the 2013 silver flux data and a summary of all the silver flux data collected in both the 2011/2012 and 2013 studies. The results of the parametric ANOVA testing for significant differences are also presented.

5.1.8.1 Silver Flux – 2013 Data

Silver was not detected in thirty-five percent of the sample results (12 out of 34 samples). This reduced (lower?) detection frequency had influenced Beacon Hill fluxes where silver was only detected in 7 of 17 samples. The MDL value was used to represent non-detected samples in flux calculations. Combining detected and non-detect results, silver fluxes were generally consistent at Beacon Hill and more variable at the Georgetown station throughout the study period (Figure 17). In paired measurements, silver fluxes were higher at Georgetown relative to the Beacon Hill station except in three samples collected in April, August and September. Silver fluxes ranged from 0.003 to 0.18 µg/m^2-day at Beacon Hill station (Table 19) with a mean of 0.03 µg/m^2-day. In comparison, silver fluxes at Georgetown station ranged from 0.02 up to 0.16 µg/m^2-day with a mean of 0.07µg/m^2-day.

A temporal pattern is not apparent in silver fluxes although the direction of change appears to match in samples at the Beacon Hill and Georgetown stations most of the time (Figure 17).

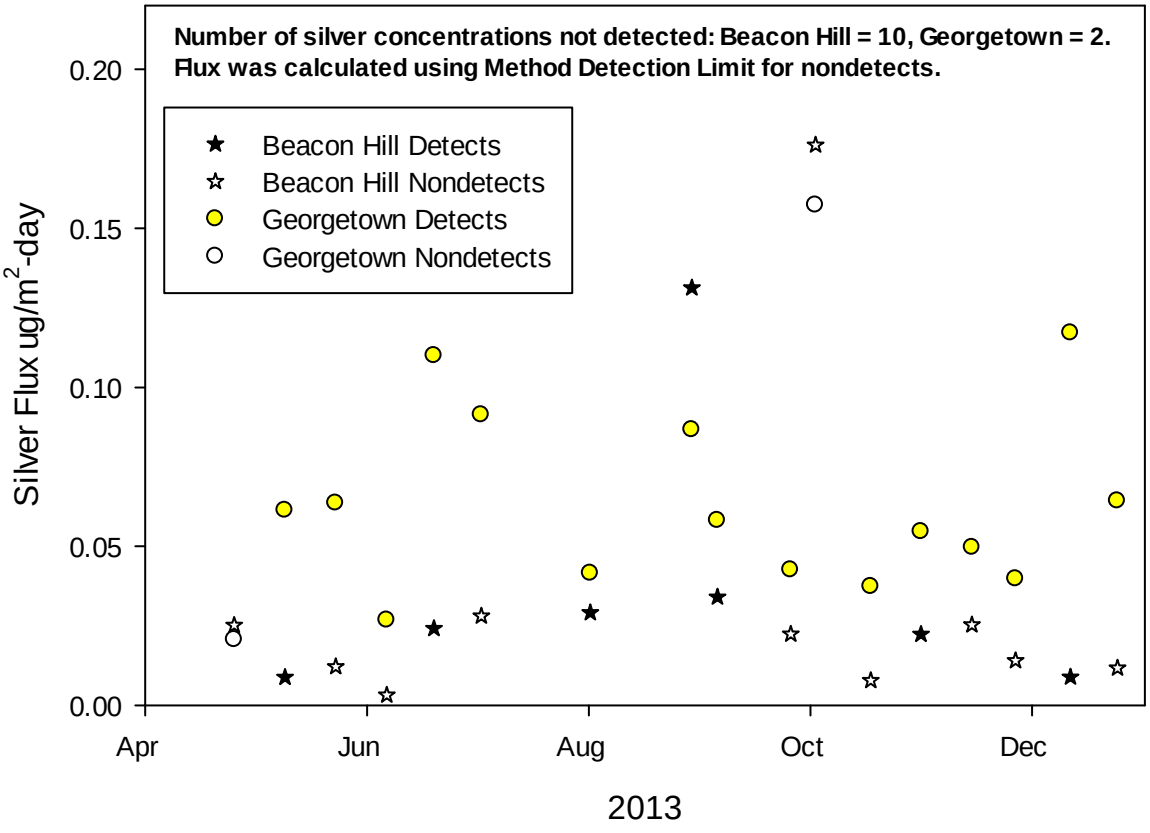


Figure 17. Silver Flux for each Collection Period by Collection Date and Station

Table 20. Summary of 2013 Silver Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
# detects/# samples	7/17	15/17
Minimum	0.003	0.02
Maximum	0.18	0.16
Median	0.02	0.06
Mean	0.03	0.07

Note: MDL values were used for nondetects in the calculation of means and medians.

5.1.8.2 Silver Flux – All Data

The silver flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Detection frequencies ranged from 10% (2/20) at Enumclaw station to 68% (17/25) at the Duwamish station. Measured silver fluxes ranged from 0.0033 µg/m^2-day at the Beacon HIll station to 0.24 µg/m^2-day at the Duwamish station (Table 21).

Table 21. Summary of All Silver Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
# Detects / Total Samples	14/39	17/25	15/17	12/25	7/25	4/7	2/20
Minimum	0.0033	0.029	0.021	0.015	0.014	0.019	0.0077
Maximum	0.18	0.24	0.16	0.15	0.18	0.053	0.11
Median	0.025	0.049	0.058	0.042	0.040	0.031	0.043
Mean	0.036	0.066	0.066	0.052	0.050	0.033	0.047

Note: MDL values were used for nondetects in the calculation of means and medians.

Figure 18 displays boxplots of log normalized silver flux distributions by station with results of testing for significant differences between means. Variability in silver flux as indicated by the 5th and 95th percentiles was largest at the Beacon Hill station and lowest at the Kent SC station. ANOVA and post-hoc testing results indicate that mean silver fluxes at Duwamish, Georgetown, and South Park are significantly higher than at Beacon Hill. Mean silver fluxes at Beacon Hill, Kent, Kent SC, and Enumclaw were not significantly different from each other. Also, mean silver fluxes at all stations except Beacon Hill were not significantly different from each other.

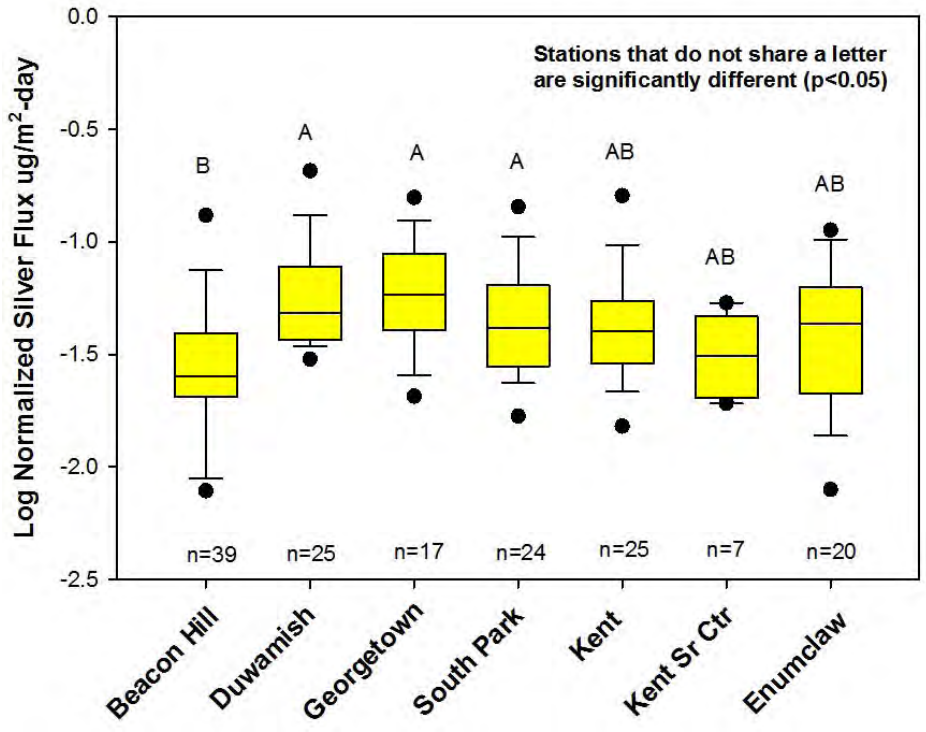


Figure 18. Boxplots of Lognormalized Silver Flux by Station

5.1.9 Vanadium

This section presents the 2013 vanadium flux data and a summary of all vanadium flux data collected in both the 2011/2012 and 2013 studies. Results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.9.1 Vanadium Flux – 2013 Data

In paired measurements, vanadium fluxes were always higher at Georgetown relative to the Beacon Hill station (Figure 19). Vanadium fluxes at the Beacon Hill station ranged from 0.53 to 2.4 µg/m^2-day with a mean of 1.2 µg/m^2-day (Table 22). In comparison, vanadium fluxes at Georgetown station ranged from 1.5 to 3.6 µg/m^2-day with a mean of 2.4 µg/m^2-day.

A temporal pattern is not apparent in vanadium fluxes but increases occur repeatedly over approximately a month long periods, followed by substantial decreases (Figure 19). This pattern is similar to that observed for other metals and is most evident at both stations during May and June.

Table 22. Summary of 2013 Vanadium Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	16	17
Minimum	0.53	1.5
Maximum	2.4	3.6
Median	1.0	2.4
Mean	1.2	2.4

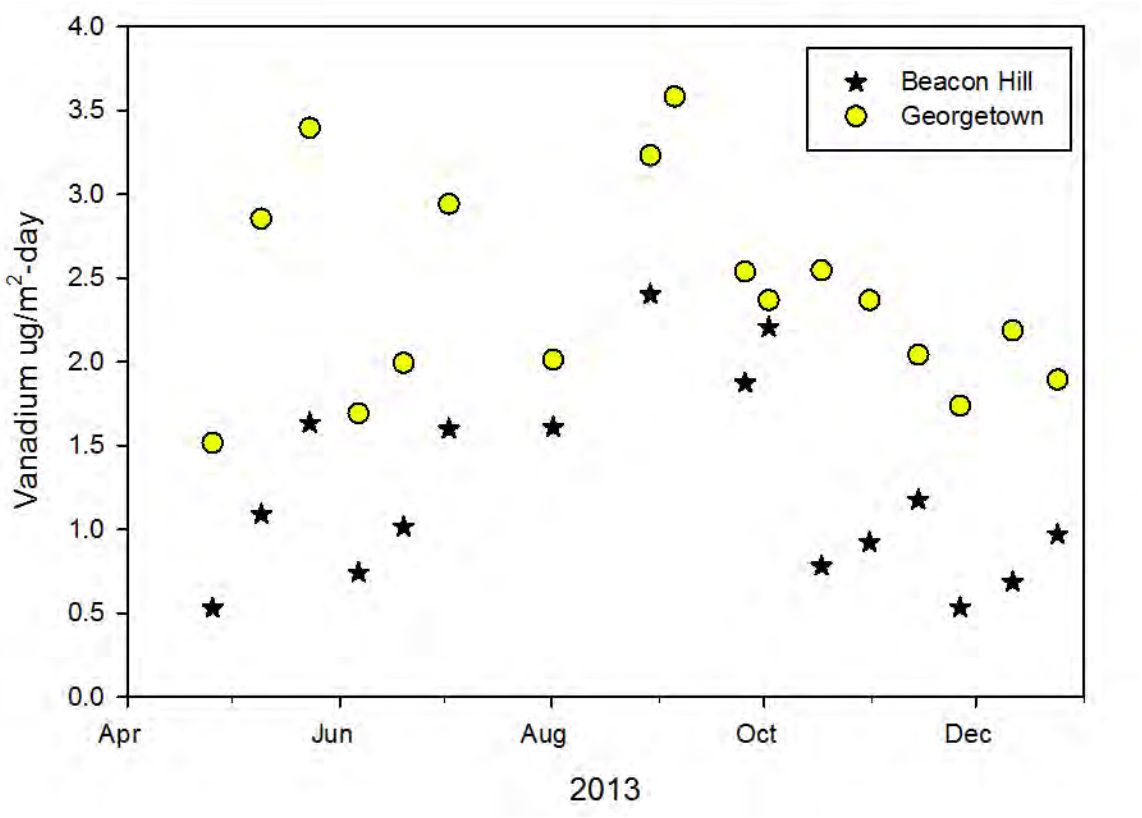


Figure 19. Vanadium Flux for each Collection Period by Collection Date and Station

5.1.9.2 Vanadium Flux – All Data

The vanadium flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured vanadium fluxes ranged from 0.23 µg/m^2-day at Enumclaw station to 9.14 µg/m^2-day at the Duwamish station (Table 23).

Table 23. Summary of All Vanadium Flux Data by Station (µg/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	38	25	17	25	25	7	20
Minimum	0.53	1.84	1.52	0.81	0.67	0.85	0.23
Maximum	3.92	9.14	3.58	5.06	3.35	3.20	3.30
Median	1.58	4.48	2.37	2.26	1.83	2.10	0.58
Mean	1.73	5.13	2.41	2.38	2.01	2.14	0.91

Figure 20 displays boxplots of vanadium flux distributions by station with results of testing for significant differences between means. Variability in vanadium flux as indicated by the

5th and 95th percentiles was largest at the Duwamish station and lowest at the Georgetown station. ANOVA by ranks and post-hoc testing results indicate that median vanadium fluxes at Duwamish were significantly higher than at the Beacon Hill, Kent and Enumclaw stations, but not significantly higher than at Georgetown, South Park or Kent SC. Median vanadium flux at Enumclaw was significantly lower than at Duwamish, Georgetown and South Park. Median vanadium fluxes at Beacon Hill, Kent, Kent SC, and Enumclaw were not significantly different from each other.

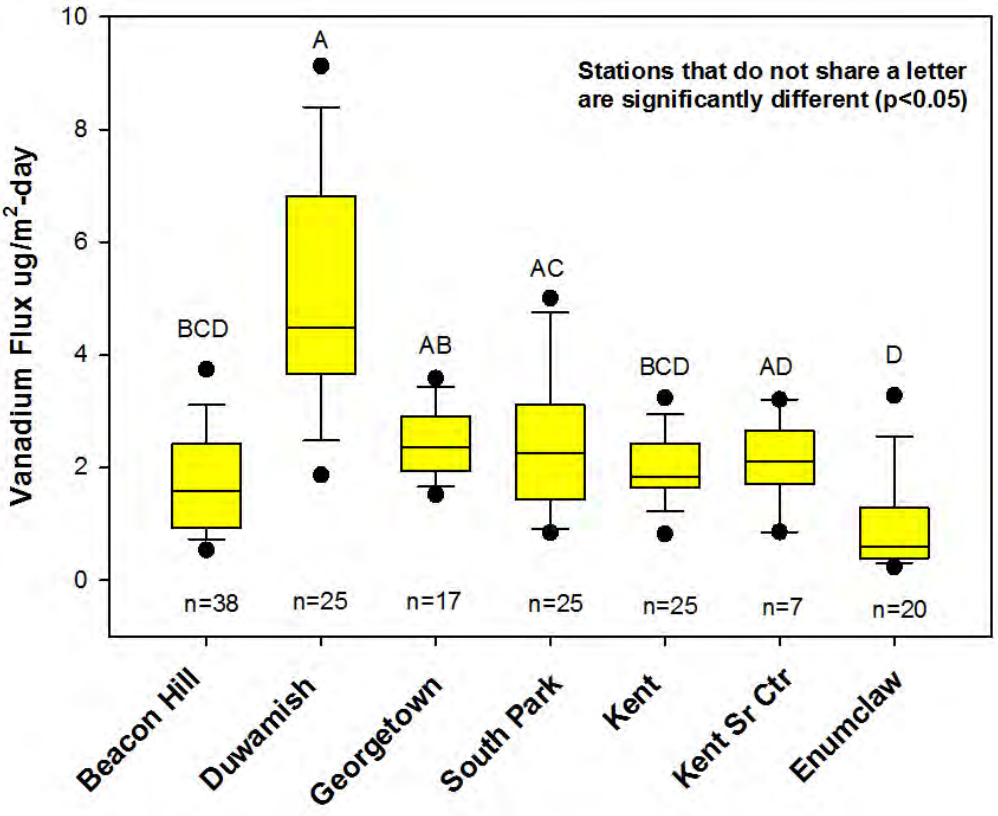


Figure 20. Boxplots of Vanadium Flux by Station

5.1.10 Zinc

This section presents the 2013 zinc flux data and a summary of all the zinc flux data collected in both the 2011/2012 and 2013 studies. The results of the nonparametric ANOVA testing for significant differences are also presented.

5.1.10.1 Zinc Flux – 2013 Data

In paired measurements, zinc fluxes were always higher at Georgetown than at the Beacon Hill station (Figure 21). Zinc fluxes at Beacon Hill station ranged from 21 to 122 µg/m^2-day with a mean of 54 µg/m^2-day (Table 23). In comparison, zinc fluxes at Georgetown station ranged from 104 to 342 µg/m^2-day with a mean of 198 µg/m^2-day.

Zinc fluxes appear to increase and decrease in a similar pattern at both the Beacon Hill as Georgetown stations during most of the study period (Figure 21). A temporal pattern is not apparent in zinc fluxes but flux increases occur repeatedly over approximately a month long period, followed by substantial decreases. This pattern is similar to that observed for other metals and is most evident at the Georgetown station during May and June.

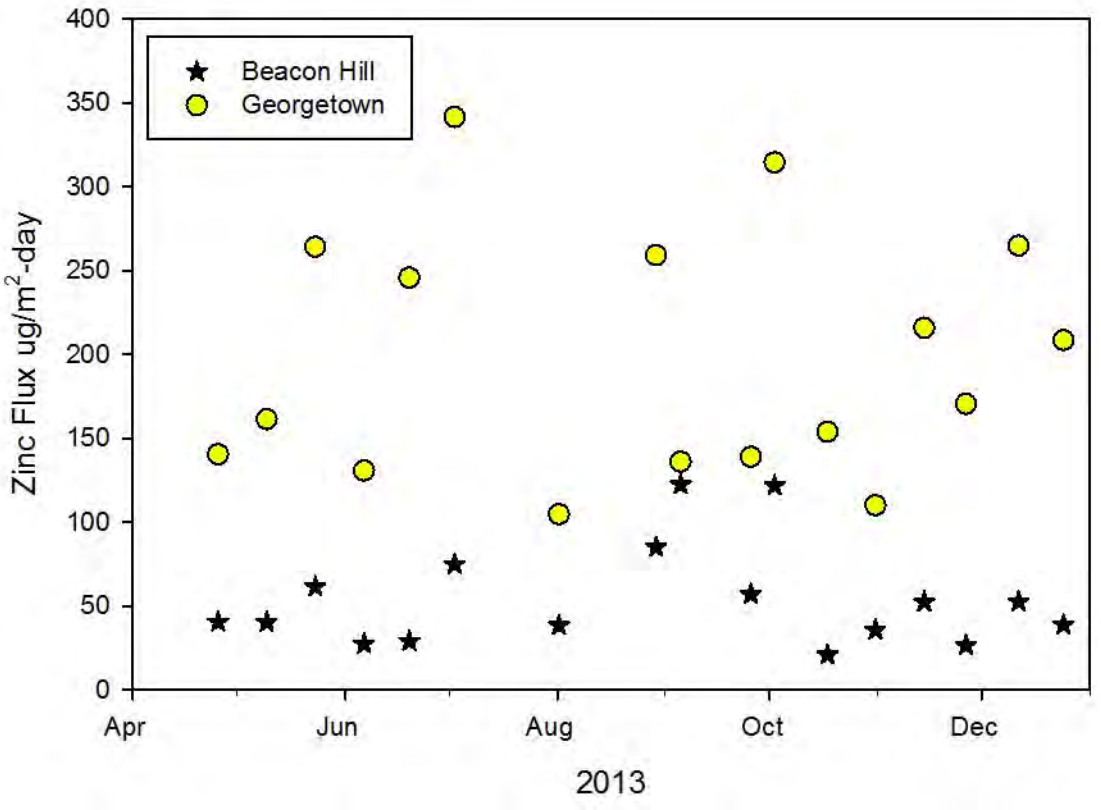


Figure 21. Zinc Flux for each Collection Period by Collection Date and Station

Table 24. Summary of 2013 Zinc Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Min	21	104
Max	122	342
Median	40	170
Mean	54	198

5.1.10.2 Zinc Flux – All Data

The zinc flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured zinc fluxes ranged from 5.47 µg/m^2-day at the Enumclaw station to a maximum of 342 µg/m^2-day at the Georgetown station (Table 25).

Table 25. Summary of All Zinc Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	25	25	7	20
Minimum	20.7	56.5	105	34.8	31.3	32.4	5.47
Maximum	122	171	342	274	153	115	99.2
Median	44.6	111	170	122	68.8	87.5	14.7
Mean	52.8	108	198	126	77.1	81.2	21.8

Figure 22 displays boxplots of zinc flux distributions by station with results of testing for significant differences between means. Variability in zinc flux as indicated by the 5th and 95th percentiles was largest at the Georgetown station and lowest at the Enumclaw station. ANOVA by ranks and post-hoc testing results indicate that median zinc fluxes at Georgetown were significantly higher than at the Beacon Hill, Kent and Enumclaw stations, but not significantly higher than at Duwamish, South Park or Kent SC. Median zinc fluxes at Enumclaw were significantly lower than all other stations except Beacon Hill. Median zinc fluxes at Beacon Hill, Kent, and Kent SC were not significantly different from each other.

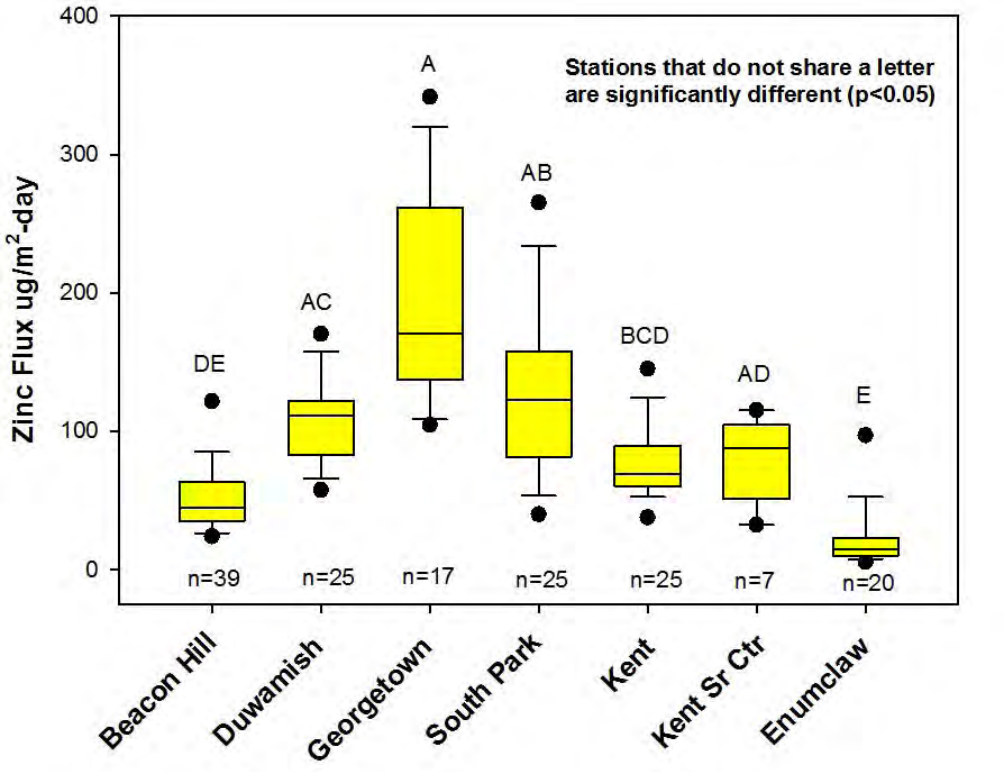


Figure 22. Boxplots of Zinc Flux by Station

5.2 PAHs

5.2.1 2013 HPAH Flux

Seventeen samples collected at both Beacon Hill and Georgetown were analyzed for PAHs. PAH flux results are discussed as HPAHs in this section. The results for LPAHs are presented and discussed in Appendix F, although, for reasons discussed below, these data are of limited usability and are provided for informational use only.

It is acknowledged that the bulk deposition methods used in this study do not capture the significant fraction of LPAH flux that occurs through gas absorption. In addition, LPAHs are volatile and loss during the sample deployment period is substantial, further magnifying the low sampling bias. Low bias from volatilization was demonstrated by quality control sample results in King County's main atmospheric deposition study (King County 2013a). Poor recovery of LPAHs using bulk atmospheric deposition sampling techniques has also been observed by other researchers (King County 2008, Brandenberger et al. 2010). Due to the low bias, the bulk atmospheric deposition data collected by this study should not be used as an absolute estimate of LPAH deposition, e.g., for loading estimates. However, it is included in an appendix because the results are still valuable for spatial comparison. HPAH recoveries in field spike blanks from the main study (King County 2013a) were high (80–98%) indicating the sampling methods did not result in substantial bias.

Measured HPAH fluxes were higher at the Georgetown station relative to the Beacon Hill station except in two samples collected in late August and September (Figure 23). HPAH fluxes at the Beacon Hill station ranged from 0.15 to 0.62 µg/m^2-day with a mean of 0.31 µg/m^2-day (Table 25). In comparison, HPAH fluxes at the Georgetown station ranged from 0.29 to 1.3 µg/m^2-day with a mean of 0.71 µg/m^2-day.

HPAH fluxes appear to follow different patterns at Beacon Hill compared to Georgetown (Figure 23). Temporal variability was lower at Beacon Hill where the highest fluxes appeared in late summer and December. HPAH flux was also relatively high in December at Georgetown, but a second peak was also detected in April. Also, longer trends appear at Georgetown; in April, HPAH fluxes are relatively high and decrease gradually through August, and then begin to rise again in September until hitting a maximum in late November before declining again in January.

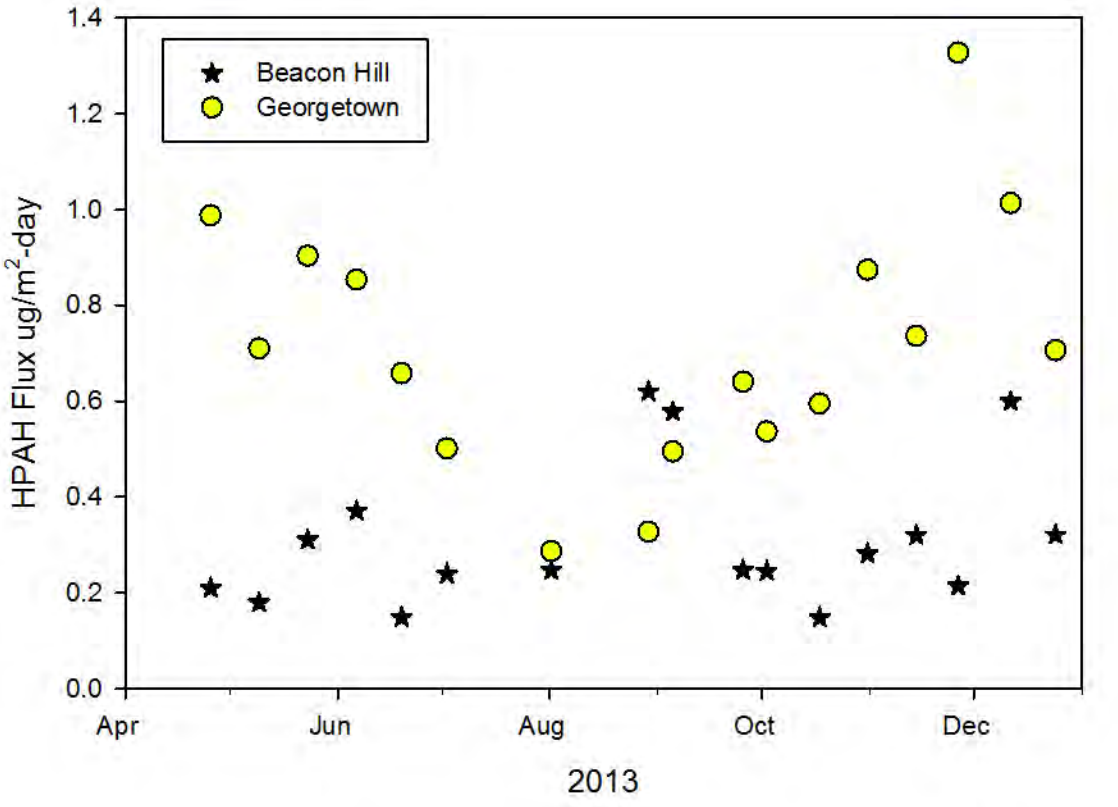


Figure 23. HPAH Flux for Each Collection Period by Collection Date and Station

Table 26. Summary of 2013 HPAH Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Georgetown
Sample Size	17	17
Minimum	0.15	0.29
Maximum	0.62	1.33
Median	0.25	0.71
Mean	0.31	0.71

5.2.2 HPAH Flux – All Data

The HPAH flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured HPAH fluxes ranged from 0.010 µg/m^2-day at the Enumclaw station to a maximum of 2.21 µg/m^2-day at the Duwamish station (Table 27). The highest median HPAH flux was at detected at the Kent station while the lowest was observed at Enumclaw.

Table 27. Summary of All HPAH Flux Data by Station (µg/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	39	25	17	24	25	7	21
Minimum	0.15	0.25	0.29	0.18	0.18	0.33	0.010
Maximum	0.62	2.21	1.33	0.93	1.68	0.56	0.21
Median	0.25	0.6	0.71	0.36	0.89	0.44	0.040
Mean	0.29	0.73	0.71	0.39	0.91	0.45	0.050

Figure 24 displays boxplots of HPAH flux distributions by station with results of testing for significant differences between means. Variability in HPAH flux as indicated by the 5th and 95th percentiles was largest at the Duwamish station and lowest at the Enumclaw station. ANOVA by ranks and post-hoc testing results indicate that the median HPAH flux at Kent was significantly higher than at the Beacon Hill, South Park and Enumclaw stations, but not significantly higher than at Duwamish, Georgetown, or Kent SC. Median HPAH flux at Enumclaw was significantly lower than at all other stations. Median HPAH fluxes at Beacon Hill, South Park, and Kent SC were not significantly different from each other.

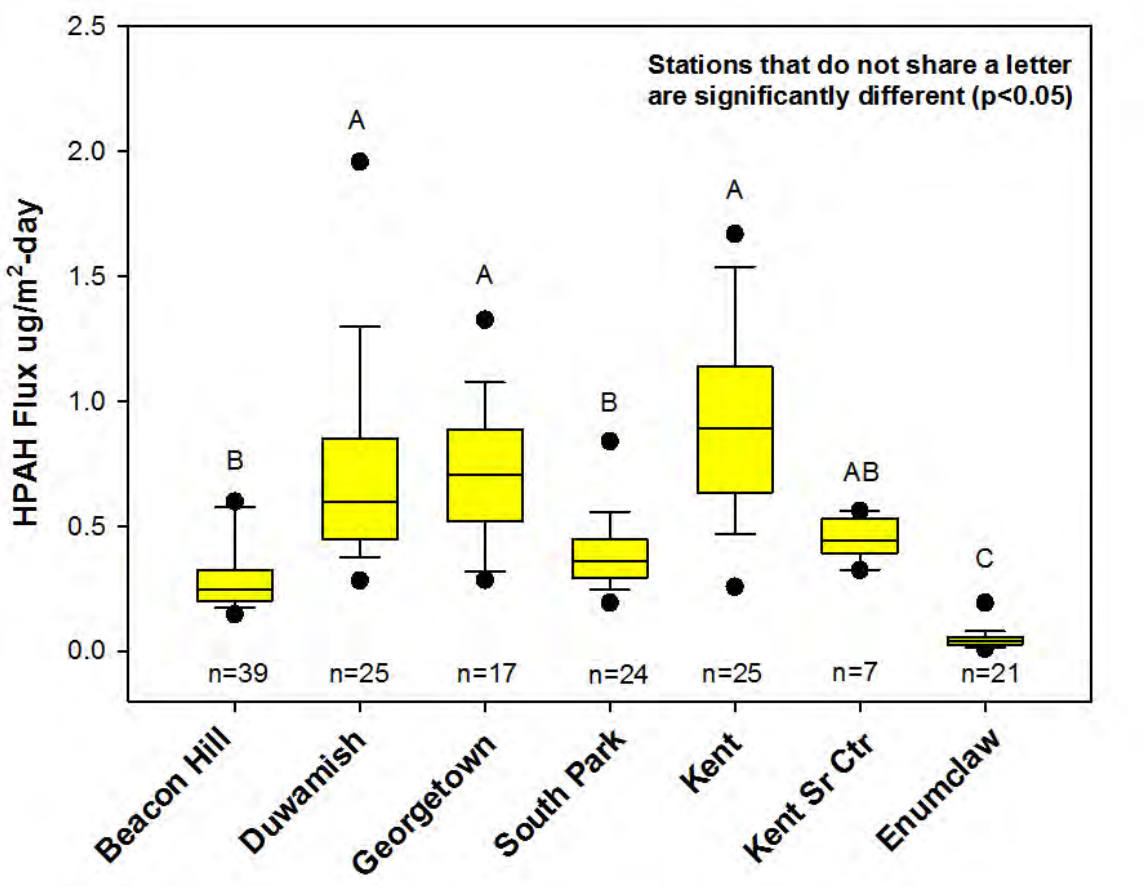


Figure 24. Boxplots of HPAH Flux by Station

5.3 PCBs

5.3.1 2013 Total PCBs Flux

Five PCB samples were collected at Duwamish, Georgetown and South Park stations for a total of fifteen samples. Measured Total PCB fluxes were higher at Georgetown relative to the Duwamish and South Park stations during four of the five sampling periods (Figure 25). Total PCB fluxes ranged from 2.9 ng/m^2-day at the Duwamish station to 205 ng/m^2-day at the Georgetown station (Table 28). Mean PCB fluxes at Duwamish and South Park were similar, but mean flux at Georgetown was almost four times higher. PCB samples were collected too infrequently over the study period to detect a temporal pattern in flux.

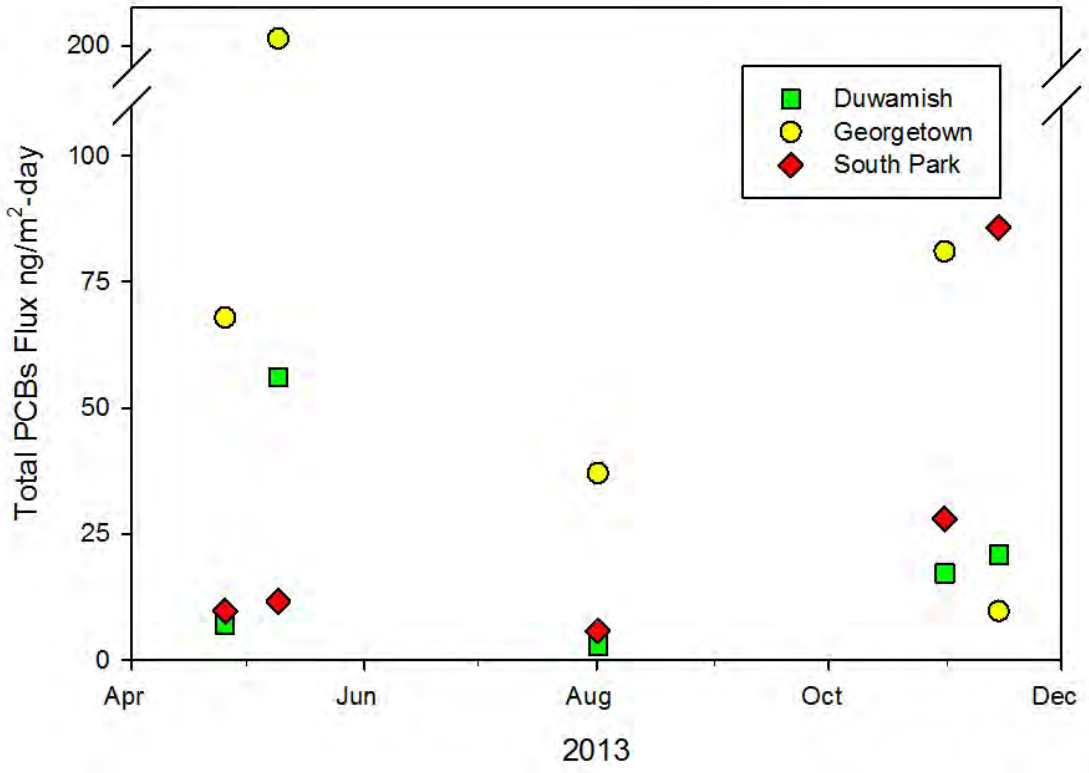


Figure 25. Total PCB Flux for each Collection Period by Collection Date and Station

Table 28. Summary of 2013 Total PCB Flux Data by Station (ng/m^2-day)

Station	Duwamish	Georgetown	South Park
Sample Size	5	5	5
Minimum	2.9	9.7	5.8
Maximum	56	205	86
Median	17	68	12
Mean	21	80	28

5.3.2 Total PCBs Flux – All Data

The PCB flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured PCB fluxes ranged from 0.35 ng/m^2-day at the Enumclaw station to 205 ng/m^2-day at the Georgetown station (Table 29).

Table 29. Summary of All PCB Flux Data by Station (ng/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	7	12	5	15	10	5	7
Minimum	2.25	2.87	9.68	4.61	0.91	1.40	0.35
Maximum	8.51	56.1	205	85.8	7.00	3.97	3.02
Median	4.99	9.65	67.9	18.0	4.35	1.99	0.75
Mean	4.98	16.2	80.0	20.6	3.87	2.48	1.12

Figure 26 displays boxplots of log-transformed PCB flux distributions by station with results of testing for significant differences between means. Variability in PCB flux as indicated by the 5th and 95th percentiles was largest at the Duwamish and Georgetown stations and lowest at the Kent SC station. ANOVA and post-hoc testing results indicate that mean PCB fluxes at Georgetown were significantly higher than at all other stations. Mean PCB fluxes were significantly lower at the Enumclaw station relative to all other stations except Kent and Kent SC. The mean PCB flux at South Park was significantly lower than Georgetown and higher than at all other stations except Duwamish. Mean PCB fluxes at Beacon Hill, Kent and Kent SC were not significantly different. Also, mean PCB flux at Beacon Hill was not significantly different from levels at the Duwamish station.

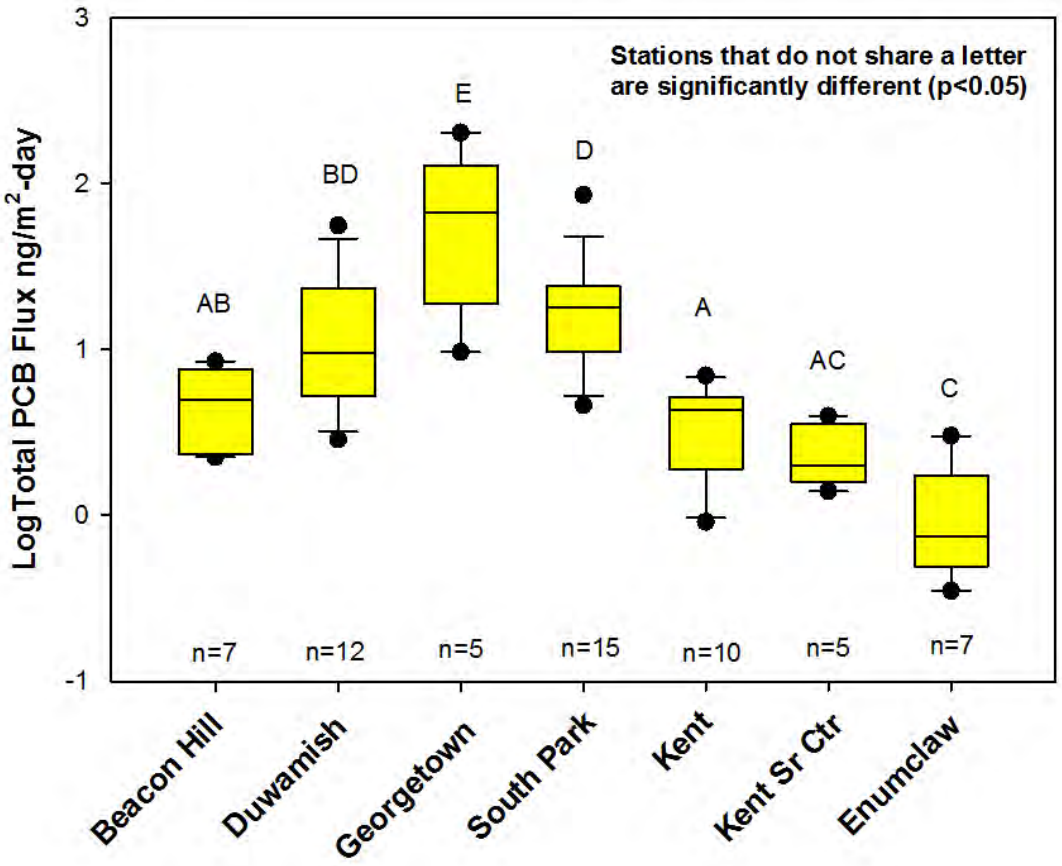


Figure 26. Boxplots of Lognormalized Total PCB Flux by Station

5.4 Dioxins and Furans

5.4.1 2013 Dioxins and Furans Flux

Five dioxin/furan samples were collected at each station for a total of fifteen samples. Measured total dioxin/furan fluxes were always higher at Georgetown relative to the Duwamish or South Park stations (Figure 27). Also, measured total dioxin/furan fluxes were generally higher at Duwamish relative to the South Park station. Total dioxin/furan fluxes ranged from 0.13 ng/m^2-day at the Duwamish station to 3.92 ng/m^2-day at the Georgetown station (Table 30). Mean dioxin/furan fluxes at Duwamish and South Park were similar, but the mean at Georgetown was more than four times higher than Duwamish.

Dioxin/furan samples were collected too infrequently over the study period to detect a temporal pattern in flux. However, variability in dioxin/furan flux at Georgetown appears higher than Duwamish or South Park stations (Figure 27).

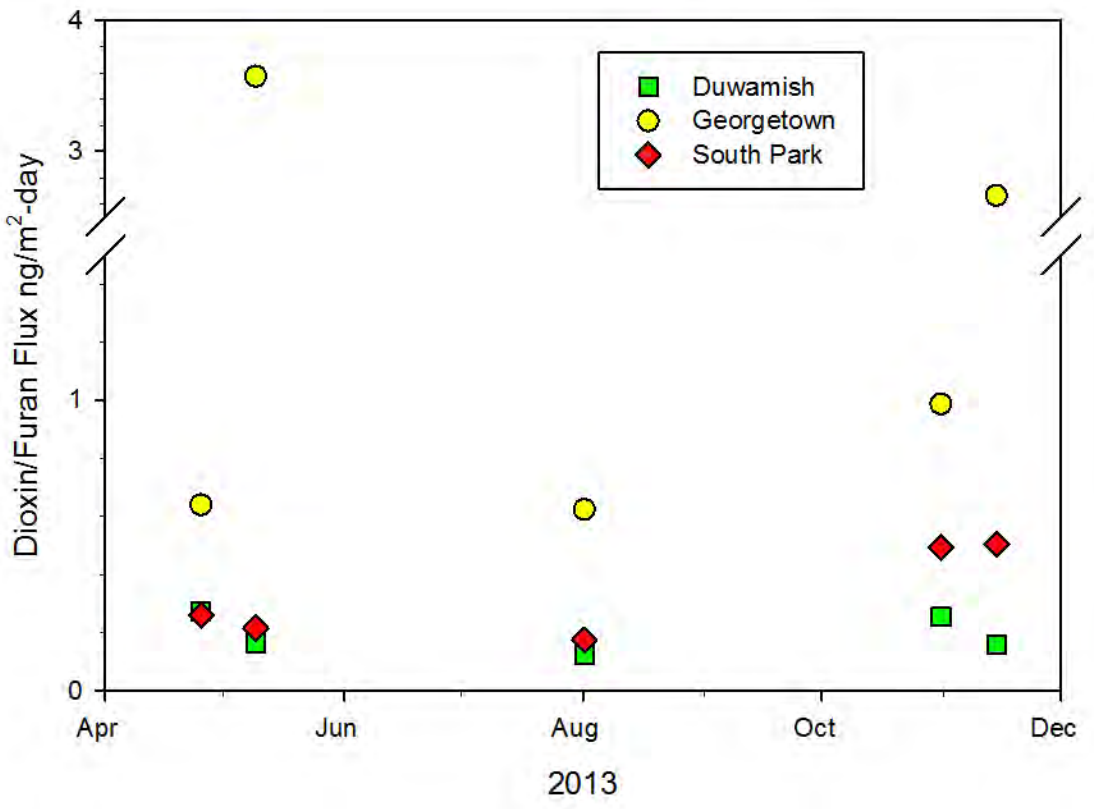


Figure 27. Total Dioxin/Furan Flux for each Collection Period by Collection Date and Station

Table 30. Summary of 2013 Total Dioxin/Furan Flux Data by Station (ng/m^2-day)

Station	Duwamish	Georgetown	South Park
Sample Size	5	5	5
Minimum	0.13	0.63	0.18
Maximum	1.14	3.92	0.52
Median	0.29	1.01	0.30
Mean	0.42	1.78	0.35

5.4.2 Dioxins and Furans Flux – All Data

The total dioxin/furan flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured total dioxin/furan fluxes ranged from 0.0023 µg/m^2-day at the South Park station to 24.4 µg/m^2-day at the Kent station (Table 31). The median total dioxin/furan flux at Kent is about half of the mean indicating a skewed distribution; the mean was heavily influenced by one or more high flux measurements.

The second Kent sampling station at Kent SC was originally installed to further evaluate the much higher total dioxin/furan fluxes detected at the original Kent station compared to other locations. The previous King County bulk atmospheric deposition report (King County 2013a) concluded that a small geographic scale effect was occurring at the Kent Station potentially related to the proximate rail line.

Table 31. Summary of All Total Dioxins and Furans Flux Data by Station (ng/m^2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	7	13	5	15	10	5	7
Minimum	0.15	0.11	0.62	0.18	0.65	0.19	0.04
Maximum	0.71	0.44	3.57	0.79	24.4	0.50	0.26
Median	0.32	0.25	0.99	0.41	3.13	0.31	0.07
Mean	0.35	0.25	1.70	0.40	6.50	0.34	0.11

Figure 28 displays boxplots of total dioxin/furan flux distributions by station with results of testing for significant differences between medians. Variability in dioxin/furan flux as indicated by the 5th and 95th percentiles was largest at the original Kent station and lowest at the Enumclaw station. The one-way ANOVA by ranks test confirms the median total dioxin/furan flux at Kent was significantly higher ($p<0.05$) than at Beacon Hill, Duwamish, and Enumclaw. The median total dioxin/furan flux was also significantly higher at Georgetown relative to Duwamish or Enumclaw. The median total dioxin/furan flux at Enumclaw was significantly lower than at Georgetown or Kent. No other significant differences were found, but small sample sizes may be limiting the ability to determine differences between stations.

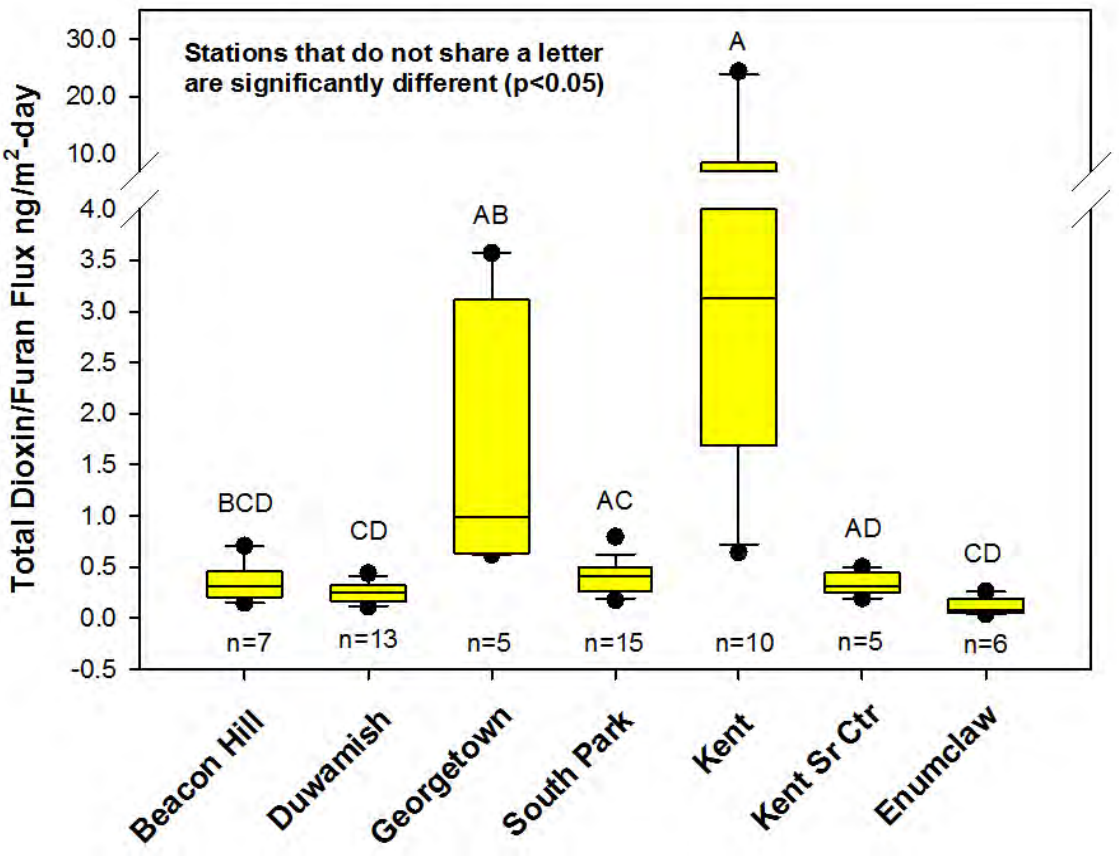


Figure 28. Boxplots of Total Dioxin/Furan Flux by Station

5.5 Dioxin TEQs

5.5.1 2013 Dioxin TEQs Flux

TEQs were calculated for all samples analyzed for dioxin/furan congeners. Dioxin TEQ based fluxes were always higher at Georgetown than the Duwamish or South Park stations (Figure 29). Dioxin TEQ fluxes ranged from 0.001 ng TEQ/m^2-day at the Duwamish station to 0.071 ng TEQ/m^2-day at the Georgetown station (Table 32). Mean dioxin TEQ fluxes at Duwamish and South Park were similar, but the mean at Georgetown was more than four times higher than at South Park. Dioxin/furan samples were collected too infrequently over the study period to detect a temporal pattern in flux (Figure 29).

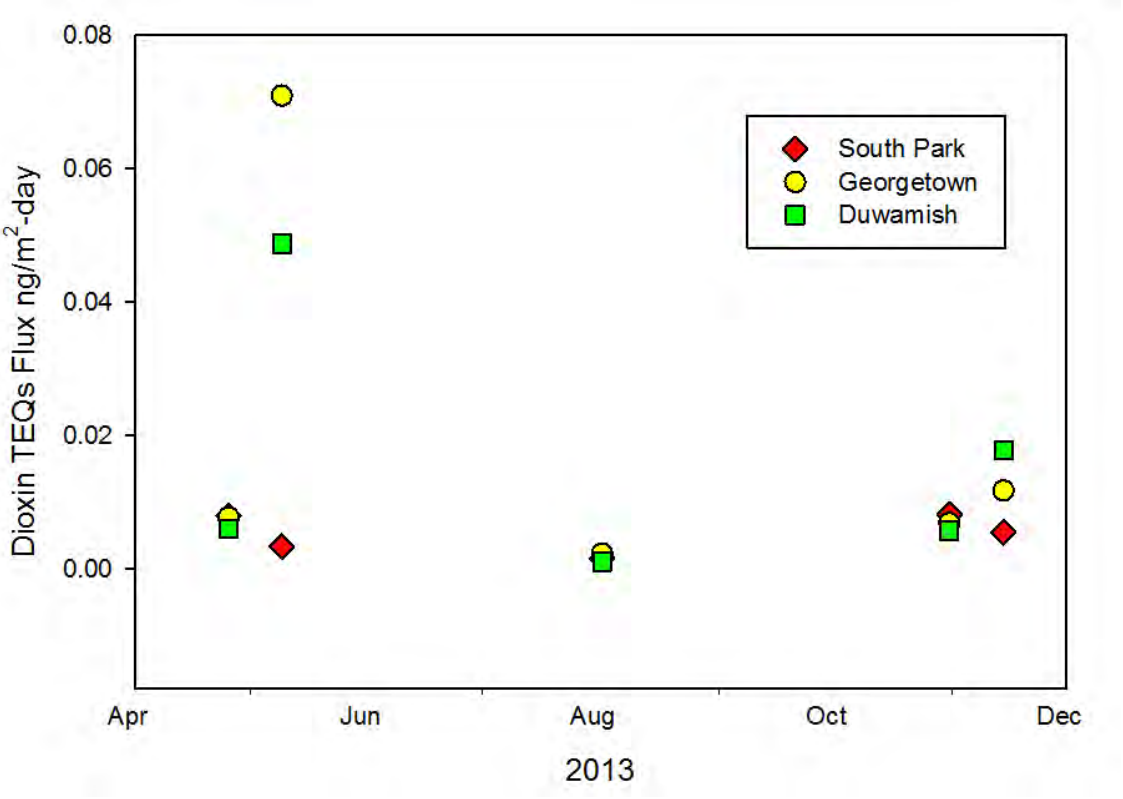


Figure 29. Total Dioxin TEQ Flux for each Collection Period by Collection Date and Station

Table 32. Summary of 2013 Dioxin TEQs Flux Data by Station (ng TEQ/m^2-day)

Station	Duwamish	Georgetown	South Park
Sample Size	5	5	5
Minimum	0.001	0.002	0.002
Maximum	0.049	0.071	0.008
Median	0.006	0.008	0.005
Mean	0.016	0.020	0.005

5.5.2 Dioxin TEQs Flux – All Data

The dioxin TEQ flux data from the 2011/2012 and 2013 studies were combined to examine overall ranges and spatial patterns. Measured dioxin TEQ fluxes ranged from 0.001 ng/m^2-day at the Duwamish and Enumclaw stations to 0.073 ng/m^2-day at the Kent station (Table 33).

Table 33. Summary of All Dioxin TEQs Flux Data by Station (ng/m2-day)

Station	Beacon Hill	Duwamish	George-town	South Park	Kent	Kent SC	Enumclaw
Sample Size	7	13	5	15	10	5	7
Minimum	0.003	0.001	0.002	0.002	0.004	0.004	0.001
Maximum	0.014	0.049	0.071	0.014	0.073	0.010	0.011
Median	0.006	0.005	0.008	0.005	0.014	0.005	0.004
Mean	0.007	0.009	0.020	0.006	0.022	0.006	0.006

Figure 30 displays boxplots of dioxin TEQ flux distributions by station with results of testing for significant differences between means. Variability in dioxin TEQ flux as indicated by the 5th and 95th percentiles was largest at the Kent and Georgetown stations. Variability at the Duwamish station was lower than that observed at Kent and Georgetown, but higher than the remaining stations. The one-way ANOVA by ranks test did not find any significant differences in medians between stations. This contrasts with spatial differences found for total dioxin/furan fluxes where the mean Kent flux was significantly higher than that observed at Duwamish, South Park and Enumclaw. If the congener content of samples at all stations was similar, similar statistical differences would be expected across stations between total dioxin/furan and total TEQ median fluxes. The lack of significant differences in total TEQ median fluxes between stations may be due to greater contributions of congeners with low TEFs at stations with high fluxes, such as Kent, compared to stations with lower median fluxes, such as Enumclaw.

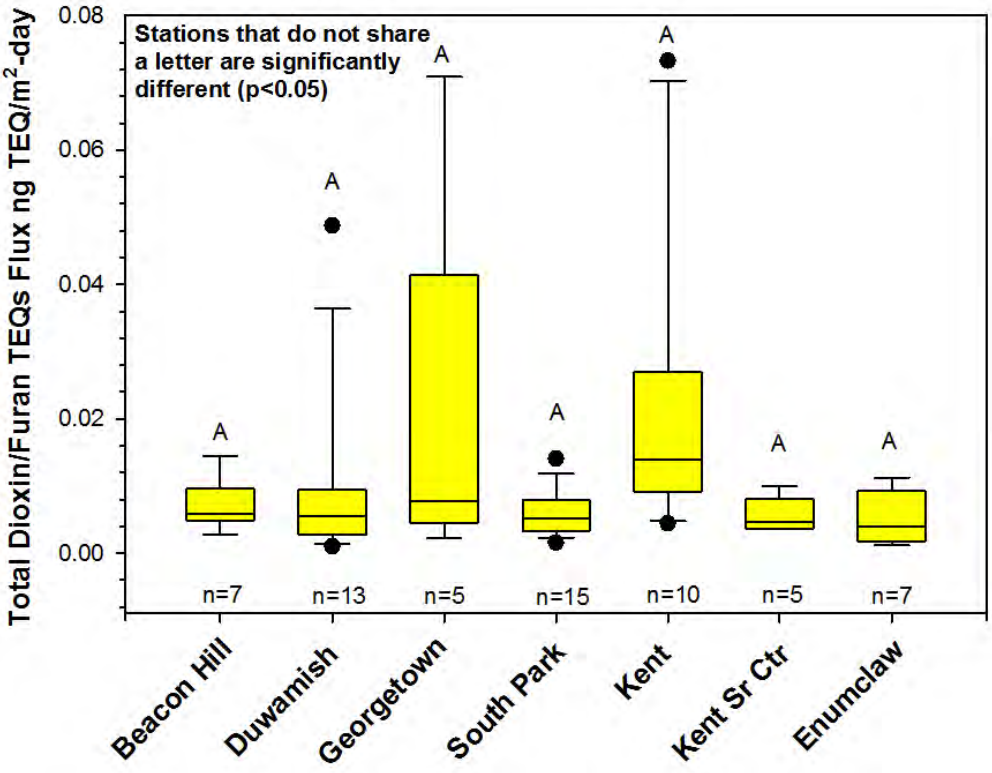


Figure 30. Boxplots of Dioxin TEQs Flux by Station

5.6 Congener Patterns – All Data

This section presents summaries of PCB and dioxin/furan congener composition to provide qualitative observations on sample variability and spatial differences. These differences may assist in understanding the nature of PCB sources to bulk atmospheric deposition.

5.6.1 PCB Congeners

The congener composition of PCB samples can vary depending on the source, including the Aroclor® mixture(s) used, and the effects of industrial/commercial use and weathering processes. For the purpose of examining differences in PCB congener composition between locations and samples, PCB congener flux data from both 2011-2012 and 2013 studies were summarized in two ways. First, for each sample the percent of each congener's contribution to the total flux of detected PCBs was calculated (field replicates were averaged). Then, for each sample, the percent contribution of each congener was summed by homologue group. The resulting percent contributions from each homologue group were plotted for each sample by station (Figures 31-37). The second method of examining PCB congeners was to average the percent contribution of each congener flux for all samples at a station. These average percentages were plotted for each station to enable visual comparison (Figures 38-44). PCB congeners that contributed at least four percent or more to the total PCBs in a sample at any station are labeled. A discussion of the results of the two PCB congener summary methods follows in this section.

The homologue profile for the Beacon Hill (Figure 31) station indicates that the pentachlorobiphenyl (Penta-CBs) and hexachlorobiphenyl (Hexa-CBs) congeners make up the largest fraction of samples collected at this location. Monochlorobiphenyls (Mono-CBs) were only detected in two of seven samples and nonachlorobiphenyls (Nona-CBs) and decachlorobiphenyls (Deca-CBs) were detected more frequently than monochlorobiphenyls, but not in all samples. The remaining seven homologue groups were present in all samples. The contributions of homologues in a sample vary with time. However, based on the limited number of samples it is not possible to discern a temporal pattern. Variability appears highest in the trichlorobiphenyls (Tri-CBs) and Penta-CBs; this is highlighted by the difference, which is nearly 20%, between the percent Tri-CBs in the 3/15/2012 sample and the 5/2/2012 sample.

The homologue profile for Duwamish (Figure 32) is similar to Beacon Hill in the dominance of Penta-CBs and Hexa-CBs and very low to no contributions from Mono-CBs and Deca-CBs. One exception is the uniquely high contribution of Nona-CBs and Deca-CBs to the 7/19/2012 sample. Percent contributions of different homologues appear to vary to a similar degree between samples.

Georgetown's homologue profile is different than the Beacon Hill or Duwamish stations. Tri and Tetra-CBs are the most dominant homologues in 3 of the 5 samples and Tetra-, Penta- and Hexa-CBs dominate the remaining two samples (Figure 33). However, there are still low to no contributions of Mono-, Nona- and Deca-CBs in Georgetown samples.

The homologue profile for South Park samples (Figure 34) has some similarities to the Duwamish and Georgetown profiles; however, some subtle differences can be observed in the relative contributions of certain homologues. For example, the contribution of Heptachlorobiphenyls (Hepta-CBs) is relatively small, but larger contributions from the Tri-CBs and Tetra-CBs are observed in samples from South Park compared to Duwamish.

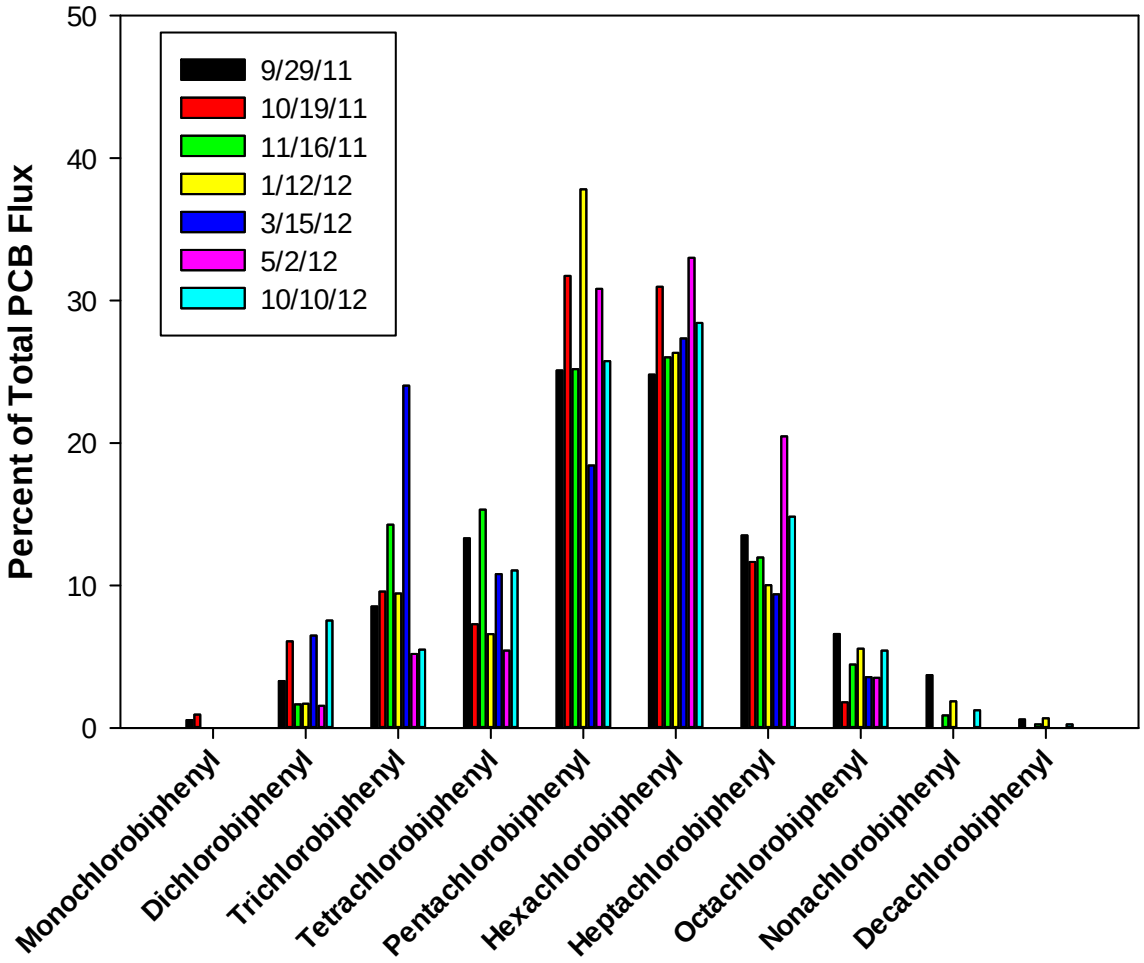


Figure 31. PCB Homologue Profile at Beacon Hill

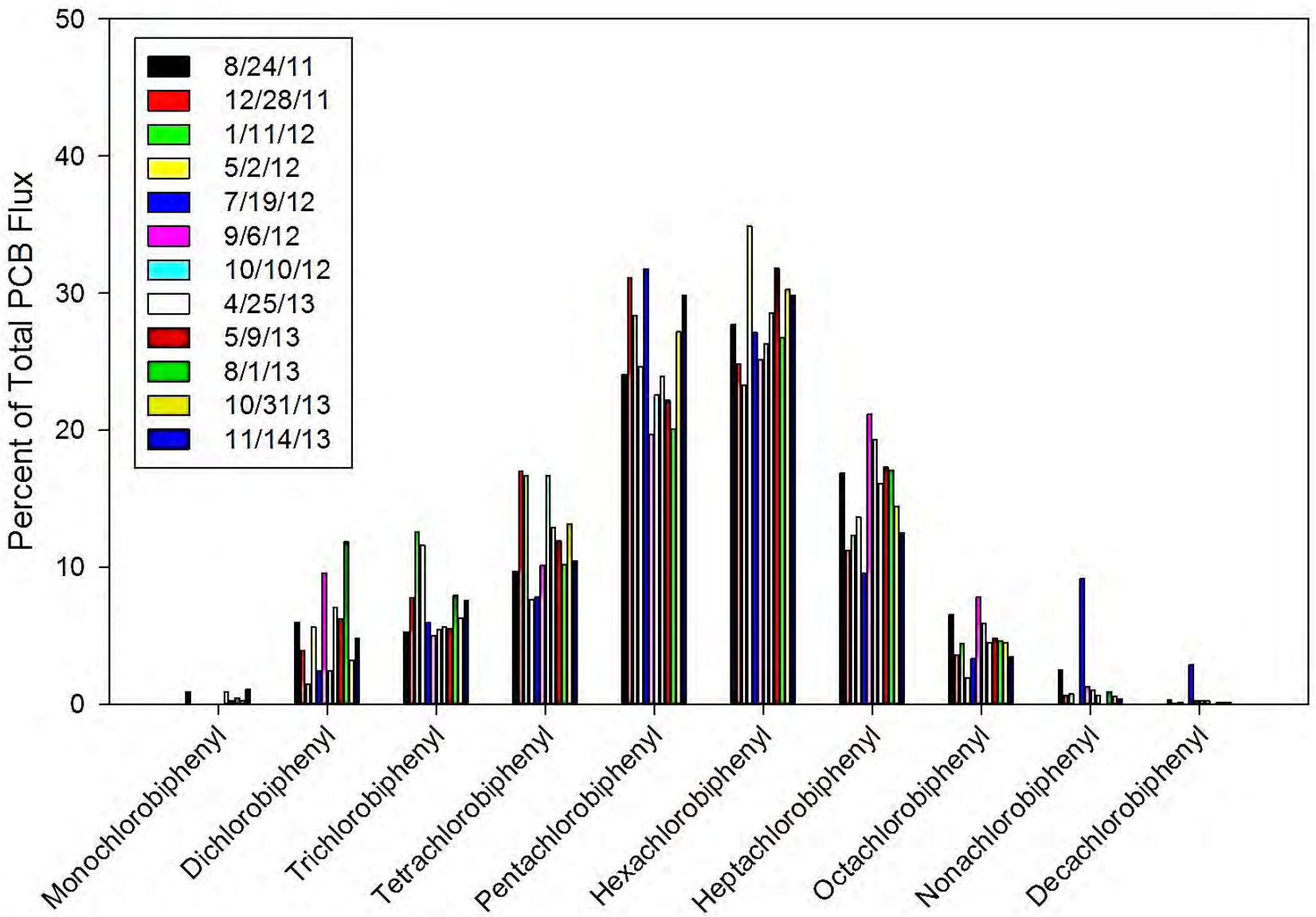


Figure 32. PCB Homologue Profile at Duwamish

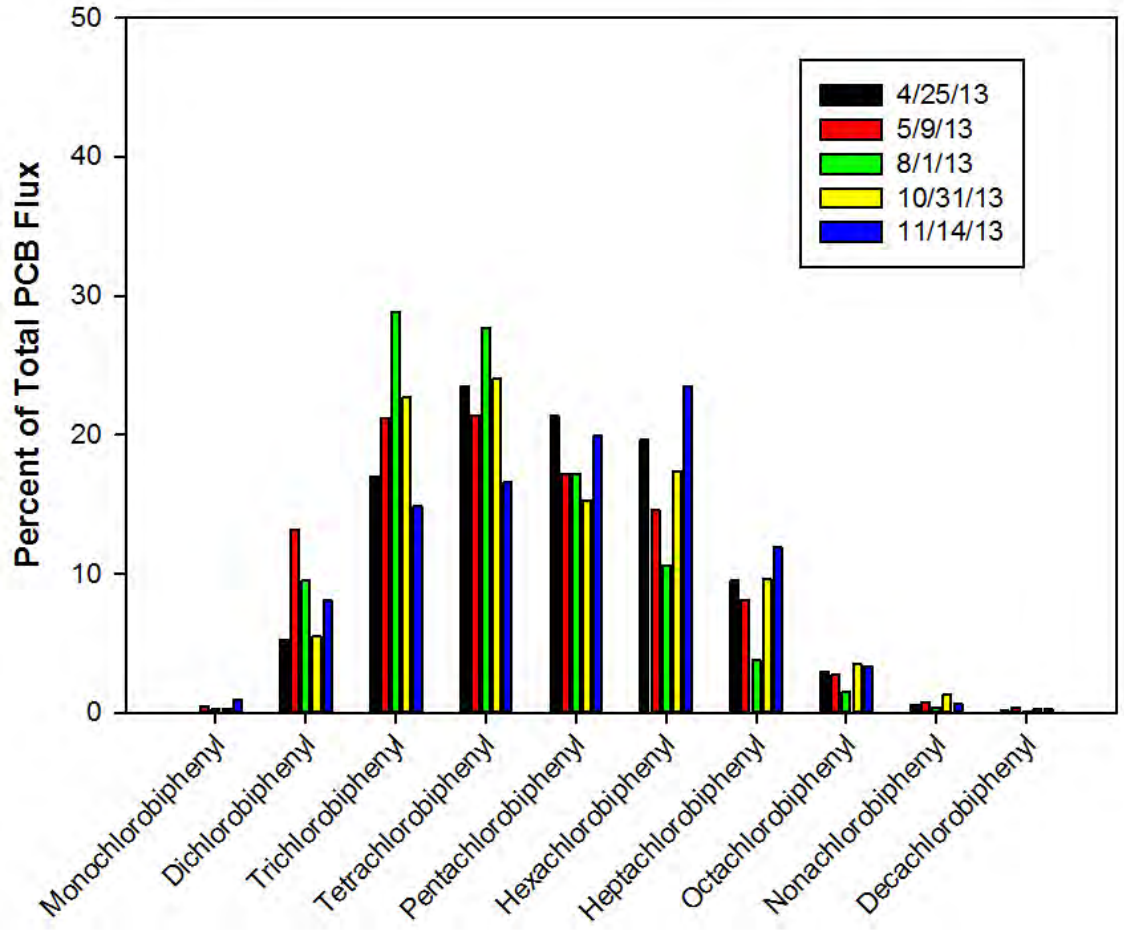


Figure 33. PCB Homologue Profile at Georgetown

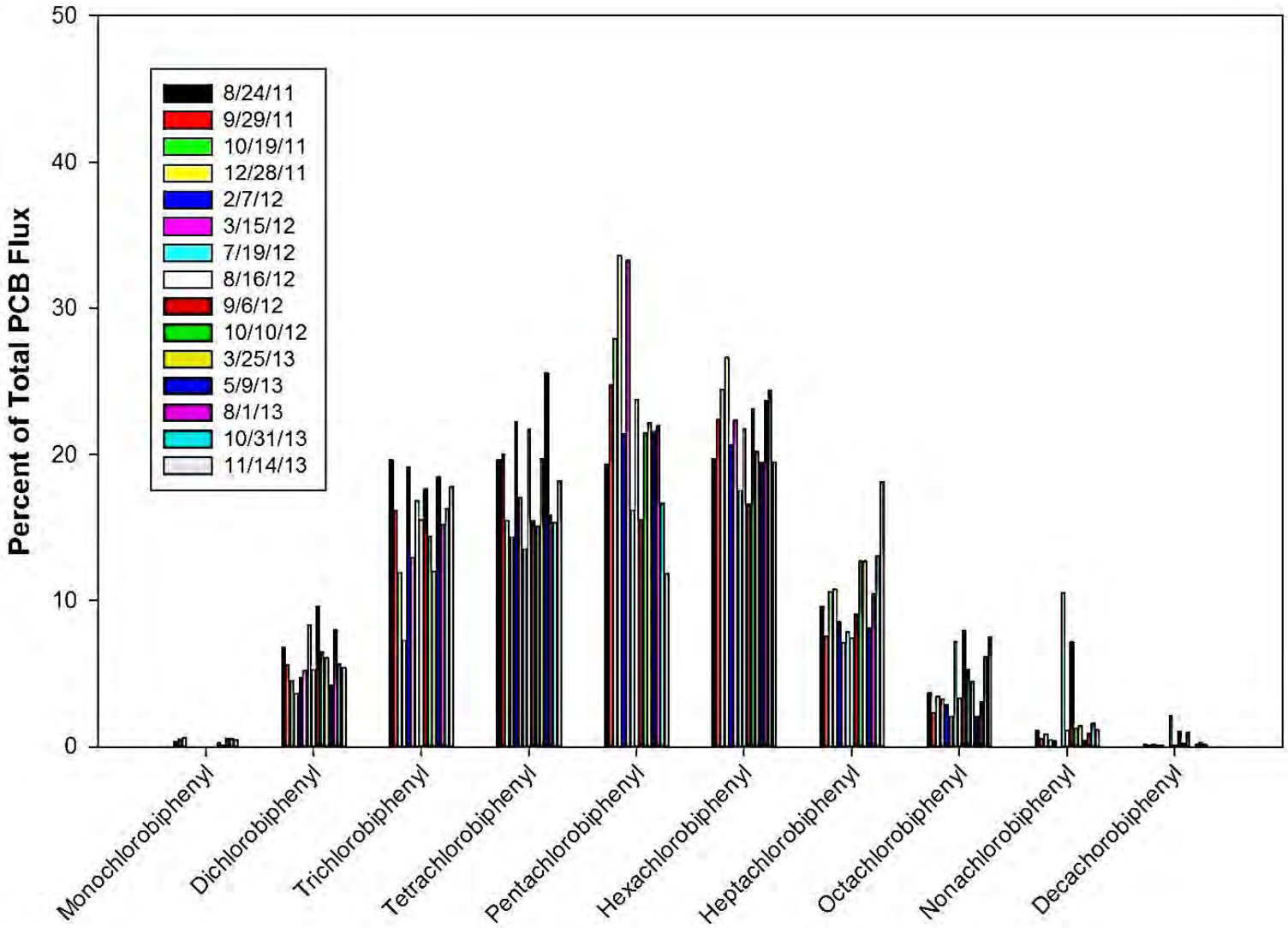


Figure 34. PCB Homologue Profile at South Park

The homologue profile at Kent (Figure 35) is similar to that observed at most other sites in the dominance of the Penta- and Hexa-CBs. Relative contributions of Tri- and Tetra-CBs were similar to Duwamish and lower than South Park. Relative contributions of Hepta-CBs at Kent were higher than at South Park and generally similar to Duwamish.

The PCB homologue profile at Kent SC (Figure 36) is limited due to the small number of samples collected at this site. Samples at this location appear to have a more even distribution of Tri-, Tetra-, Penta-, and Hexa-CBs than other stations, although in most samples Penta- and Hexa-CBs still dominate.

The PCB homologue profile for Enumclaw is the most unique of all stations (Figure 37). Mono-CBs and Nona-CBs were not detected in any samples and Deca-CBs were present in only one sample. Octa-CBs were only detected in two samples, but, typically present at other stations. The absence of some homologues in the Enumclaw samples may have been influenced by the low total PCB deposition measured in these samples which resulted in a higher number of undetected congeners. Penta- and Tri-CBs were often dominant in Enumclaw samples and not the Tetra-CBs, except in one December sample. However, the contributions of Penta- and Tri-CBs were highly variable over time ranging from 10 to 35 or 40%. The sometimes large relative contributions of Tri-CBs compared to Tetra-CBs to total PCBs are a unique characteristic at the Enumclaw station.

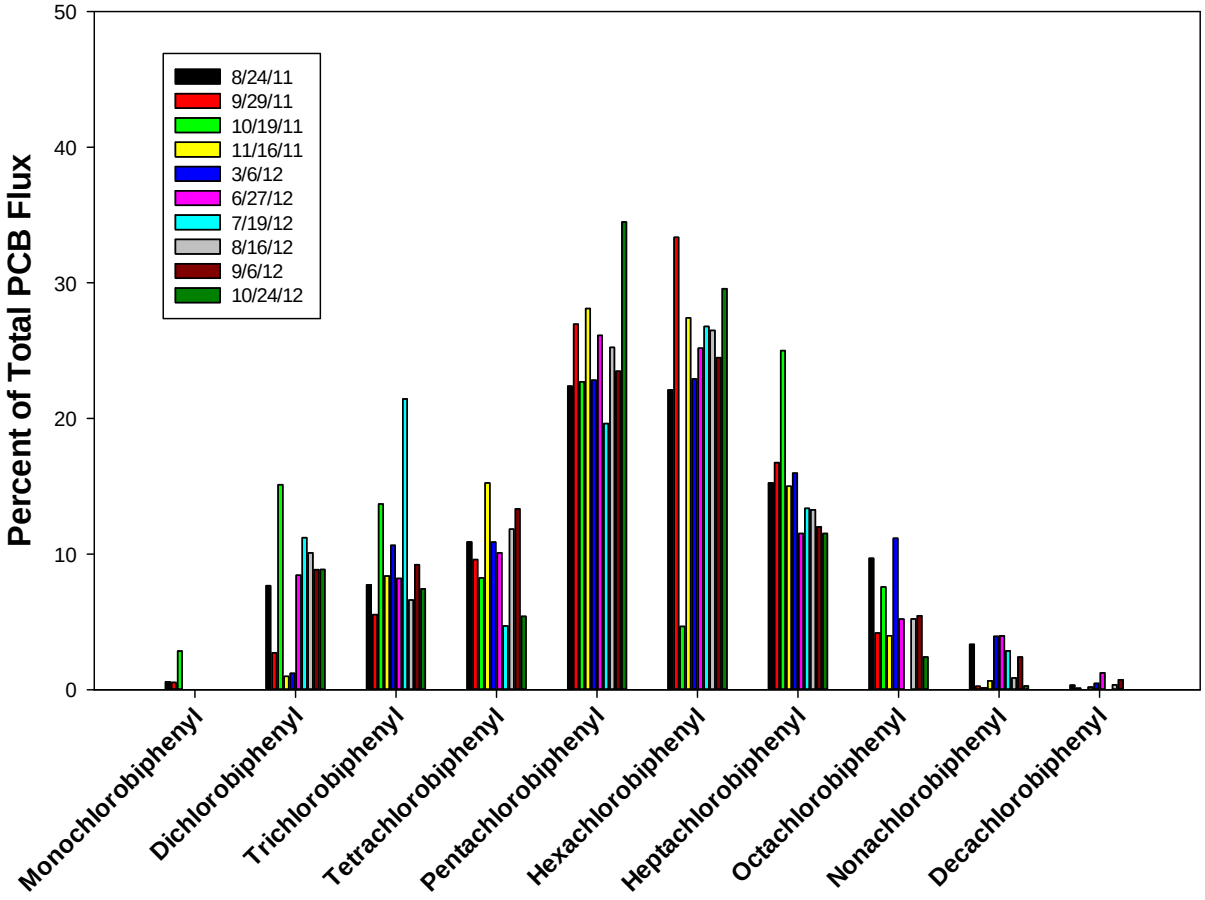


Figure 35. PCB Homologue Profile at Kent

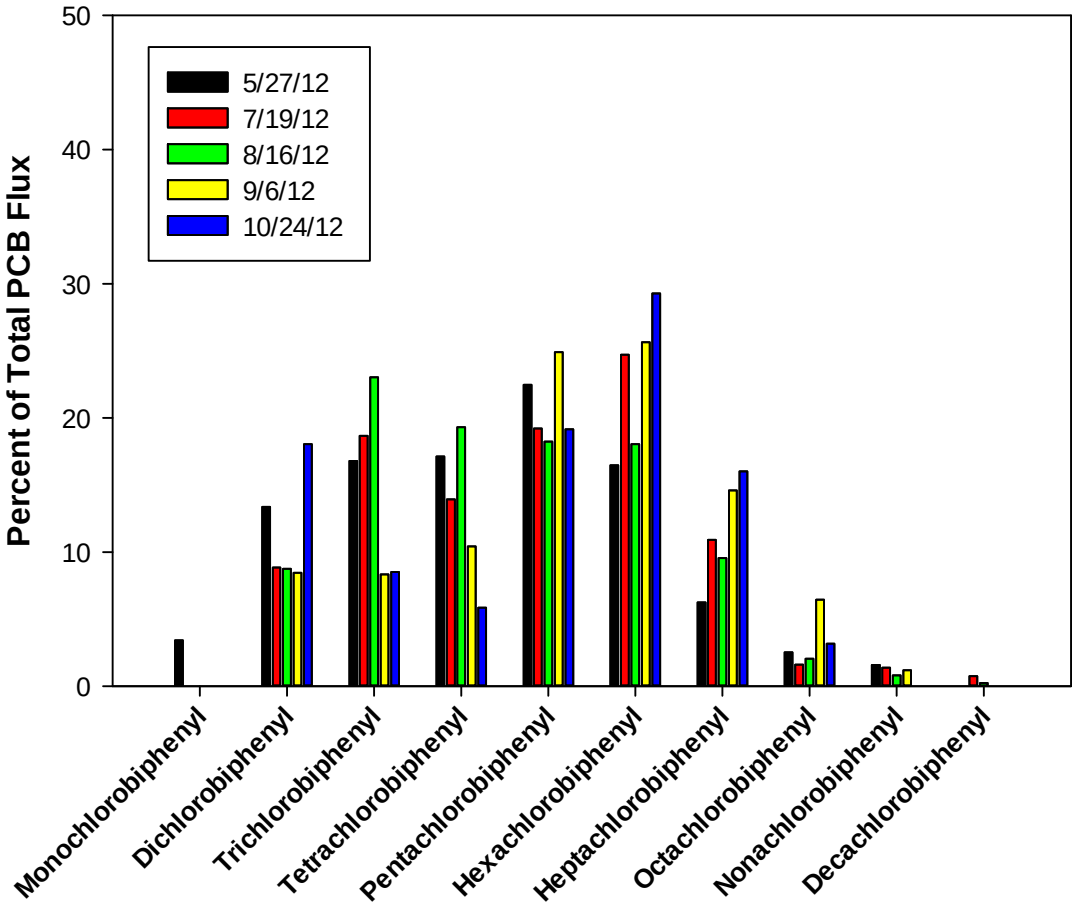


Figure 36. PCB Homologue Profile at Kent SC

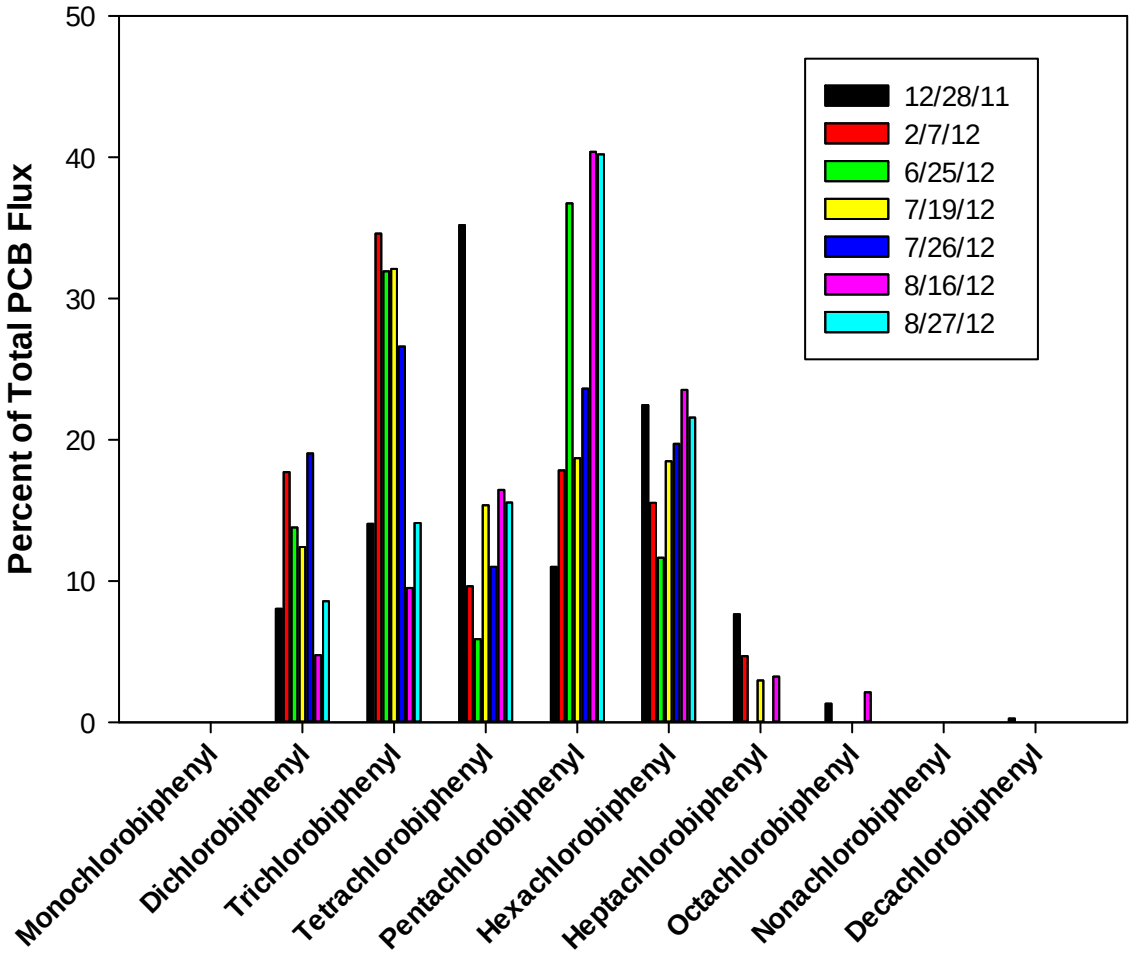


Figure 37. PCB Homologue Profile at Enumclaw

The congener profile for Beacon Hill (Figure 38) shows that many congeners are present, but on average, few contribute more than four percent to the total PCB flux. PCB-129 contributes the most at just under eight percent of the total PCB flux. Other dominant congeners at Beacon Hill include PCB-90, PCB-110, PCB-118, PCB-147, PCB-153 and PCB-180.

The congener profile for the Duwamish station (Figure 39) is similar to that of the Beacon Hill station. The main differences are the slightly lower contributions of mid-chlorinated congeners such as PCB-110 and PCB-129; decreases in this range appear to be compensated for by increases in contributions from lower-chlorinated congeners like PCB-11 and PCB-61.

The average contribution of congeners in the Georgetown station samples is more evenly distributed than at the Duwamish or Beacon Hill stations. Contributions from PCB-20,

PCB-61 and PCB-129 are greatest at Georgetown, but only contribute just over 4% each. However, the same congeners appear to be present at Georgetown as those detected at the Duwamish and Beacon Hill stations. Overall, reductions in higher-chlorinated PCB congeners are replaced by increases in lower-chlorinated congeners (e.g., PCB-20 and PCB-61).

In samples from the South Park station (Figure 41), lower-chlorinated congeners (e.g., PCB-20 and PCB-61) contribute more to the total PCB flux than at the Duwamish station, but less than at Georgetown. Key congeners in Beacon Hill and Duwamish samples, such as PCB-110, PCB-147, and PCB-153, are less dominant in samples at South Park. PCB-20 and PCB-61 and several lower-chlorinated congeners are more prominent in South Park samples than in Beacon Hill or Duwamish samples.

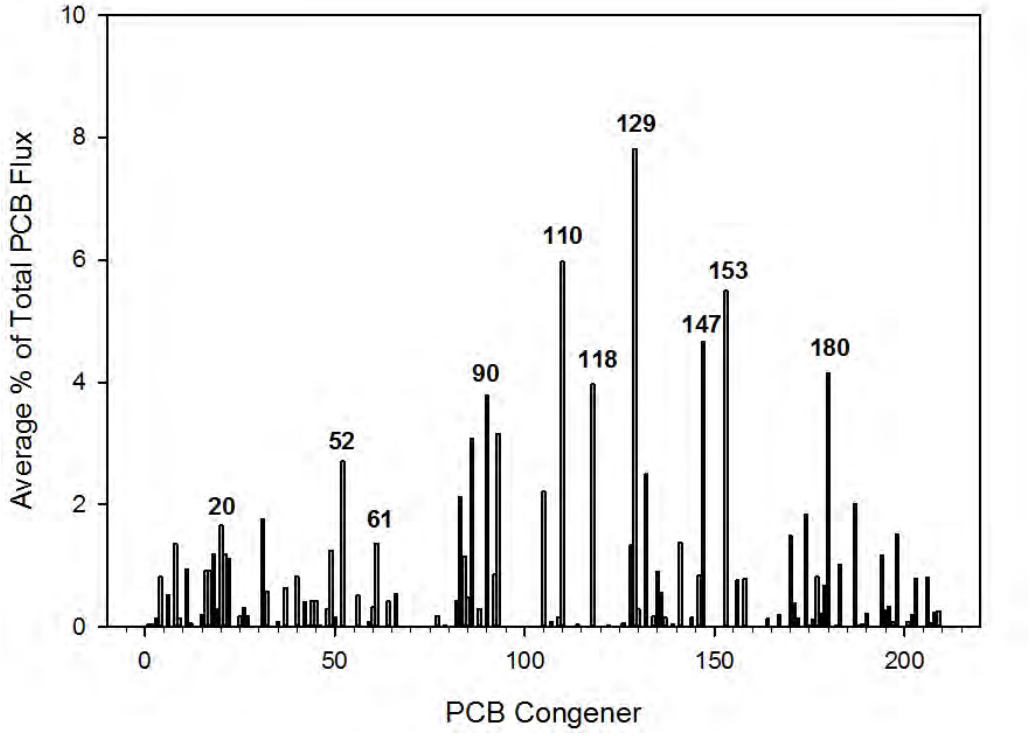


Figure 38. Average Congener Contribution to Total PCB Flux at Beacon Hill (n=7)

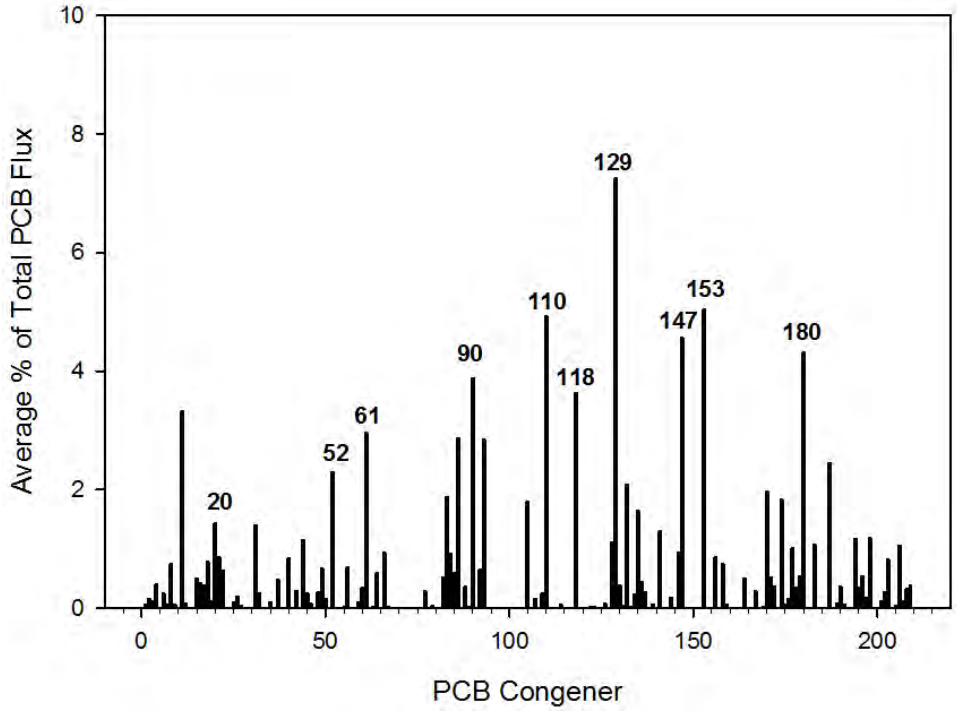


Figure 39. Average Congener Contribution to Total PCB Flux at Duwamish (n=12)

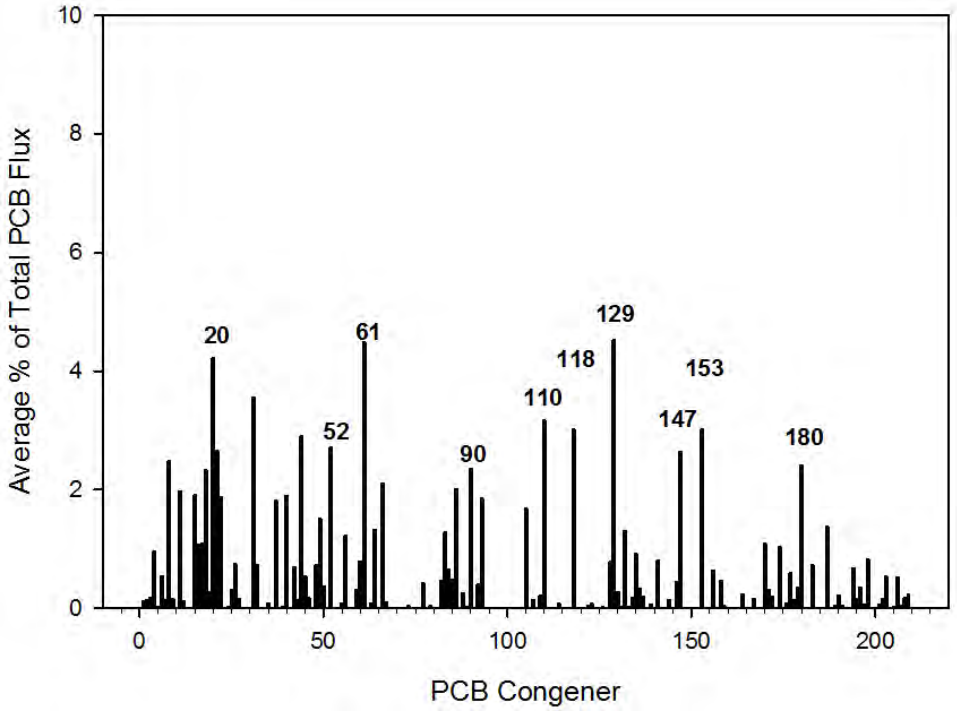


Figure 40. Average Congener Contribution to Total PCB Flux at Georgetown (n=5)

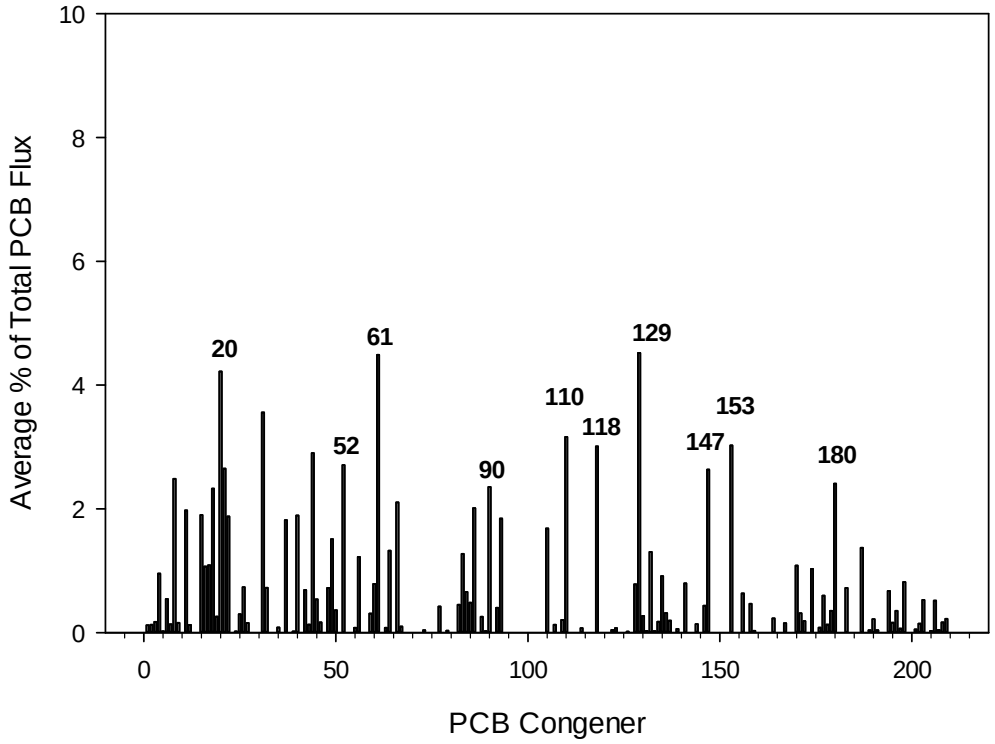


Figure 41. Average Congener Contribution to Total PCB Flux at South Park (n=15)

Although the dominant congeners in samples from Kent (Figure 42) appear similar to those observed in samples from the Beacon Hill, Duwamish and South Park stations, there are some differences in the congener patterns. Contributions from low-chlorinated congeners, such as PCB-20, to the total PCB flux are lower at the Kent station with the exception of PCB-8 and PCB-11, which collectively contribute a greater percentage to the total PCB flux than at any of the three LDW corridor stations. The dominant congener at the Kent station is PCB-110 rather than PCB-129 which dominates at the Duwamish and South Park stations.

The PCB congener profile at the Kent SC station (Figure 43) differs from that at the Kent station in multiple ways. First, the proportions of PCB-110 and PCB-129 at the Kent SC station are different than Kent with PCB-129 being the most dominant congener at Kent SC, rather than PCB-110. Also, the lower-chlorinated congeners such as PCB-20 and PCB-52 contribute more to total PCB flux at Kent SC. Lastly, PCB-147 contributes relatively more to the total at Kent than at the Kent SC station.

The congener profile at Enumclaw (Figure 44) has some similarities to the other study sites in that PCB-110 and PCB-153 are among the most dominant congeners. However, several characteristics make Enumclaw unique. First, congeners above PCB-153 (except PCB-180) contribute little to nothing to total PCB flux. Conversely, many of the lower-chlorinated

congeners contribute more to total PCB flux than at any other station. Second, PCB-129 is less dominant at Enumclaw than at other stations. Lastly, PCB-52 contributes greater than four percent to the total PCB flux at Enumclaw station – this occurs at no other station. Enumclaw shares some aspects of the congener pattern observed in the Georgetown and Kent SC samples in the prominence of lower-chlorinated congeners.

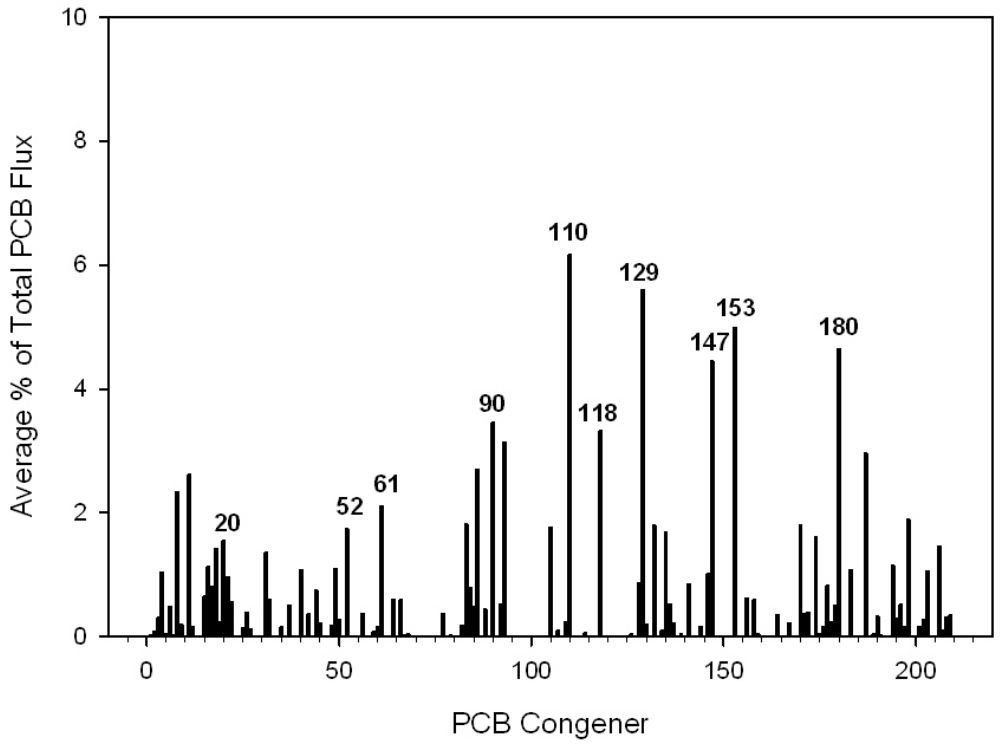


Figure 42. Average Congener Contribution to Total PCB Flux at Kent (n=10)

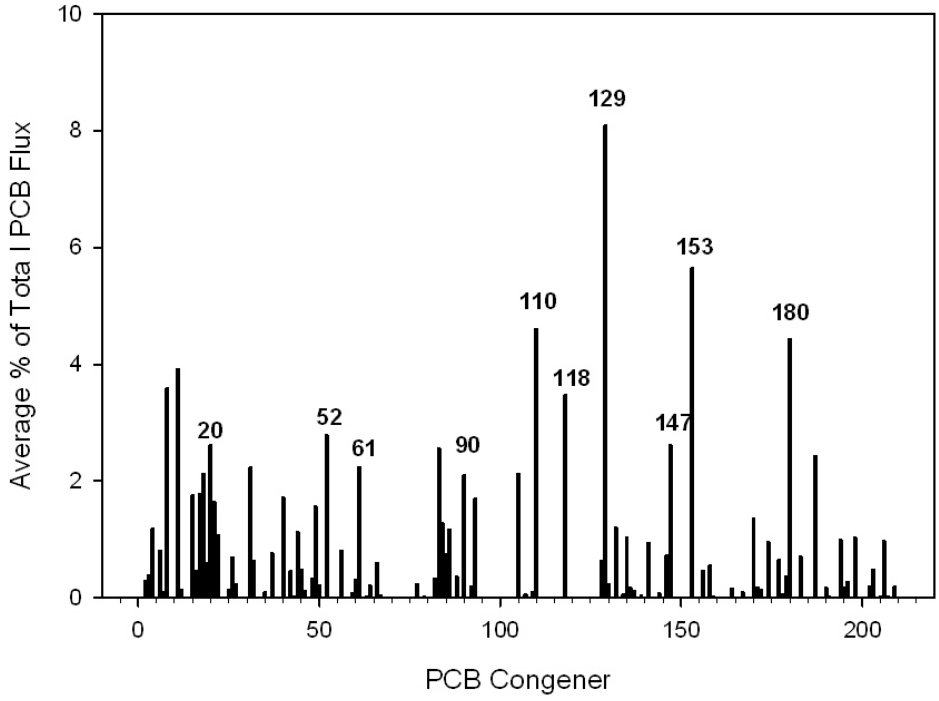


Figure 43. Average Congener Contribution to Total PCB Flux at Kent SC (n=5)

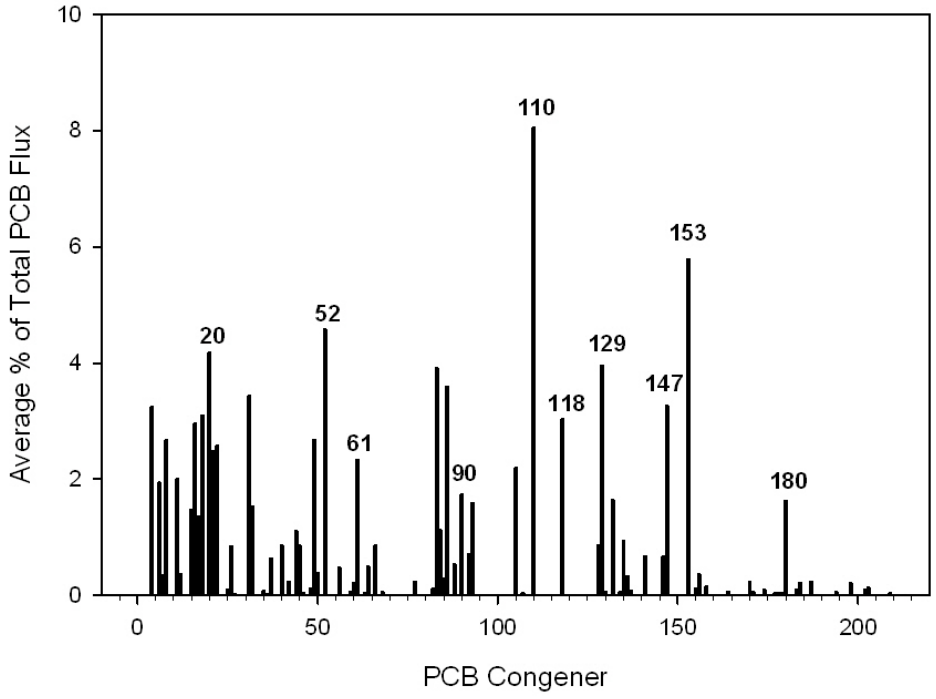


Figure 44. Average Congener Contribution to Total PCB Flux at Enumclaw (n=7)

5.6.2 Dioxins and Furans Congeners

Unlike PCBs, dioxins and furans are not commercial products, but are byproducts of the combustion of chlorinated compounds. Similar to PCB congeners, dioxin and furan congeners present in the environment may vary depending on the source type(s) and effects of industrial and weathering processes. To examine the differences in dioxin and furan congeners between samples and locations, the percent contribution of each congener to the total flux was calculated for each sample (field replicates were averaged) in the 2011-2012 and 2013 studies. The majority of the 17 dioxin/furan congeners contributed a negligible amount to the total dioxin/furan flux. For visual presentation, percentages were only graphed for congeners that contributed more than 3% in at least one sample: 1,2,3,4,6,7,8-heptachlorodibenzodioxin (1,2,3,4,6,7,8-HPCDD), octadibenzodioxin (OCDD), 1,2,3,4,6,7,8-heptachlorodibenzofuran (1,2,3,4,6,7,8-HPCDF), and octadibenzofuran (OCDF) (Figures 44–49).

At Beacon Hill, OCDD consistently dominated every sample at about 80% or more of the total dioxin/furan flux (Figure 45). The congener 1,2,3,4,6,7,8-HPCDD was detected in every sample, but 1,2,3,4,6,7,8-HPCDF and OCDF were absent from some samples. Congener contributions were generally consistent between samples except for the November 16, 2011 and May 2, 2012 sampling events where 1,2,3,4,6,7,8-HPCDD was lower or higher by approximately 4% and OCDF was also different (higher or not detected).

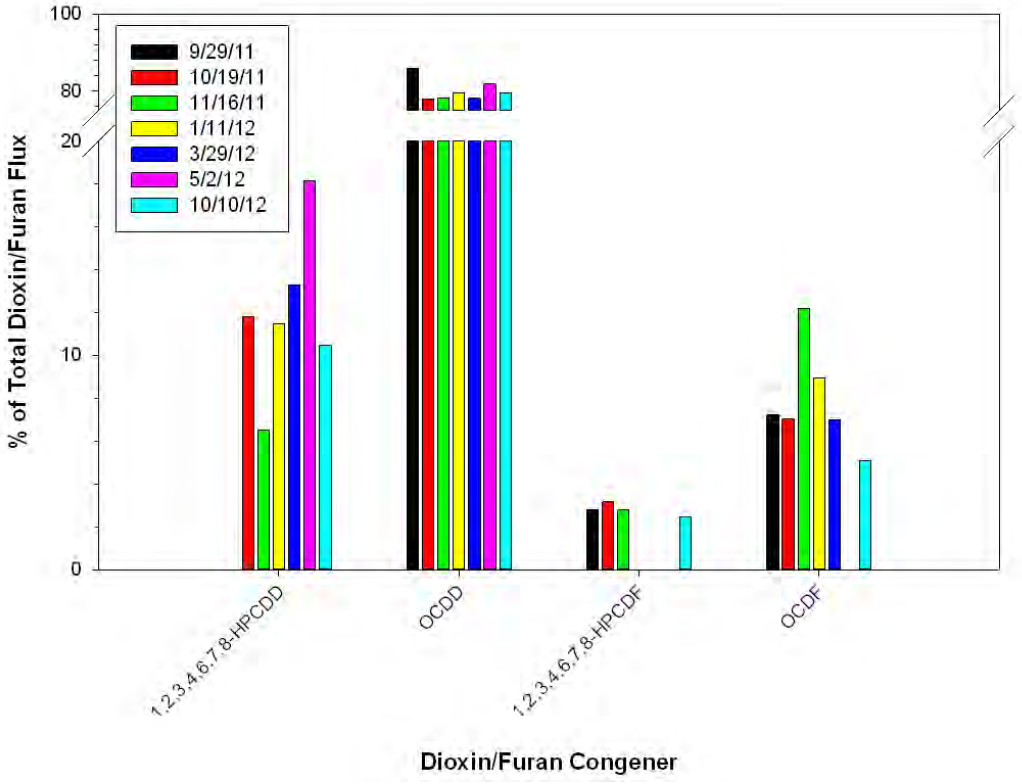


Figure 45. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Beacon Hill Station

Similar to Beacon Hill, OCDD was the dominant dioxin/furan congener in every sample except one at the Duwamish station. In the May 9, 2013 samples OCDD was K-qualified by the laboratory (K qualifiers are considered nondetect when calculating dioxin and furan sums); therefore, the majority of this sample was comprised of what is typically the next most common congener - 1,2,3,4,6,7,8-HPCDD. For all other samples, the congener 1,2,3,4,6,7,8-HPCDD contributed approximately 6-18% to total flux and 1,2,3,4,6,7,8-HPCDF and OCDF were not detected in some samples (Figure 46).

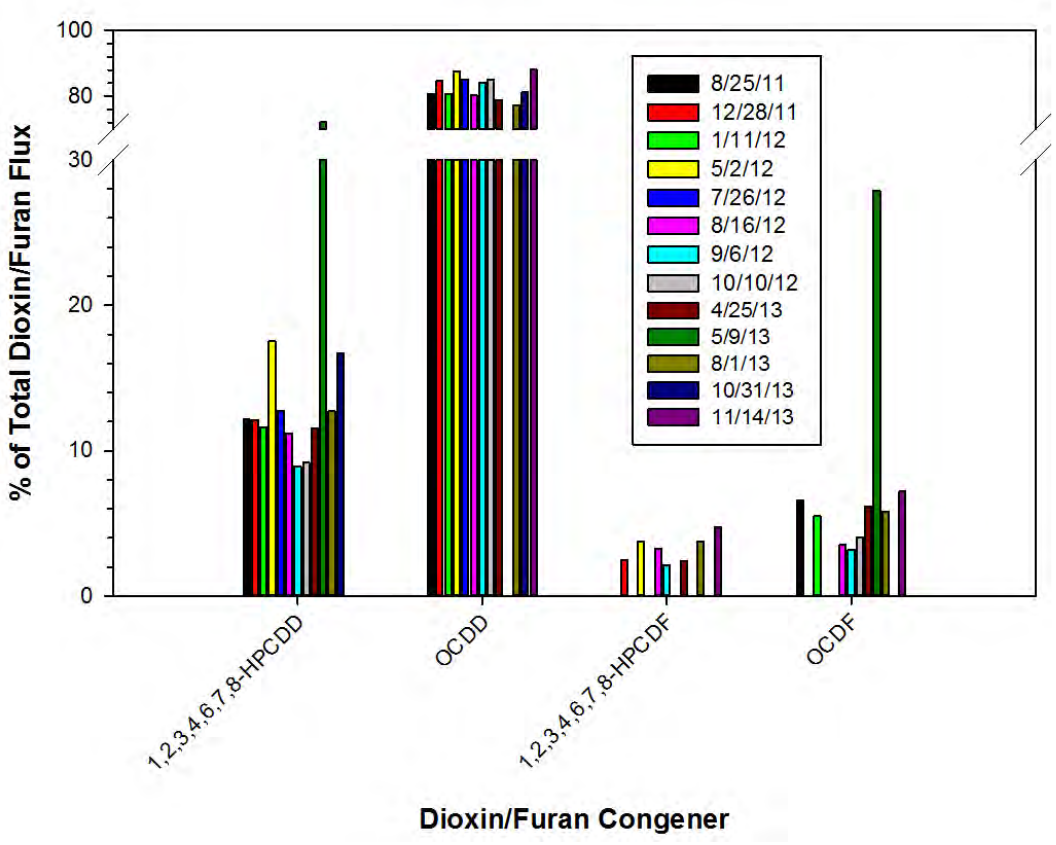


Figure 46. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Duwamish Station

Fewer samples were collected at Georgetown (n=5) than Beacon Hill (n=7) or Duwamish (n=13) stations. However, samples at Georgetown appear to have a similar congener composition to these stations as well as South Park and Kent SC (Figure 47). OCDD dominated and consistently contributed approximately 80% and 1,2,3,4,6,7,8-HPCDD contributed approximately 10% to the total dioxin/furan flux in every sample. The four dominant congeners, except 1,2,3,4,6,7,8-HPCDF, were detected in every sample.

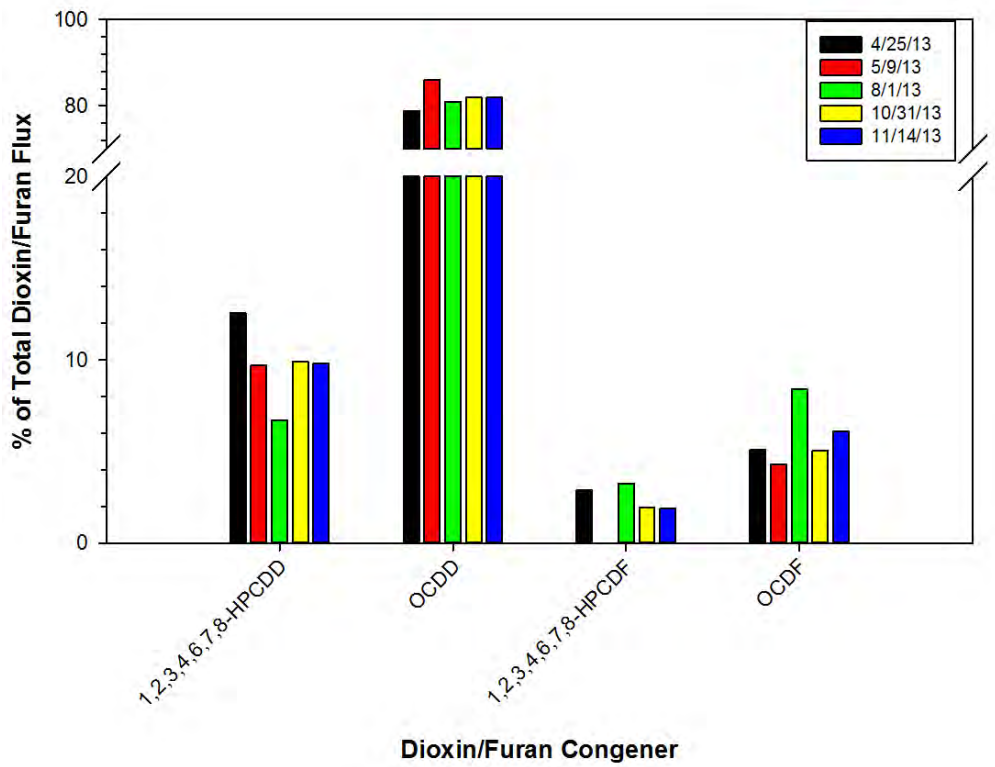


Figure 47. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Georgetown Station

The dioxin/furan congener profile at South Park station is similar to that at Duwamish station (Figure 48). OCDD dominated and consistently contributed approximately 80% and 1,2,3,4,6,7,8-HPCDD contributed approximately 10% to the total dioxin/furan flux in every sample. When detected, the two furan congeners were present at 6% percent or less.

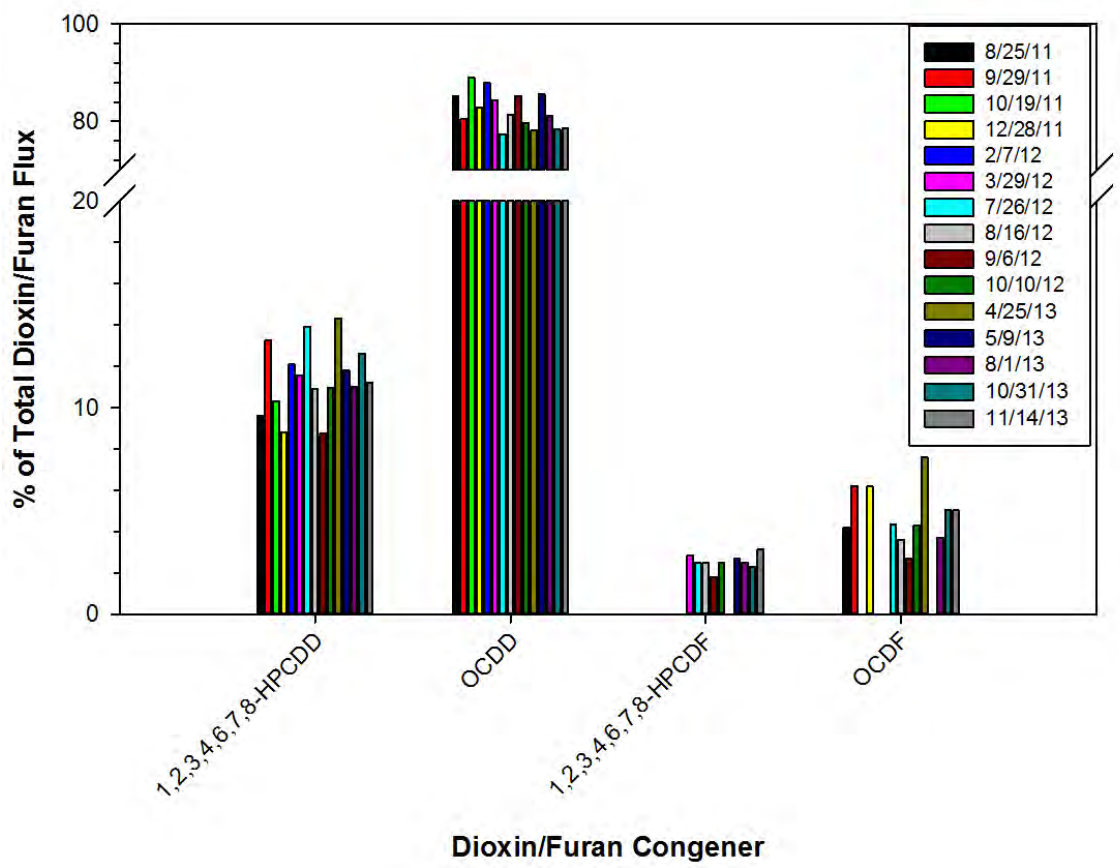


Figure 48. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at South Park Station

The dioxin/furan congener profile at Kent station (Figure 49) is different than that observed at the Beacon Hill, Duwamish, Georgetown, or South Park stations. OCDD is the dominant congener, but it contributes less than 80% in most samples and 1,2,3,4,7,8-HPCDD also contributes less than at the other stations. Also, the two furans are present in all Kent samples and contribute more to the total dioxin/furan flux; this is especially notable for OCDF relative to the other locations. Congener contributions to total dioxin/furan flux were generally consistent between samples except for OCDF in the July 19 and September 6, 2012 samples; OCDF contributed notably less to the total dioxin/furan flux estimated from these samples.

The dioxin/furan congener profile at Kent SC (Figure 50) is more similar to Beacon Hill, Duwamish, Georgetown, and South Park than Kent station. The 1,2,3,4,6,7,8-HPCDD congener contributes 10% or more at Kent SC station compared to 10% or less at Kent station to the total dioxin/furan flux. Similar to Beacon Hill, Duwamish, Georgetown, and South Park stations, 1,2,3,4,6,7,8-HPCDF is not present in every sample. Also, OCDF is present at similar contributions to these three stations.

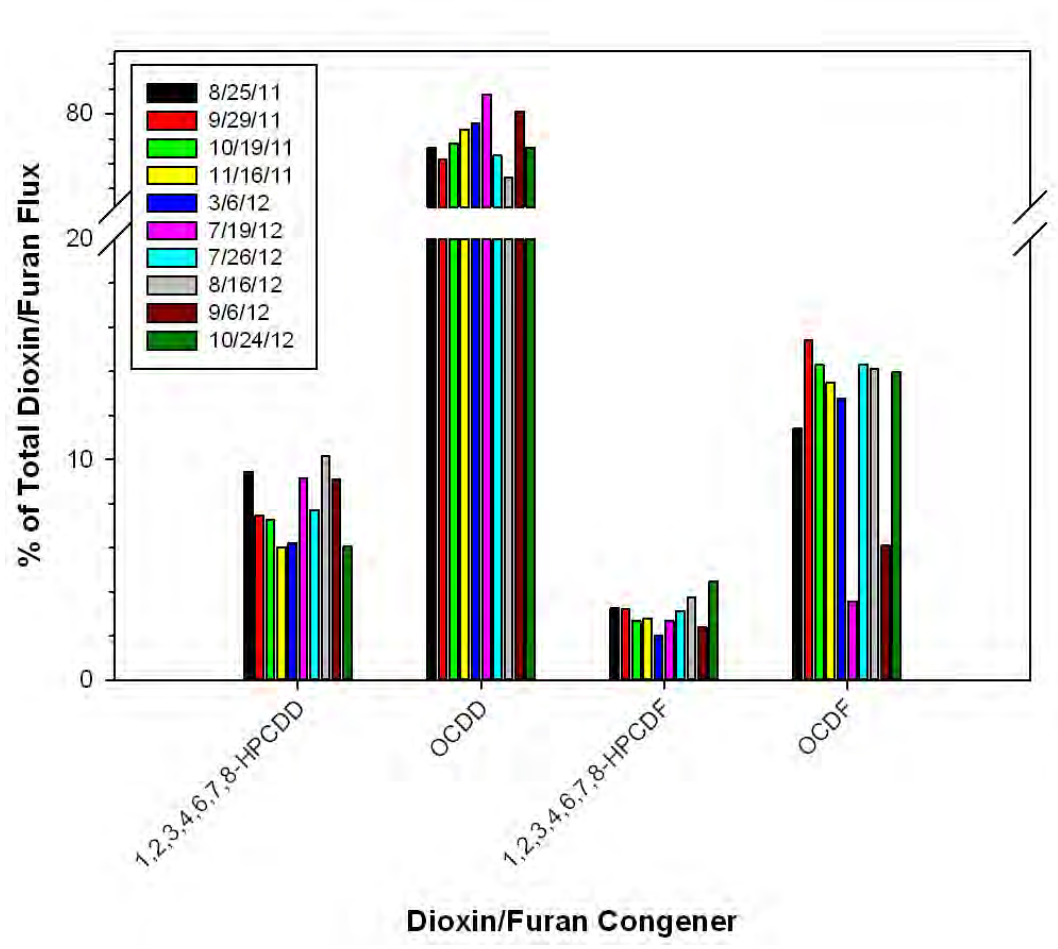


Figure 49. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Kent Station

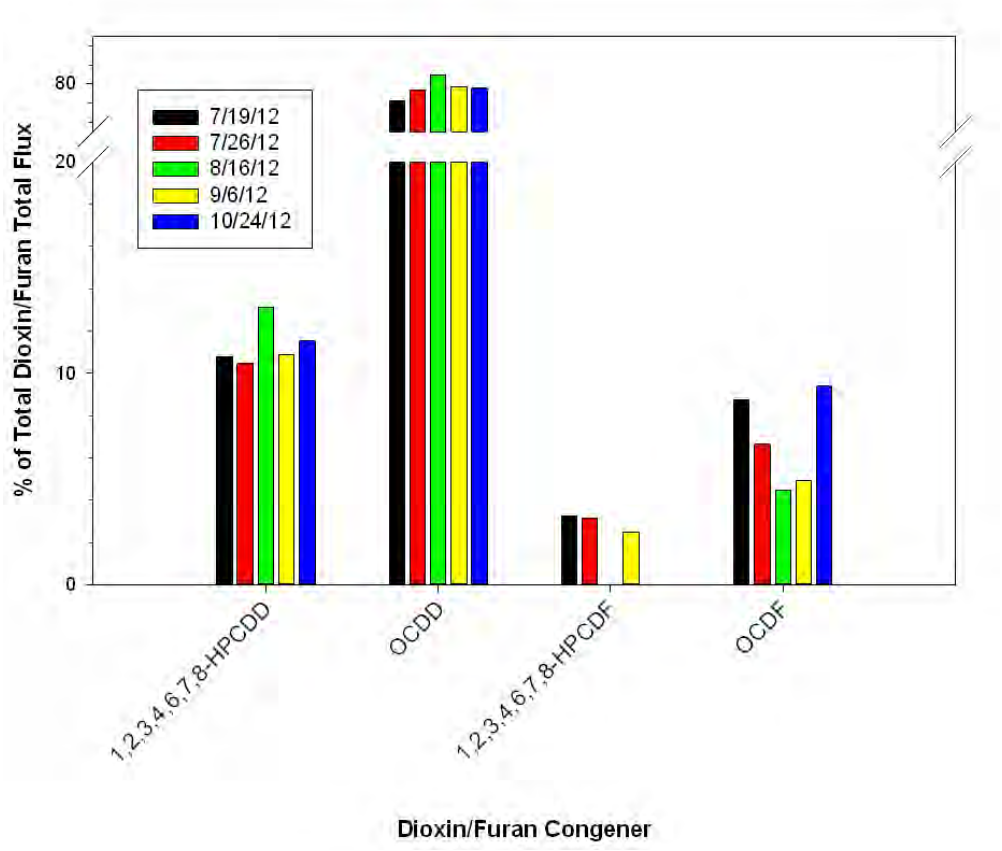


Figure 50. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Kent SC Station

The dioxin/furan congener profile at Enumclaw is unique compared to other stations (Figure 51). The two furan congeners contribute less to samples at Enumclaw than at any other station.

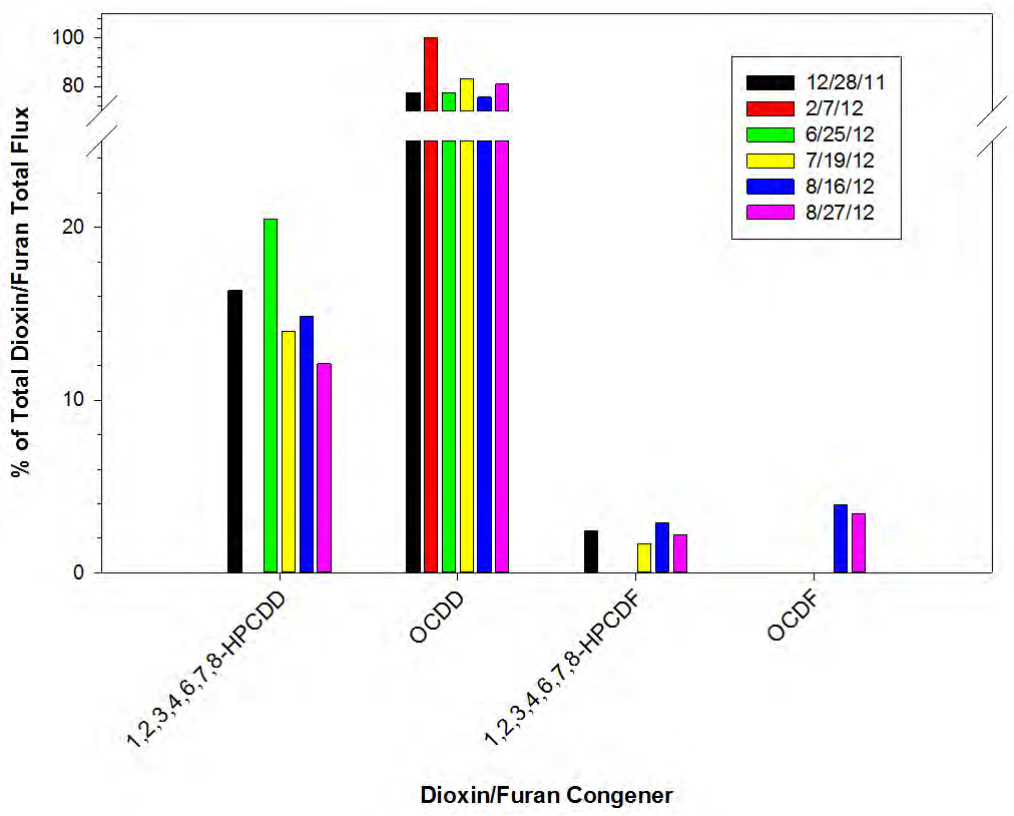


Figure 51. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Enumclaw Station

The percentage contributions for all congeners were averaged for each location and graphed together to visually examine differences between stations (Figure 52). On average, only five dioxin/furan congeners were detected at all seven stations: 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HPCDD, OCDD, 1,2,3,4,6,7,8-HPCDF, and OCDF. Average contributions of 1,2,3,4,6,7,8-HPCDD, OCDD and OCDF to total dioxin/furan flux varied the most, but only within about 10%. Of these, the highest average contributions of 1,2,3,4,6,7,8-HPCDD and OCDD were at Duwamish station while the lowest was observed at Kent. The highest average contributions of OCDF were at Kent and the lowest at Enumclaw. The most toxic congener, 2,3,7,8-TCDD, contributed (1-2%) to the total flux only at Beacon Hill, Duwamish and South Park stations. This congener was not detected in samples from Georgetown, Kent, Kent SC or Enumclaw.

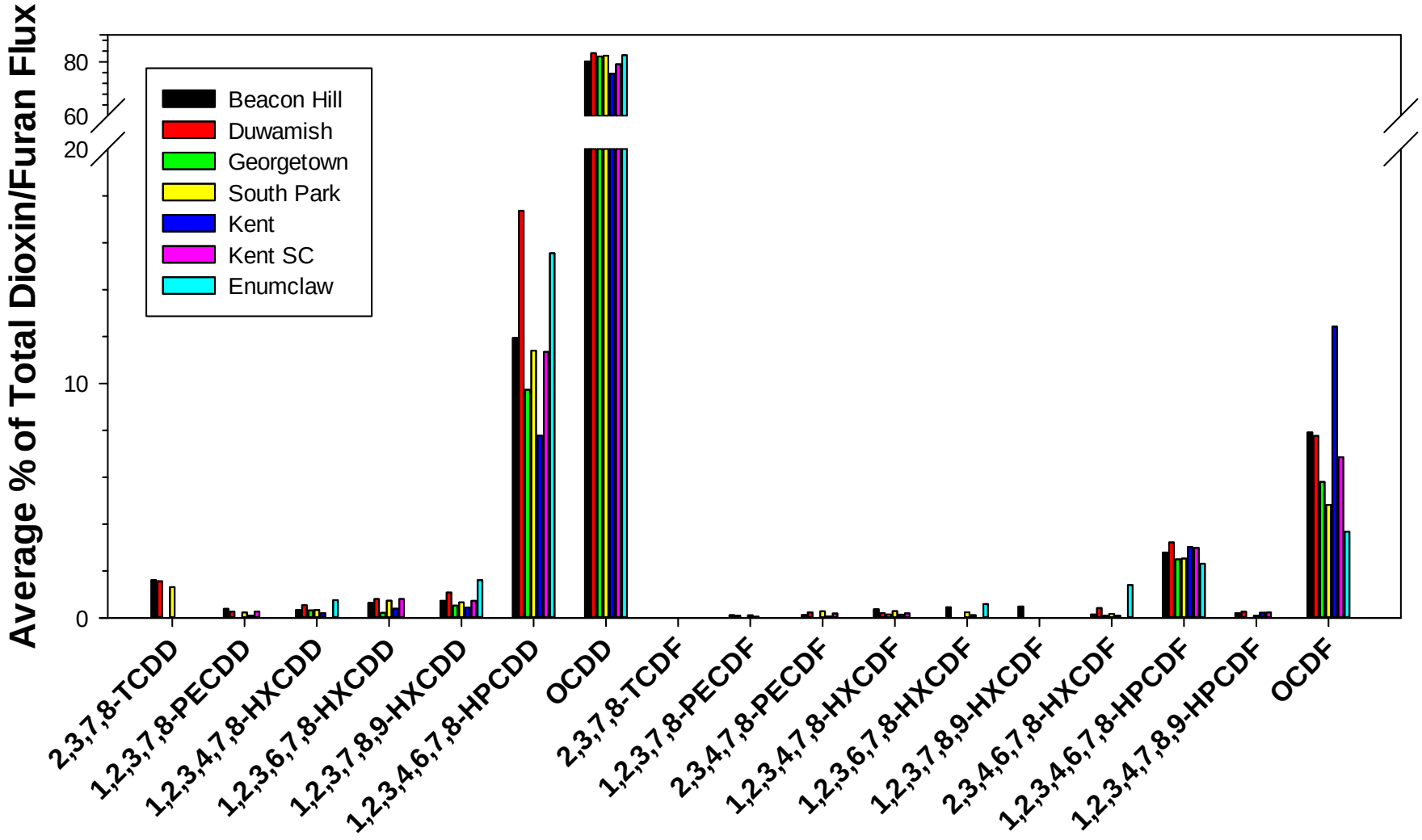


Figure 52. Average Percent Total Dioxin/Furan Congener Flux by Station

5.7 Field Replicate Samples

Field replicate samples provide an indication of combined uncertainty from microspatial variability (i.e. small differences between where the sample and replicate were collected), field sample handling, and analytical method variability. Three replicate samples were collected in 2013. The relative percent differences (RPDs) between samples and their replicates are presented here.

Maximum RPDs for three PAHs were over 40% but less than 52% (Table 34). RPDs for the remaining PAHs were below 40% with most falling below 30%. Relative percent differences were not calculated for replicate pairs where both results were not detected. There were no instances where PAHs in one sample in a pair were detected and not in other. Overall, the field replicate results indicate the greatest potential for variability in benzo(a)anthracene, benzo(a)pyrene, and chrysene and the least potential for variability for fluorene and phenanthrene.

Table 34. Relative Percent Difference (RPD) Between Field Replicates

Group	Analyte	# of Replicate Pairs	RPD Range
HPAH	Benzo(a)anthracene	3	4-52
HPAH	Benzo(a)pyrene	3	3-47
HPAH	Benzo(b,j,k)fluoranthene	3	8-39
HPAH	Benzo(g,h,i)perylene	3	5-29
HPAH	Chrysene	3	6-43
HPAH	Dibenzo(a,h)anthracene	3	2-24
HPAH	Fluoranthene	3	8-25
HPAH	Indeno(1,2,3-Cd)Pyrene	3	6-33
HPAH	Pyrene	3	9-27
LPAH	Acenaphthene	3	17*
LPAH	Acenaphthylene	3	5-36
LPAH	Anthracene	3	5-32
LPAH	Fluorene	3	4-13**
LPAH	Naphthalene	3	ND
LPAH	Phenanthrene	3	9-13**

*Value is for one replicate pair with detected results. Results for two pairs were not detected.
**Range is for pairs with detected results. Results for one pair were not detected.
ND – Results for all samples were not detected.

5.8 Chemistry Data Validation

Metals, mercury, and PAH data collected in 2013 were validated by King County using EPA National Functional Guidelines for Superfund data (EPA 2008 and 2010b) and the project SAP and SAP addendum (King County 2011; 2013a). Details of this validation are described in a data validation technical memorandum (Appendix D). Validation of PCB and

dioxin/furan congener data was completed by Laboratory Data Consultants, Inc. (LDC) in accordance with EPA Superfund guidance (EPA 1996, EPA 1995). PCB and dioxin/furan congener validation reports are provided in Appendix E. This section summarizes the major findings of the chemistry data validations.

5.8.1 Metals, Mercury, and PAHs

KCEL reviewed the metals, mercury, and PAHs data by comparing the results to reference method and SAP requirements and flagging with laboratory data qualifiers where appropriate. Data validation was conducted by Water and Land Resources Division Science Unit staff. For the metals, mercury, and PAHs validation, data anomaly forms, batch reports and analytical quality control (QC) reports were reviewed. The following QC parameters were also reviewed: holding time, method blanks, spike blanks and duplicates, matrix spikes and duplicates, laboratory duplicates and surrogates.

The majority of metals, mercury and PAH results did not receive qualification. The vanadium result for one sample was not reported by KCEL because hydrochloric acid was used to preserve the samples instead of the required nitric acid. The hydrochloric acid caused interference in analysis of vanadium, but the other metals results were not impacted. The affected sample was collected from Beacon Hill station on September 5, 2013.

Between three and eight PAH compounds were detected in every method blank associated with the PAHs samples. Except for one detection of benzo(b,j,k)fluoranthene, all of the PAH compounds detected in method blanks were at concentrations below the RDL. Thus, current EPA guidance (EPA 2008) rules were applied and results where the sample concentration was greater than the RDL and greater than 10 times the method blank concentration remained unqualified. When the method blank and sample concentrations were less than the RDL, the sample result was changed to the numeric RDL value and received a “U” validation qualifier. When the method blank concentration was less than the RDL and the sample concentration greater than the RDL but less than 10 times the method blank concentration, the sample result remained as reported but received a “U” validation qualifier. Sample results are treated as not detected when “U” validation qualifiers are applied.

The relative percent difference between spike blank and spike blank duplicate results for dibenzo(a,h)anthracene exceeded the QC limit of 40% and affected the two samples comprising that analytical batch. Dibenzo(a,h)anthracene results from these samples were qualified with a “J” validation qualifier and considered estimated with unknown bias.

5.8.2 PCBs and Dioxins/Furans

PCBs and dioxin/furan data were validated to Level III by LDC. Level III validation includes verification of custody, holding times, reporting limits, sample QC and QC acceptance criteria, and frequency of QC samples, instrument performance checks, along with initial and routine calibration checks.

Instrument performance fell within method specifications except for a few instances. All of the results for 2,3,7,8-TCDF on column DB-5 were rejected. 2,3,7,8-TCDF performs better on the second DB-225 column, and these results were used to quantify 2,3,7,8-TCDF in all samples. Therefore, this performance issue did not result in unusable data for this compound; results from the second column were used.

Contamination of method blanks was not found within five times the environmental concentration for any for dioxin or furan. Thus, no blank qualifications for dioxins were required by EPA validation guidance.

For PCBs, method blank contamination above method specifications was detected in all batches. One or more mono or di-chlorinated PCB congeners were detected in most method blanks. Several method blanks had detections across the entire PCB homolog range. Method blanks had as few as none and as many as 28 detected PCB congeners. Under this high resolution method that quantifies 209 PCB congeners with several co-elutions, it is common to detect some congeners in method blanks. Environmental sample detections were qualified as non-detect by the contract validator whenever sample concentrations were within five times the method blank concentration. This potentially resulted in some low bias for congeners detected above the method blank concentration but within five times the method blank.

Laboratory duplicate results were within method specifications for all but a few PCB congeners. RPD between laboratory duplicates are specified by the SAP to be plus or minus 50%. LDC applied this when both the parent and lab duplicate results were greater than five times the LMCL. For sample L57717-5 and its duplicate RPDs for PCB 206 and 208 were 51.4 and 50.5 percent. These congeners were flagged as estimated in this sample due to this slight method performance issue.

Internal standards for PCB analysis were within method specifications with some exceptions. The internal standard ^{13}C PCB-4 in sample L58204-9 fell below allowable recovery limits of 25 to 150% with 22.1% recovery. This resulted in flagging the mono and dichlorinated biphenyls which are quantified relative to this standard's recovery as estimated. Detects of PCB congeners 4 through 14 and associated total dichlorinated biphenyls were qualified as "J" or estimated while non-detected congeners were qualified as "UJ" for estimated detection limits.

Numerous dioxin/furan and PCB congeners were qualified by the analytical laboratory as "K" which means that not all identification and qualification criteria were met for these compounds. The maximum potential concentration is reported for "K" flagged congeners. These analytes were qualified as non-detects by the validator according to the EPA Region 10 validation guidelines (EPA 1995).

5.9 Weather and Particulate Data

Chemical concentrations in the air and atmospheric deposition rates are affected by weather conditions. Weather conditions impact chemical transport processes such as volatilization, particle resuspension (e.g., by wind), gas-to-particle partitioning, and particle scavenging (i.e. removal by rainfall) which can change atmospheric deposition rates (Poster and Baker 1997). Historical databases of weather and particle data are available for some of the stations sampled. Downloadable parameters included air temperature, rainfall, fine particle concentration and wind speed/direction. Not all parameters were available for every station (Table 35). This section summarizes the data for these parameters during the 2013 study period.

Table 35. Weather and particulate data available by station for 2013 study

Parameter	Beacon Hill	Duwamish	Georgetown	South Park
Air Temp.	√	√	N/A	N/A
Rainfall[a]	N/A	√	√	√
PM 2.5	√	√	N/A	√
Wind Rose	√	√	N/A	N/A
Wind Speed	√[b]	√	N/A	N/A

[a] There are no rainfall meters at PSCAA stations. Rainfall data were acquired from King County's Hydrological Information Center database at rainfall stations closest to the air sampling stations (See Section 5.9.2). One precipitation gage was available to represent Duwamish, Georgetown and South Park stations.
[b] Wind data available measured by propeller. Wind data for the Duwamish station were measured using sonic methods.
N/A – not available

5.9.1 Air Temperature

Historical air temperature data were available at the PSCAA air quality graphing tool website (http://airgraphing.pscleanair.org/) only for the Beacon Hill and Duwamish air monitoring stations sampled in the 2013 study. Hourly air temperature data were downloaded for these stations for the study period (Figure 53). Temperatures at the Duwamish station were typically warmer than those measured at the Beacon Hill station.

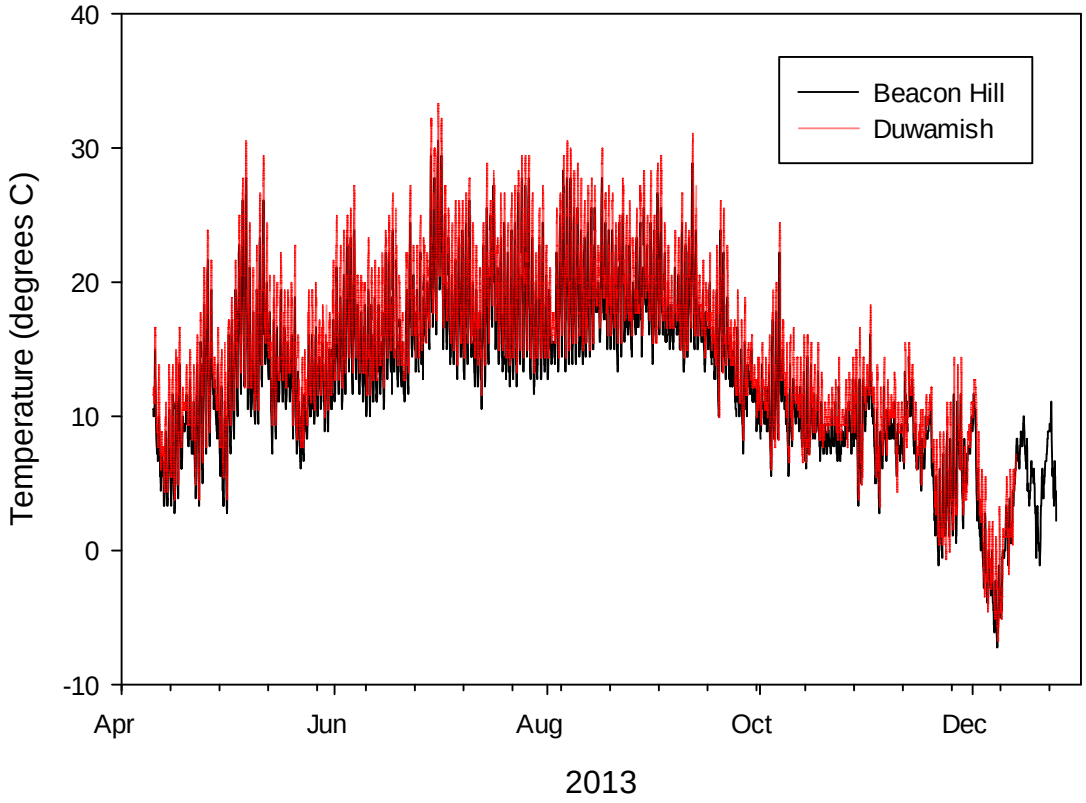


Figure 53. Hourly Temperature Over the 2013 Study Period at Beacon Hill and Duwamish Stations

5.9.2 Rainfall

PSCAA does not provide downloadable precipitation data for their monitoring stations. Therefore, daily rainfall data were downloaded from the King County HIC database (http://green.kingcounty.gov/WLR/Waterres/hydrology/GaugeTextSearch.aspx) for the Hamm Creek ("hau") gage in the Duwamish River Valley. There is only one rain gage in this database located near the Duwamish, Georgetown and South Park stations. No rainfall gages were located near Beacon Hill station. The maximum daily rainfall over the study period occurred in October (1.5 inches) (Figures 54). July was distinctly dry with only two days of measurable rain each less than 0.1 inches. Early August was also relatively dry, but moderate rain events (>0.5 inches/day) occurred at the end of the month.

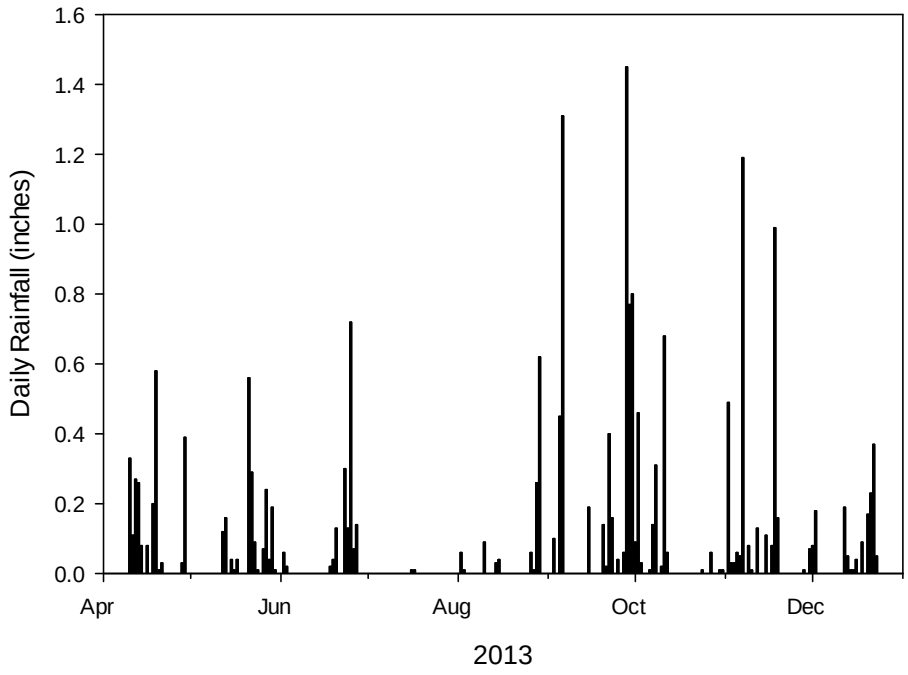


Figure 54. Total Daily Rainfall During the 2013 Study Period at the Hamm Creek gage in the Duwamish River Valley

5.9.3 Fine Particulates (PM 2.5)

Air concentrations of fine particles (<2.5 µm or PM 2.5) are monitored at all the PSCAA air monitoring stations sampled for this study. However, the Georgetown station is not part of the PSCAA air monitoring network and there was no other source of PM 2.5 data for this location. Daily PM 2.5 data measured by nephelometer or partisol[10] were downloaded from the PSCAA air quality graphing tool for Beacon Hill, Duwamish, and South Park stations. Ecology no longer monitors the larger size fraction of particle size concentrations (PM 10) at any of the corresponding air quality monitoring stations that were part of this project. Therefore, data records were only available for fine particulates. Average daily concentrations of fine particulates were lowest at Beacon Hill and were highest at the Duwamish station (Figures 55-57). The average daily concentration of fine particulates reached values at Duwamish approximately three times higher than those measured at the Beacon Hill station in November and December. Average daily PM 2.5 concentrations were generally similar at all three stations from April to October, although Beacon Hill concentrations were slightly lower than the other two stations. Spikes in concentrations that occurred at all stations from October through December were lowest at Beacon Hill, higher at South Park and highest at Duwamish station. Although the magnitude of concentration peaks vary by site, the pattern of PM 2.5 peaks and valleys are generally similar across stations.

[10] Nephelometer data was preferred to partisol data because daily measurements are available. Partisol data was only available every third day. Where only partisol data were available, an average was calculated across available days.

Higher particulate concentrations are often measured during periods of greater home-heating needs. In winter months, the largest sources of particulates to the atmosphere are wood-stove and fireplace burning (PSCAA 2013). Other sources include mobile sources (e.g., rail and truck), outdoor fires, and industry. Residential land use in the vicinity of South Park station and proximal industrial and mobile sources near Duwamish station may result in elevated concentrations of PM 2.5 in these areas. Comparatively lower PM 2.5 levels at Beacon Hill may be due to the higher elevation of this station (i.e. higher winds and greater air mixing) and fewer industrial and intense mobile sources. Higher PM 2.5 concentrations at Duwamish station compared to Beacon Hill is congruent with data collected by Kim and Hopke (2008). These researchers characterized particle sources in the Seattle area including Duwamish and Beacon Hill stations. Using PM 2.5 data, they estimated that the average contributions of diesel and wood-burning particles at Duwamish station were higher than at Beacon Hill station.

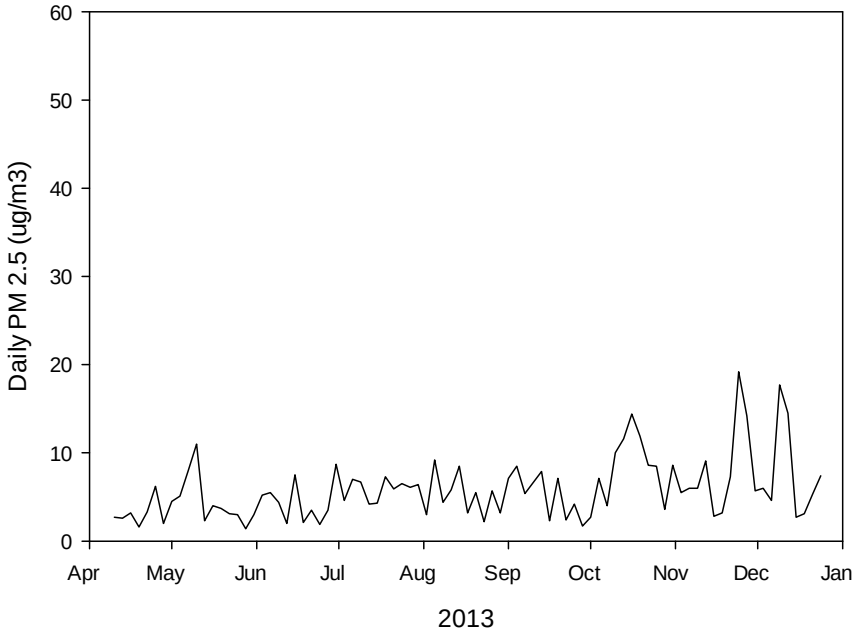


Figure 55. Average Daily Fine Particulate Concentration at Beacon Hill

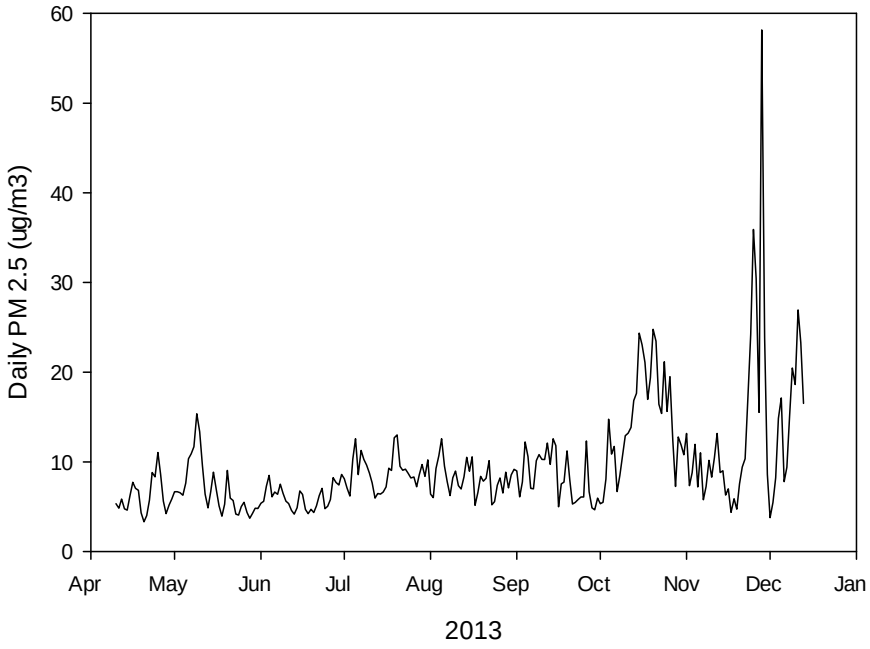


Figure 56. Average Daily Fine Particulate Concentration at Duwamish

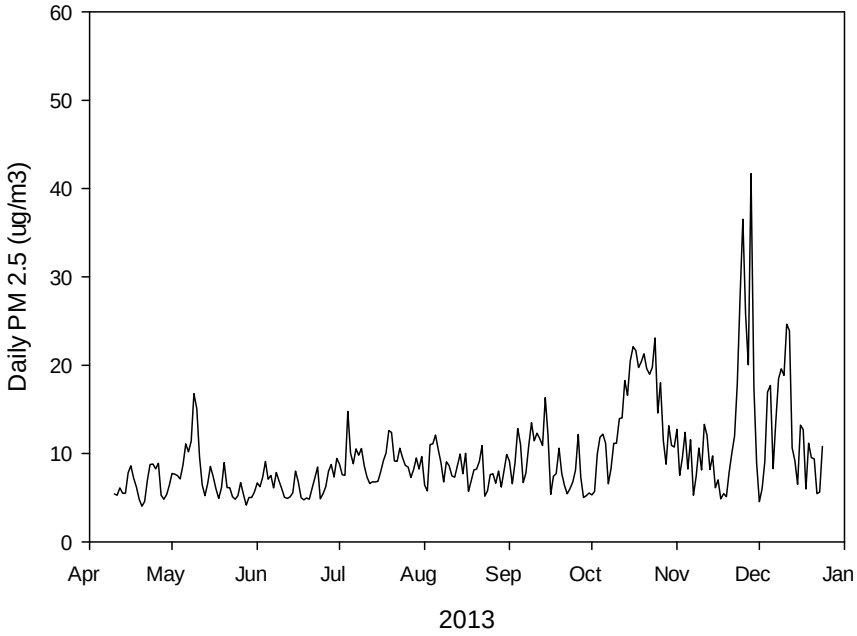


Figure 57. Average Daily Fine Particulate Concentration at South Park

5.9.4 Wind

As a transport mechanism, wind may play a role in the deposition rates of contaminants. The influence of wind speed on atmospheric deposition of the measured chemicals is tested in the Multivariate Analysis Section (Section 5.10). Wind speed data are presented here for both the 2011-2012 and 2013 study periods because these data were not included in the previous King County report (King County 2013a). Average daily wind speed data were downloaded from the PSCAA air quality graphing tool website for Beacon Hill, Duwamish, Kent, and Enumclaw stations for the 2011-2012 study period; wind speed data for the South Park and Georgetown stations were not available. Wind speed data were average daily values calculated from midnight to midnight in Pacific Standard Time. Wind speed data for Kent and Enumclaw stations are not presented for the 2013 study because these stations were not sampled.

Average daily wind speeds at Beacon Hill ranged from approximately 2 and 8 miles per hour (mph) during the 2011-2012 and 2013 studies (Figures 58 and 59). Daily wind speed data were not available from August 1 to September 16, 2013. Average daily wind speed was generally higher in January and February of 2011/2012 but still remained below 10 mph. This time of year was not part of the 2013 sampling period.

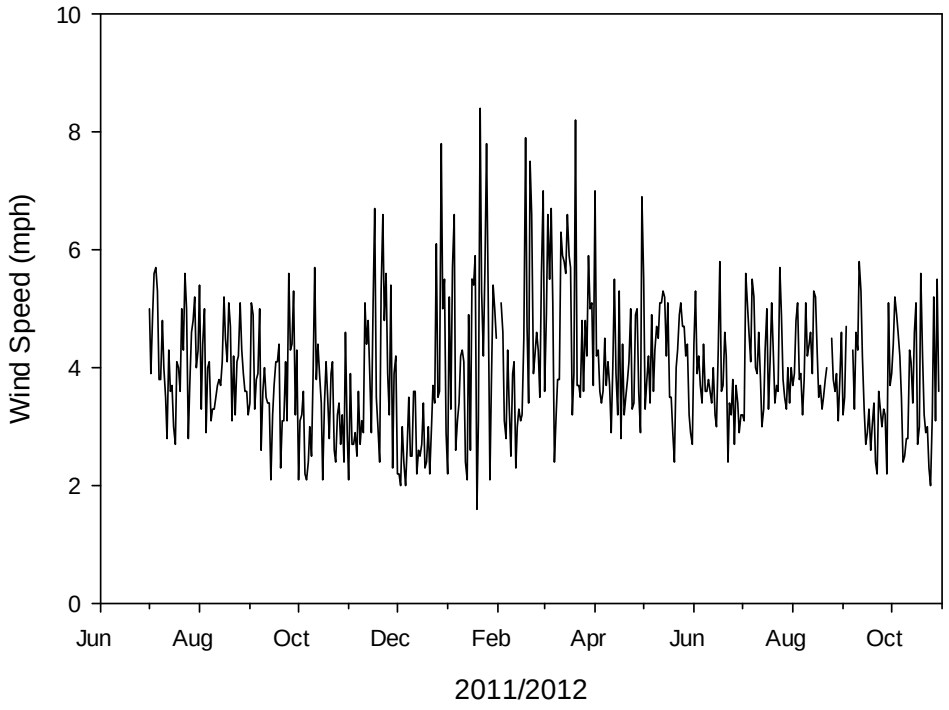


Figure 58. Ecology Wind Speed for Beacon Hill During the 2011/2012 Study Period

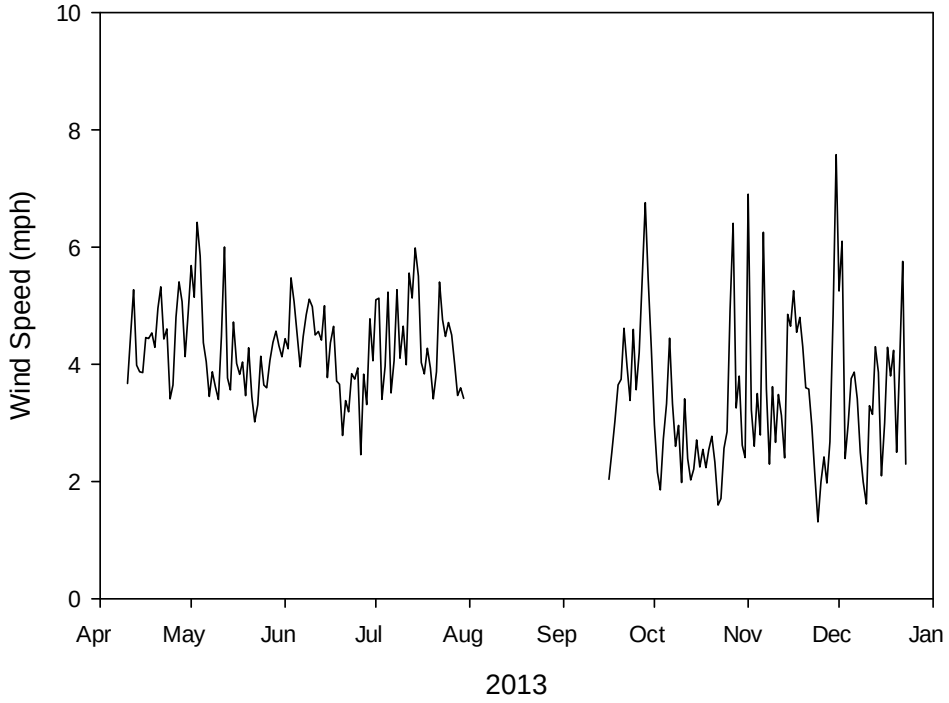


Figure 59. Ecology Wind Speed for Beacon Hill During the 2013 Study Period

Average daily wind speeds at Duwamish station ranged from approximately 2 to 12 mph in 2011/2012 (Figure 60). Average daily wind speed during the 2013 study was similar, but slightly lower, ranging from 2- 10 mph (Figure 60). The time period with highest average daily wind speed in 2011/2012, January and February, was not sampled in 2013. During both studies, average daily wind speeds at the Duwamish station reached higher maxima than at Beacon Hill.

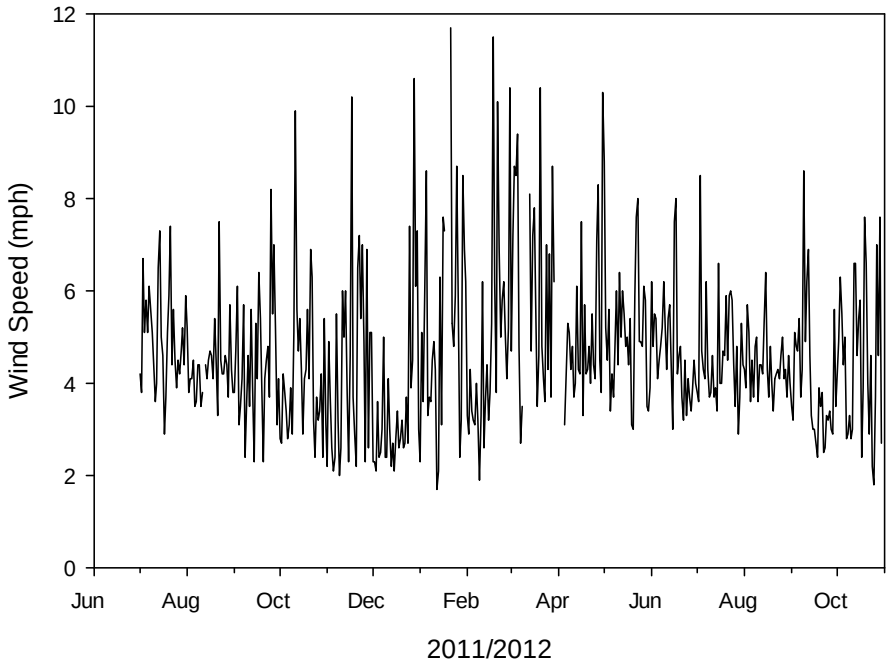


Figure 60. PSCAA Wind Speed for Duwamish Station During the 2011-2012 Study Period

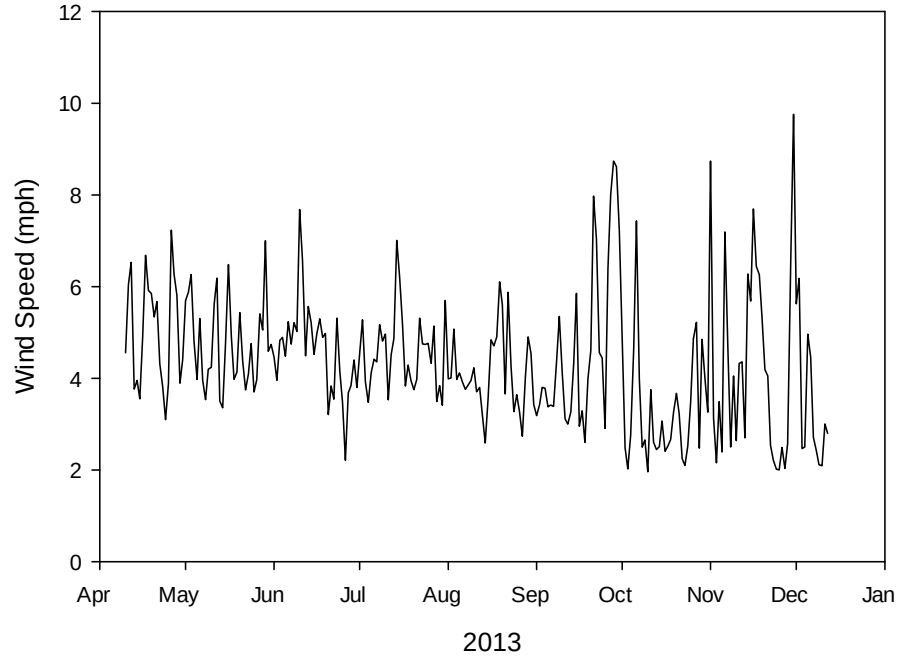


Figure 61. PSCAA Wind Speed for Duwamish Station During the 2013 Study Period

Average daily wind speeds at the Kent station in the 2011-2012 study period were similar to Duwamish over the same time period and ranged from 2 to just over 10 mph (Figure 62).

In contrast, average daily wind speeds at Enumclaw were higher and more variable, ranging from 1 to almost 18 mph (Figure 63). Samples were not collected from the Kent and Enumclaw stations in 2013.

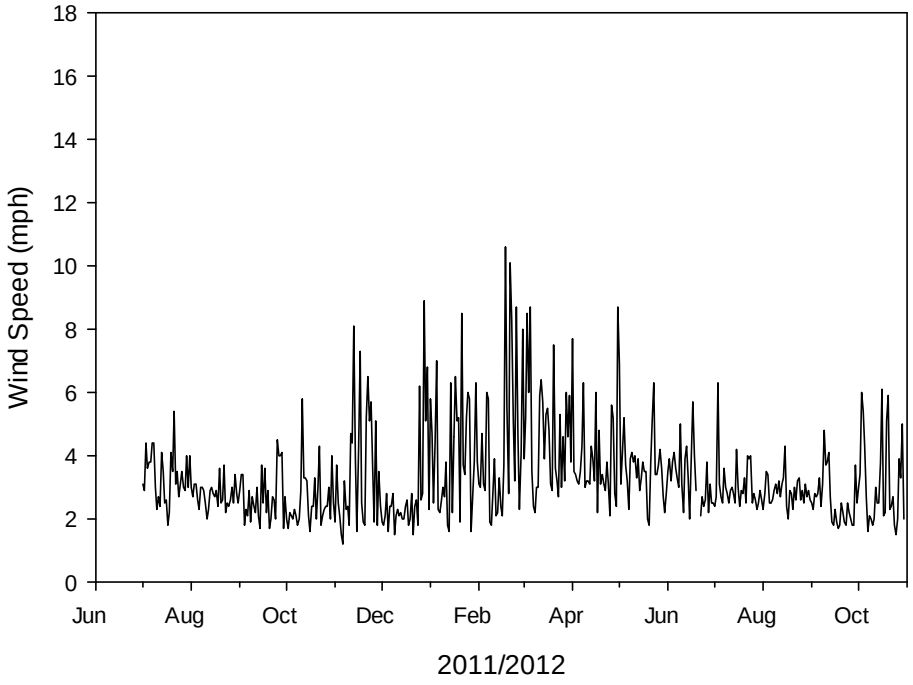


Figure 62. PSCAA Wind Speed for Kent Station During the 2011-2012 Study Period

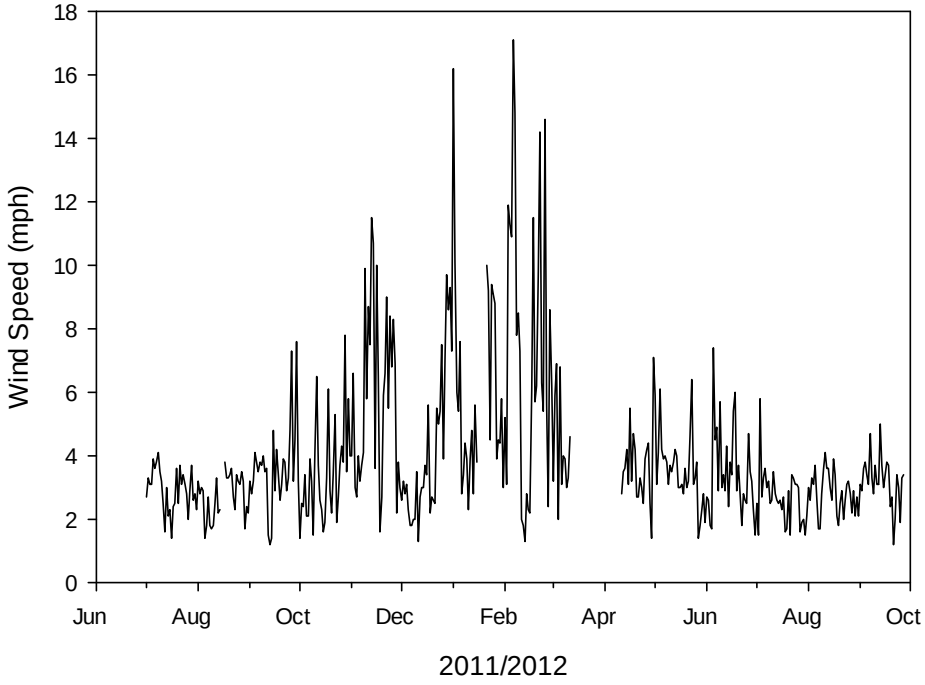


Figure 63. Ecology Wind Speed for Enumclaw Station During the 2011-2012 Study Period

The PSCAA website has recently been modified and the wind rose tool has been eliminated. The Ecology air monitoring data website creates wind roses but only provides a wind rose for the Duwamish station during the 2013 study period (https://fortress.wa.gov/ecy/enviwa/). Over the 2013 study period, the prevailing winds at the Duwamish station came from the Northwest and South (Figure 64).

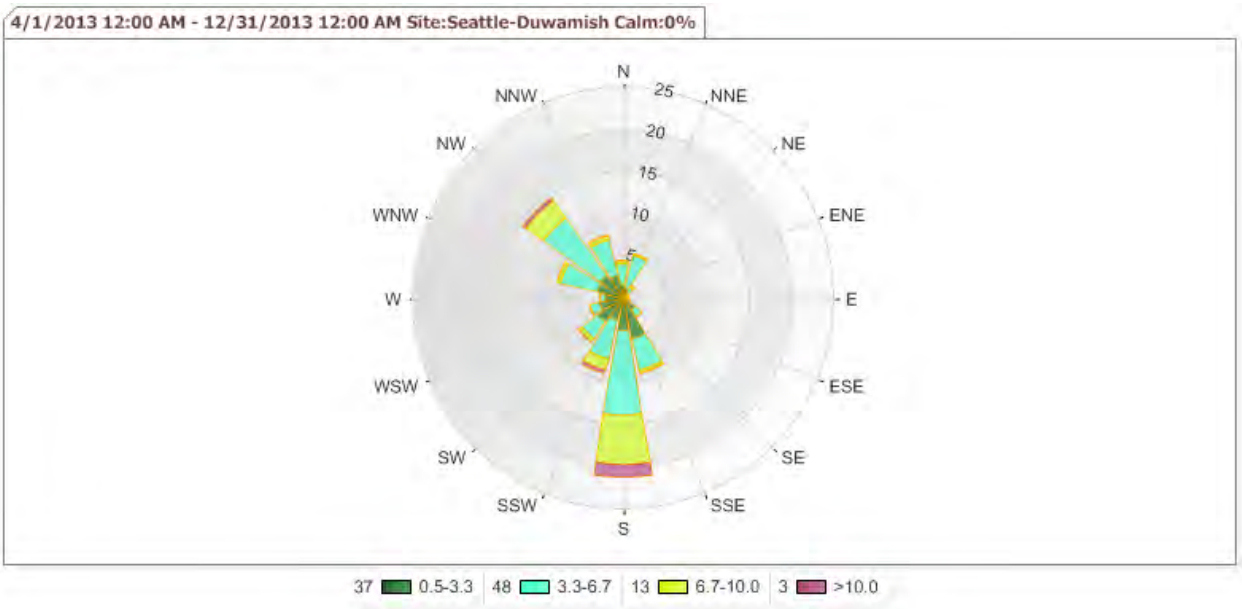


Figure 64. PSCAA Wind Rose for Duwamish During the 2013 Study Period

5.10 Multivariate Analysis

Principle components analysis conducted on pooled metals flux data found site differences spatially consistent with the statistical analysis in Section 5.1. For example, the lowest metals fluxes were at Enumclaw, the highest were at Duwamish and Georgetown stations, and fluxes at South Park, Kent, and Beacon Hill were in between (Figure 65). Only the first PCA axis was statistically significant by Monte Carlo permutation tests and used for interpretation. Significant differences between sites were difficult to identify from PCA ordination with no distinct hull[11] separation evident. However, considering both the first and second axis, Enumclaw visually appears different from other stations and this was confirmed by results of the PerMANOVA and pairwise testing (Figure 66; stations not sharing letters are significantly different). Overall metals fluxes were significantly different at Enumclaw compared to all other stations ($p<0.05$). Metals fluxes at Beacon Hill, Duwamish, and South Park stations were similar to each other. In addition, metals fluxes at Duwamish, Georgetown and Kent were similar. However, metals fluxes at Georgetown and Kent were significantly different than Beacon Hill, South Park and Enumclaw.

[11] A hull is a term for a polygon drawn around data from the same station.

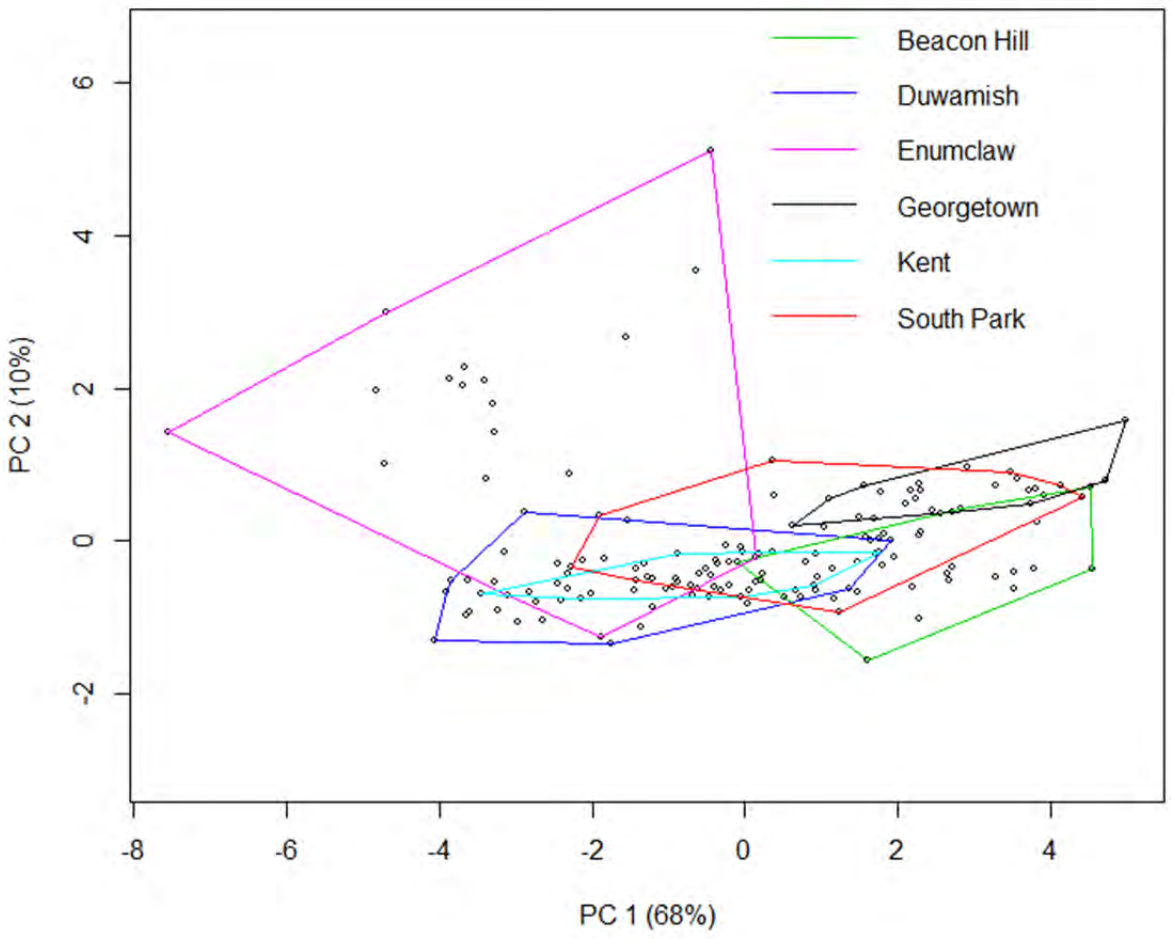


Figure 65. Principle Components Analysis of metal flux data at six King County sites

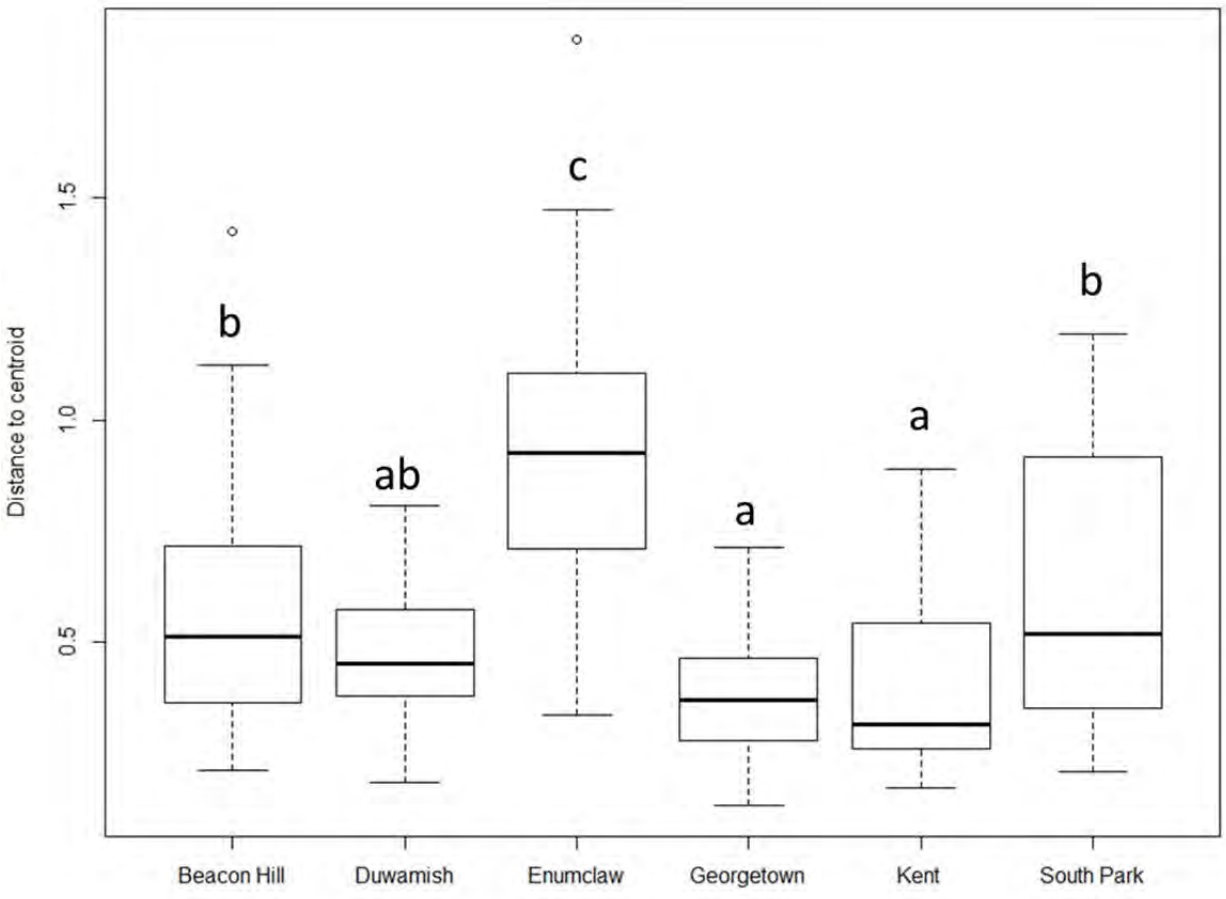
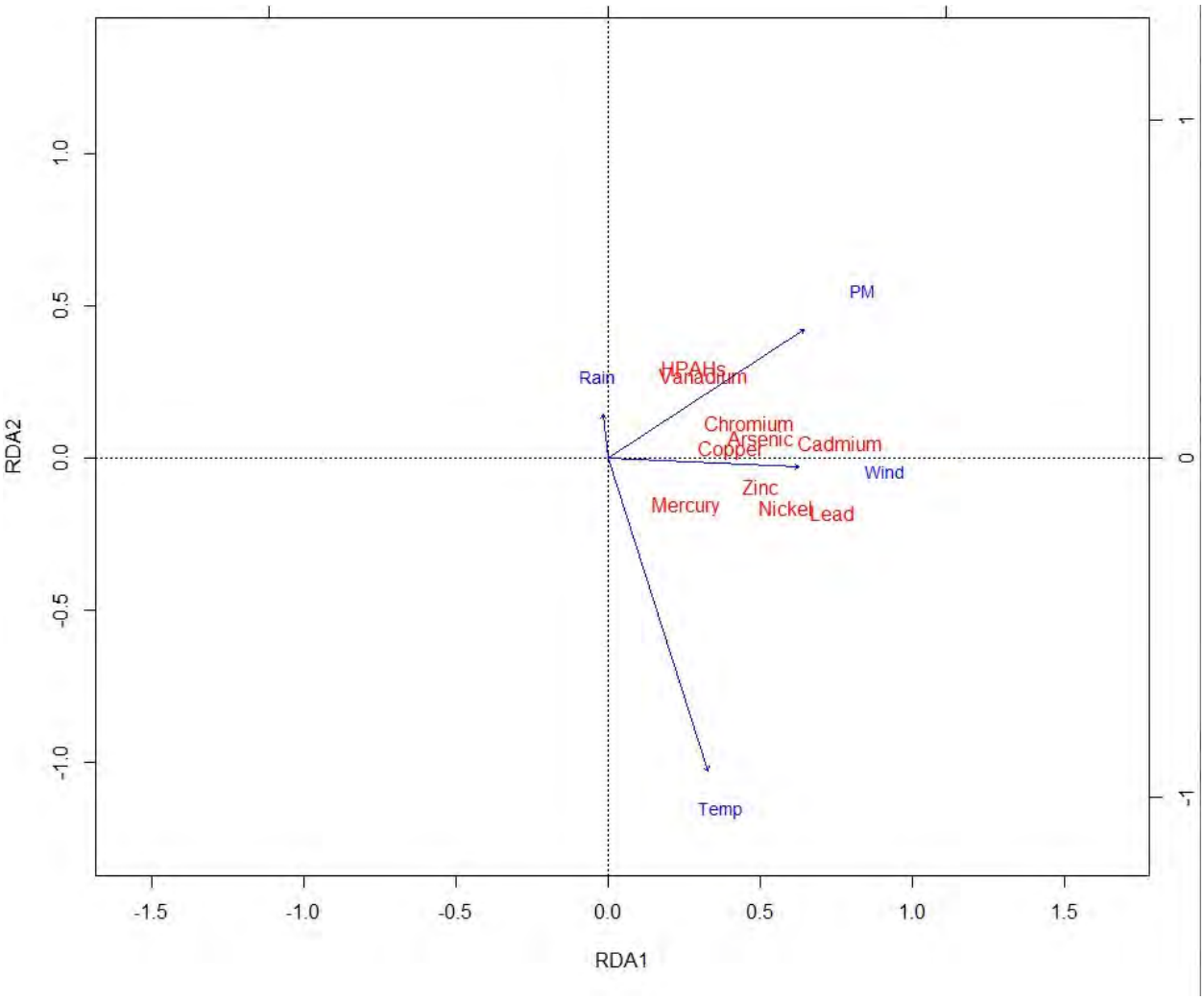


Figure 66. Boxplot of perMANOVA site variation of metals fluxes

RDA results showed that the variance captured by the environmental variables explains 34% of the total variance in metals fluxes (Figure 67). The first axis explained the majority of this variance at 29% of 34%. Loading on this first axis can indicate the strength of associations between environmental variables and metals fluxes. RDA determined average wind speed to be the strongest driver of metals flux (First axis loading = 0.58), followed closely by PM 2.5 (First axis loading = 0.56) and average temperature (First axis loading = 0.30) being a lesser driver (Figure 67). Zinc, nickel and lead flux were strongly influenced by wind and temperature. Cadmium, arsenic, copper and chromium were strongly influenced by wind and PM 2.5. Vanadium and HPAHs were more influenced by PM 2.5 and wind than temperature.



Note: Temp = average temperature; PM = average PM 2.5; Rain = total rainfall; Wind = average wind speed

Figure 67. Redundancy Analysis graph of metal deposition and environmental variables at Beacon Hill, Duwamish, Georgetown, and Kent stations

Table 36 shows the environmental variables that significantly contribute to individual metal flux based on multiple regression analysis. These results generally concur with those of the RDA ordination for metals. Total rainfall did not significantly contribute to the flux of most chemicals, except for mercury. PM 2.5 was a significant driver of chemical flux except for mercury and total dioxin/furans. Wind speed was also a significant driver to all metals but not any organic chemicals. Temperature significantly influenced chemical flux of all organics and most metals except arsenic, chromium, and copper. F-statistics from ANOVA on pooled metals fluxes showed that PM 2.5 ($F=26.9$, $p = 0.01$) is the most important contributing factor followed by wind speed ($F=16.4$, $p = 0.01$), and temperature ($F=8.2$, $p = 0.02$). Total rainfall was an insignificant driver of metal deposition ($F=1.8$, $p = 0.16$).

Table 36. Significant contributing environmental variables to metal and organics deposition at Beacon Hill, Duwamish, and Kent sites

Analyte	Environmental Variables			
	Temp	Rain	Wind	PM 2.5
Arsenic			x	x
Cadmium	x		x	x
Chromium			x	x
Copper			x	x
Lead	x		x	x
Mercury	x	x	x	
Nickel	x		x	x
Vanadium	x		x	x
Zinc	x		x	x
HPAHs	x			x
Dioxins/Furans	x			
PCBs	x			x

Variables with a p-value < 0.05 are marked with "x". Temp = average temperature; PM = PM 2.5 concentration; Rain = total rainfall; Wind = average wind speed.

Spearman's rank correlations between analyte deposition and environmental variables show similar results to the RDA ordination and multiple regression analysis (Table 37). Total rainfall shows little to no correlation to flux for most analytes; mercury flux was positively correlated with total rainfall but the correlation was not significant ($p = 0.06$). Average wind speed and PM 2.5 were significantly correlated to the flux of every metal except mercury. The strongest correlation factors were between PCB flux and PM 2.5 (rho = 0.58), PCB flux and temperature (rho = 0.48), and lead flux and temperature (rho = 0.41). Correlation factors for other contaminants were less than 0.4. Average wind speed was not correlated to organics fluxes.

Table 37. Spearman's correlation coefficients and associated pairwise p-values of metal, HPAH, dioxin/furan, and PCB deposition at Beacon Hill, Duwamish, Georgetown and Kent sites

Spearman's rho	Temp	Wind	PM 2.5	Rain
Arsenic	0.18	0.34	0.33	-0.03
Cadmium	0.14	0.33	0.32	0.10
Chromium	0.23	0.23	0.38	-0.12
Copper	0.23	0.26	0.33	-0.04
Lead	0.41	0.30	0.36	-0.16
Mercury	0.32	0.36	-0.04	0.19
Nickel	0.37	0.36	0.28	-0.08
Vanadium	-0.01	0.29	0.26	-0.05
Zinc	0.34	0.25	0.31	-0.08
HPAHs	-0.17	0.00	0.33	0.09
Dioxins/Furans	-0.21	-0.06	-0.04	0.10
PCBs	0.48	0.02	0.56	-0.18
Pairwise P-values				
	Temp	**Wind**	**PM 2.5**	**Rain**
Arsenic	0.08	**0.00**	**0.00**	0.80
Cadmium	0.16	**0.00**	**0.00**	0.30
Chromium	**0.02**	**0.02**	**0.00**	0.24
Copper	**0.02**	**0.01**	**0.00**	0.69
Lead	**0.00**	**0.00**	**0.00**	0.10
Mercury	**0.00**	**0.00**	0.66	0.06
Nickel	**0.00**	**0.00**	**0.00**	0.40
Vanadium	0.94	**0.00**	**0.01**	0.62
Zinc	**0.00**	**0.01**	**0.00**	0.42
HPAHs	0.08	0.99	**0.00**	0.37
Dioxins/Furans	0.34	0.80	0.87	0.66
PCBs	**0.03**	0.92	**0.01**	0.42

Note: Significant correlations with a p-value < 0.05 are bold. Temp = average temperature; PM = minimum particulate size; Rain = total rainfall; Wind = average wind speed.

6.0 DISCUSSION

Observed spatial differences in chemical flux and temporal patterns in metals flux are discussed in this section. Also discussed is the impact of sampling method and analytical biases and the influence of environmental factors.

6.1 Comparisons between Stations

Over both studies, chemical fluxes varied with location, sometimes significantly. Overall, fluxes for the three stations located in the Duwamish Valley (Duwamish, Georgetown and South Park) proved to be higher than stations outside the Valley. For metals, the Georgetown station median flux ranked highest of all stations for seven of ten metals analyzed (Table 38). The median flux at Duwamish ranked highest for the remaining three metals analyzed. In addition, fluxes at the Duwamish and Georgetown stations were often found to be statistically significantly higher than one or more other stations. For example, arsenic, cadmium, copper, lead, and nickel fluxes were significantly higher at Duwamish and Georgetown than Kent or Enumclaw stations. In contrast, the median flux at Enumclaw ranked lowest of all stations for most metals. Multivariate testing, examining pooled flux data from all stations except Kent SC, found that metals fluxes were significantly different at Enumclaw compared to other stations, confirming individual metal ANOVA results.

Table 38. Station Rankings Relative to Median Flux

	Beacon Hill	Duwamish	Georgetown	South Park	Kent	Kent SC	Enumclaw
Arsenic	7	1	2	3	5	4	6
Cadmium	6	2	1	3	4	5	7
Chromium	6	1	2	4	3	5	7
Copper	6	2	1	3	5	4	7
Lead	7	3	1	2	6	4	5
Mercury	5	3	1	2	6	4	7
Nickel	5	2	1	3	6	4	7
Silver	7	2	1	4	5	6	3
Vanadium	6	1	2	3	5	4	7
Zinc	6	3	1	2	5	4	7
HPAHs	6	3	2	5	1	4	7
PCBs	4	3	1	2	5	6	7
Dioxin/Furans	4	6	2	3	1	5	7
Dioxin TEQs	3	4	2	4	1	4	7

Note: Stations are ranked high (1) to low (6) based on median flux

The ratio of each station's median flux to the lowest median flux at any station for each metal demonstrate the magnitude of difference in median flux between locations (Figure 68). The lowest median flux was at Enumclaw for all metals except chromium, where the lowest median flux was at Beacon Hill. The largest differences between stations

occur for copper, nickel, vanadium and zinc. For example, the median copper flux at Georgetown is fourteen times higher than at Enumclaw, the station with the lowest median flux. The median copper fluxes at all other stations were at least six times higher than Enumclaw.

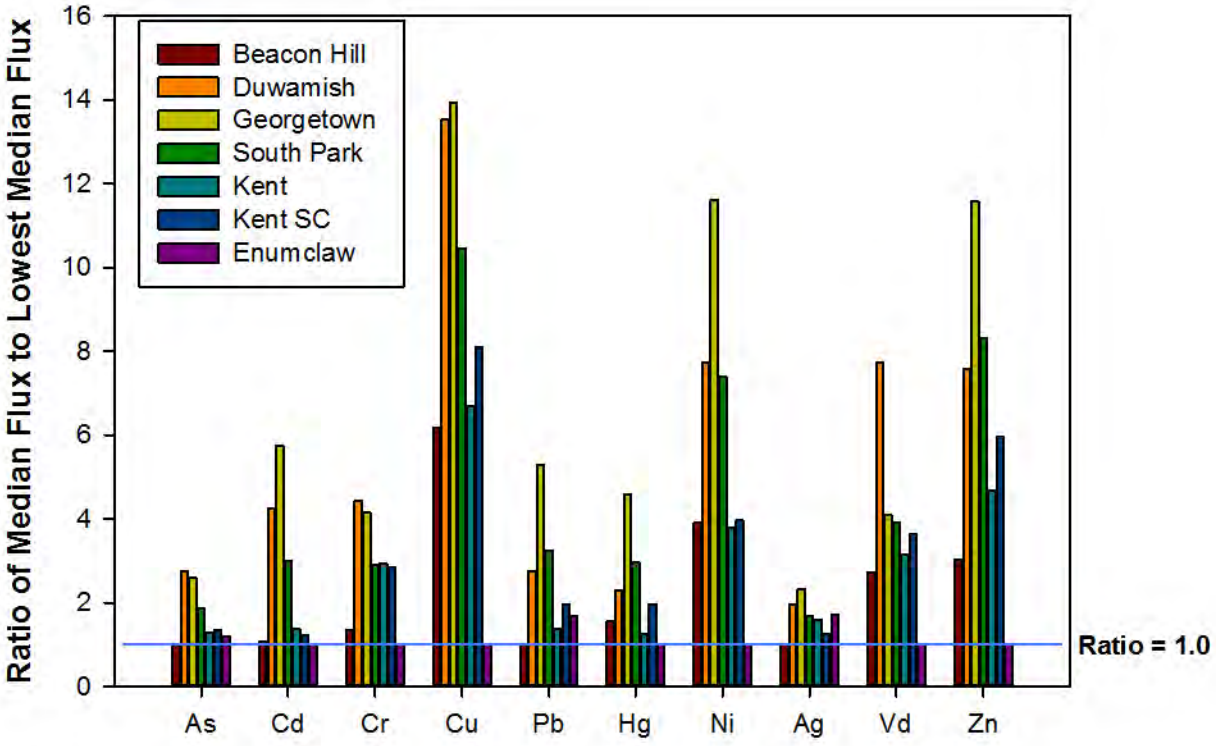


Figure 68. Ratios of Median Flux to Lowest Median Flux For Metals

Rankings of median fluxes for organic compounds were somewhat different mainly because of microscale effects on HPAHs and dioxins/furans at Kent. Ranked second after Kent for HPAHs and dioxins/furans is the Georgetown station. HPAH fluxes also tested significantly higher at Kent, Georgetown, and Duwamish stations compared to Beacon Hill, South Park, and Enumclaw (Section 5.2). Dioxin/furan fluxes were significantly higher at Kent and Georgetown than Enumclaw and those at Kent were also significantly higher than South Park and Duwamish stations (Section 5.4). PCB fluxes did not appear affected by microscale effects at the Kent station. Mean PCB fluxes were significantly higher at Georgetown than any other station. Although mean PCB flux was higher at South Park when compared to Duwamish, mean fluxes were not significantly different between the two stations; mean PCB flux at South Park was significantly different than all other stations (Section 5.3). Mean and median HPAHs, PCB, and dioxin/furan fluxes were always lowest at Enumclaw.

Ratios of median flux to the lowest median flux for each organic chemical demonstrate the magnitude of difference between locations (Figure 69). The greatest differences are seen with PCBs and dioxin/furan totals. The median dioxin/furan fluxes at Kent station are

almost 50 times higher than at Enumclaw, the station with the lowest median dioxin/furan totals. Other than Kent, smaller differences exist between stations for dioxin/furan totals – within a factor of fourteen. PCB fluxes at Georgetown were 90 times higher than Enumclaw and more than 3 times higher than any other station. South Park and Duwamish stations rank second and third for PCB flux.

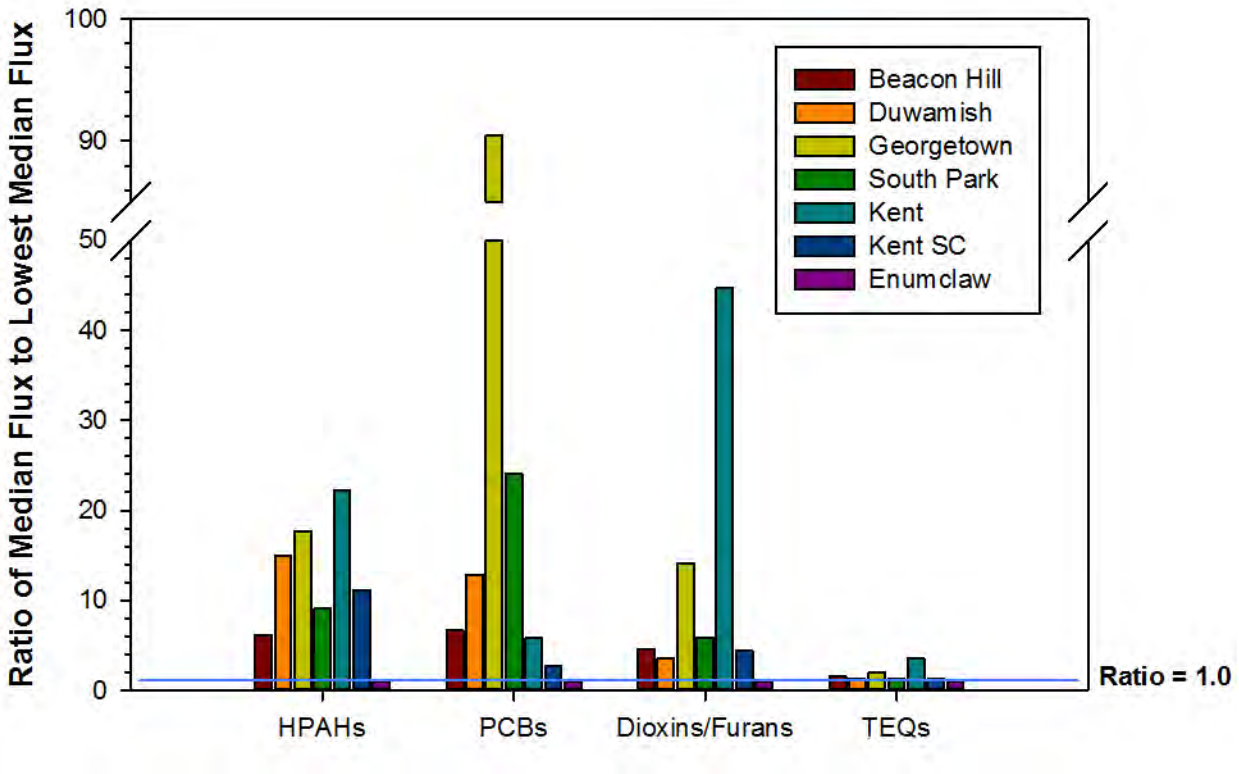


Figure 69. Ratios of Median Flux to Lowest Median Flux for Organics

A comparison of flux data in the previous main study (King County 2013a) to other regional studies showed that stations in areas with industrial land use such as Duwamish and South Park have substantially higher metals and PCB fluxes than areas on the Puget Sound shoreline sampled in other studies using the same methods. The Georgetown station also fits this pattern, characterized with residential, commercial, and industrial land uses. Although high winter fluxes of some contaminants (e.g., HPAHs, PCBs) at this station may be related to home-heating use in this neighborhood, this does not explain the top rank of this station for most of the contaminants measured. Georgetown is surrounded by major transportation corridors, such as the King County International Airport, rail lines, I-5 and East Marginal Way, all of which can be sources of air contaminants. Proximity to local PCB sources likely accounts for the substantial differences in median fluxes at these stations. However, at this time the exact sources are unknown.

HPAH ratios are over 20 times higher at Kent than Enumclaw. However, HPAH median fluxes at other stations were also much higher than Enumclaw (over five times higher).

6.2 Congener Profiles

The relative contribution of PCB congeners to the total flux varied between samples but PCB-129 was a dominant congener at Beacon Hill, Duwamish, Georgetown, South Park, and Kent SC with PCB-20 and PCB-61 co-dominating at Georgetown and South Park stations. PCB-110 was the most dominant congener in samples at Kent and Enumclaw. Although median PCB flux is higher at Duwamish station than Beacon Hill, PCB congener and homologue patterns at Beacon Hill and Duwamish are similar. Penta- and Hexa-CBs are clearly dominant homologues at these and the two Kent stations. The Tri- and Tetra-CBs contribute almost as much as Penta- and Hexa-CBs at South Park and Kent SC. Tri- and Tetra-CBs contribute nearly the same amount or more than Penta- and Hexa-CBs at Georgetown and Enumclaw. The PCB congener profiles at the two Kent stations are notably different suggesting different types of sources are present in the vicinity of these stations. Overall PCB congener contributions to Duwamish and Beacon Hill samples appear similar to each other as do those at South Park and Georgetown. Enumclaw samples appear different than other stations in the small contribution or absence of the higher chlorinated congeners (> hexa-CB).

The OCDD congener consistently comprised at least 70% of total dioxin/furan flux. Average dioxin/furan congener contributions are generally consistent between Beacon Hill, Duwamish, Georgetown, South Park and Kent SC stations; Kent and Enumclaw each differ from the others. The dioxin/furan congener profile at Enumclaw differed from all other stations in having greater relative contributions from dioxins compared to furans, particularly compared to OCDF. The opposite pattern was seen at Kent station.

6.3 Identified Bias

Two large sources of bias were identified which impact how this study's results should be interpreted: one source is related to detection limits for silver, and the other source is related to the sampling method used. First, it should be noted that fluxes measured for silver are biased high because the MDL value was assumed to represent fluxes when silver was not detected. The high percentage of 2011-2012 (39%) and 2013 samples (35%) where results were not detected may have limited the ability to observe significant differences between stations.

An important conclusion from evaluation of the field blank spike samples in 2011-2012 for LPAHs was that the fluxes measured for acenaphthylene and anthracene were biased low due to loss during field deployment. As previously mentioned in Section 5.2, the passive sampling method used is not able to capture deposition from the gaseous phase as absorption. This low bias should be considered when interpreting the LPAH and HPAH results from these air deposition studies. In addition, poor recovery of benzo(a)pyrene was observed sporadically in laboratory spike blanks during the 2011-2012 study resulting in a low bias for HPAH totals. However, the low bias may not substantially impact HPAH totals as indicated by comparison of Beacon Hill flux statistics between years (Table 39). This was the only station in both studies where HPAHs were analyzed. The median HPAH flux was the same and the mean was slightly higher (0.28 to 0.31 $\mu g/m^2$-day) in 2013 than 2012, but this may be due to natural variability as much as analytical bias. Overall, the range of HPAH

fluxes from both studies appear similar and it was concluded that the analytical bias in benzo(a)pyrene had little, if any impact, on the total HPAH flux values.

Table 39. HPAH Flux (µg/m^2-day) Statistics at Beacon Hill Station for Each Study and Combined

	2011-2012 Beacon Hill	2013 Beacon Hill	All Years Beacon Hill
Sample Size	22	17	39
Minimum	0.17	0.15	0.15
Maximum	0.59	0.62	0.62
Median	0.25	0.25	0.25
Mean	0.28	0.31	0.29

6.4 Environmental Factors

Multivariate analysis of pooled 2011-2012 and 2013 metals flux (metals and mercury combined) and environmental data determined 34% of the variance in metals fluxes was explained by PM 2.5, average wind speed, average temperature, and total rainfall. Total rainfall is not an important driver of metals (including mercury) or organics flux, except perhaps for mercury. PM 2.5 was a significant driver of metals and organics flux except for mercury and total dioxin/furans. Wind speed and PM 2.5 were found to have the strongest influence on metals flux, while temperature was a lesser driver. Temperature significantly influenced flux of all organics and most metals except for arsenic, chromium, and copper. PCB fluxes were significantly influenced by temperature and PM 2.5. The strongest significant correlation was between PCB flux and PM 2.5 (rho = 0.58) suggesting that PM 2.5 is moderately predictive of PCB flux and more predictive than temperature. Zinc, nickel, and lead fluxes were strongly influenced by wind and temperature. Cadmium, arsenic, copper, and chromium fluxes were strongly influenced by wind and PM 2.5. Vanadium and HPAH fluxes were more influenced by PM 2.5 and wind than temperature.

The temporal relationship between metals flux and rainfall after prolonged dry periods is discussed below in the context of precipitation scavenging. In addition, the spatial differences in HPAH flux and the possible link to PM 2.5 are discussed in this section.

6.4.1 Precipitation Scavenging

Precipitation scavenging is a documented process affecting wet deposition rates of trace metals, particularly mercury and lead (Sakata and Koji 2004, Sakata and Asakura 2007, Brandenberger et al. 2010). Precipitation scavenging can occur as gas or particle scavenging. Gas scavenging is driven by equilibrium partitioning of gases to water droplets; i.e. rain drops. Particle scavenging is the removal of particulates with adhered contaminants from the atmosphere by rainfall via various physical forces (Poster and Baker 1997).

Atmospheric washout of metals from particle scavenging could potentially explain the observed temporal metals flux patterns during the summer/fall of 2011-2012 and summer

2013 study periods. As described in the previous main data report (King County 2013a), metals fluxes in the first study period (2011/2012) tended to be highest in late summer of 2011 and sequentially decreased during the early wet season. Daily precipitation during this period was low until the end of September, when rain events began on a regular basis. After rain events occurred consecutively without long dry periods, metals fluxes showed a declining trend. The concept here is that rainfall is scavenging (i.e. "flushing") particles from the atmosphere, lowering their density, thereby leaving fewer particles to be scavenged in the next successive rain event.

During the 2013 study period, most metals fluxes climbed and plummeted three times from May through August. Unlike flux patterns at other times of year, this pattern is consistent between most metals and is most evident at the Georgetown station. Overlaying the total daily rainfall in 2013 on metals flux data demonstrates that metals fluxes related to the timing of rain events and were proportional to antecedent dry period length. Figures 70 and 71 illustrate how flux relates to total daily rainfall for arsenic and copper. Fluxes measured in seven samples are displayed. The time period shown was limited to two examples of flux rise (between Samples 1-3, 4-6) and fall (between Samples 3 and 4, 6 and 7) between April and early August to ease viewing. Each sample represents bulk deposition that occurred over the 2–4 week sampling period (i.e. the time between vertical hashed lines). The highest fluxes (i.e. Samples 3 and 6) were for samples collecting deposition when rain events occurred subsequent to a week or more of dry weather. Samples collected after peak fluxes covered time periods when rainfall events successively followed previous rainfall events (Sample 4) or when no rainfall had occurred to scavenge the particulates and associated metals from the atmosphere (Sample 7). The increase in flux from Sample 4 to 5 is likely due to the initiation of rain following a relatively long antecedent dry period, the peak of which fell within the next sample period and further increased flux for Sample 5 to 6.

Precipitation scavenging is just one of potentially many factors that could cause the observed temporal pattern in metals flux during the 2013 study. Further data collection and analysis would be required to determine if precipitation scavenging alone or other processes are affecting metals deposition in the study area.

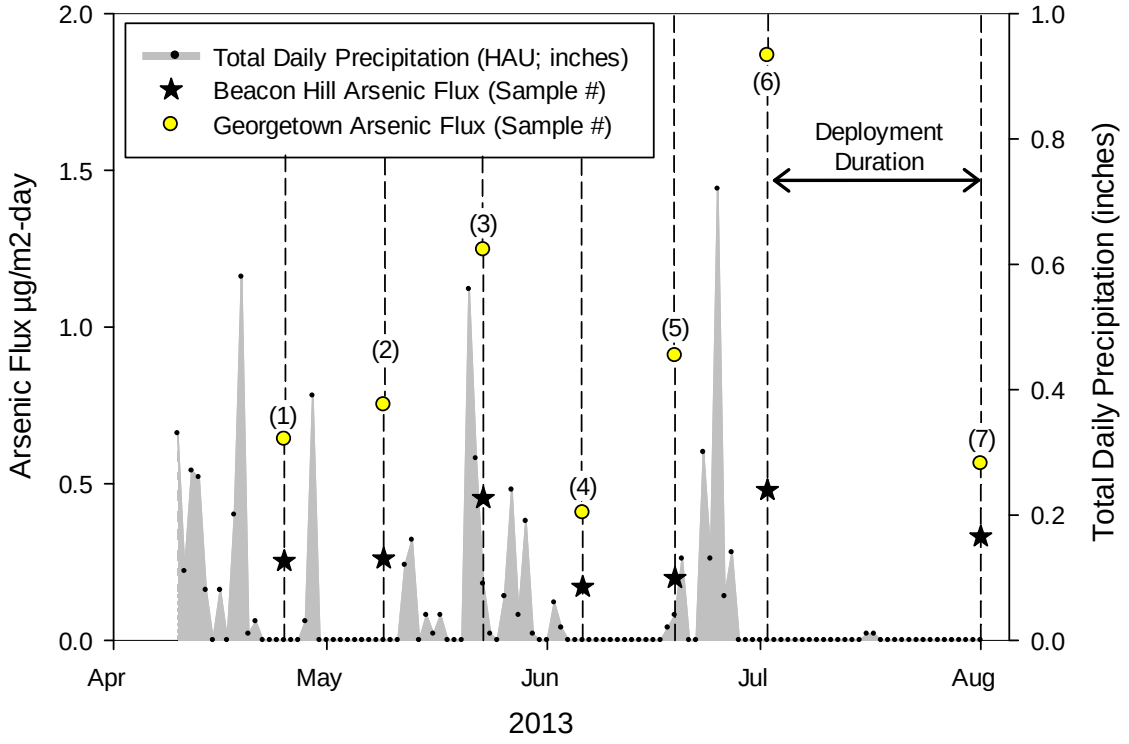


Figure 70. Particle Scavenging of Metals – 2013 Total Daily Rainfall and Arsenic Flux

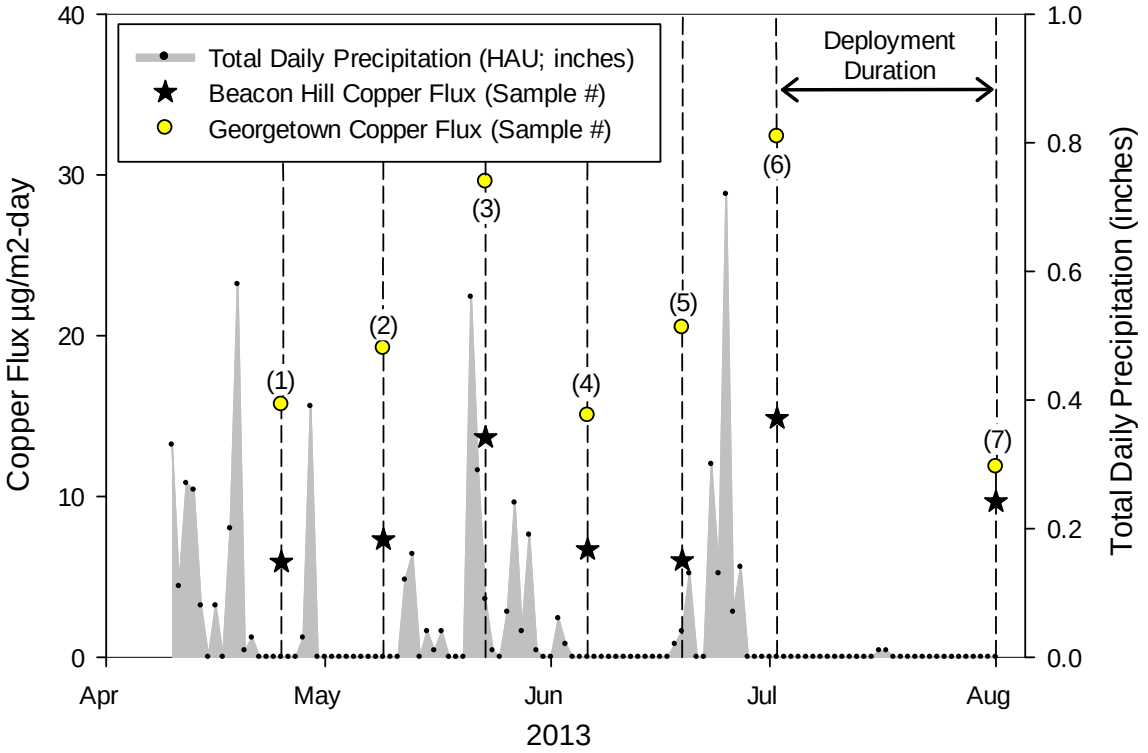


Figure 71. Particle Scavenging of Metals – 2013 Total Daily Rainfall and Copper Flux

6.4.2 Spatial Differences in HPAH Flux and PM 2.5

In 2013, higher HPAH fluxes were measured in winter months at Georgetown than Beacon Hill which is consistent with timing of home-heating. Residential wood-burning is the primary source of particulates in winter months in the Puget Sound area (PSCAA 2015) and the primary statewide source of PAHs to air (Ecology 2012b). The current study congruently determined that PAH fluxes are significantly and positively influenced by PM 2.5 (See Section 5.10). Data on home-heating use for the Georgetown and Beacon Hill areas were not available from PSCAA; thus, it is unknown if differences in home-heating may account, at least in part, for the observed HPAH flux patterns. However, Kim and Hopke (2008) characterized particle sources in the Seattle area including the same Duwamish and Beacon Hill stations sampled in this King County study and a different station in Georgetown. Using five years of PM 2.5 chemical speciation data, they estimated using positive matrix factorization (a multivariate approach) that the average contribution of wood-burning particles to PM 2.5 at Duwamish station were two times higher than at Beacon Hill station. The Duwamish station was found to have more significant particle contributions from vehicle and industrial emissions than wood combustion which is consistent with the areas dominant land uses. At Georgetown station, Kim and Hopke (2008) estimated that wood burning particles contributed three times more to total PM 2.5 than Beacon Hill station and that vehicle and wood burning sources were the highest contributors to PM 2.5 at Georgetown station. Thus, these results support the idea that local sources may explain differences in HPAH fluxes between stations.

7.0 CONCLUSION

This report summarizes the results of the supplemental atmospheric deposition sampling conducted in 2013. In addition, this report combines 2013 data with 2011/2012 data from a previous study to help evaluate how atmospheric deposition of pollutants in the Green/Duwamish River Watershed varies with different land use combinations and across a gradient of urbanization. The measured metals, mercury, PAHs, PCBs and dioxin/furans fluxes also provide information to assist in understanding atmospheric sources to the LDW.

Four stations were sampled for bulk air deposition in 2013; three of these stations were previously sampled in the 2011-2012 study and one station (Georgetown) was added in 2013. Three of the four stations were located in the LDW Valley (Duwamish, South Park and Georgetown) and one station was located in the urban residential neighborhood of Beacon Hill. Three additional stations were sampled in the 2011-2012 study: Kent, Kent SC and Enumclaw. Together, the stations range in degree of urbanization (urban to rural) and vary in their mix of land uses (industrial, commercial, and residential).

Metals (including mercury) and organics fluxes generally relate positively to the degree of urbanization at stations. The Enumclaw station typically experienced the lowest fluxes while Duwamish, Georgetown, or South Park generally had the highest fluxes. Metals fluxes at Duwamish and Georgetown were often statistically significantly higher than other stations. For example, arsenic, cadmium, copper, lead, nickel, and vanadium fluxes were significantly higher at Duwamish than at the Beacon Hill or Kent stations. Median metals fluxes at Georgetown station were most often the highest of any station and mean PCB fluxes were significantly higher than at any other station. Major transportation activity located around Georgetown may influence contaminant fluxes at this station, but the particular source of elevated fluxes at Georgetown is unknown. The observed large spatial differences in PCB and HPAH fluxes are likely due to differences in local sources. Limited existing PM 2.5 data indicate spatial flux differences may be related to the sources of particulates. Large differences in dioxin/furan flux were observed on a very small spatial scale in 2011-2012 at the two Kent stations. Only 0.3 miles apart, these stations demonstrate how spatially variable contaminant flux can be. This spatial variability indicates that the deposition rates measured at the stations sampled do not likely represent the average deposition rates for the neighborhoods where they are located.

Overall, PCB congener contributions to Duwamish and Beacon Hill samples appear similar to each other as do those at South Park and Georgetown. Congener patterns at Enumclaw appear different than at other stations in the small contribution or absence of congeners more chlorinated than hexa-CBs. This preliminary PCB congener analysis indicates that local sources vary by location. Average dioxin/furan congener contributions are generally consistent between Beacon Hill, Duwamish, Georgetown, South Park and Kent SC stations; Kent and Enumclaw each differ from the others. Further PCB and dioxin/furan congener analyses could be conducted to look more closely at potential sources.

Precipitation scavenging may influence metals and mercury fluxes and explain temporal flux patterns observed during the late dry and early wet seasons of both 2011 and 2013. Further study and analysis is needed to investigate the temporal trends in metals flux observed in the dry to wet period transition.

Average wind speed and PM 2.5 were found to be the most important environmental drivers of metals flux of those tested. Average temperature and total rainfall were not as important for metals flux. PM 2.5 was found to be a significant driver of HPAH and PCB flux but not for dioxin/furan flux. Average temperature was also found to be a significant driver for PCBs. PM 2.5 and average temperature are moderately strong predictors of PCB flux and weak to moderate predictors of HPAH flux.

Air deposition is highly variable over time and space; however, urbanization does appear to result in higher local air deposition of the metals and organics measured in this study. Additional PCB and dioxin/furan congener analysis, such as fingerprinting or positive matrix factorization, and acquisition of more particulate data may provide more insight regarding the types of sources contributing to the air fluxes in the Lower Duwamish Waterway.

8.0 REFERENCES

Brandenberger, J.M., P. Louchouarn, L-J Kuo, E.A. Crecelius, V. Cullinan, G.A. Gill, C. Garland, J. Williamson, and R. Dhammapala. 2010. Control of Toxic Chemicals in Puget Sound, Phase 3: Study of Atmospheric Deposition of Air Toxics to the Surface of Puget Sound. Washington Department of Ecology, Olympia WA. Ecology Publication No. 10-02-012. http://www.ecy.wa.gov/pubs/1002012.pdf

Ecology. 2013. Sediment Management Standards, Chapter 173-204 WAC. Washington State Department of Ecology. Olympia, Washington. Publication #13-09-055.

Ecology. 2012a. 2012 Ambient Air Monitoring Network Report. Air Quality Program, Washington State Department of Ecology, Olympia, WA. Publication #12-02-008. www.ecy.wa.gov/biblio/1102017.html

Ecology. 2012b. PAH Chemical Action Plan. Waste 2 Resources, Washington State Department of Ecology, Olympia, WA. Publication No. 12-07-48 www.ecy.wa.gov/biblio/1207048.html

EPA. 2010a. Method 1668, Revision C: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. EPA No. EPA-820-R-10-005. United States Environmental Protection Agency, Office of Water. Washington, D.C. Accessed April 15, 2013 at http://water.epa.gov/scitech/methods/cwa/upload/M1668C_11June10-PCB_Congeners.pdf

EPA. 2010b. USEPA Contract Laboratory Program National Functional Guidelines for Superfund Inorganic Data Review. OSWER 9240.1-51, USEPA-540-R-10-011. United States Environmental Protection Agency. Washington, D.C. January 2010.

EPA. 2009. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use. EPA 540-R-08-005 Accessed April 8th, 2013. http://www.epa.gov/superfund/policy/pdfs/EPA-540-R-08-005.pdf

EPA. 2008. USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review. OSWER 9240.1-48, USEPA-540-R-08-01. United States Environmental Protection Agency. Washington, D.C.

EPA. 2000. Low Impact Development: A Literature Review. EPA-841-B-00-005. United States Environmental Protection Agency, Office of Water. Washington, D.C.

EPA. 1996. EPA Region 10 SOP for the Validation of Polychlorinated Dibenzodioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data. EPA Region 10. Seattle, WA.

EPA. 1995. EPA Region 10 SOP for the Validation of Method 1668 Toxic, Dioxin-Like, PCB Data. EPA Region 10, Seattle WA. http://yosemite.epa.gov/r10/OMP.NSF/b380f72ce20f16c188256f0100719be8/77c4f4ee8e0e02a98825731a0069a5fd/$FILE/qar01668.pdf .

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

Kim, E, and Hopke, P.K. 2008. Source characterization of ambient fine particles at multiple sites in the Seattle area. Atmospheric Envir. 42: 6047-6056.

King County. 2015. Lower Duwamish Waterway Source Control: Upper and Middle Green River Surface Water Data Report. Prepared by Carly Greyell, Richard Jack, and Debra Williston, Water and Land Resources Division. Seattle, Washington.

King County. 2014a. Sediment Quality in the Green River Watershed. Prepared by Dean Wilson, Carly Greyell, and Debra Williston, King County Water and Land Resources Division. Seattle, Washington.

King County. 2014b. Lower Duwamish Waterway Source Control: Green River Watershed Surface Water Data Report. Prepared by Carly Greyell, Debra Williston, and Deb Lester. Water and Land Resources Division. Seattle, Washington.

King County. 2013a. Lower Duwamish Waterway Source Control: Bulk Atmospheric Deposition Study – Final Data Report. Prepared by Jenée Colton, Carly Greyell, and Richard Jack, Water and Land Resources Division. Seattle, Washington.

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

King County. 2013c. Draft Lower Duwamish Waterway Bulk Atmospheric Deposition Study Sampling and Analysis Plan – 2013 Addendum. Prepared by Jenée Colton, King County Water and Land Resources Division. Seattle, Washington.

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

King County. 2011a. Duwamish River Basin Combined Sewer Overflow Data Report for Samples Collected from September 2007 to January 2010. King County Water and Land Resources Division, Seattle, WA

King County. 2011b. Lower Duwamish Waterway Source Tracing - Sampling and Analysis Plan. Prepared by Debra Williston and Richard Jack, Water and Land Resources Division. Seattle, Washington.

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

King County. 2011d. 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.

King County. 2008. Lower Duwamish Waterway Source Control Project: Passive atmospheric deposition sampling monitoring report – October 2005 to April 2007. Prepared by Bruce Tiffany, Industrial Waste Program/Wastewater Treatment Division, King County Department of Natural Resources and Parks, Seattle, WA.

Poster, D.L. and J.E. Baker. 1997. Mechanisms of atmospheric wet deposition of chemical contaminants. Chapter 4 in Atmospheric deposition of contaminants to the Great Lakes and coastal waters. Baker, J.E. editor. Proceedings from a session of the Society of Environmental Toxicology and Chemistry (SETAC) 15th Annual Meeting: 30 Oct – 3 Nov. 1994; Denver CO. Published by SETAC Press, Pensacola, FL. 451 pp.

PSCAA. 2015. Puget Sound Clean Air Agency Criteria Air Pollutants webpage. http://www.pscleanair.org/airquality/airqualitybasics/airpollutants/Pages/default.aspx

PSCAA. 2013. Puget Sound Clean Air Agency, "Particulate Matter" website. http://www.pscleanair.org/airq/basics/criteria/particulate.aspx

Sakata, M. and K. Asakura. 2007. Estimating contribution of precipitation scavenging of atmospheric particulate mercury to mercury wet deposition in Japan. Atmosph. Environ. 41:1669-1680.

Sakata, M. and M. Koji. 2004. Annual changes in wet deposition fluxes of trace metals and scavenging of mercury by precipitation in the Western Tokyo Metropolitan Area. J. Env. Chem. 14(3):555-565.

Van den Berg, M., L.S. Birnbaum, M. Denison, M. De Vito, et al. 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicological Sciences 93(2):223-241