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

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King County

Department of Natural Resources and Parks
Water and Land Resources Division

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Prepared for:

King County Wastewater Treatment Division
Department of Natural Resources and Parks

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- Appendix D Metals and PAHs Data Validation Technical Memorandum
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Appendix F LPAH Flux Results and Discussion

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	octadibenzodioxin
OCDF	octadibenzofuran
PAHs	polycyclic aromatic hydrocarbons

PCBs	polychlorinated biphenyls
pg/L	picograms per liter
PM	parts per million
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 equivalent factors
TEQs	toxicity equivalents
WTD	King County Wastewater Treatment Division

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EXECUTIVE SUMMARY

King County Wastewater Treatment Division (WTD) wants to better understand the potential atmospheric sources of chemicals of concern (COCs) identified in the Lower Duwamish Waterway Superfund site that contribute chemical inputs through stormwater runoff to Lower Duwamish Waterway (LDW) combined sewer overflow (CSO) basins¹. King County has eight CSOs and two emergency overflows that discharge into the LDW. Therefore, King County launched atmospheric deposition studies in the Green/Duwamish River Basin. King County conducted and previously reported on atmospheric deposition sampling in the LDW basin from 2005 to 2007. This data report presents and discusses the results of the 2011/2012 sampling program with respect to spatial and temporal observations and differences between geographic locations.

Five stations representing various land uses located in the Lower Duwamish Valley and the Green River watershed were sampled for bulk atmospheric deposition (wet and dry deposition) of metals and organics from July 27, 2011 through October 24, 2012. Two stations were located in the urban areas of the LDW: Duwamish and South Park stations. The Duwamish station represents the most industrial area whereas South Park station represents a mix of industrial/commercial and residential land uses. Of the remaining stations, one station was in an urban residential neighborhood (Beacon Hill), one station was located in a suburban/commercial area (Kent), and one station was located in the rural area of Enumclaw (Mud Mountain). A sixth station was added in the Kent area towards the end of the study period for paired comparison with the original Kent station; microscale effects (deposition rate differences due to differences in local sources and conditions) were suspected in Kent after interim review of the dioxin/furan congener data. Samples were analyzed for metals, mercury, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) congeners and dioxin/furan congeners. Metals, mercury and PAHs samples were collected at each station continuously over the study period and PCBs and dioxin/furan congener samples were collected intermittently.

The main findings of this bulk air deposition study are:

- Metals and organics deposition rates (i.e., amount of chemical deposited in one square meter of land surface) generally relate positively to the degree of urbanization at stations with Enumclaw usually having the lowest rates and Duwamish or South Park often having the highest rates.
- Metals deposition rates at Duwamish and South Park stations were often significantly higher than other stations. For example, arsenic, cadmium, copper, lead, nickel and vanadium deposition rates were significantly higher at Duwamish than Beacon Hill or Kent stations.

¹ CSOs include discharges of both industrial and municipal wastewater and stormwater.

- Microscale effects can explain substantial differences between local stations as seen at the Kent station where significantly higher PAH and dioxin/furan deposition rates were measured than another station in Kent located 0.3 miles away.
- Stations in areas with industrial land use such as Duwamish and South Park have substantially higher metals and PCB deposition rates than areas on the Puget Sound shoreline sampled in other studies using the same methods.
- PCB deposition rates at South Park were more than two times higher than Duwamish. The reasons for this difference are unknown.
- The PCB congener profile² at Duwamish station was most similar to Beacon Hill; however, profiles at all stations but Enumclaw were generally similar. The PCB congener profile at Enumclaw was the most unique. More of the lower chlorinated PCB congeners were present in Enumclaw samples compared to other stations.
- Mean relative contributions of dioxin/furan congeners³ to the total deposition were similar between Beacon Hill, Duwamish, South Park and Kent SC stations; there were some notable differences at Kent and Enumclaw stations.
- Metals deposition rates generally decreased during the fall months into early winter, potentially due to precipitation scavenging (scouring of pollutants by rainfall).
- Metals deposition rates are significantly higher in the dry season (July through September) than the wet season (October through June).
- Fine particulates (PM 2.5) concentrations were significantly correlated with most metals and PCBs deposition rates, but the correlations were only weakly to moderately predictive. Fine particulates concentrations were highest at Kent and lowest at Beacon Hill stations.
- Multivariate analysis found that PM 2.5, wind speed and temperature significantly influenced metals deposition rates at Beacon Hill, Duwamish and Kent stations but rainfall did not. Also, PM 2.5 was the only environmental factor to significantly influence high-molecular-weight polycyclic aromatic hydrocarbon (HPAH) deposition at these three stations.
- Based on the laboratory quality control results, there is a potential for significantly low bias for all benzo(a)pyrene results in this study.
- Low-molecular-weight polycyclic aromatic hydrocarbon (LPAH) results are biased low and only provided for relative spatial comparison.

² PCBs are comprised of 209 chemicals of similar structure called “congeners”. Looking at the proportions of congeners in different samples, or the profile, gives an indication of different PCB sources.

³ There are 210 different congeners of dioxins and furans, however, only 17 were measured in this study. These are the 17 congeners reported to cause human health effects.

1.0. INTRODUCTION

King County is collecting data to help evaluate how the atmospheric deposition of pollutants in the Green/Duwamish River Basin varies with land use type and proximity to various levels of urbanization. The objectives of this study are to compare the measurements of bulk deposition (dry particulates and precipitation) at a small number of stations in areas of different land uses within the Green/Duwamish River Basin and to provide information to assist in understanding atmospheric sources to the Lower Duwamish Waterway (LDW).

This data report presents and discusses the results of the 2011/2012 sampling program with respect to spatial and temporal observations and differences between geographic locations. 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 results (Section 5.0) of the study. A discussion of the findings and preliminary conclusions of this study are in Section 6.0. Supporting appendices include chain of custody forms, laboratory data results, chemistry flux⁴ data, and chemistry data validation reports.

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), EPA, City of Seattle, and the Port of Seattle. The Source Control Work Group collaborates to understand potential sources of contaminants to the LDW Superfund site and works to control and reduce sources that can contaminate sediments in the waterway. King County wants to better understand the potential sources of chemicals of concern (COCs) identified in the LDW Superfund site that contribute chemical inputs through stormwater runoff to LDW combined sewer overflow (CSO) basins⁵, LDW separated stormwater basins, and the Green/Duwamish River upstream of the LDW. King County has eight CSOs and two emergency overflows that discharge into the LDW.

King County has completed sampling of whole waters at various CSOs in the Duwamish Basin (King County 2011a) and has been characterizing solids within the combined sewer structures and lines that discharge to the LDW (King County 2011b). Also, King County is sampling water, sediment and suspended solids in the Green River Basin (King County 2011c, King County 2012, King County 2013). To complement these data, King County has launched atmospheric deposition studies in the Green/Duwamish River Basin.

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

⁴ “Flux” is used in this report to refer to the mass of a chemical deposited on one square meter of land surface per day.

⁵ CSOs include discharges of both industrial and municipal wastewater and stormwater.

collected for polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyl (PCB) Aroclors. In this study, additional bulk 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 deposition across the range of land uses within the Green/Duwamish River Basin. The COCs include metals, including mercury, PAHs, and dioxin/furan and PCB congeners. The bulk deposition data collected in this study assists in understanding atmospheric sources across the watershed including areas with combined sewer systems, separated stormwater basins, and less developed basins upstream 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 distributional differences, and as a line of evidence in evaluating sources to the LDW.

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 study area encompasses the LDW, Lower Green and Middle Green River portions of the Green/Duwamish River Basin. The land use within the Basin includes industrial, commercial, residential, and transportation corridors. The study area also includes parks and relatively undeveloped locations, consisting of evergreen and deciduous forests, riparian shorelines, and wetlands. The amount of developed land varies greatly between subbasins, ranging from heavily urbanized to almost entirely undeveloped. The study area has been expanded beyond LDW to evaluate the degree to which urban residential, suburban, and rural bulk deposition differs from the LDW.

2.0. FIELD SAMPLING METHODS

This section reviews the field sampling methods used in this study. The field procedures are described in greater detail in the project Sampling and Analysis Plan (SAP) (King County 2011d). The locations where air 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 that occurred in field sampling compared to the project SAP (King County 2011d). Copies of completed chain-of-custody forms used to track sample custody are presented in Appendix A.

2.1 Sample Locations

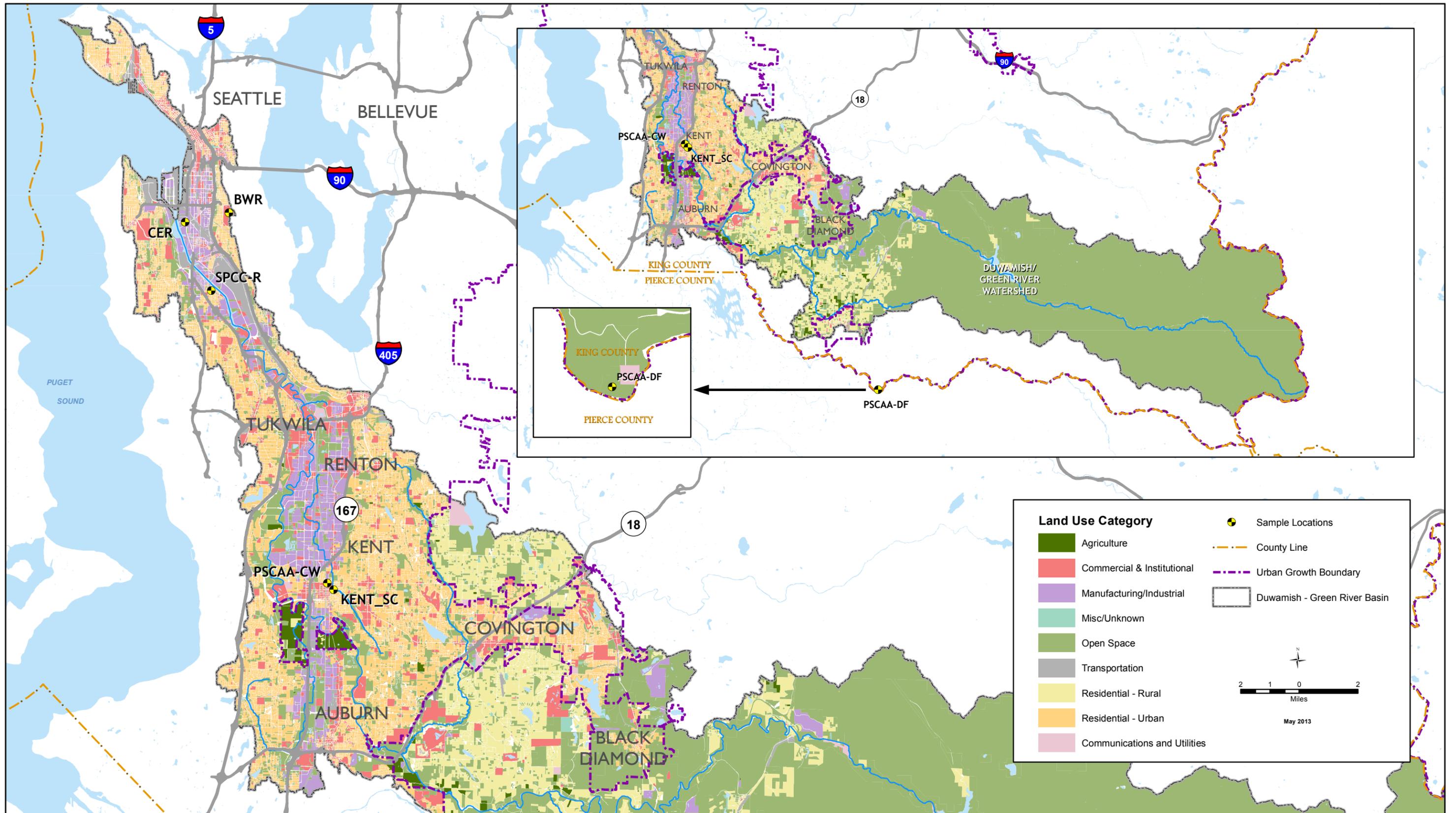
Five stations were originally selected for sampling (see Figure 1, Table 1). All of these stations selected are part of the Puget Sound Clean Air Agency's (PSCAA) regional network of air quality monitoring stations. Selecting PSCAA stations provides not only complementary meteorological data where possible, but also congruence with the concept of these locations supplying locally representative air quality data. Two stations were selected within the LDW corridor to supply some spatial variability in the main area of interest. The "Duwamish" station represents industrial and urban land uses and the South Park location represents a mix of suburban, industrial and residential land uses. These two sites are positioned relatively centrally in the LDW corridor, yet spaced about 4 km apart and on opposite sides of the Duwamish River. A station was selected in each of two areas upstream in the Green River. The Kent station represents suburban and commercial land use while the Enumclaw station represents rural and forestry land uses. Lastly, a fifth station at Beacon Hill was selected as representative of urban residential land use. This station was also selected by the U.S. Environmental Protection Agency (EPA) to represent urban scale air toxics in the Pacific Northwest (Ecology 2012). This station is owned and operated by Ecology. All other stations are owned and operated by PSCAA.

After an interim review of measured bulk atmospheric deposition and calculated daily fluxes, it was observed that dioxin/furan daily fluxes appeared much higher at the Kent station than all other stations. The proximity of the Kent station to a local rail line (~250 feet) was suspected to affect the bulk atmospheric deposition measurements (Figure 2). The rail line is used by the commuter Sounder train which supports nine northbound and nine southbound trains on weekdays that stop at Kent station (<http://www.soundtransit.org/Schedules/Sounder-Lakewood-Seattle>). In addition, there are passenger trains (Amtrak Cascades⁶ and Coast Starlight⁷) and freight trains that use the same rail line to pass through Kent (<http://www.wsdot.wa.gov/Rail/passengertypes.htm>). Therefore, an additional station was selected for paired sampling in Kent to test for variability in atmospheric deposition due to local (microscale) influences. The new station

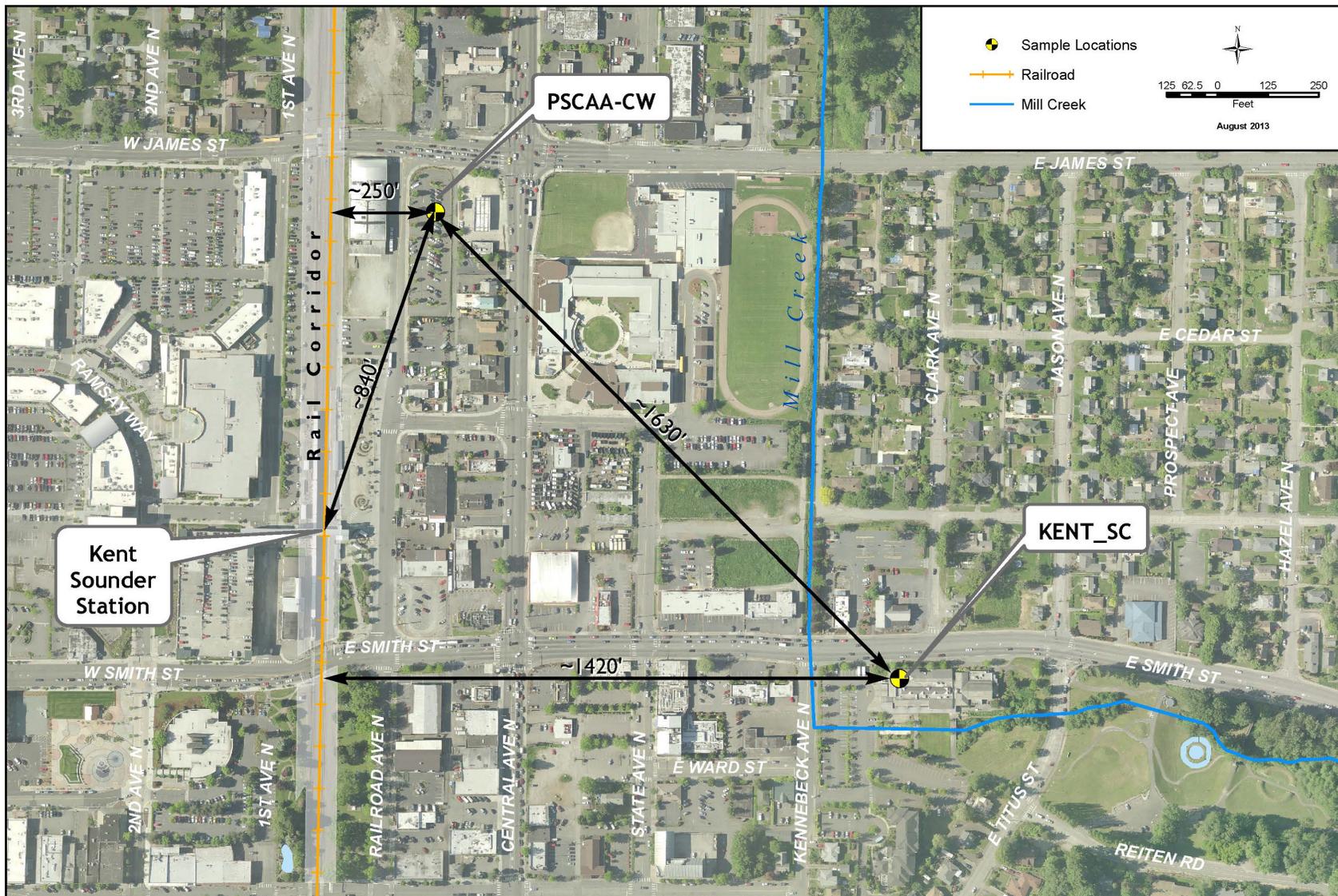
⁶ Amtrak Cascades runs four northbound and four southbound trains through Kent each day.

⁷ The Coast Starlight train runs once northbound and once southbound each day.

was located on the roof of the Kent Senior Activity Center (Kent SC) and was sampled on the same schedule as the Kent station, beginning on May 2, 2012 and continuing for the remainder of the study (Figure 1, Table1). This location is not part of the PSCAA station network but was selected to represent the suburban center of Kent, similar to the original Kent station but without the proximal rail line. The rail line is located ~1420 feet from the Kent SC station.



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Figure 2
**Kent and Kent SC
 Bulk Atmospheric Deposition
 Sampling Stations
 in Relation to Railroad Features**

Table 1. Air Sampling Locations and Locator Names

Station Location	KC Locator	PSCAA ID	Location	State Plane Easting	State Plane Northing
Beacon Hill, relocated ¹	BWR	BW	15th S. and Charlestown, Seattle	1276200	210777
Duwamish relocated ²	CER	CE	4401 E. Marginal Wy. S., Seattle	1268326	209111
South Park	SPCC-R	DD	8201 10th Ave S. Seattle	1273043	196688
Kent	PSCAA-CW	CW	James St. & Central Ave., Kent	1293960	144039
Kent Senior Center ³	KENT_SC	None	600 East Smith St., Kent	1295105	142885
Enumclaw	PSCAA-DF	DF	30525 SE Mud Mountain Rd, Enumclaw	1365590	53337

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

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

³ The Kent Senior Center was added for sampling in May, 2012 for comparison to the original Kent station data because of higher dioxin/furan flux measurements which were suspected to be due to nearby sources, particularly the rail line.

2.2 Sample Collection and Processing

Sampling systems were constructed by hand according to the design described in the project SAP (King County 2011d) and consisted of a wood-framed structure supporting 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 two organics samplers, 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 congeners and dioxin/furan congener analyses and a second organics sampler collected samples for PAHs analysis. Mercury samplers collected wet and dry deposition with a plastic funnel (high-density polyethylene) connected to a 500 mL fluoropolymer sample bottle. The metals sampler was identical to the mercury sampler during the dry season, but when the wet season began, a 2 L plastic bottle was deployed for total metals.

Larger diameter (45 cm) funnels were deployed with the organics samplers during the dry season while smaller diameter (23 cm) funnels were deployed during the wet season. This funnel size change was necessary to collect sufficient mass for analysis in the dry season yet prevent overflowing the collection vessels in the wet season.

Carboys, funnels, and other 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: filling each bottle with 1:1 nitric acid and soaking in a hot water bath for 24 hours, rinsing with reagent water, then repeating these two steps filling the bottle with 1% hydrochloric acid instead of nitric acid.

Samples were collected 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. For all samples, shorter collection periods occurred during the wet season (i.e., October–May) to reduce risk of sampler container 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 sample container, a known quantity of reverse osmosis (RO) water was used to rinse dry particulates 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. Then, the funnel was disconnected, and the collection vessel was capped and stored on ice during return to the lab. The rinse volume and funnel area were recorded on field sheets and entered along with deposition volume into the King County Laboratory Information Management System (LIMS).

Initially, the trace metals sample volume was determined using a volumetric method according to the SAP. The deposition volume was marked on the sample container using lab tape and a marking pen. After analysis of the samples was complete, the deposition volume was determined. The excess sample was discarded, the sample bottle filled with RO water to the marked volume line, and then poured out into a graduated cylinder for measurement. Beginning on November 16, 2011, the trace metals sample volumes were determined by weighing the sample containers before sample collection and comparing that to the weight of the sample container with the sample inside. The difference in grams was equivalent to the volume in milliliters.

The organics sampler for PCBs and dioxins/furans was removed from the field between sampling periods and re-cleaned and stored at KCEL before redeployment⁸. 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.

⁸ Samples for PCB and dioxin/furan congeners were collected at a lower frequency; samples for all other parameters were collected continuously.

A total of three field replicates were collected for metals, mercury, PAHs, PCBs and dioxins/furans analyses. One equipment blank was collected for metals and mercury analyses and one equipment blank was collected for PCBs and dioxin/furan analyses. One spike blank was collected for metals and mercury analyses and two spike blanks were collected for PCBs and dioxin/furans analyses. One wipe sample was collected for PAHs, PCBs and dioxin/furan analyses. No wipe samples were collected for metals analysis because the background contamination on the pre-used wipe was too high. In lieu of a metals wipe sample, a second type of equipment blank was collected by capturing RO rinse water run through a funnel after a sample had been collected at Duwamish station. This sample was named "Post-sample equipment blank."

2.3 Sampling Schedule

Bulk atmospheric deposition sampling began on July 27, 2011 and the last sample was collected on October 24, 2012. Samples for PAHs, metals and mercury analyses were collected more or less continuously at all stations (Table 2). Exceptions occurred when high wind conditions caused blow over of collection funnels or sample containers were overfilled from greater than predicted rainfall. Samples were typically not retained under these conditions except on two collection dates, when samples were retained and analyzed because the overflow was believed to be small (i.e., <200 mL). The specific dates of these two events can be viewed in Table 2; the analytical results for these samples were flagged to indicate the overflow event (See Section 5.6 and Appendix B). The deployment period ranged from 6 to 29 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 ranged from 7 to 29 days for PCBs and dioxin/furan samples.

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

Deployment End Date	Days Deployed	Beacon Hill	Duwamish	South Park	Kent	Kent SC	Enumclaw
8/25/2011	29	X	X ^R	X	X	--	X
9/21/2011	27	X	X	X	X	--	X ¹
9/29/2011	8	X	X	X	X	--	X
10/19/2011	20	X	X	X	X	--	X
11/2/2011	14	X	X	X	X	--	X
11/16/2011	14	X	X	X	X	--	X
11/22/2011	6	--	--	--	--	--	X
11/23/2011	7	X	X	X	X	--	--
11/29/2011	6	X	X	X	X	--	X
12/28/2011	29	X	X	X	X	--	X
1/11/2012	14	X	X	X	X	--	X
1/24/2012	13	X	X	X	X	--	X
2/7/2012	14	X	X	X	X	--	X
2/21/2012	14						X
2/22/2012	15	X	X	X	X	--	
3/6/2012	13	X	X	X	X	--	W
3/15/2012	9	X	X	X ^{RM}	X ^{RP}	--	X
3/29/2012	14	X	X	MH ²	X	--	P ³
4/19/2012	21	X	X	X	X	--	X
5/2/2012	13	X	X	X	X	--	X ⁴
5/31/2012	29	X	X	X	X	X	
6/25/2012	25	--	--	--	--	--	X
6/27/2012	27	X	X	X	X	X	--
7/19/2012	22	X	X ^{RP}	X	X	X	PM
7/26/2012	7	--	X	X	X	X	X
8/16/2012	21	--	X	X	X	X	X
9/6/2012	21	--	X	X	X ^{RM}	X	--
9/6-9/13/2012	--	--	--	--	--	--	--
10/10/12	27	X	X	X	--	--	--
10/24/12	14	--	--	--	X	X	--

-- No sample collected

X = PAHs, metals and mercury analyses

W = Samplers overturned due to wind

P = PAHs analysis

M = Metals analysis

H = Mercury analysis

¹ PAHs, metals and mercury samplers overflowed by small amount. Sample results have been flagged.

² PAH samples were not collected because wind blew over the funnels

³ Metals and mercury samples were not collected because wind blew over the funnels

⁴ PAHs sampler overflowed by small amount. Sample results have been flagged.

^R = field replicate was collected for PAHs and metals

^{RM} = field replicate was collected for metals and mercury

^{RP} = field replicate was collected for PAHs

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

Deployment End Date	Days Deployed	Beacon Hill	Duwamish	South Park	Kent	Kent SC	Enumclaw
8/25/2011	29		X	X	X		
9/29/2011	8	X		X	X ^R		
10/19/2011	20	X		X	X ^R		
11/16/2011	14	X			X		
12/28/2011	29		X	X			X
1/11/2012	14	X	X				
2/7/2012	14			X			X
3/6/2012	13				X		
3/29/2012	14	X		X			
5/2/2012	13	X	X ^R				O
6/25/2012	25						X
7/19/2012	22				X	X	X
7/26/2012	7		X	X	X	X	X
8/16/2012	21		X	X	X	X	X
8/27/2012	10						X
9/6/2012	21		X	X	X	X	
10/10/2012	27	X	X	X			
10/24/2012	14				X	X	

O = PCB and D/F samplers were not retained because the sample container overflowed from rain.

X = PCBs and dioxin/furan analyses

^R = field replicate was collected for PCBs and dioxin/furan analysis

The original sampling schedule spanned one year. However, the sampling was extended to obtain samples that could not be collected as scheduled (e.g., due to overturning from wind at Enumclaw), to add additional paired events at the two sites in Kent, and to obtain more dry period samples at all sites. The total number of samples, including field replicates, collected at each station ranged from 31 at the Kent SC station to 101 at the Kent station (Table 4). At all stations except Kent SC, 20 or more samples were collected for PAHs, metals and mercury analyses. The number of samples by station for PCBs and dioxin/furan analyses ranged from 5 to 12 per station.

Table 4. Sample Totals for Each Analyte Group by Station

Analyte Group/Station	Beacon Hill	Duwamish	South Park	Kent	Kent_SC	Enumclaw
PAHs	22	27	24	26	7	21
Metals	22	27	26	26	7	20
Mercury	22	25	25	25	7	19
PCBs	7	8	10	12	5	7
Dioxins/Furans	7	9	10	12	5	7
Totals	80	96	95	101	31	74

2.4 Deviations from the SAP

Sampling methods that differed from the project SAP are summarized in the following list:

- After the first deployment, it became clear that the 500 mL capacity of the metals and mercury sample bottles was too small to prevent overflow due to rainfall on a two week deployment. Thus, the metals sample bottles were changed to a 2L capacity for the second sampling period. Use of a 500 mL capacity sample bottle for mercury was continued due to limited 2L bottle supply. See Section 3.5 below for a description of laboratory procedures for sample splitting when the mercury sample bottle overflowed.
- Deposition volume on all sample bottles was first determined volumetrically, according to the SAP, using a graduated cylinder. However, starting November 16, 2011, this method was improved for the metals and mercury sample deposition volume measurement to be based on mass. This method is generally more accurate because it does not rely on visual estimation. However, this approach was not used for the organics sample bottles because the 4L bottle was too heavy for the available laboratory scales. Therefore, the measurement method described in the SAP was retained for organics samples.
- As described in Section 2.1, a second Kent station was added for sampling on May 2, 2012 at Kent SC. This station was used to evaluate presence of a microscale effect for dioxins/furans at the original Kent station.
- The project SAP stated that 10 field replicates would be collected for metals, mercury and PAHs samples. After the SAP was finalized, it was realized that more regular samples would be collected than scoped because of the desire to sample continuously and the need to limit deployment times to prevent overflow. Thus, the field replicates were reduced to three for metals, mercury and PAHs analysis to help compensate for the increase in regular samples. Although the total number of field replicates was reduced from the SAP for metals and PAHs, the resulting number of field replicates is considered adequate for a qualitative indication of replicate variability. Three field replicates were collected and analyzed for PCBs and

dioxins/furans, one more than designated in the SAP. The extra field replicate was collected because the first field replicate was only deployed for 8 days; it was collected early to prevent overflowing from incoming rain. It was uncertain if this short deployment would result in detectable amounts of deposition. Therefore, the field replicate was deployed again at the same location (i.e., Kent station).

3.0. LABORATORY METHODS

A summary of analytical methods for PAHs, metals, 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 SDL may be 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. Nominal MDL and RDL values were based on results of an MDL study completed on June 23, 2011.

3.3 PCB Congeners

PCB congener analysis followed EPA Method 1668A Revision A (EPA 2003), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. The analysis included all 209 PCB congeners. AXYS switched to Revision C of Method 1668 (EPA 2010) during this project upon promulgation of this method by EPA. Method 1668C also provides reliable analyte identification and very low detection limits. Both versions of this method add an extensive suite of labeled surrogate standards before sample extraction. Data are “recovery-corrected” for losses in extraction and clean-up, and analytes are quantified

against their labeled analogues. The principle difference between Method 1668A and 1668C is the replacement of individual laboratory acceptance criteria with interlaboratory developed acceptance criteria. This change is not anticipated to modify result values, although there might have been minor differences in data qualifiers not affecting usability. Samples collected and analyzed for PCBs through October 13, 2011, were analyzed by Method 1668A, and the remainder were analyzed by Method 1668C.

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. Labeled native and surrogate standards are added before samples are extracted. Data are “recovery-corrected” for losses in extraction and cleanup, and analytes are quantified against their labeled analogues or a related labeled compound. AXYS performed this analysis according to their Standard Operating Procedure MLA-017 which is based on EPA Method 1613B Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.

3.5 Deviations from the SAP

The following procedures differed from the project SAP:

- When the mercury sample bottle overflowed, the 2L metals sample bottle volume was split in the laboratory so that half the volume was used for metals analysis and the other half for mercury analysis. The split samples were preserved as appropriate for their respective method requirements. This sample splitting change is not expected to impact data quality.
- For the determination of MDL/RDL values for PAH analysis, the MDL study was completed using a sample volume of two liters instead of the one liter stated in the SAP.
- For PAHs, individual field spike concentrations were 0.0667 µg/L (0.133 µg/L for benzo(b,j,k)fluoranthene) instead of 0.750 µg/L as stated in the SAP.
- An error was noticed in Table C-2 of the SAP. The native compound spike amounts should be in pg/mL and not pg/L.

- Quality control (QC) wipes were not analyzed for trace metals. The testing of the wipes showed they were contaminated with metals of interest. A second equipment rinse blank was collected instead.

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 to each other because differences exist between bulk air deposition samples in deployment duration, sample rinse volume, rainfall volume and the funnel size used for collection. 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:

$$\text{Concentration } (\mu\text{g/L}) \times (\text{Rainfall volume (L)} + \text{Sample rinse volume (L)}) / \text{Funnel area (m}^2\text{)} / \text{Deployment duration (days)} = \text{Flux } (\mu\text{g/m}^2\text{-day)}$$

All data analyses were conducted using flux values.

4.2 Summation for PAHs, PCB Congeners 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 1995): 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:

- Concentrations were converted to fluxes first⁹.
- When sample results were non-detect (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 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 interpreting 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 equivalent 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 was not detected, the TEF was applied to the flux based on the full non-detect value (or U qualified value)¹⁰.

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

⁹ 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.

¹⁰ 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
1,2,3,7,8,9-HXCDD	0.1
1,2,3,7,8-PECDD	1
Furans	
2,3,7,8-TCDF	0.1
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 results. One plot was made for each analyte (i.e., metals and mercury) or analyte group (i.e., LPAHs, HPAHs, PCBs, dioxins/furans). Boxplots were also created to examine data distributions by location. In preparation for testing for significant differences between fluxes with location, the assumption of normality was tested for each analyte or analyte group using the Shapiro-Wilk test. Also, the assumption that the data groups had equal variances was 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 for silver, vanadium, LPAHs, total PCBs, and dioxin TEQs. 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 five chemicals that passed for normality and equal variance assumptions were tested using a parametric one-way analysis-of-variance test for significant differences. Differences were considered statistically significant with a p value less than 0.05.

To analyze differences in fluxes between the wet and dry seasons, where applicable, data were grouped by analyte and season combining data for all stations. The Shapiro-Wilk test ($p < 0.050$) was used to test for normality. All data groups failed the Shapiro-Wilk test, signifying the need for a nonparametric test. Therefore, a Mann-Whitney Rank Sum test was used to compare analyte fluxes at all stations between the dry and wet seasons. Differences were considered statistically significant with a p value less than 0.05.

Correlation analysis was conducted to examine relationships between weather parameters and fluxes. Normality was tested for each analyte or analyte group using the Shapiro-Wilk test. Then, corresponding parametric or nonparametric correlations were tested using polynomial linear regression or Spearman rank order correlation, respectively. Linear, quadratic, or cubic equations provided the best fit in parametric regressions. The strength

of the correlation was judged based on the corresponding test correlation coefficient (i.e., R^2 for linear regression or r_s for nonparametric Spearman rank test) with values closer to 1.0 being strongest. All statistical testing was completed using the software program SigmaPlot® 12.

A principal component analysis (PCA) correlation matrix was employed to summarize patterns of metal deposition at Beacon Hill, Duwamish, Enumclaw, Kent, South Park sites. Permutation multivariate analysis of variance (perMANOVA) using Euclidian distance was also performed to examine metal deposition differences among stations. In addition, a redundancy analysis was conducted to examine the influence of environmental (weather and particulate) parameters on fluxes of metals at the three stations: Beacon Hill, Duwamish and Kent. These stations were selected because they had the most complete environmental data. Stepwise regression was employed to determine which environmental variable(s) influence HPAH presence. Stepwise regression was also used to verify ordination results for metals. Multivariate analyses were not conducted with PCBs or dioxins/furans flux data because too few samples were collected to make the analysis meaningful. A detrended correspondence analysis indicated that a linear model was appropriate for redundancy analysis. The environmental variables included were average temperature, wind speed, total rainfall, total inversion days (assuming >50% hours = inversion) and PM 2.5 concentration. The first two ordination axes were used for interpretation because they explained the majority of the variance within the dataset. Metals flux data were log-transformed prior to analysis to linearize the data. PCA and redundancy analysis is sensitive to outliers; therefore, data screening was performed to identify extreme outliers. In addition, environmental variables were standardized by z-score prior to analysis due to the different measurement units for each variable. All analyses were performed with R statistical programming version 3.0.1 using the “vegan” package.

5.0. RESULTS

Summary results for chemistry (presented as flux measurements) and associated measurements of temperature, rainfall, fine particulates and wind are presented in this section. 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 also included (Section 5.9). The complete data validation reports are included in Appendices D and E. Some figures in this section are in a boxplot format following a consistent symbology. Figure 3 presents the symbology used for all boxplots in this report. All field replicates were averaged before calculation of boxplot statistics.

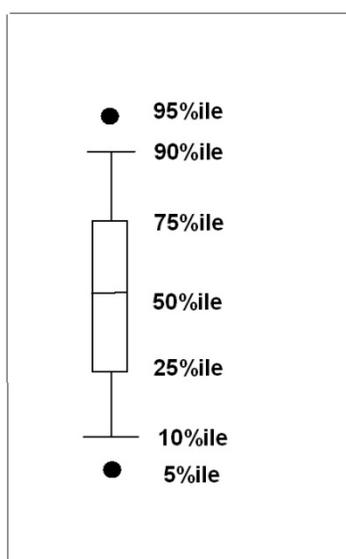


Figure 3. Box Plot Legend

5.1 Metals

The number of metals results varied by station, ranging from 20 to 25 with the exception of the Kent SC station, where only seven metals samples were collected. The results for each metal are presented in this section.

5.1.1 Arsenic

Arsenic fluxes were usually lowest at either the Beacon Hill or Enumclaw stations (Figure 4). The lowest arsenic flux occurred at the Enumclaw station and was estimated at 0.13 $\mu\text{g}/\text{m}^2\text{-day}$. The highest arsenic fluxes occurred at the Duwamish station (maximum of 2.7 $\mu\text{g}/\text{m}^2\text{-day}$) except for the summer months of 2012 (Figure 4, Table 6). Arsenic fluxes measured at Beacon Hill, South Park, and the two Kent stations were most often between the Enumclaw and Duwamish fluxes.

Arsenic fluxes decreased to a low point in late December to mid-January at most stations then increased in the following months; this was particularly evident at the Duwamish and Kent stations. During late July and August, arsenic fluxes were highest at Enumclaw. Although arsenic fluxes at the South Park station were typically lower than at the Duwamish station, the patterns of change over time were similar at these stations. In addition, changes in arsenic fluxes at Beacon Hill and Kent stations were similar over time.

Ignoring temporal differences by grouping fluxes by station shows that the Duwamish had the highest median and mean and greatest variability in arsenic fluxes (Figure 5). Arsenic fluxes at Beacon Hill and Kent were relatively low in variability. The median arsenic flux at South Park was second highest. When both Kent stations were sampled, median arsenic fluxes were similar at the two stations but the mean arsenic flux was higher at Kent SC. Notably, variability at the Enumclaw station was relatively high and its median flux (0.41 $\mu\text{g}/\text{m}^2\text{-day}$) was close to the lowest, that at Beacon Hill (0.36 $\mu\text{g}/\text{m}^2\text{-day}$). The one-way ANOVA by ranks test showed arsenic fluxes at Duwamish were significantly higher ($p < 0.05$) than all other stations except South Park. Also, arsenic fluxes were found to be significantly higher at South Park than Beacon Hill; notably arsenic fluxes at South Park were not significantly different than Kent. No other significant differences were found.

Table 6. Summary of Arsenic Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	0.18	0.49	0.28	0.14	0.33	0.13
Maximum	0.80	2.67	1.19	0.64	1.12	1.67
Median	0.36	0.93	0.63	0.44	0.46	0.41
Mean	0.38	1.10	0.67	0.44	0.54	0.56

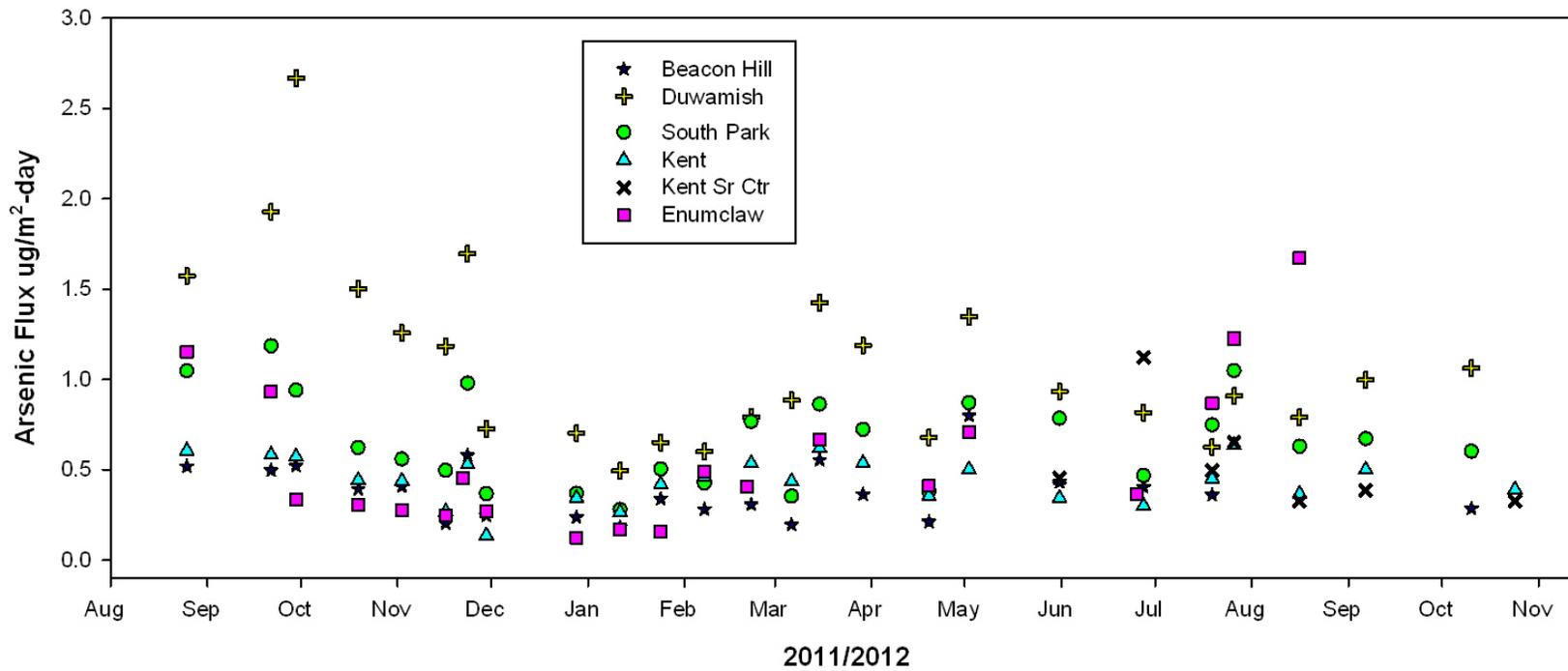


Figure 4. Arsenic Flux for each Collection Period by Collection Date and Station.

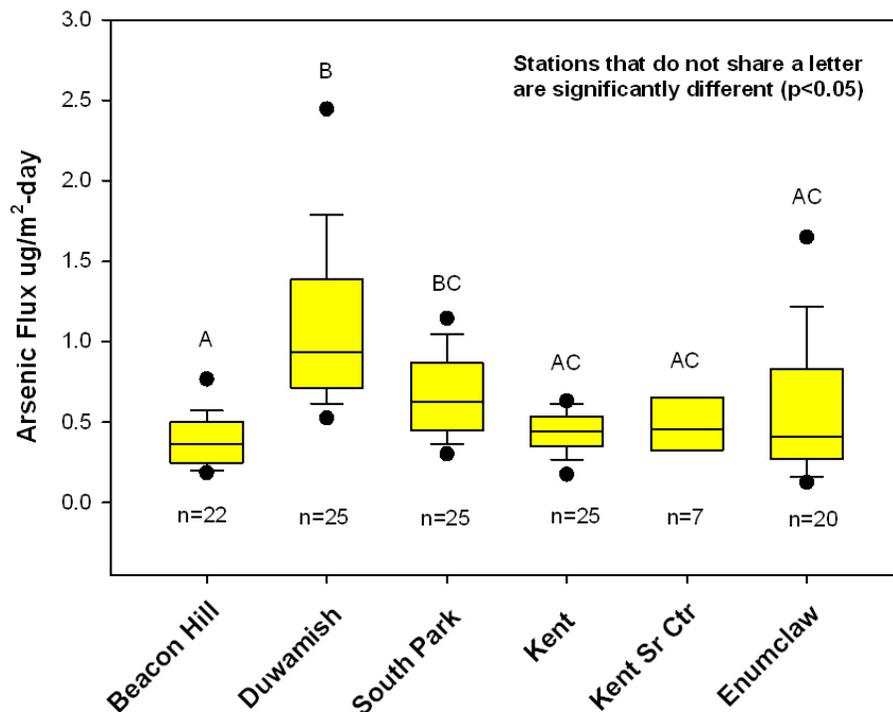


Figure 5. Boxplots of Arsenic Flux by Station.

5.1.2 Cadmium

Cadmium fluxes were often but not consistently the lowest at the Enumclaw station. The single lowest flux occurred at the Enumclaw station and was estimated at $0.010 \mu\text{g}/\text{m}^2\text{-day}$. The highest fluxes were most often at either South Park or Duwamish stations (Table 7). However, the single highest cadmium flux ($1.57 \mu\text{g}/\text{m}^2\text{-day}$) was measured at Beacon Hill. Cadmium fluxes measured at Beacon Hill and the two Kent stations were usually below Duwamish and South Park fluxes and above Enumclaw fluxes.

Cadmium fluxes decreased to a low point in late November 2011 at South Park and then increased in the following months; this trend was not apparent at other stations (Figure 6). Cadmium fluxes at Duwamish were sometimes very similar to South Park (e.g., October 2011) and sometimes divergent (e.g., March 2012). Cadmium fluxes at Beacon Hill and Enumclaw were relatively stable and similar except for a sampling event in late November. The late November flux at Beacon Hill was particularly high but fluxes at other stations also increased to some degree during the same sampling event.

Ignoring temporal differences by grouping fluxes by station shows that the Duwamish median cadmium fluxes were highest (Figure 7). The median cadmium flux at South Park was second highest. The median cadmium fluxes at the remaining four stations were similar to each other with Enumclaw being lowest. At Beacon Hill, 95th percentile flux was the highest, reflecting the high flux sampling event in November 2011. When both Kent stations were sampled, cadmium fluxes were similar at the two stations. The one-way

ANOVA by ranks test showed cadmium fluxes at Duwamish were significantly higher ($p < 0.05$) than all other stations except South Park. Also, cadmium fluxes were found to be significantly higher at South Park than Beacon Hill or Enumclaw. No other significant differences were found.

Table 7. Summary of Cadmium Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	0.039	0.13	0.048	0.046	0.050	0.010
Maximum	1.57	0.79	0.73	0.71	0.13	0.20
Median	0.084	0.34	0.24	0.11	0.10	0.080
Mean	0.15	0.38	0.27	0.16	0.095	0.080

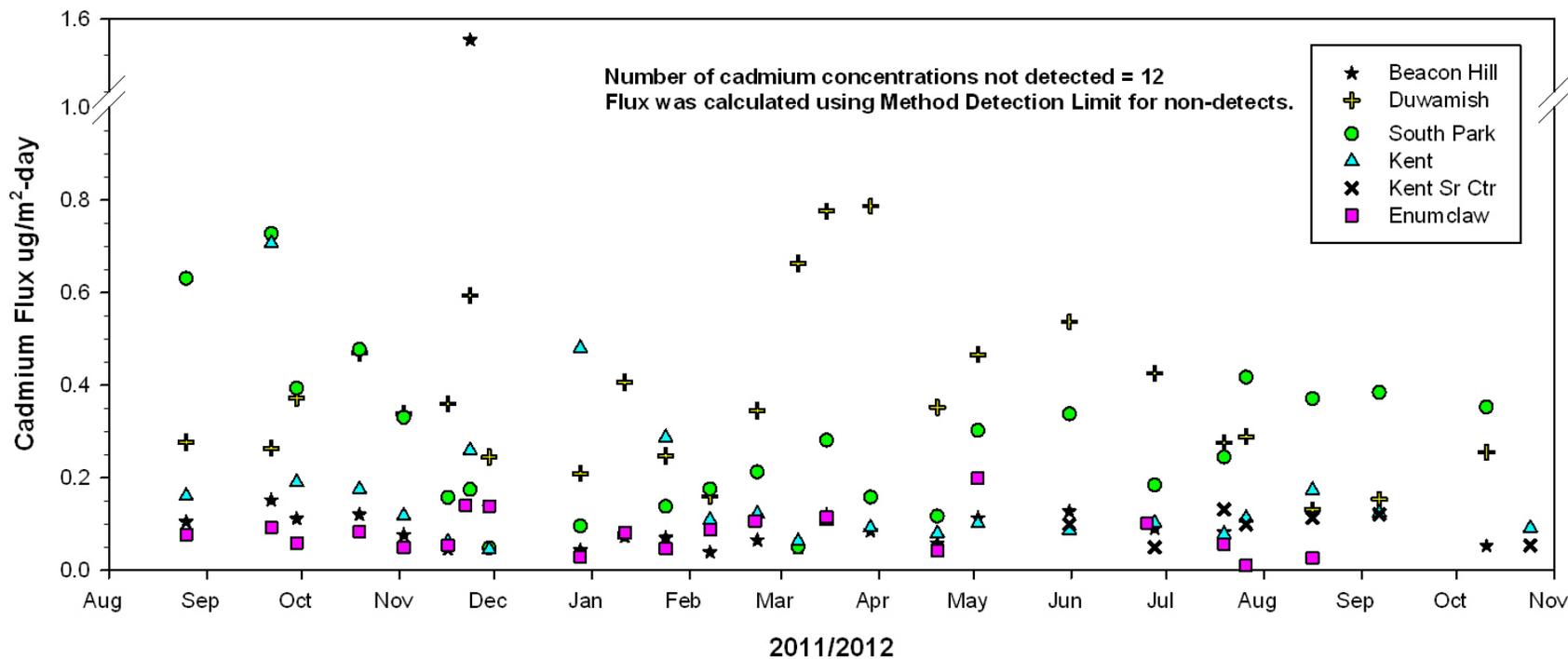


Figure 6. Cadmium Flux for each Collection Period by Collection Date and Station.

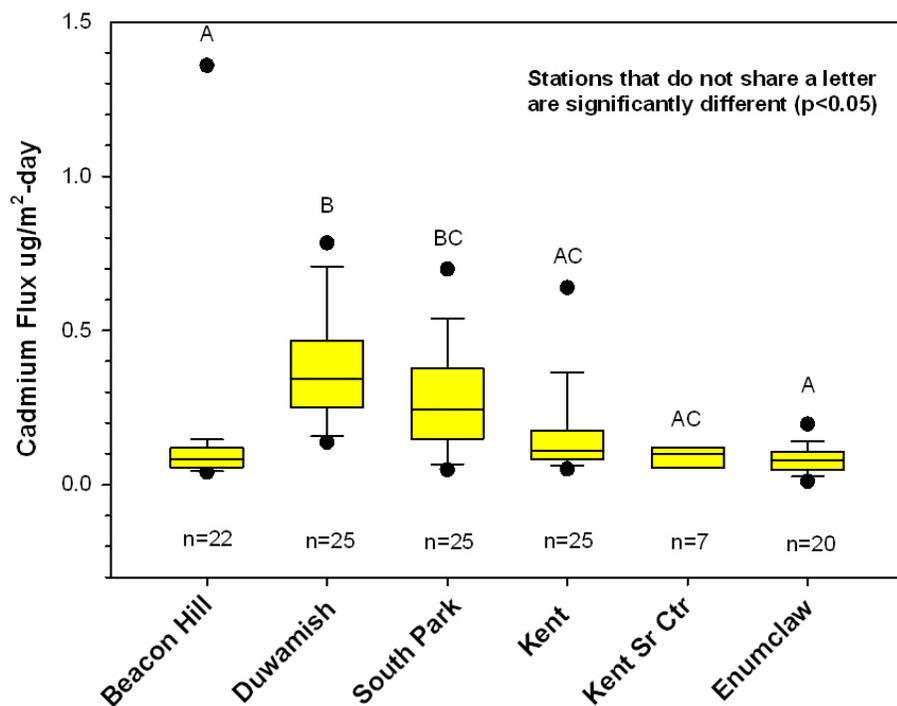


Figure 7. Boxplots of Cadmium Flux by Station.

5.1.3 Chromium

Chromium fluxes were often but not consistently the lowest at the Enumclaw station. The lowest flux occurred at the Enumclaw station and was estimated at $0.14 \mu\text{g}/\text{m}^2\text{-day}$ (Figure 8). The highest fluxes were most often at the Duwamish station (Table 8). The single highest chromium flux ($8.8 \mu\text{g}/\text{m}^2\text{-day}$) was measured at Duwamish station. Chromium fluxes measured at Beacon Hill, South Park and the two Kent stations were usually below Duwamish but above Enumclaw fluxes.

In general, chromium fluxes decreased to a low point in November/December then increased in subsequent months; this pattern was less apparent at some stations such as Enumclaw. Chromium fluxes at each station appear to follow their own unique patterns of change over the sampling period with no consistent seasonal trends.

Ignoring temporal differences by grouping fluxes by station shows that the Duwamish median chromium flux was highest (Figure 9). The median chromium fluxes at the South Park, Kent and Kent SC stations were lower than Duwamish and all similar. Variability in chromium fluxes was greater at Enumclaw than Beacon Hill but the median chromium fluxes were similar at these two stations. When both Kent stations were sampled, the median chromium fluxes were similar at the two stations. The one-way ANOVA by ranks test showed chromium fluxes at Enumclaw and Beacon Hill were significantly lower

($p < 0.05$) than Duwamish, Kent and South Park stations. No other significant differences were found.

Table 8. Summary of Chromium Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	0.55	1.97	0.77	1.07	0.96	0.14
Maximum	2.63	8.78	5.69	4.59	3.86	5.48
Median	1.22	3.94	2.57	2.61	2.53	0.89
Mean	1.33	4.15	2.62	2.61	2.50	1.28

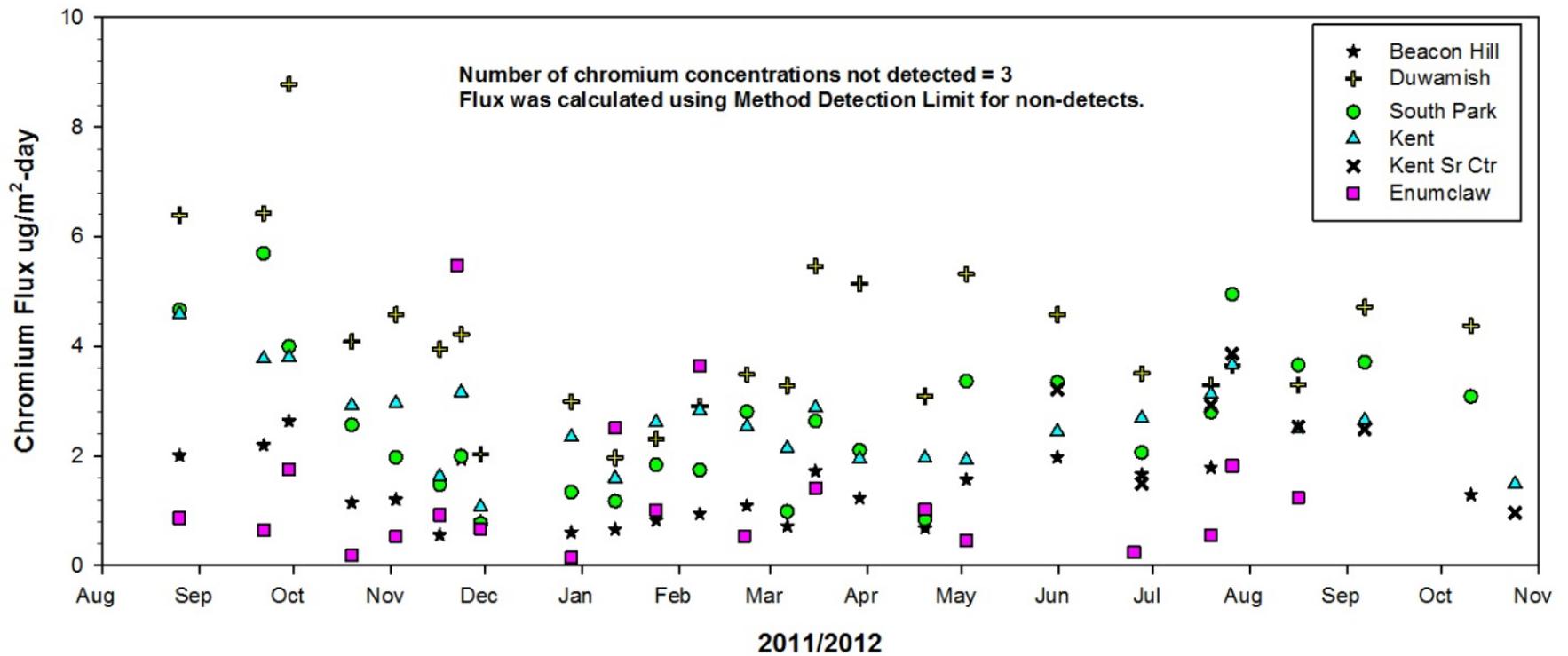


Figure 8. Chromium Flux for each Collection Period by Collection Date and Station.

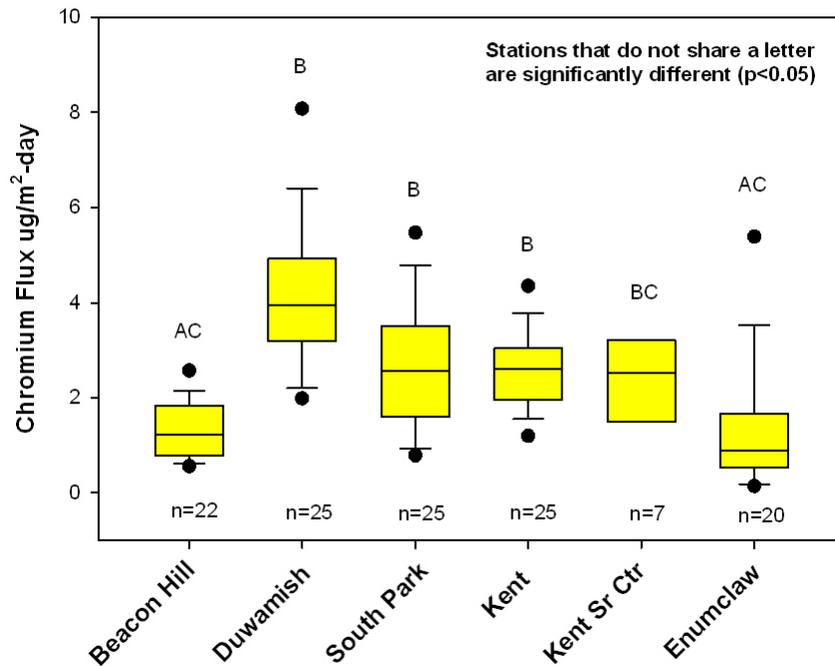


Figure 9. Boxplots of Chromium Flux by Station.

5.1.4 Copper

Copper fluxes were consistently the lowest at the Enumclaw station (Figure 10). The single lowest flux measured at the Enumclaw station was 0.63 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 9). The highest copper fluxes were most often at either Duwamish or South Park stations throughout the study period; the maximum was 43.8 $\mu\text{g}/\text{m}^2\text{-day}$ at Duwamish. Copper fluxes measured at Beacon Hill, South Park, and the two Kent stations were usually below the Duwamish and South Park stations.

Copper fluxes at the Enumclaw stations were relatively stable throughout the study period with maxima occurring in the summer months (July-September). Temporal changes in copper fluxes at the Duwamish and South Park stations were dynamic with large peaks and valleys. The general decrease in fluxes seen with other metals during the late November and December timeframe is also present for copper. Changes in copper fluxes at Beacon Hill and Kent stations were similar over time and less dynamic than at Duwamish and South Park stations. Copper fluxes did not show definitive seasonal changes other than the higher flux at Enumclaw in the summer months.

Ignoring temporal differences by grouping fluxes by station shows that the Duwamish had the highest median copper flux (Figure 11). The median at South Park was next highest. The median copper fluxes at Beacon Hill and Kent were similar and lower than South Park. When both Kent stations were sampled, the median copper flux was higher at Kent SC. The median copper flux was lowest at the Enumclaw station. The one-way ANOVA by ranks test showed copper fluxes were significantly lower ($p < 0.05$) at Enumclaw than all other stations. Also, copper fluxes at Duwamish were found to be significantly higher than at Kent

and Beacon Hill. No other significant differences were found. Notably, at the other station with industrial land use (South Park), copper fluxes were not found to be significantly different from Kent or Beacon Hill.

Table 9. Summary of Copper Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	5.36	13.1	7.60	5.92	8.30	0.63
Maximum	22.0	43.8	38.4	26.5	29.0	6.41
Median	11.0	23.7	18.3	11.7	14.2	1.75
Mean	11.3	23.5	18.8	13.3	15.8	2.46

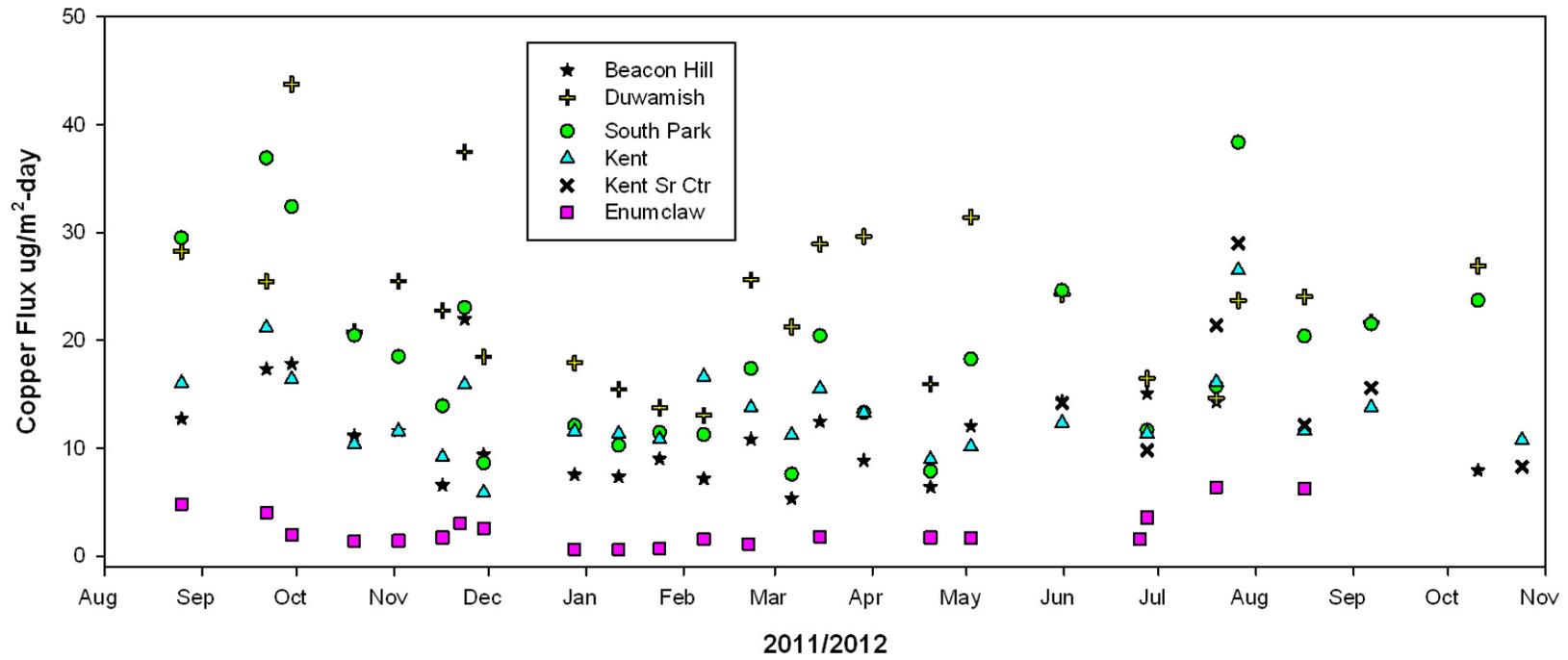


Figure 10. Copper Flux for each Collection Period by Collection Date and Station.

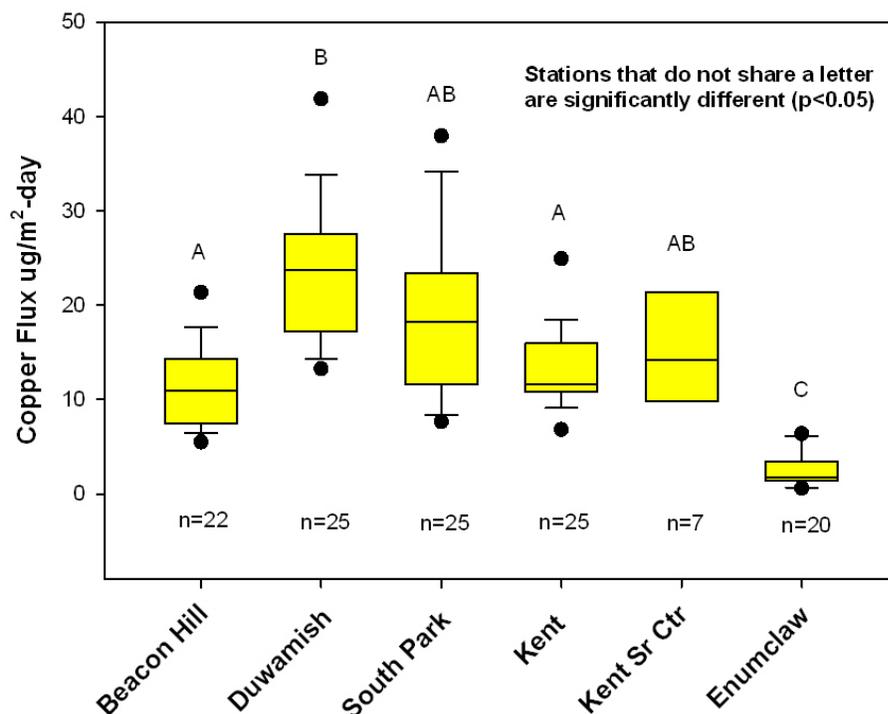


Figure 11. Boxplots of Copper Flux by Station.

5.1.5 Lead

No single station was consistently lowest for lead flux throughout the study period; lead fluxes at Beacon Hill or Enumclaw were most frequently lowest (Figure 12). The lowest flux measured was 1.51 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 10) measured at Enumclaw. The highest lead fluxes were most often at South Park station but the highest single lead flux was measured at Enumclaw (275 $\mu\text{g}/\text{m}^2\text{-day}$) and was over twice as high as the next highest lead flux. Lead fluxes measured at the two Kent stations were usually below the Duwamish and South Park stations.

In general, lead fluxes decreased to a low point in November or December then increased in subsequent months. Lead fluxes at the Enumclaw station were dynamic during the study period reaching both overall minimum and maximum fluxes. Lead fluxes measured at two different events were particularly high at Enumclaw; one event occurred in late November and the other in mid-February. Temporal changes in lead fluxes at South Park and Duwamish stations were less dynamic than at Enumclaw. When both Kent stations were sampled, lead fluxes were similar. Changes in lead fluxes at Beacon Hill and Kent stations were also similar over time.

Ignoring temporal differences by grouping fluxes by station shows that the South Park had the highest median lead flux (Figure 13). The median at Duwamish was next highest but similar to South Park. The median lead fluxes at Kent and Enumclaw were similar and

lower than South Park. Lead fluxes were highly variable at South Park and Enumclaw. The mean for Enumclaw is strongly influenced by an unusually high late November maximum flux¹¹. When both Kent stations were sampled, lead fluxes were higher at Kent SC. The median lead flux was lowest at the Beacon Hill station. The one-way ANOVA by ranks test showed lead fluxes at Duwamish and South Park were significantly higher ($p < 0.05$) than both Beacon Hill and Kent stations. No other significant differences were found.

Table 10. Summary of Lead Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	1.76	3.68	3.00	1.75	3.25	1.51
Maximum	7.93	24.1	42.3	11.0	10.1	275
Median	4.03	11.1	13.1	5.54	7.87	6.85
Mean	4.42	11.8	16.3	5.96	7.15	26.7

¹¹ The mean lead flux at Enumclaw without the single highest flux value is $13.6 \mu\text{g}/\text{m}^2\text{-day}$.

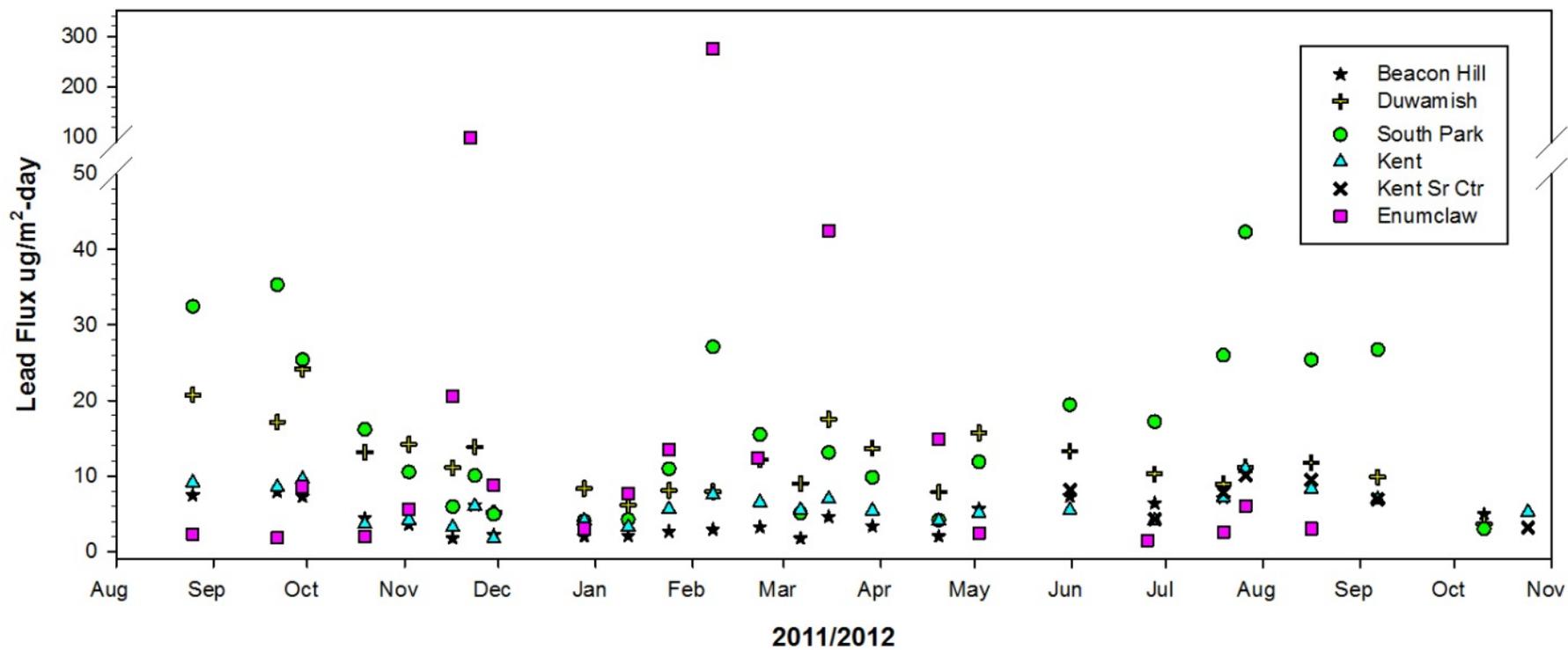


Figure 12. Lead Flux for each Collection Period by Collection Date and Station.

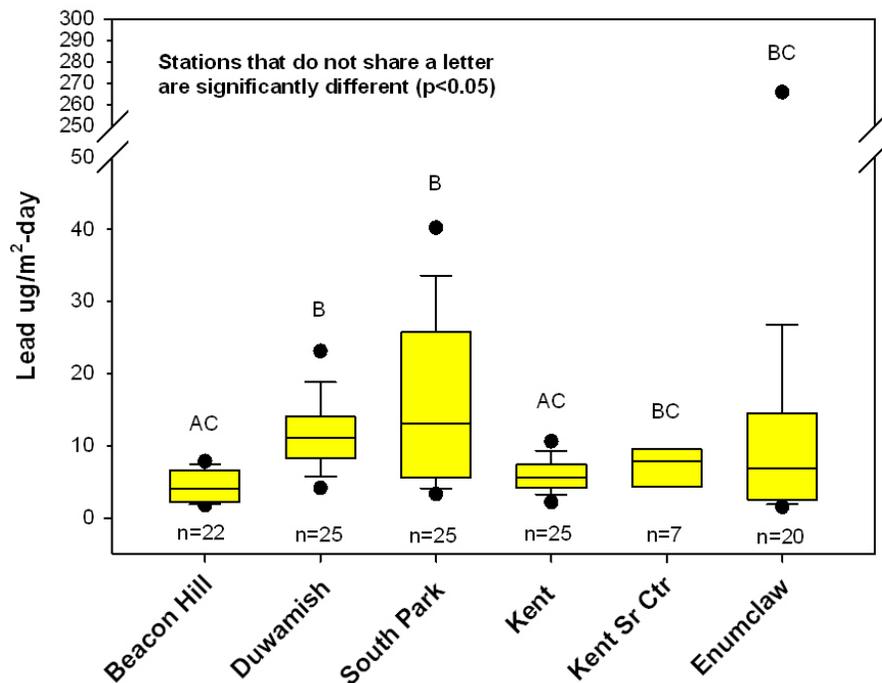


Figure 13. Boxplots of Lead Flux by Station.

5.1.6 Mercury

No single station was consistently lowest for mercury flux throughout the study period; mercury fluxes at Enumclaw were most frequently lowest (Figure 14). The lowest flux measured was 0.0035 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 11) at Enumclaw. The highest mercury fluxes were most often at either South Park or Duwamish stations. The single highest mercury flux was measured at the Duwamish station in late March reaching 0.15 $\mu\text{g}/\text{m}^2\text{-day}$ or nearly three times the next highest flux. Mercury fluxes measured at the remaining four stations were frequently similar and below fluxes at Duwamish and South Park stations.

Mercury fluxes were relatively variable at both the Duwamish and South Park stations during the study period but did not follow the same temporal pattern. In contrast, changes in mercury fluxes at Beacon Hill and Kent stations were similar over time. When both Kent stations were sampled, mercury fluxes were also similar. A decline in flux followed by an increase in subsequent months was seen in late December at all stations, similar to that observed for other metals. Overall, mercury fluxes did not show definitive seasonal changes.

Ignoring temporal differences by grouping fluxes by station shows that the South Park had the highest median mercury flux (Figure 15). However, the median mercury fluxes were similar across all stations. When both Kent stations were sampled, median mercury fluxes were similar. The median mercury flux was lowest at the Enumclaw station. The one-way ANOVA by ranks test showed mercury fluxes at Duwamish and South Park were

significantly higher ($p < 0.05$) than at the Enumclaw station and significantly higher at South Park than Kent and Beacon Hill stations. No other significant differences were found. Notably, mercury fluxes at the other station with industrial land use (Duwamish), were not significantly different from Kent or Beacon Hill stations.

Table 11. Summary of Mercury Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	19
Minimum	0.0029	0.0049	0.0055	0.0040	0.0043	0.0035
Maximum	0.022	0.149	0.063	0.041	0.043	0.025
Median	0.009	0.014	0.018	0.008	0.012	0.0061
Mean	0.011	0.023	0.022	0.010	0.015	0.0089

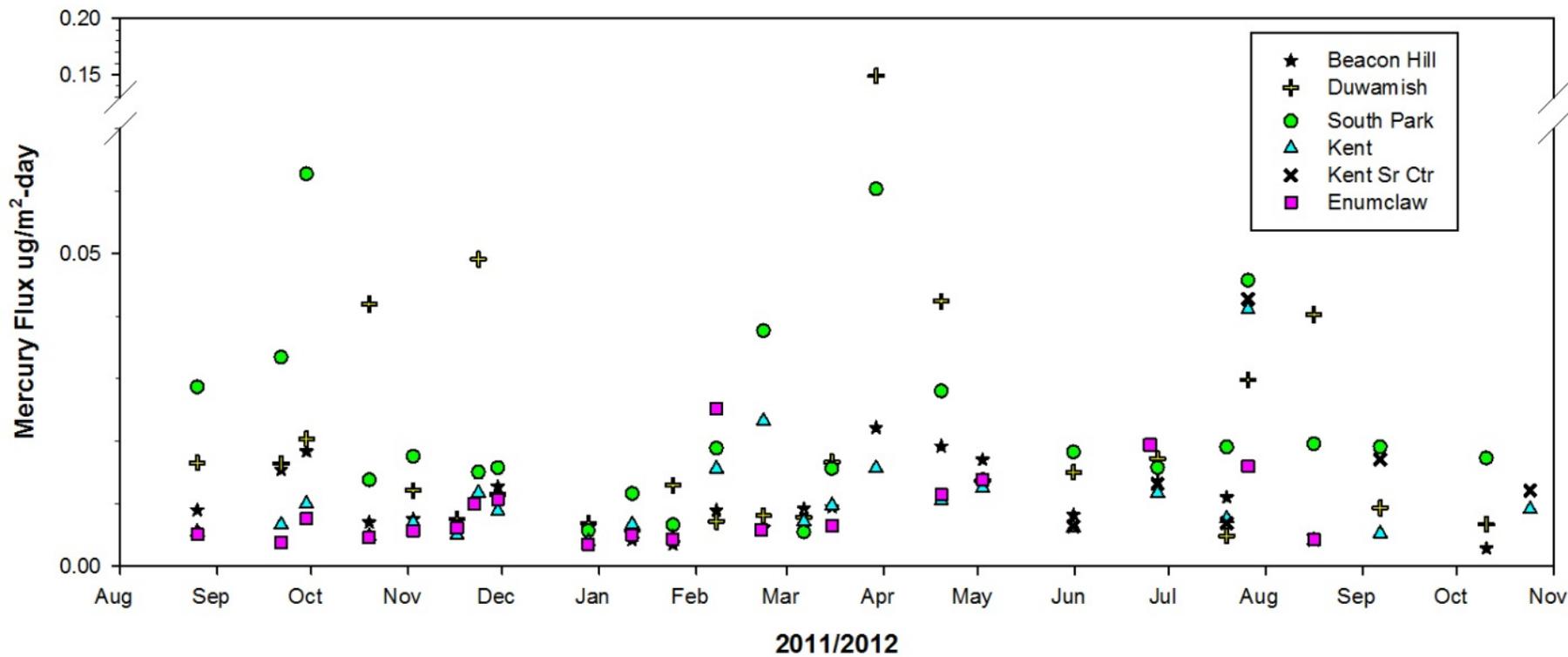


Figure 14. Mercury Flux for each Collection Period by Collection Date and Station.

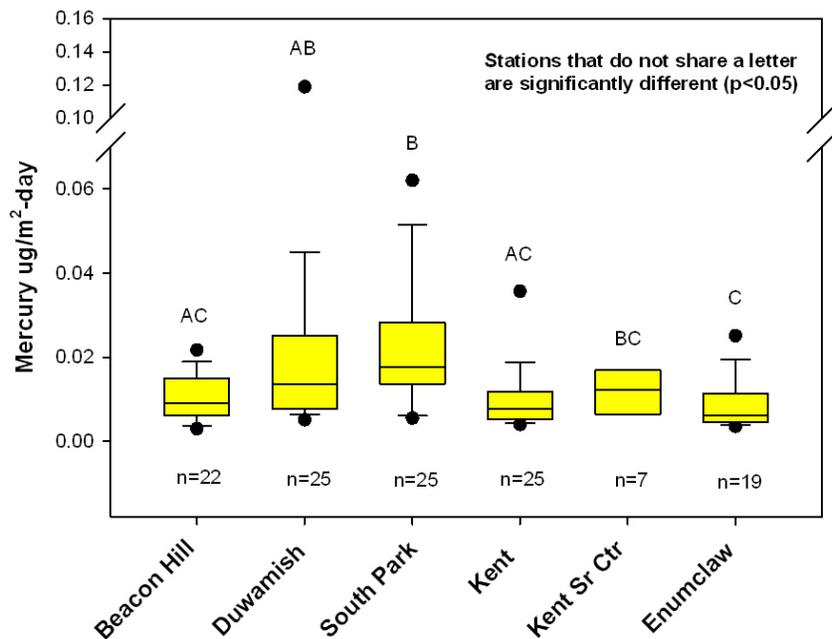


Figure 15. Boxplots of Mercury Flux by Station.

5.1.7 Nickel

Nickel fluxes at Enumclaw were consistently lowest throughout the study period (Figure 16). The lowest single flux measured was 0.22 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 12). The highest nickel fluxes were at either Duwamish or South Park stations with the single highest nickel flux measured at South Park (6.2 $\mu\text{g}/\text{m}^2\text{-day}$). Nickel fluxes measured at Beacon Hill and the two Kent stations were usually below the Duwamish and South Park stations and above Enumclaw.

Nickel fluxes were variable at all stations over the study period; however; two events are notable. The first event was a decrease from summer into late November or December and subsequent increase in nickel fluxes at all stations, particularly South Park. The second event was a rapid and brief increase in nickel flux at all stations in July. This increase reached nickel fluxes similar to summer months of 2012 but only in July. When both Kent stations were sampled, nickel fluxes were generally similar. Changes in lead fluxes at Beacon Hill and Kent stations were generally similar over time.

Ignoring temporal differences by grouping fluxes by station shows the highest median nickel flux was at Duwamish station (Figure 17). The median at South Park was next highest but similar to Duwamish. The median nickel fluxes at Beacon Hill and the two Kent stations were all similar and lower than South Park. The median nickel flux was lowest at the Enumclaw station. Nickel fluxes at Duwamish and South Park were most variable and those at Kent and Enumclaw were least variable. The one-way ANOVA by ranks test showed nickel fluxes at Duwamish and South Park were significantly higher ($p<0.05$) than the Beacon Hill, Kent, and Enumclaw stations. No other significant differences were found.

Table 12. Summary of Nickel Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	0.71	1.83	1.03	0.92	0.75	0.22
Maximum	3.37	6.05	6.16	2.69	3.68	1.81
Median	1.70	3.48	3.33	1.70	1.78	0.46
Mean	1.72	3.69	3.22	1.70	1.89	0.69

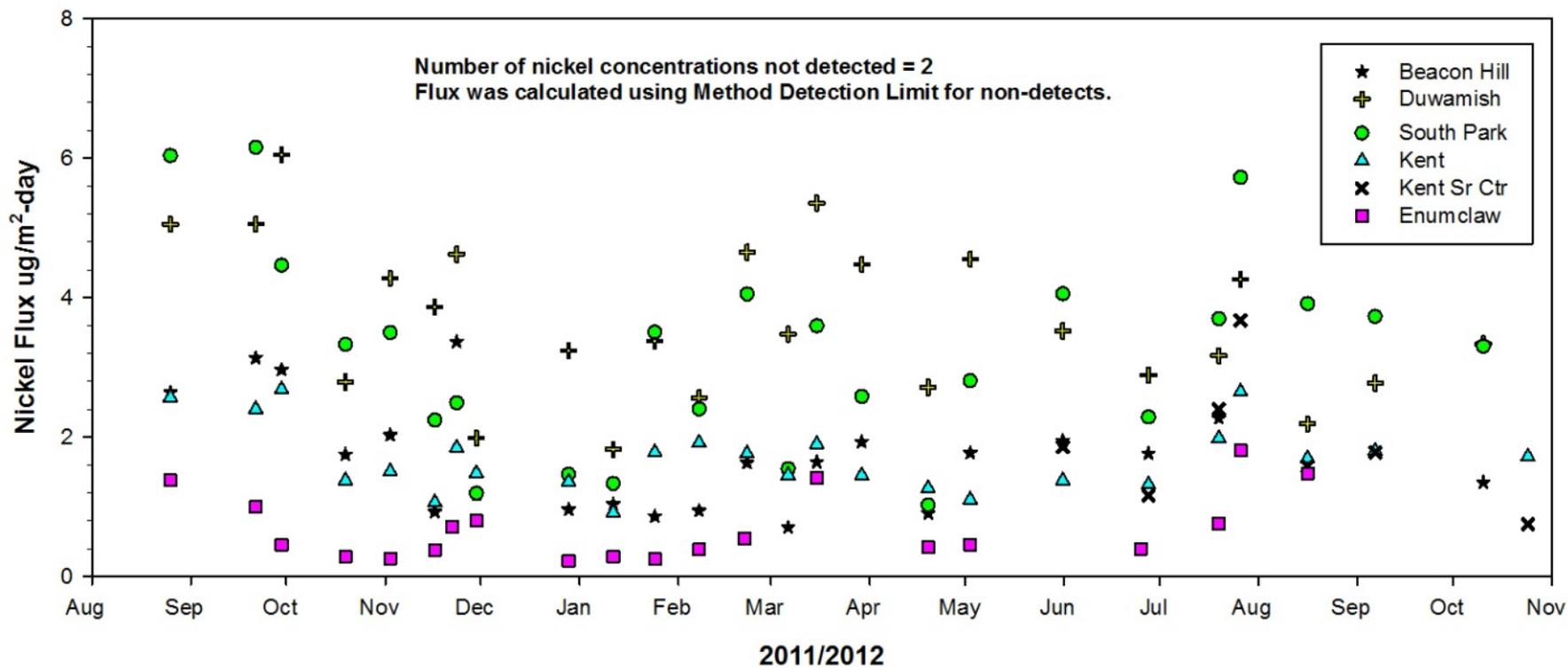


Figure 16. Nickel Flux for each Collection Period by Collection Date and Station.

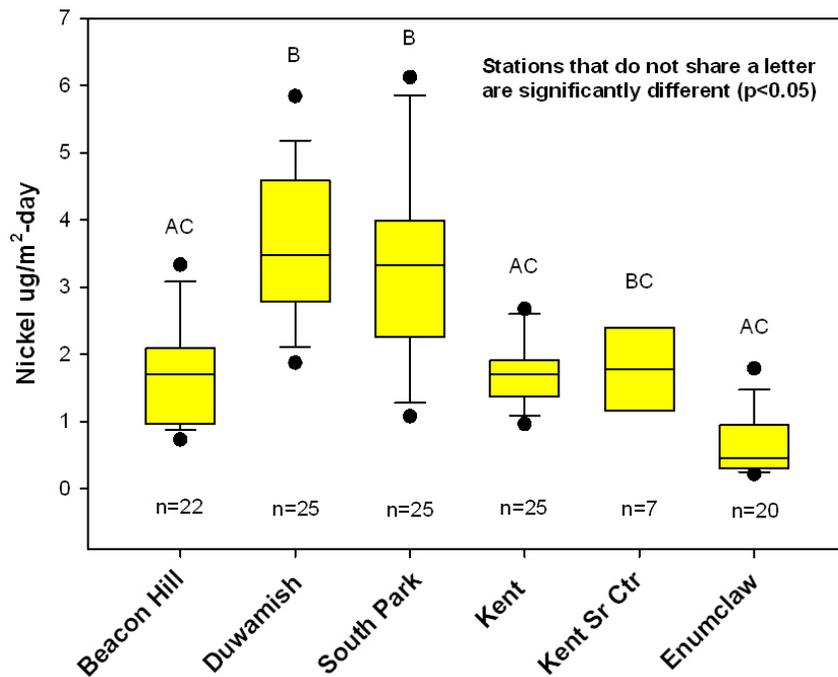


Figure 17. Boxplots of Nickel Flux by Station.

5.1.8 Silver

Sixty percent of the sample results for silver were not detected (75 out of 124 samples). This heavily impacted Enumclaw fluxes where silver was detected in only 2 of 20 samples. For samples with nondetects, the MDL value was used in calculations of flux. The minimum and maximum MDLs for nondetect results were 0.0070 and 0.20 $\mu\text{g}/\text{m}^2\text{-day}$, respectively. The minimum and maximum MDLs for detected results were 0.0077 and 0.51 $\mu\text{g}/\text{m}^2\text{-day}$, respectively. Combining detect and nondetect results, silver fluxes were variable among all stations throughout the study period (Figure 18). Silver fluxes ranged from 0.0077 to 1.48 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 13), with the minimum from Enumclaw station and the maximum from Duwamish station. There was no consistency in the location of the highest or lowest silver flux.

Silver fluxes varied inconsistently with time at all stations; however, silver fluxes converged during several sampling events, particularly in months other than August and September. When both Kent stations were sampled, silver fluxes were sometimes similar and sometimes divergent with Kent being higher than Kent SC.

Ignoring temporal differences by grouping fluxes by station shows the highest median silver flux was at Duwamish station (Figure 19). However, the median silver fluxes were similar among all stations with the most variability at the Duwamish station. The one-way ANOVA test showed silver fluxes at Duwamish station were significantly higher ($p < 0.05$) than at Beacon Hill. No other significant differences were found. The high number of non-

detect results for silver artificially raises the lower end of the sample distribution, thereby limiting the ability to detect differences between stations.

Table 13. Summary of Silver Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
# Detects/Total Samples	7/22	17/25	12/25	7/25	4/7	2/20
Minimum	0.012	0.029	0.015	0.014	0.019	0.0077
Maximum	0.11	0.24	0.15	0.18	0.054	0.11
Median	0.035	0.049	0.042	0.040	0.031	0.043
Mean	0.038	0.066	0.052	0.050	0.033	0.047

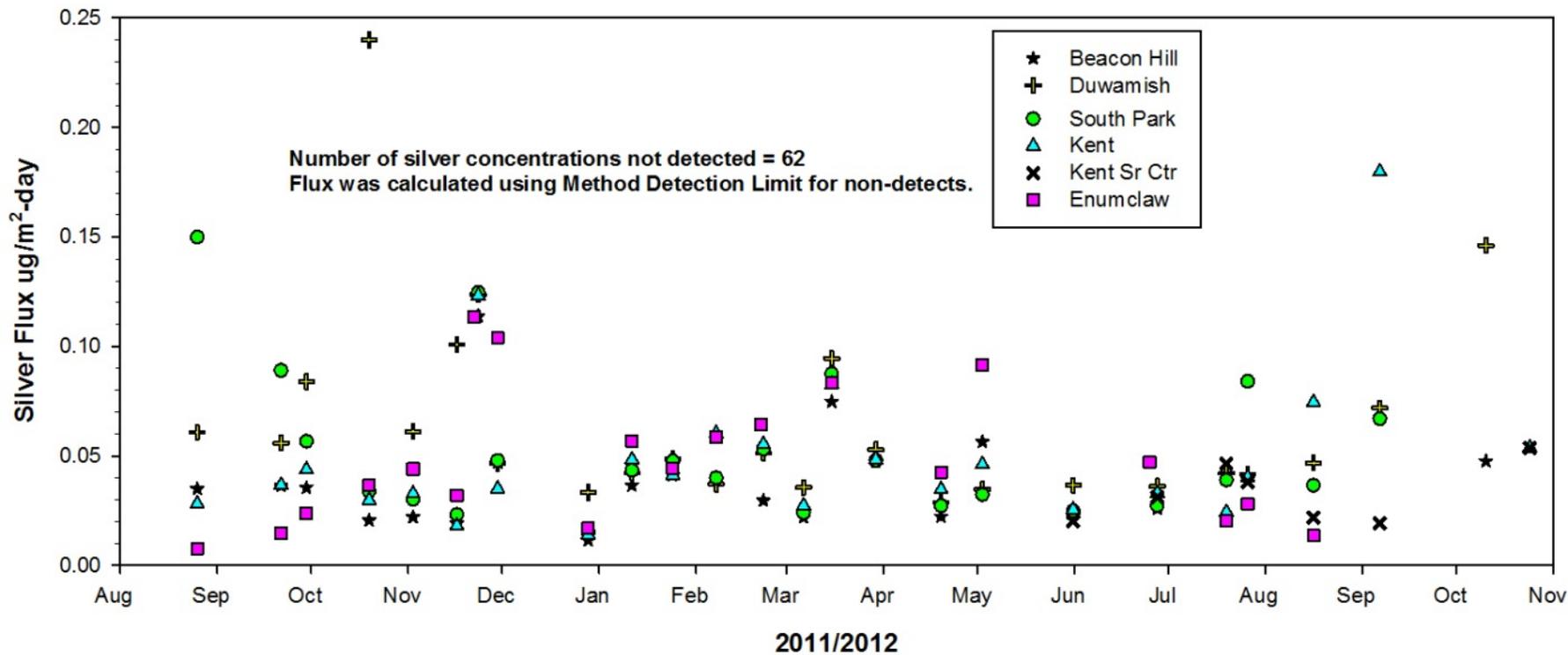


Figure 18. Silver Flux for each Collection Period by Collection Date and Station.

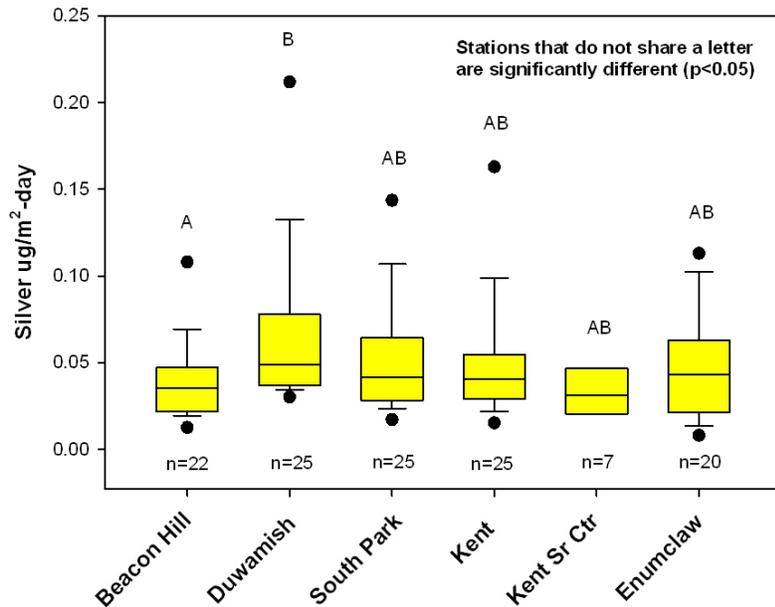


Figure 19. Boxplots of Silver Flux by Station.

5.1.9 Vanadium

Vanadium fluxes were lowest at Enumclaw throughout the study period with exceptions in two sampling events in July and August 2012 (Figure 20). The single lowest flux measured was 0.23 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 14) at Enumclaw. Vanadium fluxes were consistently highest at the Duwamish station and the single highest vanadium flux was 9.14 $\mu\text{g}/\text{m}^2\text{-day}$. Vanadium fluxes measured at Beacon Hill, South Park and the two Kent stations were usually between the Duwamish and Enumclaw stations.

Vanadium fluxes at the Enumclaw station were lowest in the winter and increased during summer months. At other stations, the same general trend was present, although an additional peak in vanadium flux was seen in the late winter/early spring months (February-April). Peaks were substantially larger at the Duwamish station reaching twice the maxima at South Park, the station with the next highest fluxes. When both Kent stations were sampled, vanadium fluxes were similar. Vanadium fluxes at Beacon Hill, South Park and Kent generally followed similar temporal patterns of change.

Ignoring temporal differences by grouping fluxes by station shows that the median vanadium flux at Duwamish was highest (Figure 21). The median vanadium flux at Enumclaw was lowest. Median vanadium fluxes at Beacon Hill, South Park and the two Kent stations were similar. The Duwamish station had the highest variability in vanadium fluxes. The one-way ANOVA test showed vanadium fluxes at Duwamish were significantly higher ($p < 0.05$) than all other stations. Also, vanadium fluxes were significantly lower at Enumclaw than all other stations. No other significant differences were found. Notably, no

significant differences were found between fluxes at Beacon Hill, South Park, Kent, or Kent SC.

Table 14. Summary of Vanadium Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	0.73	1.84	0.81	0.67	0.85	0.23
Maximum	3.92	9.14	5.06	3.35	3.20	3.30
Median	2.02	4.48	2.26	1.83	2.10	0.58
Mean	2.10	5.13	2.38	2.01	2.14	0.91

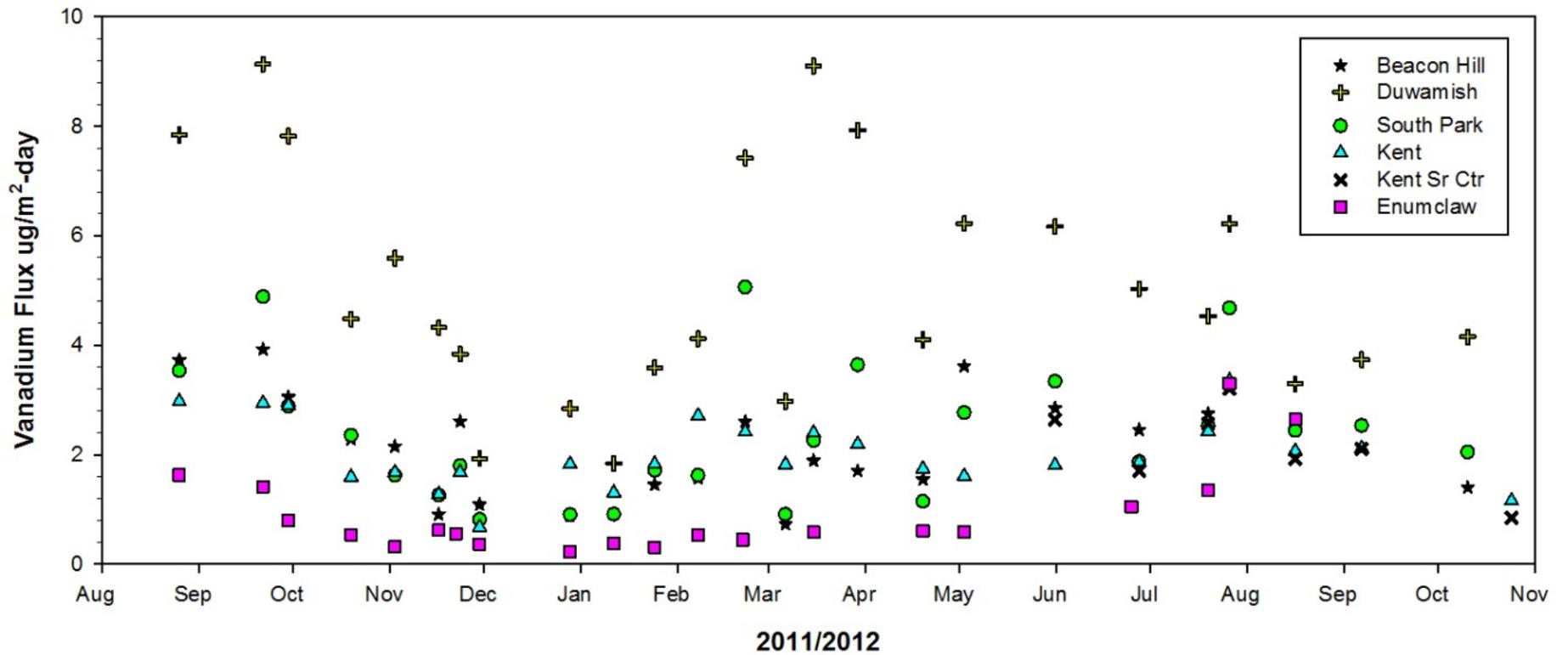


Figure 20. Vanadium Flux for each Collection Period by Collection Date and Station.

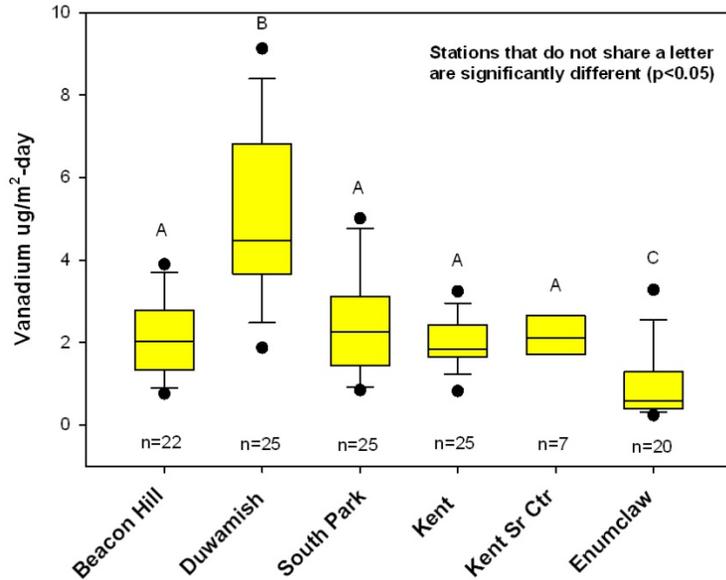


Figure 21. Boxplots of Vanadium Flux by Station.

5.1.10 Zinc

Zinc fluxes were lowest at Enumclaw throughout the study period with one exception in February 2012 (Figure 22) when Enumclaw fluxes were highest. The single lowest flux was measured at Enumclaw ($5.5 \mu\text{g}/\text{m}^2\text{-day}$) (Table 15). Zinc fluxes were most frequently highest at either the Duwamish or South Park stations and the single highest zinc flux was at South Park ($274 \mu\text{g}/\text{m}^2\text{-day}$). Zinc fluxes measured at Beacon Hill and the two Kent stations were usually between the other three stations.

Zinc fluxes at Beacon Hill, South Park and Kent stations declined in the winter and increased during August through October months. No other seasonal patterns were evident at other stations. When both Kent stations were sampled, zinc fluxes were similar.

Ignoring temporal differences by grouping fluxes by station shows that the median zinc flux at South Park was highest (Figure 23) with the Duwamish median flux just below.

Variability in zinc fluxes was also greatest at South Park. Variability and the median zinc flux were lowest at Enumclaw. The Beacon Hill median zinc flux was lower than all other stations except Enumclaw. When both Kent stations were sampled, the median zinc fluxes were higher at Kent SC and both were above Beacon Hill and below Duwamish and South Park median fluxes. The one-way ANOVA by ranks test showed zinc fluxes at Enumclaw were significantly lower ($p < 0.05$) than all other stations except Beacon Hill. In addition, zinc fluxes at Beacon Hill were significantly lower than at South Park or Duwamish stations. No other significant differences were found.

Table 15. Summary of Zinc Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	25	25	7	20
Minimum	24.1	56.5	34.8	31.3	32.4	5.47
Maximum	107	171	274	153	115	99.2
Median	45.7	112	122	68.8	87.5	14.7
Mean	51.6	108	126	77.1	81.2	21.8

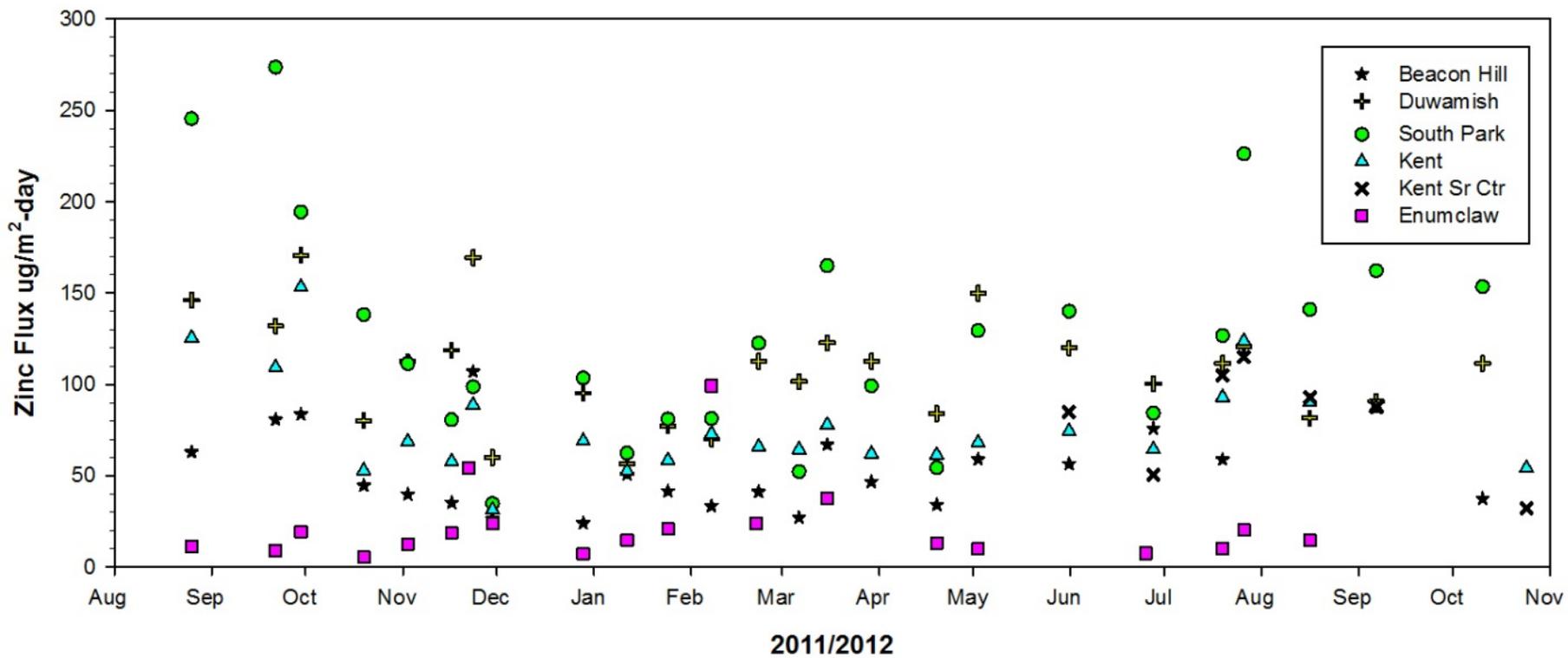


Figure 22. Zinc Flux for each Collection Period by Collection Date and Station.

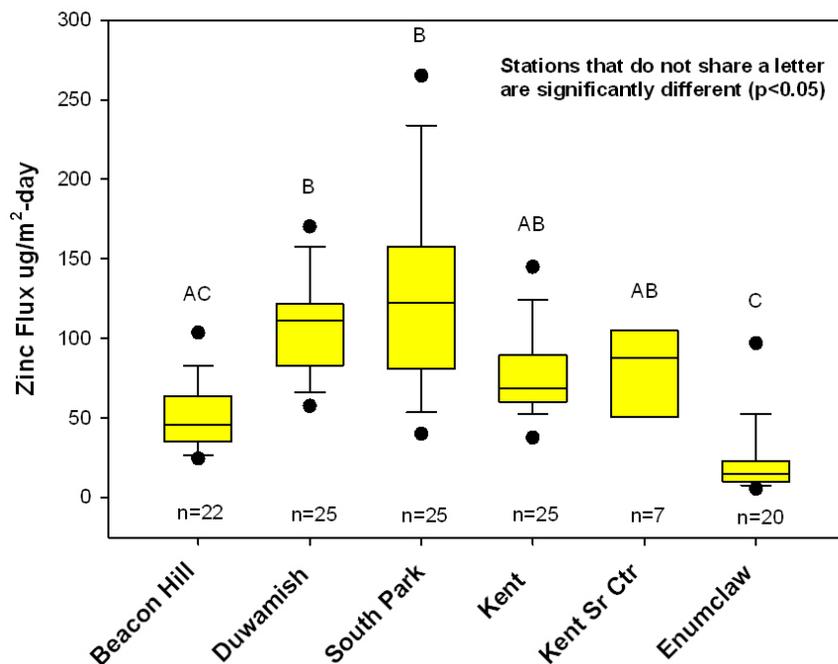


Figure 23. Boxplots of Zinc Flux by Station.

5.2 PAHs

The number of PAH results varied by station ranging from 21 at the Enumclaw station to 25 at the Kent station with the exception of Kent SC station where only seven PAH samples were collected. PAH flux results are discussed as HPAHs in this section. The results for LPAHs are presented and discussed in Appendix F, although these data are of limited usability and are provided for informational use only.

It is acknowledged that LPAH sampling with the bulk deposition methods used in this study does 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. The low bias from volatilization is indicated by the results of the PAH field spike blank samples (see Section 5.8.2 for details) where recovery of particular LPAHs was less than 20% (acenaphthalene, anthracene) and other common LPAHs, such as naphthalene, experienced modest recovery of less than 65%. Poor recovery of LPAHs using bulk atmospheric deposition sampling techniques has also been observed by other researchers (King County 2008, King County/Seattle 2005, Brandenberger et al. 2010). Because of this low bias, the bulk atmospheric deposition data collected in 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.

The HPAH fluxes were consistently lowest at Enumclaw (Figure 24). The minimum HPAH flux at Enumclaw was 0.01 $\mu\text{g}/\text{m}^2\text{-day}$ (Table 16). HPAH fluxes were highest at either Kent or Duwamish stations throughout the sampling period reaching maxima of 1.7 and 2.2 $\mu\text{g}/\text{m}^2\text{-day}$, respectively. HPAH fluxes at Beacon Hill, South Park and Kent SC stations generally fell in the middle, between the fluxes at the other three stations.

Variability in HPAH flux generally increased from January through March at the Kent and Duwamish stations. This pattern of increases in HPAH fluxes was also observed at South Park and Beacon Hill at a smaller scale during this time period. HPAH fluxes at Enumclaw did not follow this pattern and remained relatively similar throughout the year. When HPAH fluxes were measured at Kent SC, they were consistently lower than at the Kent station indicating microscale effects of location on HPAH flux.

Ignoring temporal differences by grouping fluxes by station reveals that the median HPAH flux at Enumclaw was lower than any other station (Figure 25). Variability in HPAH flux was also lowest at Enumclaw. The widest variation in HPAH fluxes occurred at the Duwamish station and the highest median of 0.89 $\mu\text{g}/\text{m}^2\text{-day}$ was at the Kent station (Table 17). Similar to LPAHs, the median HPAH flux at Kent was higher than Kent SC which may reflect the influence of the adjacent rail line. Beacon Hill, South Park, and Kent SC median HPAH fluxes were between Duwamish and Enumclaw fluxes. The one-way ANOVA by ranks test showed HPAH fluxes at Kent and Duwamish were significantly higher ($p < 0.05$) than at Beacon Hill, South Park, or Enumclaw stations. Also, HPAH fluxes at Enumclaw station were significantly lower than all other stations except Beacon Hill. No other significant differences were found. Notably, HPAH fluxes at South Park were not significantly different from Beacon Hill or Kent SC.

Table 16. Summary of HPAH Flux Data by Station ($\mu\text{g}/\text{m}^2\text{-day}$)

Station	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	22	25	24	25	7	21
Minimum	0.17	0.25	0.18	0.18	0.33	0.01
Maximum	0.59	2.21	0.93	1.68	0.56	0.21
Median	0.25	0.60	0.36	0.89	0.44	0.04
Mean	0.28	0.73	0.39	0.91	0.45	0.05

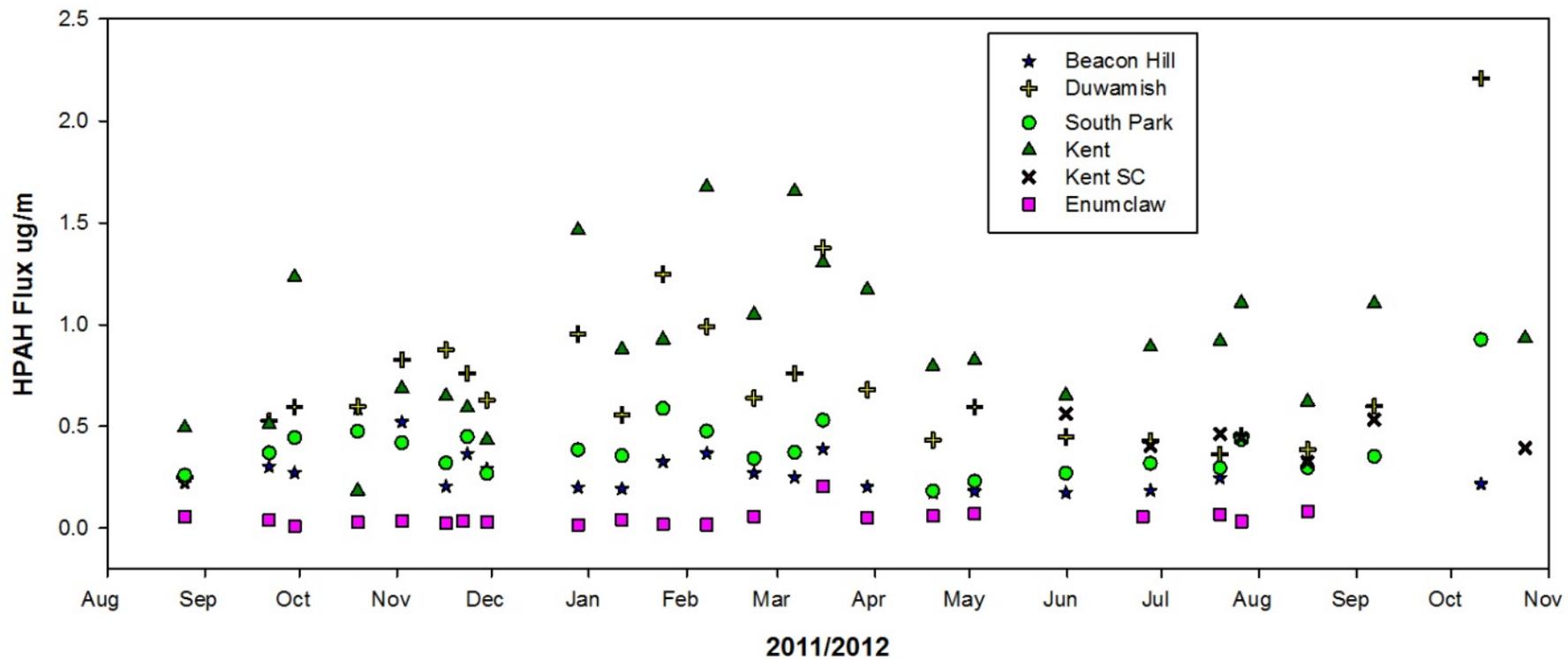


Figure 24. HPAH Flux for Each Collection Period by Collection Date and Station.

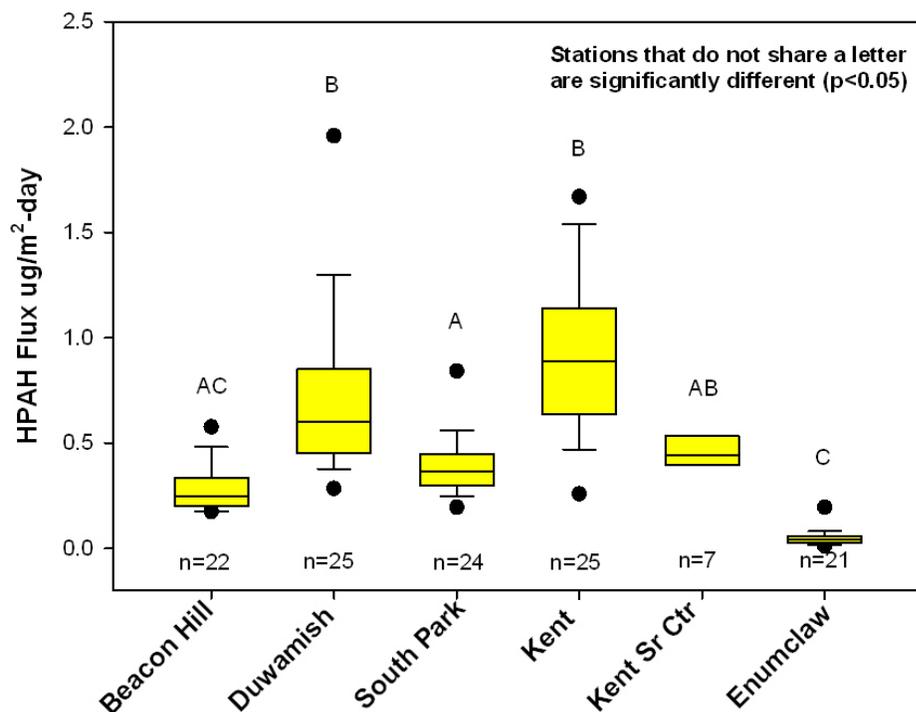


Figure 25. Boxplots of HPAH Flux by Station.

5.3 PCBs

The number of PCB samples varied by station ranging from 5 at Kent SC station to 12 at Kent station. PCB fluxes varied by location during almost all sampling periods (Figure 26). Temporal differences can't be determined from the low number of samples collected and the variation in number of stations sampled. When PCB flux was measured at the Enumclaw station, it was always the lowest of any station. The highest PCB fluxes were observed at the Duwamish and South Park stations and were usually 2-3 times higher than fluxes at other stations sampled during the same time period. PCB fluxes at Beacon Hill, Kent and Kent SC stations were more consistent than at Duwamish and South Park stations and were slightly greater than fluxes measured at the Enumclaw station.

Grouping fluxes by station shows the median PCB flux at the Enumclaw station ($0.75 \mu\text{g}/\text{m}^2\text{-day}$) was just below Kent SC station (Figure 27). Variability in measurements was also lowest at the Enumclaw station. Median PCB fluxes at Kent and Beacon Hill stations were similar and above Kent SC station (Table 17). Variability in measurements was greatest at the Duwamish station but the median PCB flux was highest for the South Park station, reaching over twice the median at the Duwamish station. The one-way ANOVA test showed PCB fluxes at Duwamish and South Park were significantly higher ($p < 0.05$) than at Kent, Kent SC or Enumclaw stations. Also, PCB fluxes at Enumclaw station were significantly lower than any other station. No other significant differences were found.

Notably, PCB fluxes at the Duwamish station were not significantly different than Beacon Hill. The sample sizes for PCB flux data are small which may limit the ability to detect differences between stations in statistical tests.

Table 17. Summary of Total PCB Flux Data by Station (ng/m²-day)

	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	7	8	10	10	5	7
Minimum	2.25	4.06	4.61	0.91	1.40	0.18
Maximum	7.68	31.0	32.8	7.00	3.97	3.02
Median	4.26	7.51	18.1	4.35	1.99	0.75
Mean	4.38	12.1	16.9	3.87	2.48	1.10

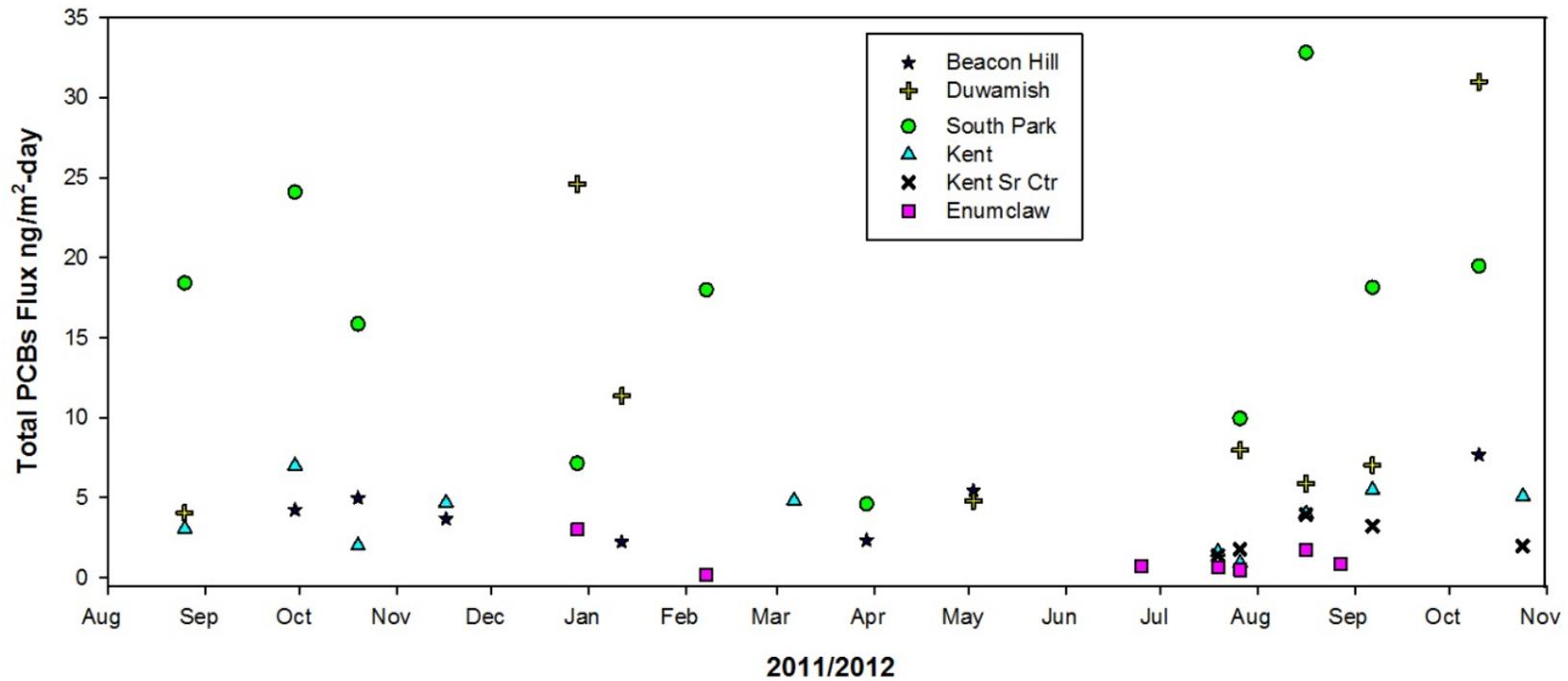


Figure 26. Total PCB Flux for each Collection Period by Collection Date and Station.

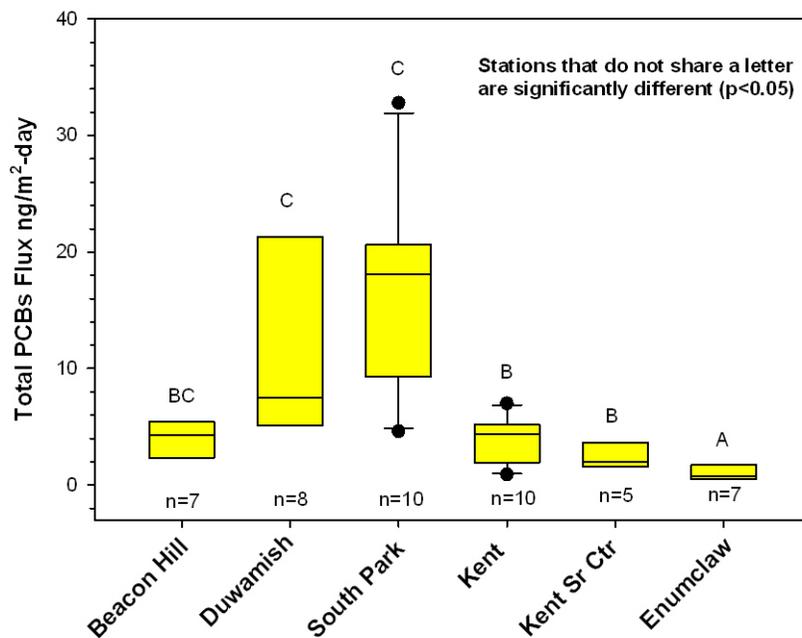


Figure 27. Boxplots of Total PCB Flux by Station.

5.4 PCB Congener Patterns

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 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, the percent contributions of each congener were summed by homologue group for each sample. The resulting percent contributions from each homologue group were plotted for each sample by station (Figures 28-33). 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 34-39). 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 28) station shows that the pentachlorobiphenyl (Penta-CBs) and hexachlorobiphenyl (Hexa-CBs) congeners make up the largest fractions of samples collected from this location. Monochlorobiphenyls (Mono-CBs) were only seen in two of seven samples and nonachlorobiphenyls (Nona-CBs) were seen more frequently but not in all samples. The other seven homologue groups were present in all samples. The contributions of homologues vary with time. However, with the

limited number of samples, any temporal patterns can't be detected. 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 to the 5/2/2012 sample.

The homologue profile for Duwamish (Figure 29) is similar to Beacon Hill in the dominance of Penta-CBs and Hexa-CBs and very low to no contributions from Mono-CBs and Nona-CBs. One exception is the uniquely high contribution of Nona-CBs to the 7/19/2012 sample. Percent contributions of different homologues appear to vary to a similar degree between samples.

Although more samples were collected at South Park (Figure 30), the homologue profile for these samples is generally similar to the Duwamish but some subtle differences can be observed in the relative contributions of certain homologues. There are smaller contributions of Heptachlorobiphenyls (Hepta-CBs) but larger contributions from the Tri-CBs and Tetra-CBs in samples from South Park.

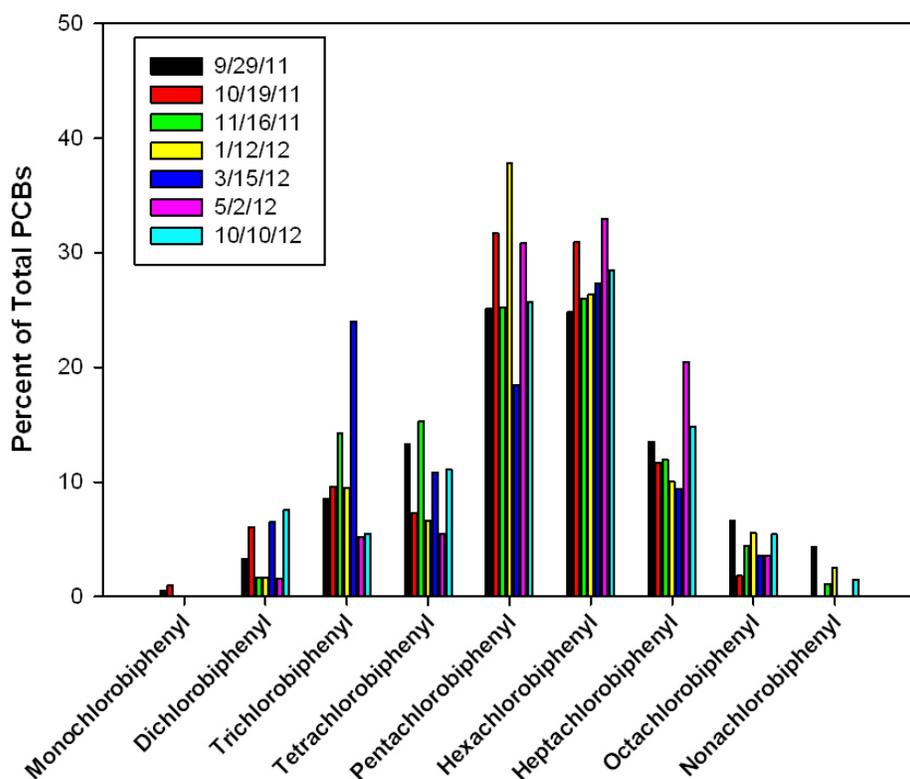


Figure 28. PCB Homologues Profile at Beacon Hill

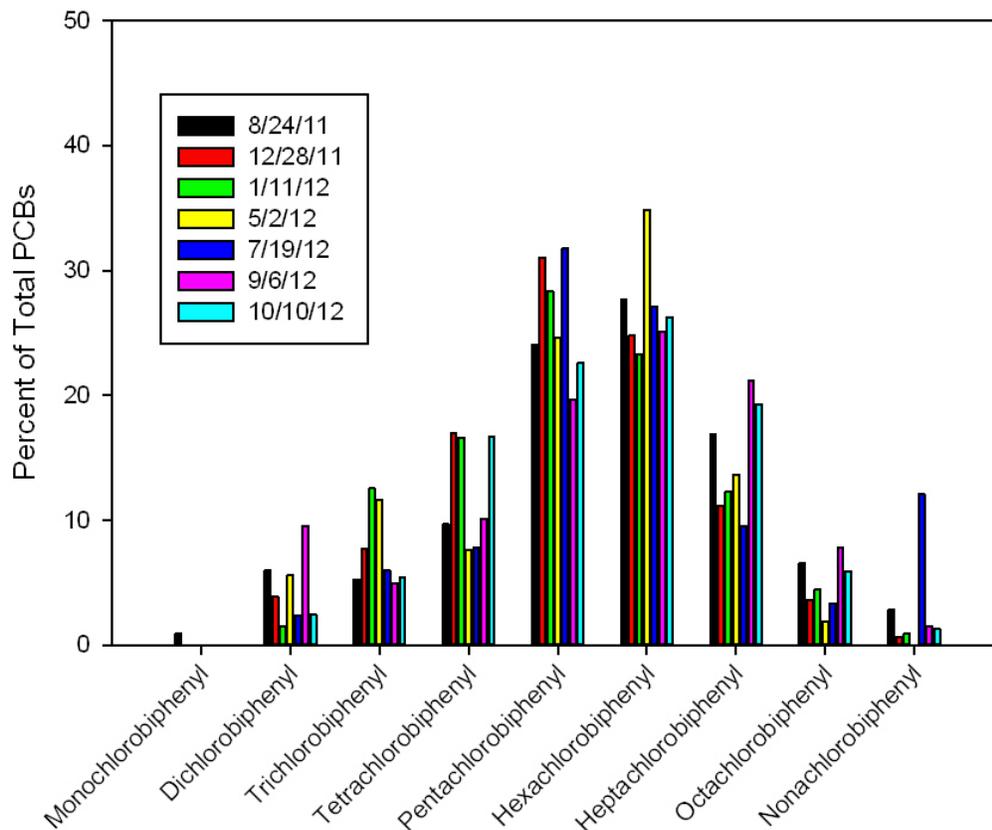


Figure 29. PCB Homologues Profile at Duwamish

The homologue profile at Kent (Figure 31) is similar to 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 32) is limited due to the small number of samples collected. Samples at this location appear to have a more even distribution of Tri-, Tetra-, Penta-, and Hexa-CBs than other stations although Penta- and Hexa-CBs in most cases still dominate.

The PCB homologue profile for Enumclaw is the most unique of all stations (Figure 33). Mono-CBs weren't in any samples and Nona-CBs were present in only one sample. Only two samples had any Octa-CBs typically present at other stations. Penta- and Tri-CBs were most often dominant in samples and not the Tetra-CBs. Penta-CBs contributed up to 40% of some samples which is the largest contribution of any single homologue in a sample at any station.

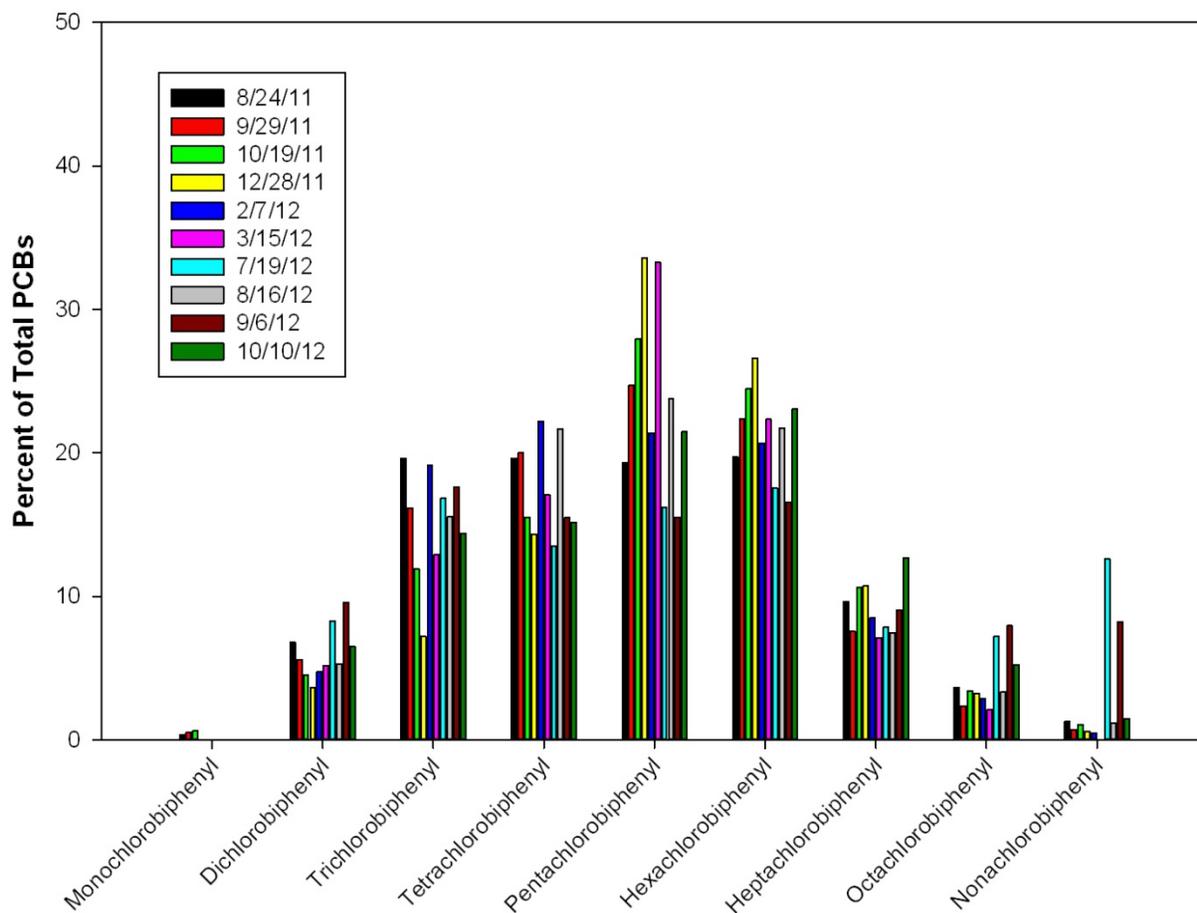


Figure 30. PCB Homologues Profile at South Park

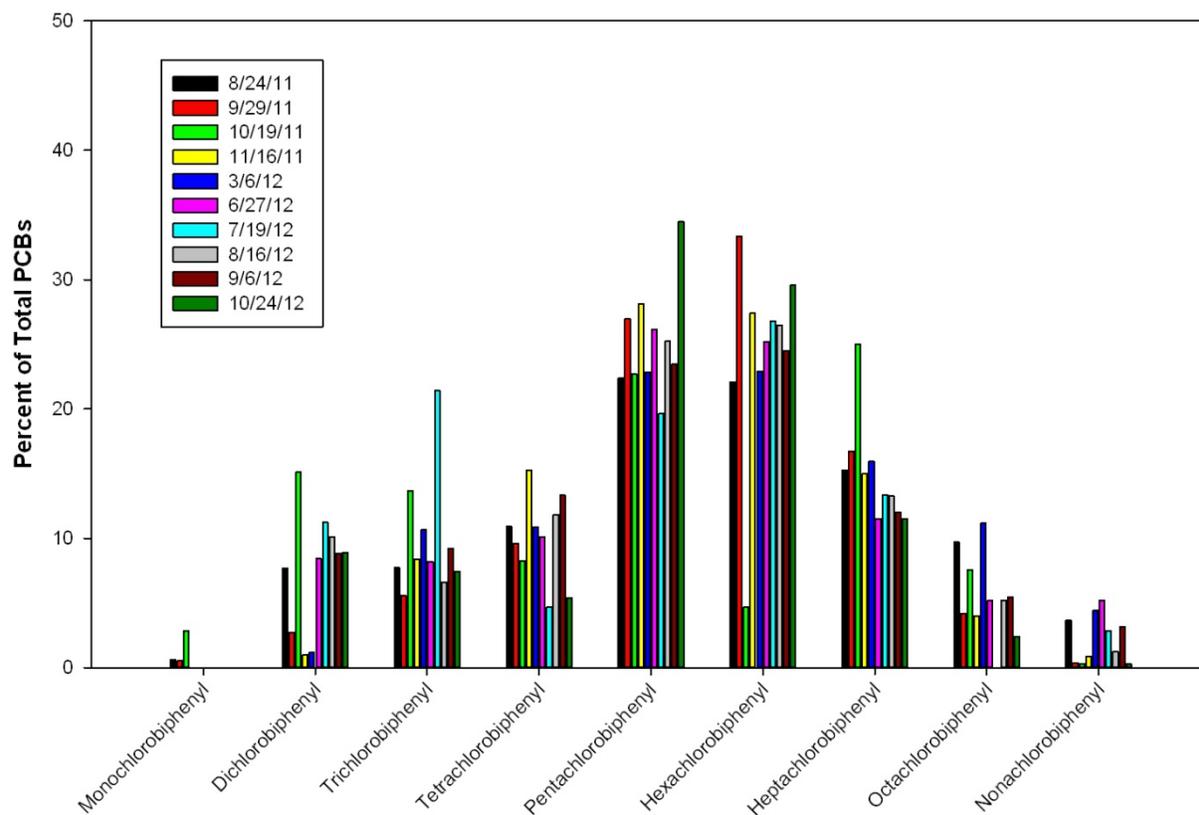


Figure 31. PCB Homologues Profile at Kent

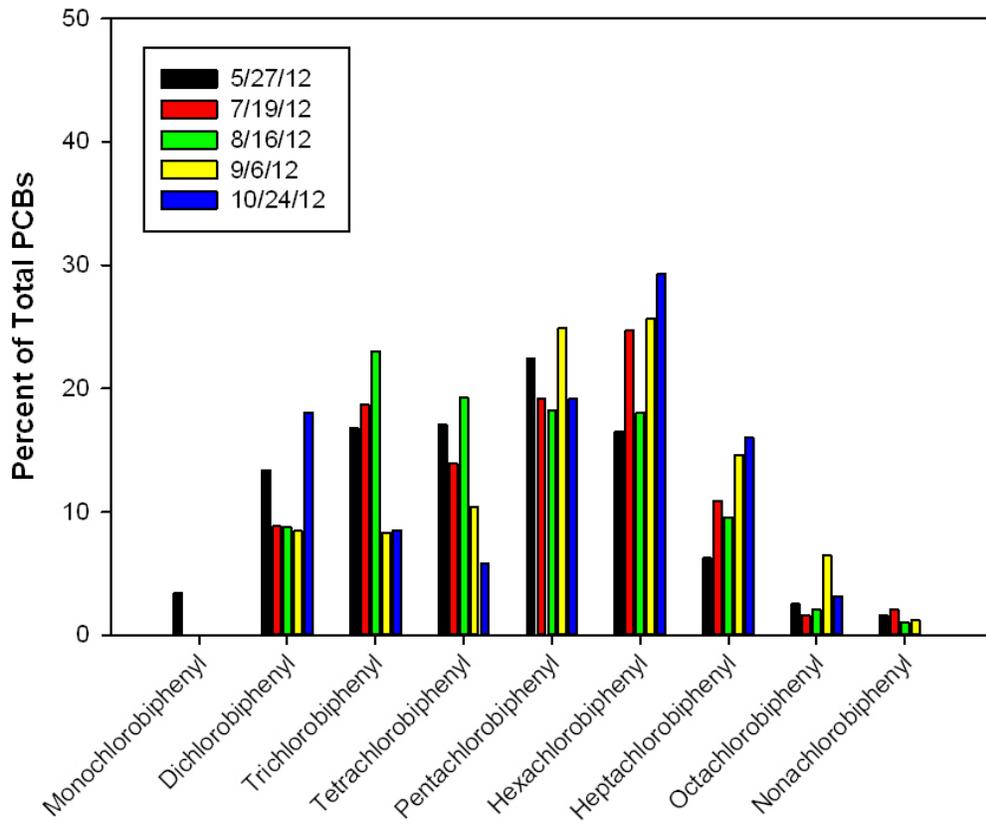


Figure 32. PCB Homologues Profile at Kent SC

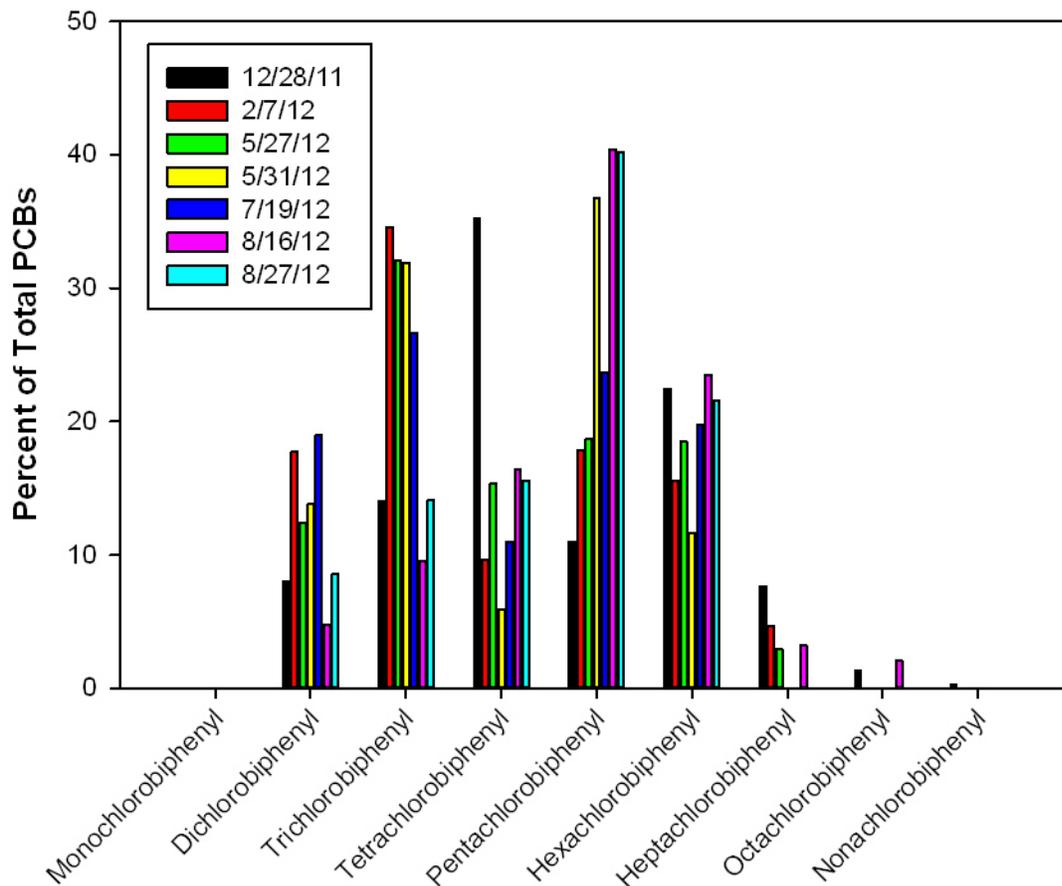


Figure 33. PCB Homologues Profile at Enumclaw

The congener profile for Beacon Hill (Figure 34) shows that many congeners are present but few contribute more than four percent to the total PCB flux on average. 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 35) is similar to that of 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 low-chlorinated congeners like PCB-11 and PCB-61.

In samples from the South Park station (Figure 36), low-chlorinated congeners (e.g., PCB-20 and PCB-61) contribute even more to the total PCB flux than at the Duwamish station. The mid- and high-chlorinated congeners contribute less to the total PCB flux. Key congeners in Beacon Hill and Duwamish samples, such as PCB-110, PCB-147, and PCB-153,

are less important in samples at South Park. Compared to Beacon Hill, PCB-129 at South Park contributes approximately two percent. PCB-20 and PCB-61 and several low-chlorinated congeners are more prominent in South Park samples than Beacon Hill or Duwamish samples.

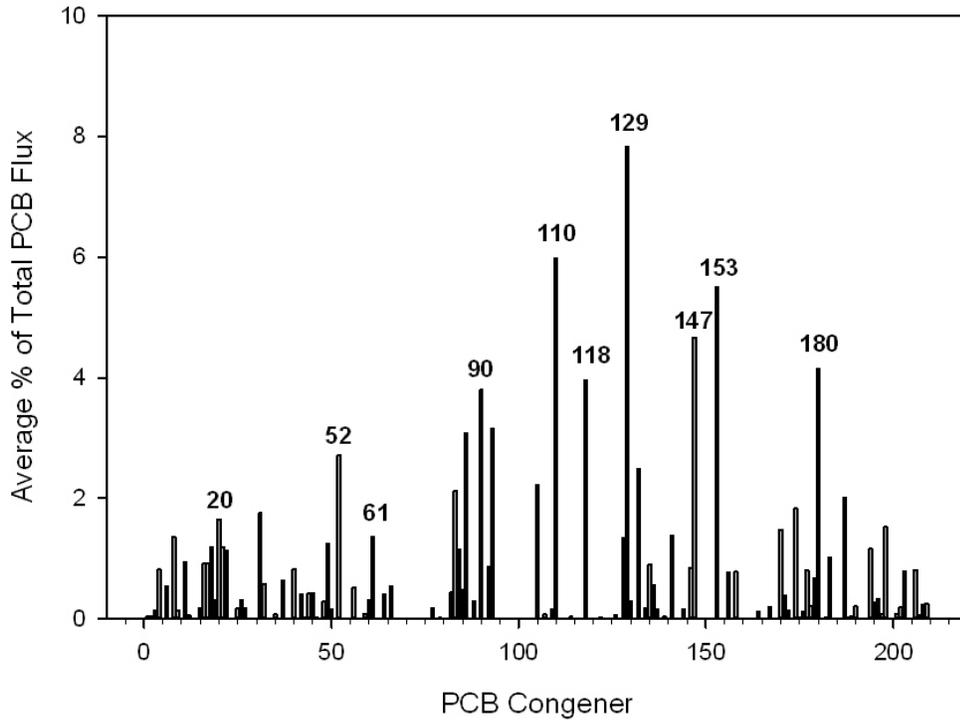


Figure 34. Average Congener Contribution to Total PCB Flux at Beacon Hill

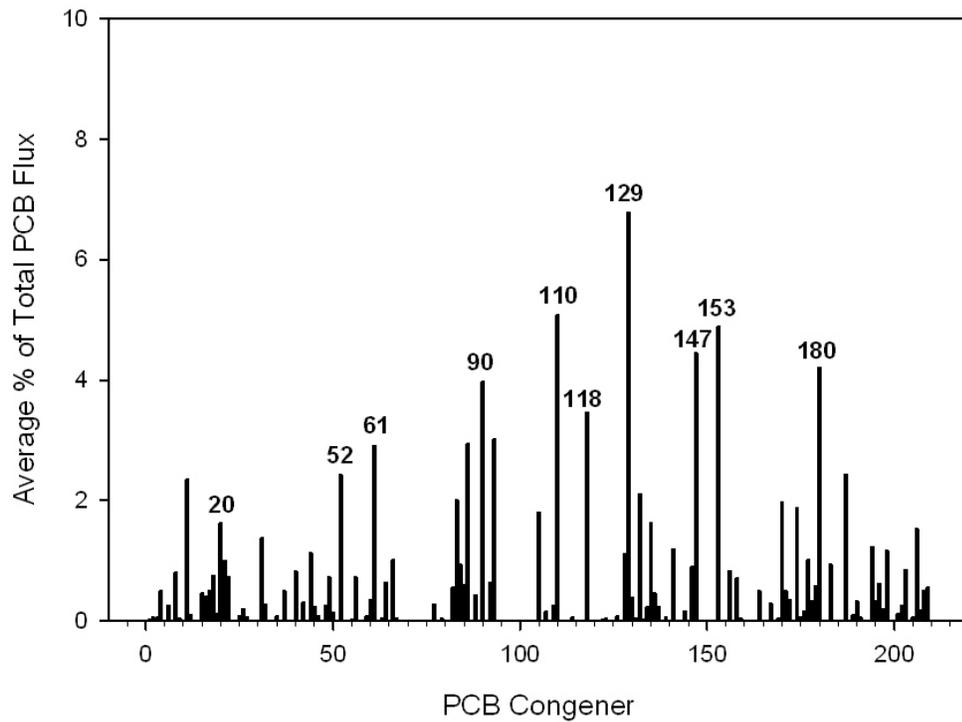


Figure 35. Average Congener Contribution to Total PCB Flux at Duwamish

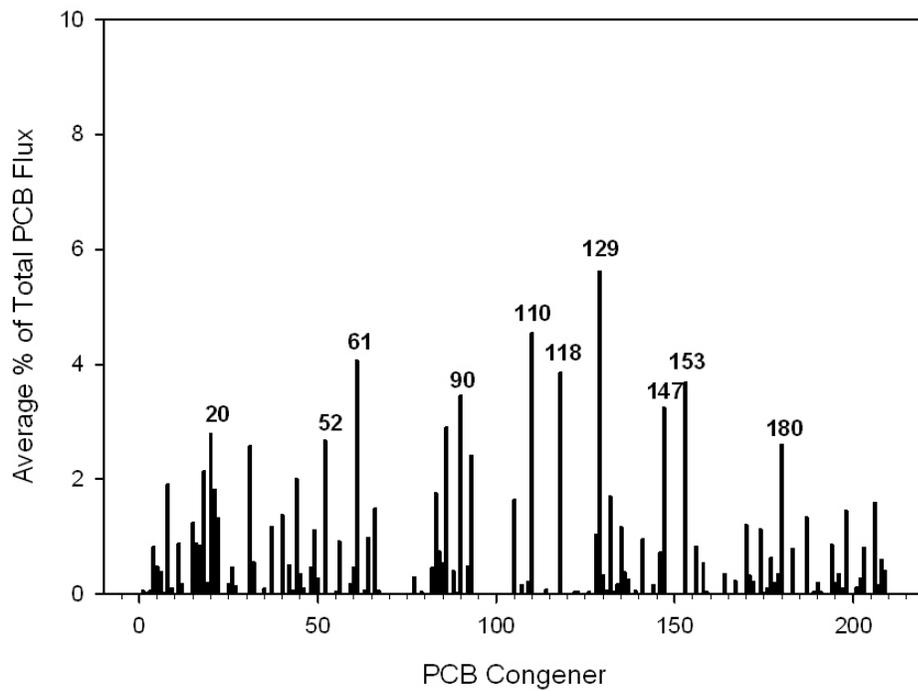


Figure 36. Average Congener Contribution to Total PCB Flux at South Park

Although the dominant congeners in samples from Kent (Figure 37) appear similar to samples at Beacon Hill, Duwamish and South Park stations, there are some substantial differences in the congener patterns. Contributions from low-chlorinated congeners, such as PCB-20, to the total PCB flux are less at Kent station with the exception of PCB-8 and PCB-11, which collectively contribute a greater percentage to total PCB flux than at any of the three Lower Duwamish area stations. Also, the contribution of PCB-129 is substantially lower than in samples from Beacon Hill or Duwamish stations. The dominant congener at Kent station is PCB-110 instead of PCB-129 which dominates at each of the three Lower Duwamish area stations.

The PCB congener profile at Kent SC station (Figure 38) differs from that at Kent station in multiple ways. First, the proportions of PCB-110 and PCB-129 at Kent SC station are different than Kent with PCB-129 being the dominant congener instead of PCB-110. Also, the low-chlorinated congeners such as PCB-20 and PCB-52 contribute more to total PCB flux at Kent SC. Lastly, several high-chlorinated congeners contribute less to the total PCB flux such as PCB-147 and PCB-187.

The congener profile at Enumclaw (Figure 39) has some similarities to most other 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 contribute little to nothing to total PCB flux. PCB-20 and PCB-52 contribute greater than four percent to the total PCB flux – this occurs at no other station. Also, many of the low-chlorinated congeners contribute more to total PCB flux than at any other station.

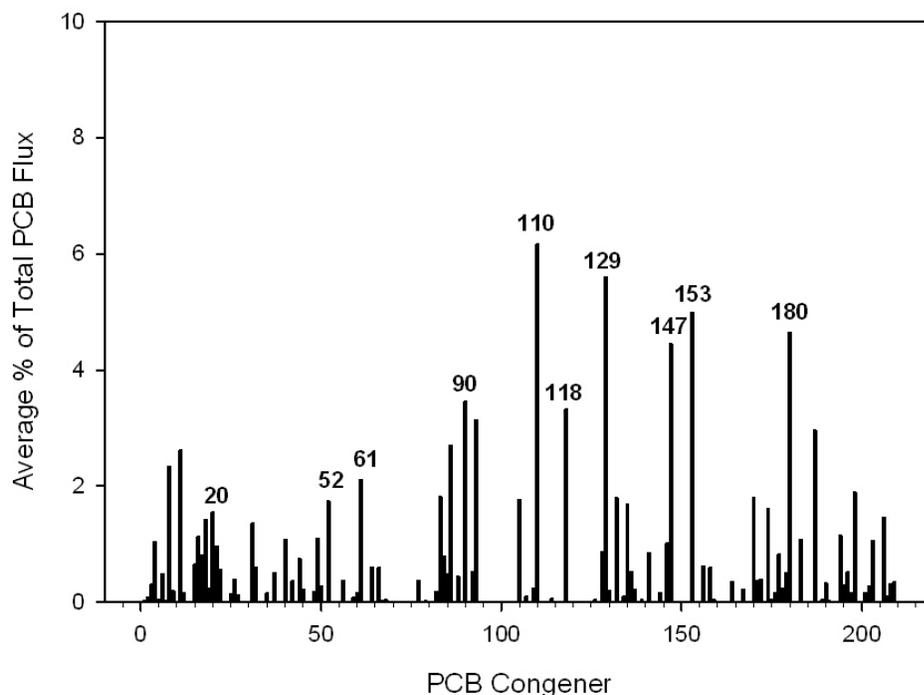


Figure 37. Average Congener Contribution to Total PCB Flux at Kent

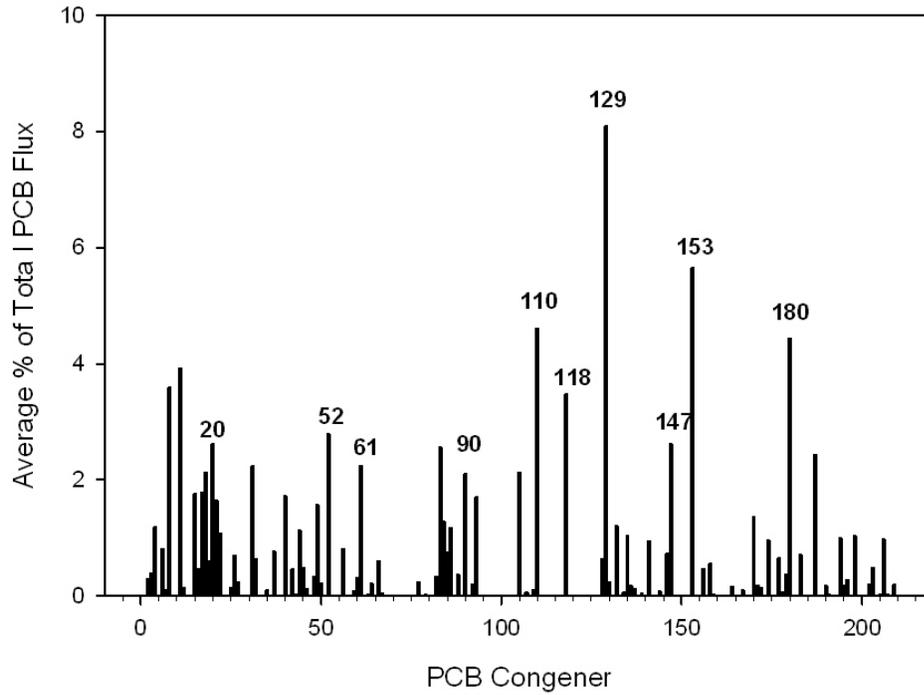


Figure 38. Average Congener Contribution to Total PCB Flux at Kent SC

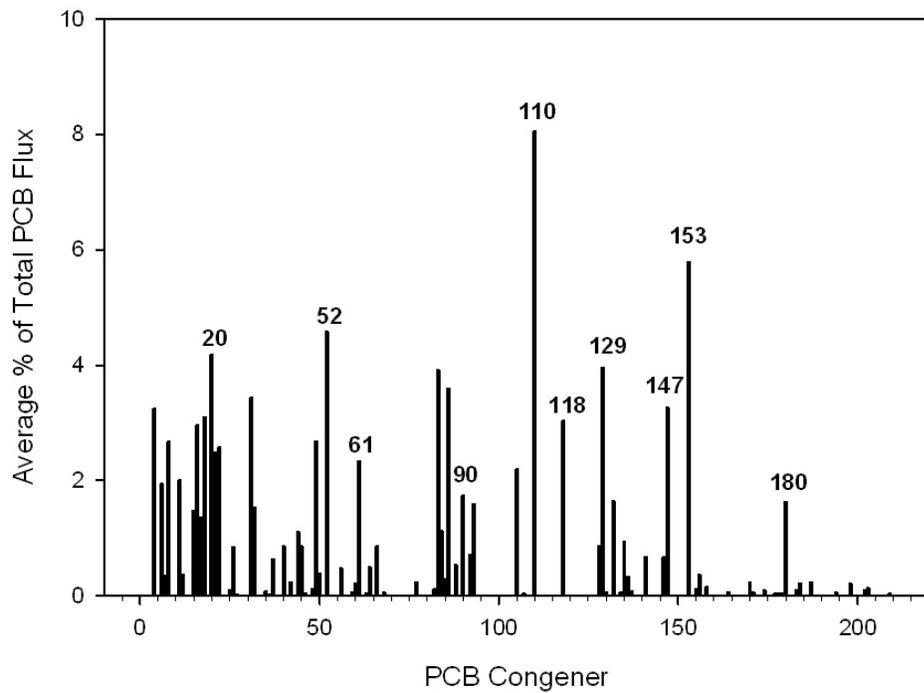


Figure 39. Average Congener Contribution to Total PCB Flux at Enumclaw

5.5 Dioxins and Furans

The number of dioxin/furan samples varied by station ranging from 5 at Kent SC station to 10 at the Kent station. Total dioxin/furan fluxes were generally consistent with location except at Kent station (Figure 40). Temporal differences can't be determined from the low number of samples collected and the variation in number of stations sampled. When dioxin/furan flux was measured at the Enumclaw station, it was the lowest of any station. The highest dioxin/furan fluxes were observed at the Kent station; the maximum flux was over 20 times higher than that measured at Kent SC during the same time period. Dioxin/furan fluxes at Beacon Hill, South Park and Kent SC stations were lower and more stable than at Kent station.

Grouping fluxes by station shows the median total dioxin/furan flux at the Enumclaw station (0.064 ng/m²-day) was lowest of all stations (Figure 41). Variability in measurements was also lowest at the Enumclaw station. Variability was relatively low for all stations except Kent. Median fluxes at Kent were much higher than any other station (Table 18). The median fluxes at Beacon Hill, Duwamish and Kent SC were similar, the Enumclaw station median flux was lowest and the South Park median flux was highest. The second sampling station at Kent SC was originally installed to further evaluate the much higher total dioxin/furan fluxes at Kent compared to other locations. Based on the available paired sampling data from Kent and Kent SC, the median dioxin/furan flux was much higher at the Kent station (3.13 vs 0.31 ng/m²-day). These differences in flux indicate a microscale effect is occurring with the Kent Station presumably being influenced by the rail line (the feature that differs most clearly between the two Kent stations). The one-way ANOVA by ranks test confirms total dioxin/furan fluxes at Kent were significantly higher (p<0.05) than at Duwamish or Enumclaw stations. Total dioxin/furan fluxes at South Park were also significantly higher than at Enumclaw. No other significant differences were found. The sample sizes for dioxin/furan flux data are small which may limit the ability to detect differences between stations in statistical tests.

Table 18. Summary of Total Dioxin/Furan Flux Data by Station (ng/m²-day)

	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	7	8	10	10	5	7
Minimum	0.15	0.11	0.20	0.65	0.19	0.037
Maximum	0.71	0.44	0.80	24.4	0.50	0.26
Median	0.32	0.30	0.42	3.13	0.31	0.064
Mean	0.35	0.28	0.44	6.50	0.34	0.10

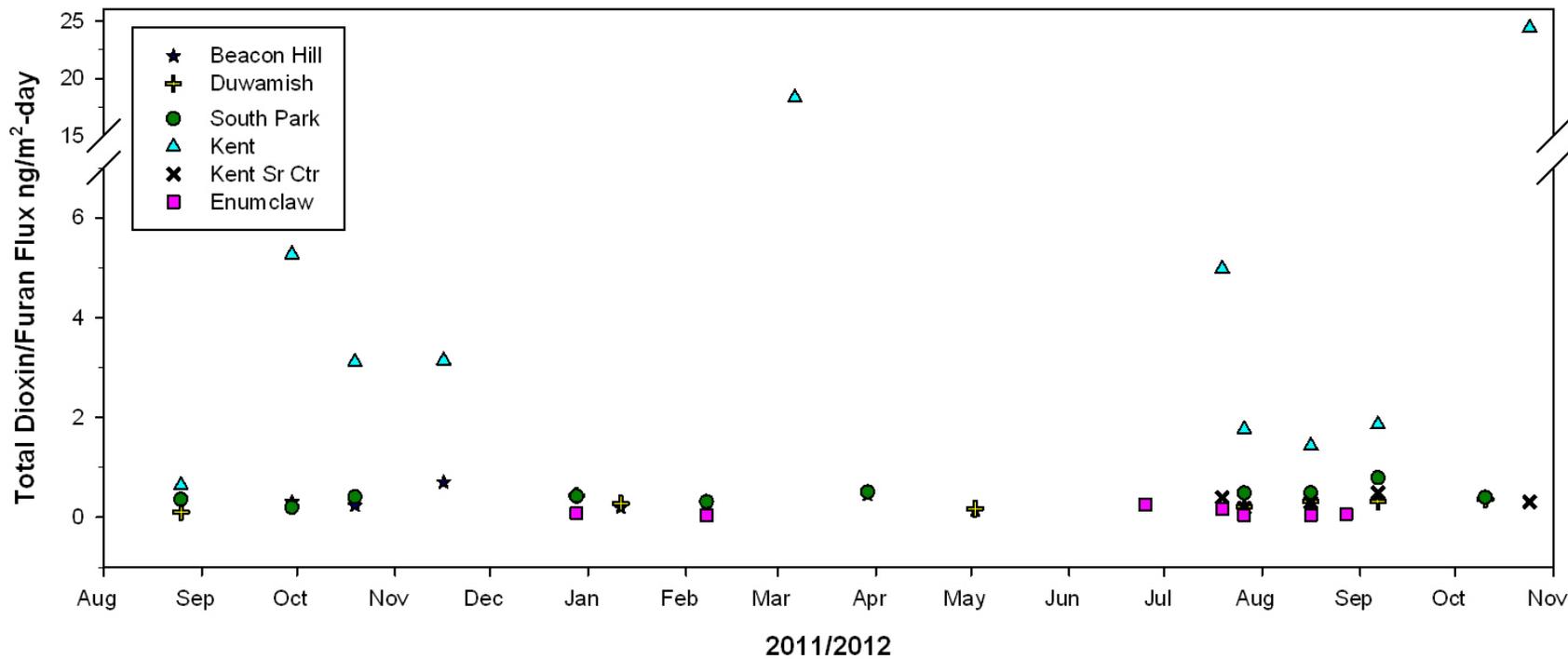


Figure 40. Total Dioxin/Furan Flux for each Collection Period by Collection Date and Station.

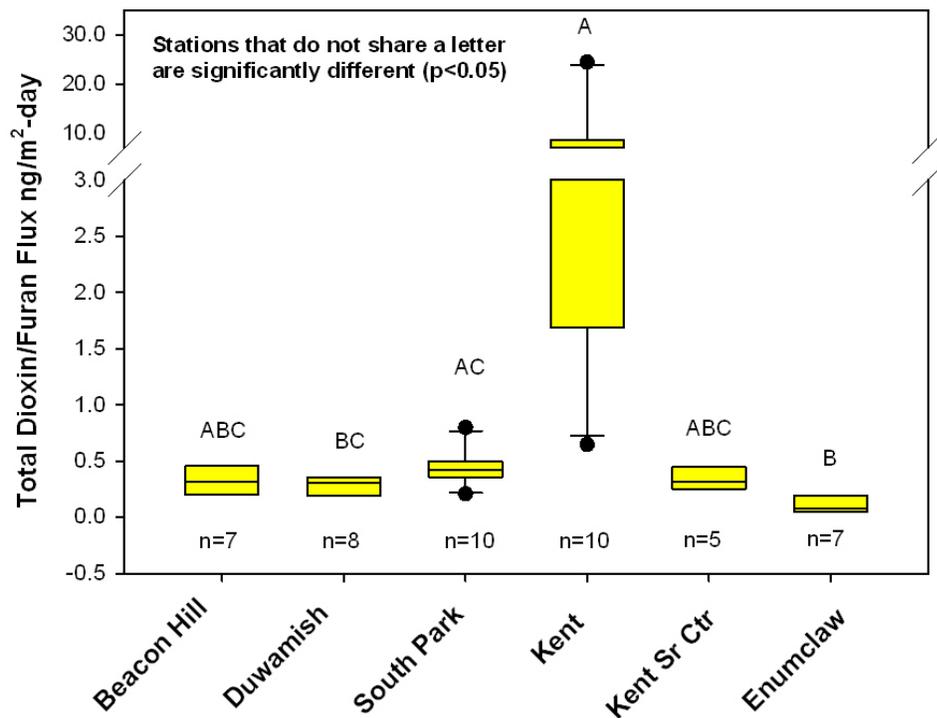


Figure 41. Boxplots of Total Dioxin/Furan Flux by Station.

5.6 Dioxin TEQs

Dioxin TEQ fluxes varied by location during most sampling periods (Figure 42). Temporal differences can't be determined from the low number of samples collected and the variation in number of stations sampled. When dioxin TEQ flux was measured at the Enumclaw station, it was usually the lowest of any station. The highest dioxin TEQ fluxes were observed at the Kent station; the maximum flux was over five times higher than that measured at Kent SC during the same time period. TEQ fluxes at all other stations were lower and more stable than at Kent station.

Grouping fluxes by station shows the median dioxin TEQ flux at Enumclaw (4.03 pg TEQ/m²-day) was lowest of all stations (Figure 43). Variability in measurements was also lowest at the Enumclaw station and highest at Kent. Median TEQ fluxes at Kent were higher than any other station. The median TEQ fluxes at all stations except Kent were similar (Table 19). The second sampling station at Kent SC was originally installed to further evaluate the much higher dioxin TEQ fluxes at Kent compared to other locations. Based on the available paired sampling data from Kent and Kent SC, the median dioxin TEQ flux was approximately three times higher at the Kent station (14.0 vs 4.6 pg TEQ/m²-day). The data indicate a microscale effect at the Kent Station presumably driven by the rail line (the feature that differs most clearly between the two Kent stations). The one-way ANOVA test showed dioxin TEQ fluxes at Kent were significantly higher ($p < 0.05$) than at Duwamish,

Kent SC and Enumclaw. No other significant differences were found. The sample sizes for dioxin TEQ flux data are small which may limit the ability to detect differences between stations in statistical tests. It should be noted that dioxin TEQs are calculated using detected and undetected results in contrast to total dioxin/furans which are calculated using only detected results. This difference, combined with the application of TEFs, makes direct comparison of total dioxin/furans and dioxin TEQs imprudent.

Table 19. Summary of Dioxin TEQs Flux Data by Station (pg TEQ/m²-day)

	Beacon Hill	Duwamish	South Park	Kent	Kent Sr Ctr	Enumclaw
Sample Size	7	8	10	10	5	7
Minimum	2.77	1.87	2.76	4.42	3.55	1.15
Maximum	14.5	10.2	14.1	73.3	9.96	11.2
Median	5.87	3.98	5.01	14.0	4.58	4.03
Mean	7.22	4.95	6.05	21.7	5.62	5.80

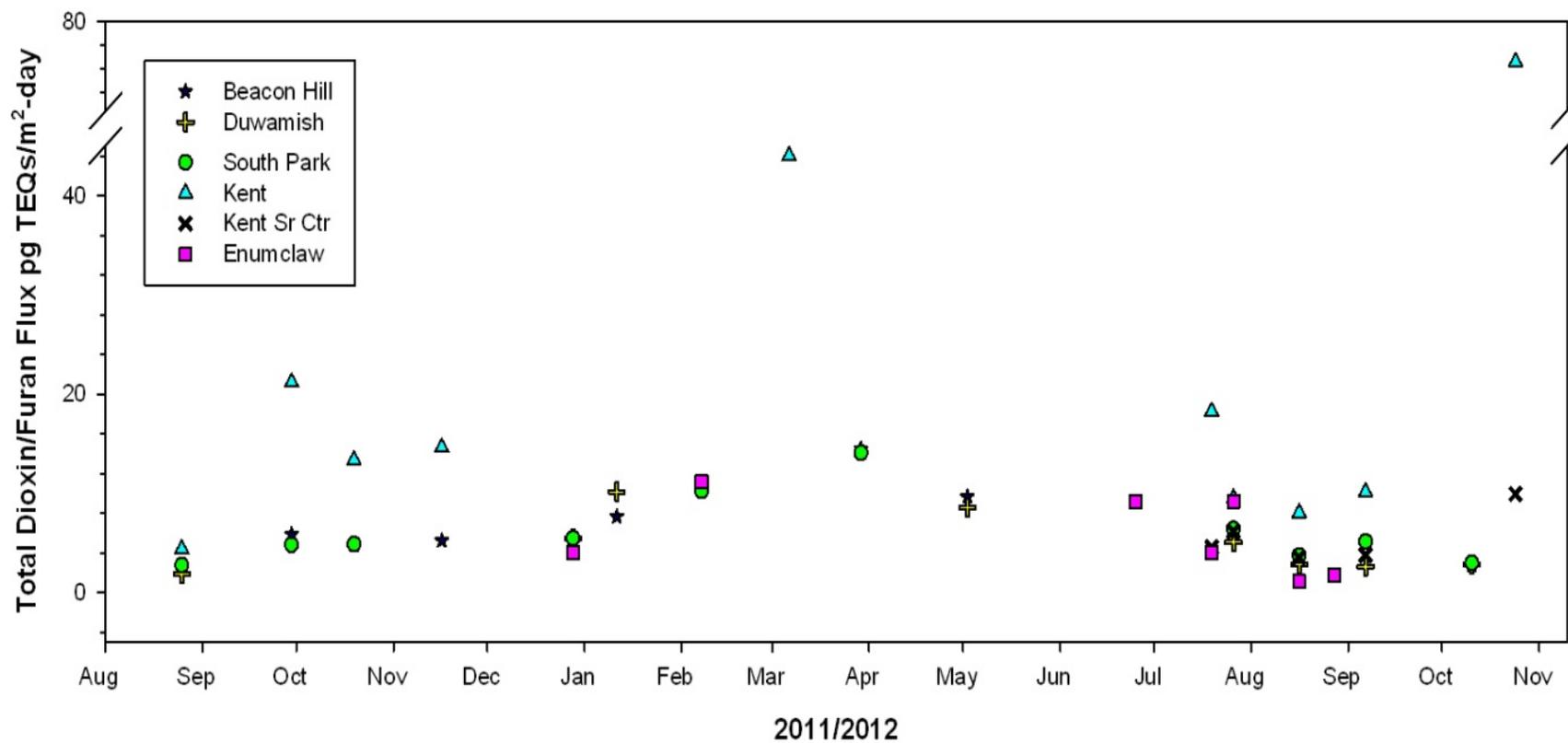


Figure 42. Dioxin TEQ Flux for each Collection Period by Collection Date and Station.

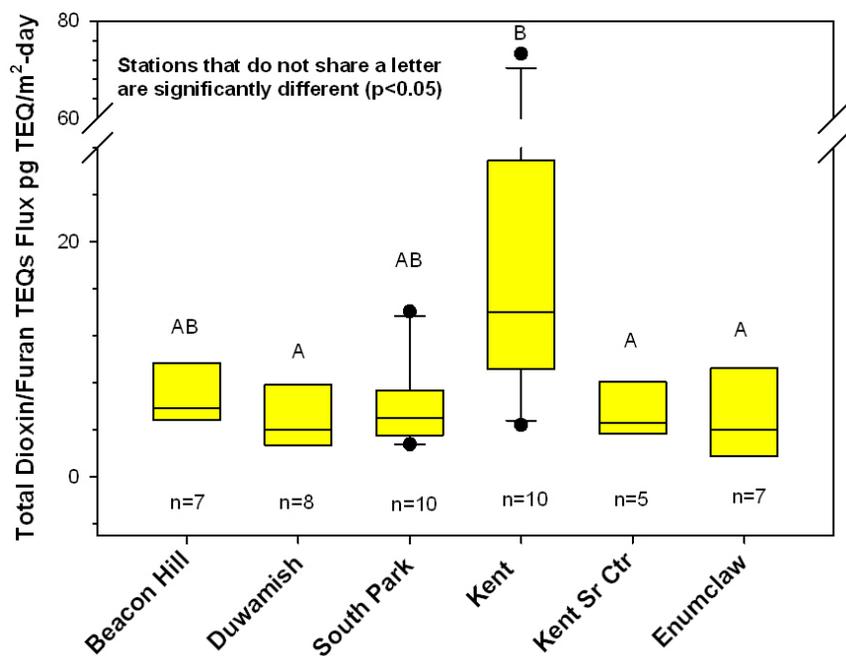


Figure 43. Boxplots of Dioxin TEQs Flux by Station.

5.7 Dioxins and Furans Congener Pattern

Unlike PCBs, dioxins and furans are not commercial products themselves, but byproducts of 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/or 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). The majority of dioxin/furan congeners contributed a negligible amount to the total dioxin/furan flux. For visual presentation, percentages were graphed only 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 44). The congener 1,2,3,4,6,7,8-HPCDD was present 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 substantially different.

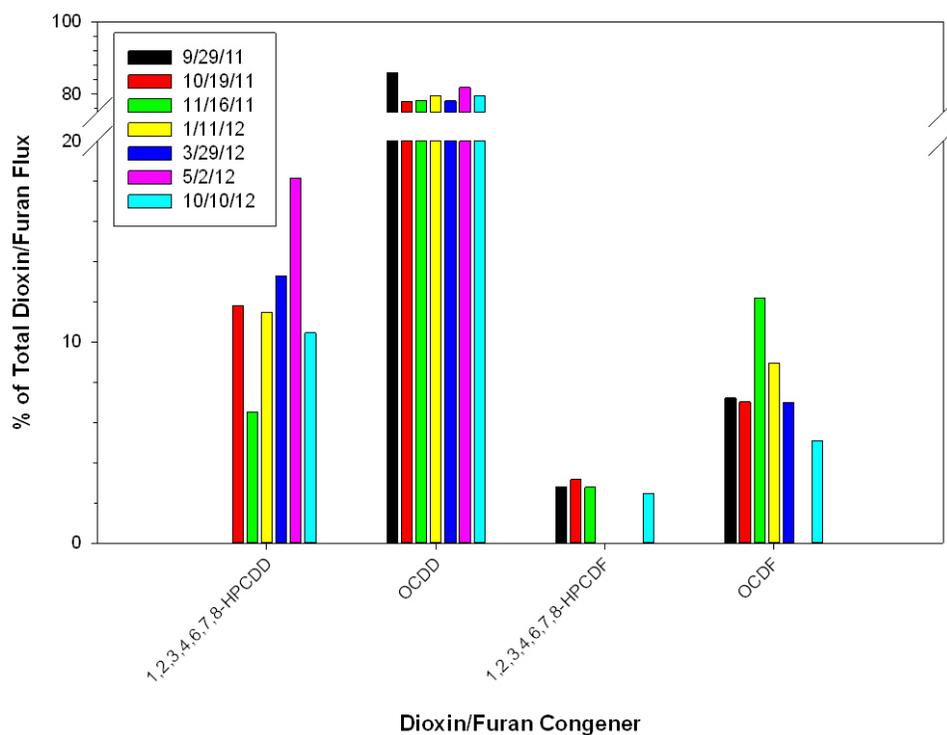


Figure 44. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Beacon Hill Station.

Similar to Beacon Hill, OCDD was the dominant dioxin/furan congener in every sample at Duwamish station. Also, the congener 1,2,3,4,6,7,8-HPCDD was consistently present contributing approximately 10% to total flux and 1,2,3,4,6,7,8-HPCDF and OCDF were absent from some samples (Figure 45). OCDF was absent from more samples at Duwamish than Beacon Hill and when present, contributed slightly less to total flux.

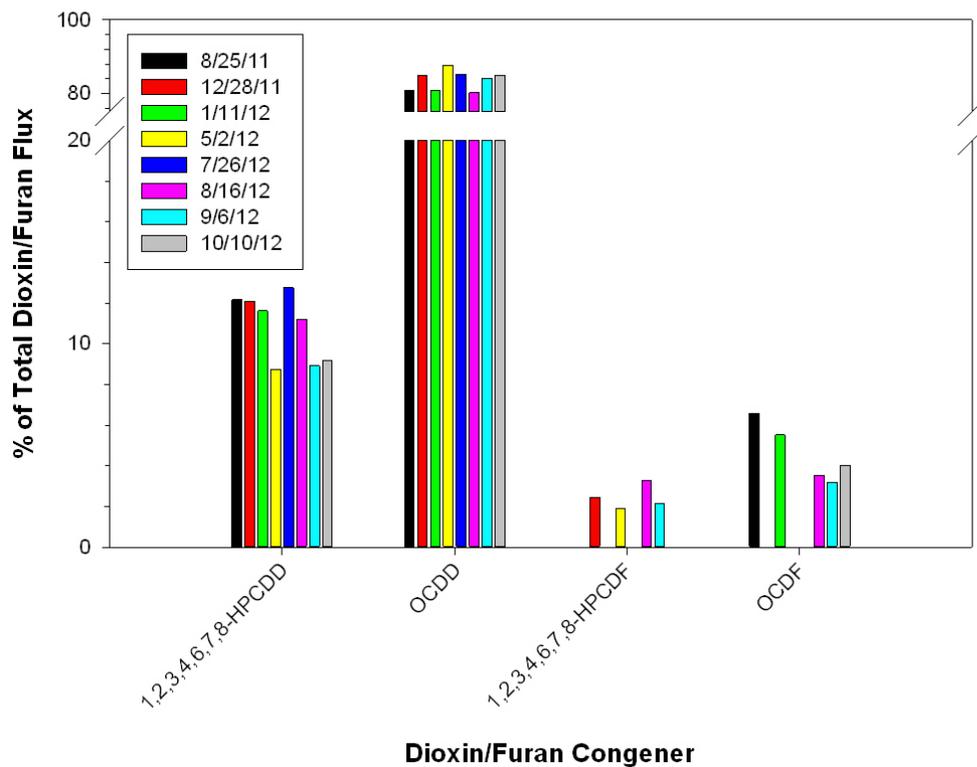


Figure 45. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Duwamish Station.

The dioxin/furan congener profile at South Park station is similar to that at Duwamish station (Figure 46). 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 two furan congeners were present at 6% percent or less where they were detected.

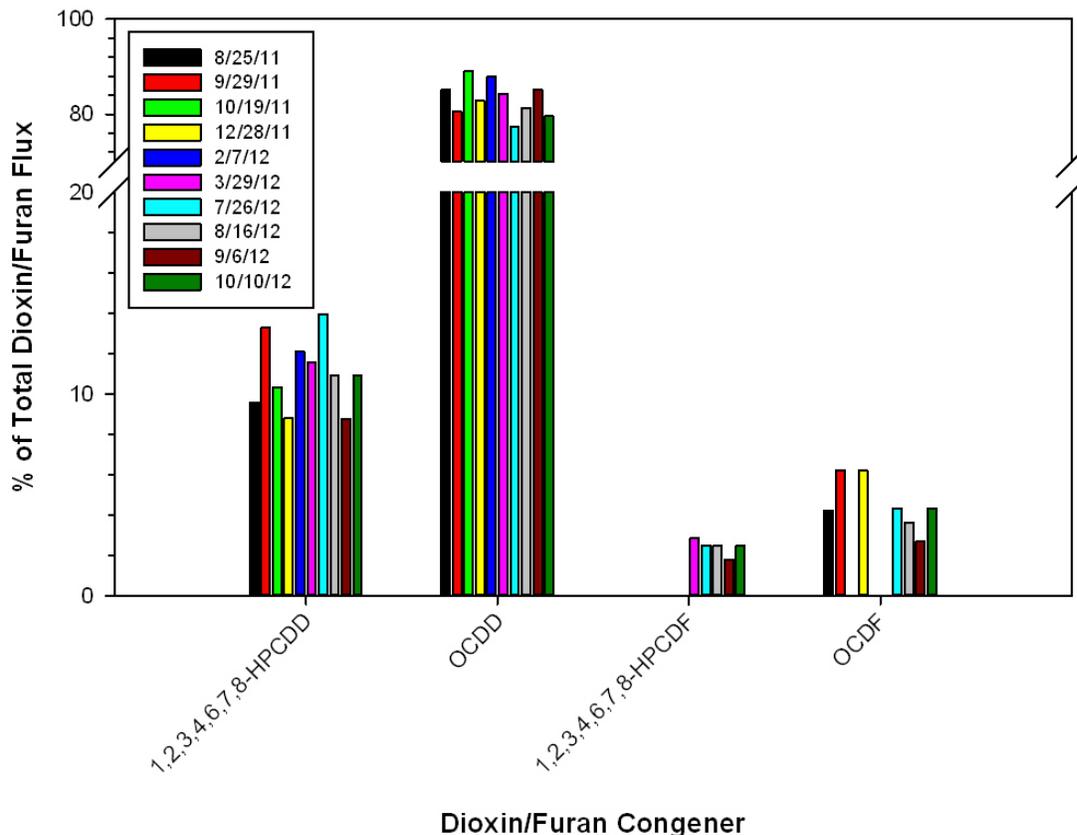


Figure 46. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at South Park Station.

The dioxin/furan congener profile at Kent station (Figure 47) is different than Beacon Hill, Duwamish, 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 compared 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 48) is more similar to Beacon Hill, Duwamish and South Park than Kent station. Contributions of OCDD in Kent SC samples are closer to 80% 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 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.

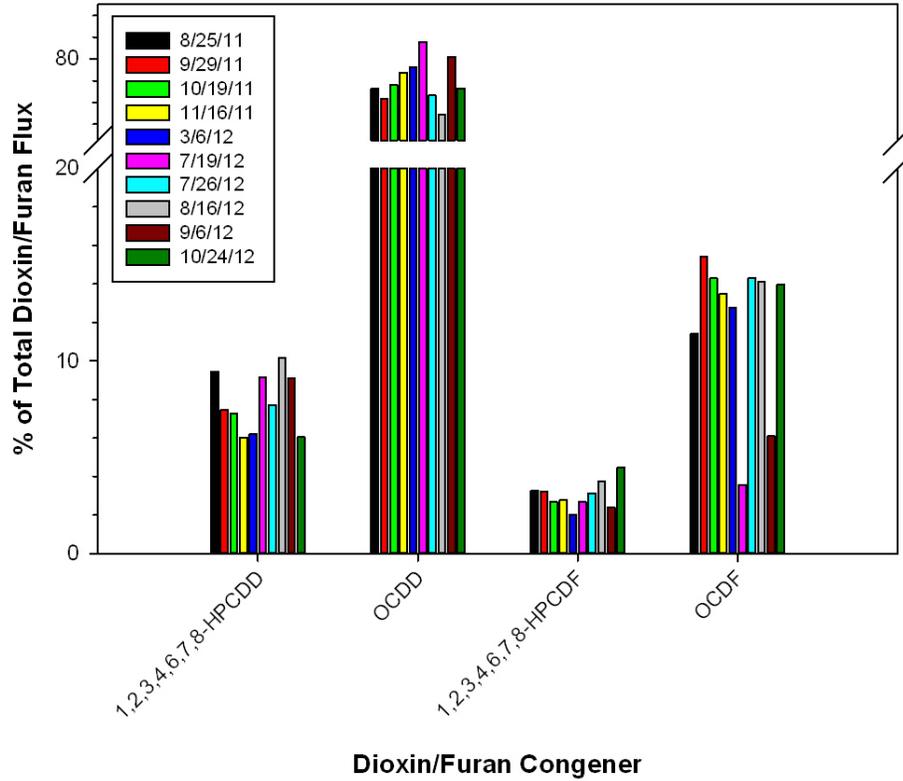


Figure 47. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Kent Station.

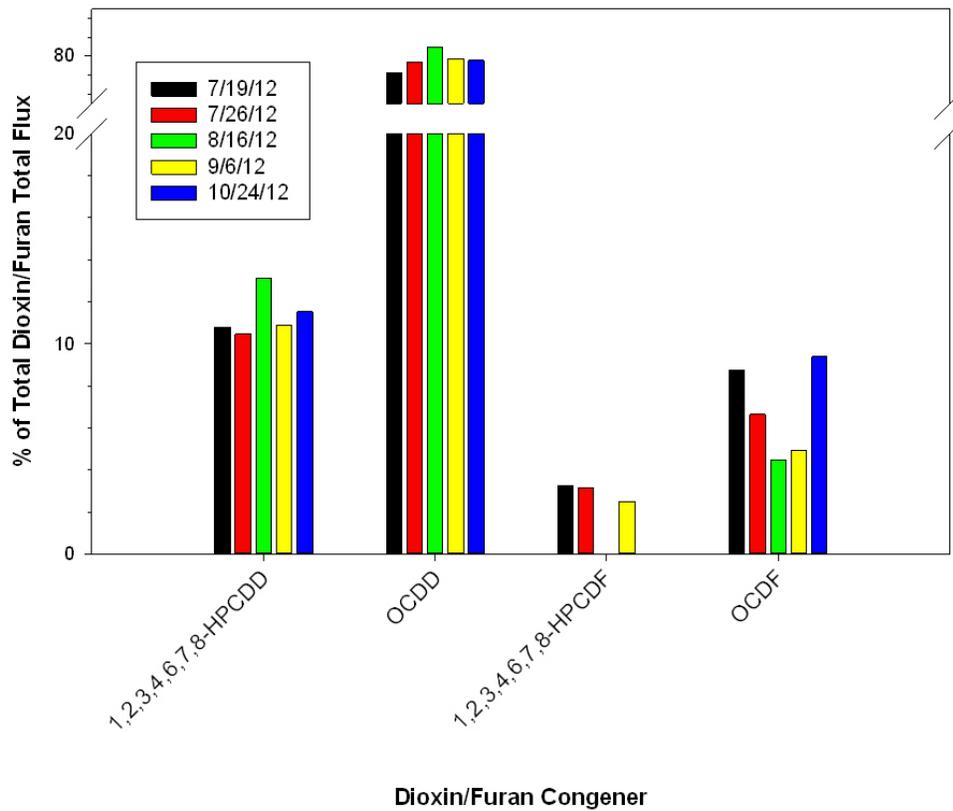


Figure 48. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Kent SC Station.

The dioxin/furan congener profile at Enumclaw is unique compared to other stations (Figure 49). OCDD is dominant similar to other stations but it is close to 100% in one sample from October 19, 2011. The other three congeners are not present in some samples. The two furan congeners contribute less to samples at Enumclaw than at any other station.

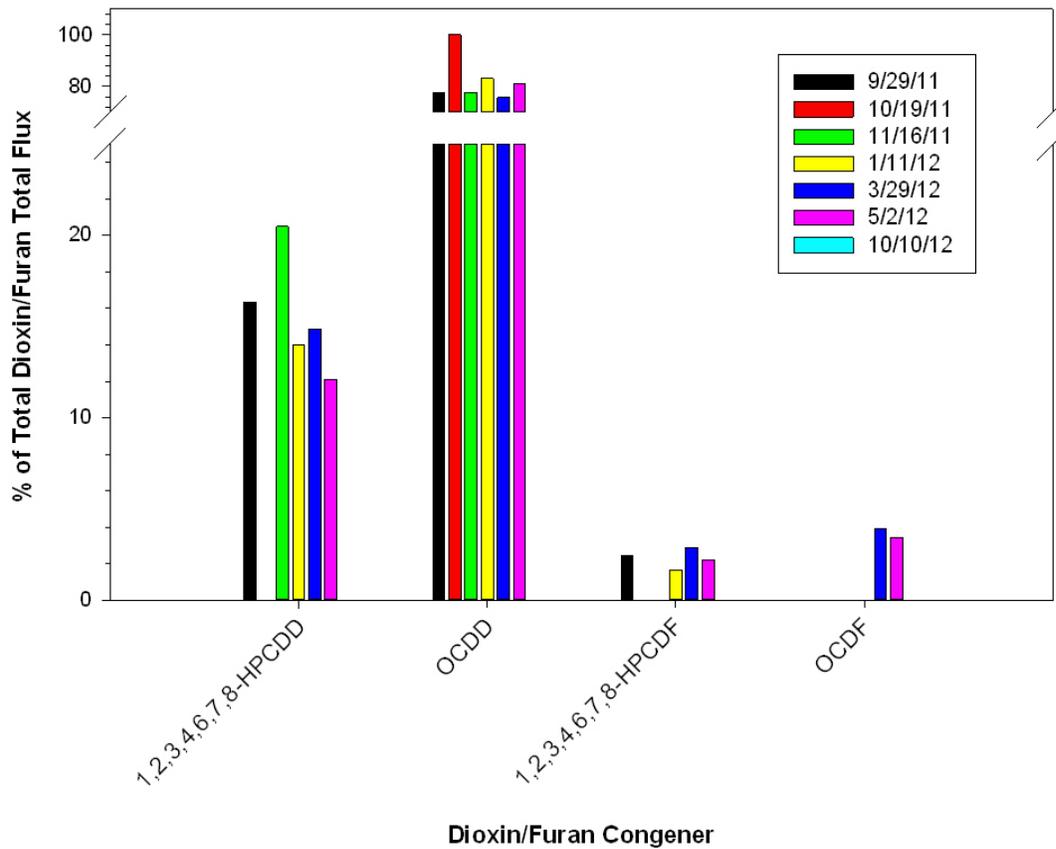


Figure 49. Congener Profile for Four Most Prominent Dioxin/Furan Congeners at Enumclaw Station.

The percentages for all congeners were averaged for each location and graphed together to look at differences between stations (Figure 50). Average dioxin/furan congener contributions are consistent between Duwamish and South Park stations. The Beacon Hill and Kent SC stations were similar to Duwamish and South Park with the exception of OCDF, which contributed more. The Kent and Enumclaw stations were most different from the others (Figure 50). OCDF contributions to total dioxin/furan flux varied the most but only within about 10%. At the Kent station, 1,2,3,4,6,7,8-HPCDD contributed at least 2% less to total dioxin/furan flux than other stations. Also, the average contributions of 1,2,3,4,6,7,8-HPCDF and OCDF at Kent station were markedly higher than any other station. Two dioxin congeners, 1,2,3,4,6,7,8-HPCDD and 1,2,3,7,8,9-hexachlorodibenzodioxin, contributed at least 1% more to total dioxin/furan flux at Enumclaw than any other station. OCDF contributed at least 1% less to total dioxin/furan flux at Enumclaw than any other station.

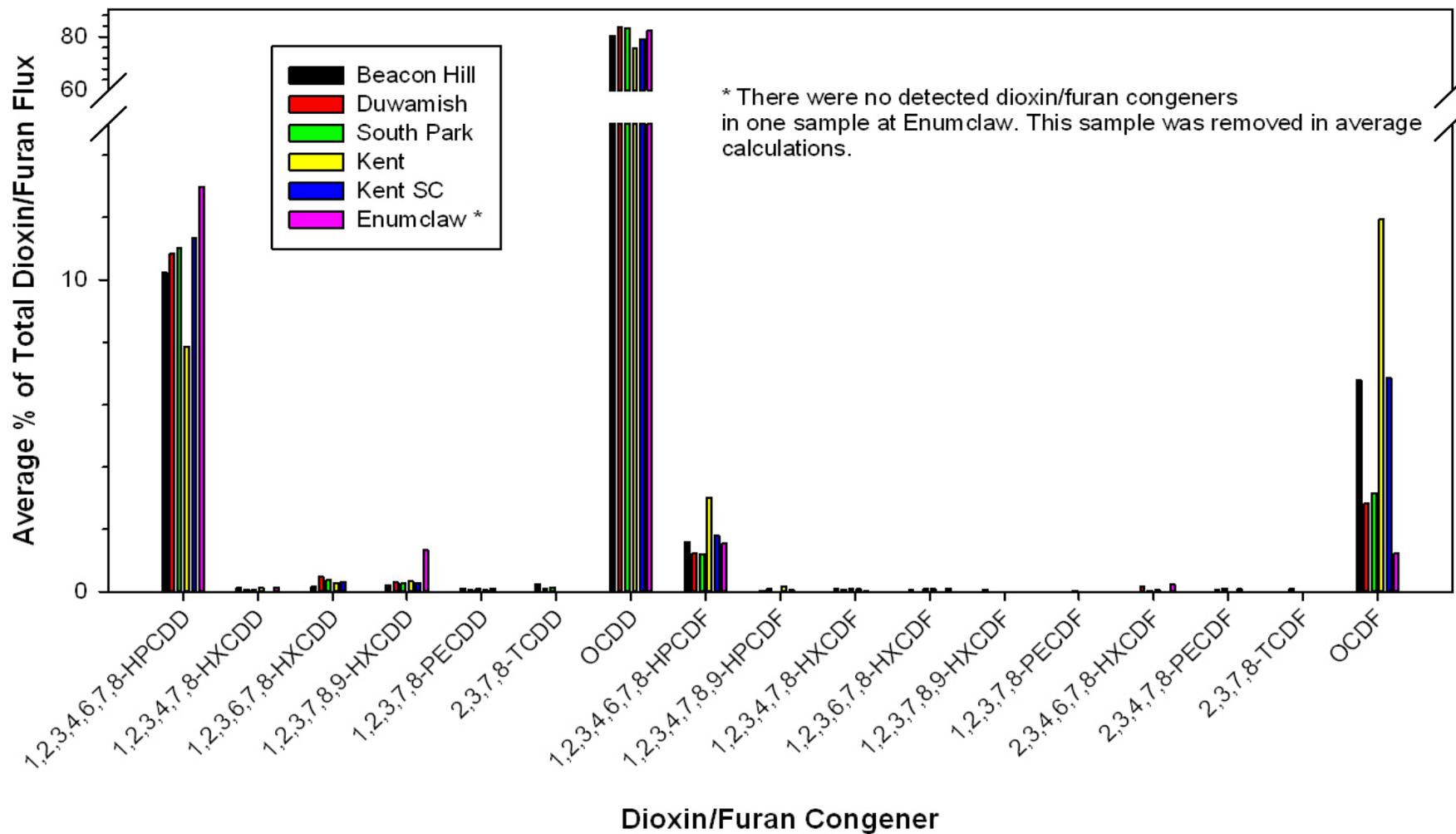


Figure 50. Average Percent Total Dioxin/Furan Congener Flux by Station.

5.8 Field Quality Control Samples

Four types of field quality control samples results are presented: field replicates, field spike blanks, wipe samples and equipment blanks.

5.8.1 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. The maximum relative percent difference (RPD) was less than or equal to 30% for six out of ten metals (Table 20). The maximum RPD for lead was 31%, for cadmium was 44%, for mercury was 140% and for silver was 158%. The RPDs are reasonably low for all metals except mercury and silver where variability is significant. Maximum RPDs for PAHs were lower than metals with all but three PAHs having RPDs less than or equal to 30%. Acenaphthylene and dibenzo(a,h)anthracene maximum RPDs were 37 and 41%, respectively. The highest RPD for PAHs was for anthracene at 79% indicating relatively moderate variability. Field replicate RPDs for total PCBs and total dioxins/furans ranged from 12 to 68% and from 1.3 to 35%, respectively. Overall, the field replicate results indicate moderate variability potential for anthracene and PCBs and high variability potential for mercury and silver. Field replicate variability was relatively low for all other COCs.

Table 20. Relative Percent Difference (RPD) Between Field Replicates

Group	Analyte	# of Replicate Pairs	RPD Range
Metal	Arsenic, Total, ICP-MS	3	9-29
Metal	Cadmium, Total, ICP-MS	3	27-44
Metal	Chromium, Total, ICP-MS	3	5-21
Metal	Copper, Total, ICP-MS	3	2-29
Metal	Lead, Total, ICP-MS	3	0-31
Mercury	Mercury, Total, CVAF	3	11-140
Metal	Nickel, Total, ICP-MS	3	2-30
Metal	Silver, Total, ICP-MS	2	140-158
Metal	Vanadium, Total, ICP-MS	3	2-27
Metal	Zinc, Total, ICP-MS	3	3-26
HPAH	Benzo(a)anthracene	3	0-7
HPAH	Benzo(a)pyrene	3	3-14
HPAH	Benzo(b,j,k)fluoranthene	3	0.3-7
HPAH	Benzo(g,h,i)perylene	3	1-4
HPAH	Chrysene	3	4-6
HPAH	Dibenzo(a,h)anthracene	3	2-41
HPAH	Fluoranthene	3	2-26
HPAH	Indeno(1,2,3-Cd)Pyrene	3	0.5-12
HPAH	Pyrene	3	2-25
LPAH	Acenaphthene	3	3-23
LPAH	Acenaphthylene	3	10-37
LPAH	Anthracene	3	1-79
LPAH	Fluorene	3	11-30
LPAH	Naphthalene	3	0-21
LPAH	Phenanthrene	3	4-15
PCB	Total PCBs	3	12-68
Dioxins/Furans	Total Dioxin/furan	3	1.3-35

5.8.2 Field Spike Blank Samples

Clean water samples spiked with metals, PAHs, PCB congeners and dioxin/furan congeners were placed in atmospheric deposition sample bottles and deployed and analyzed in the same way as regular samples. These field spike blanks were collected to measure the potential loss of analytes occurring mainly from volatilization during deployment (adhesion to the sample bottle is also possible). The percent recovery of metals was high, ranging from 93 to 110% (Table 21). Recovery of PAHs was lower, particularly for LPAHs. More volatilization would be expected for LPAHs compared to HPAHs because of their lower molecular weight. All PAH recoveries were above 50% except for acenaphthylene

(19%), anthracene (15%) and benzo(a)pyrene (2.2%). The high benzo(a)pyrene loss is unexpected given the lower volatility of this compound compared to anthracene and other LPAHs. However, spike recovery of benzo(a)pyrene was often low in spike blanks as well indicating the loss was not necessarily related to field volatilization or jar adhesion (See discussion in Section 5.9.1). Given the high loss rates for acenaphthylene, anthracene and benzo(a)pyrene, flux rates for these three PAHs should be considered to be biased low. The loss of benzo(a)pyrene is not believed to be related to actual loss during deployment but due to an analytical issue causing poor spike recovery, as was observed sporadically in the laboratory spike blanks (See Section 5.9 for more discussion).

Table 21. Recovery of Metals and PAHs in Field Spike Blank

Parameter	% Recovery
Arsenic, Total, ICP-MS	98.5%
Cadmium, Total, ICP-MS	103.5%
Chromium, Total, ICP-MS	98.5%
Copper, Total, ICP-MS	105.0%
Lead, Total, ICP-MS	105.0%
Mercury, Total, CVAF	93.2%
Nickel, Total, ICP-MS	104.0%
Silver, Total, ICP-MS	107.0%
Vanadium, Total, ICP-MS	100.0%
Zinc, Total, ICP-MS	109.5%
Acenaphthene	53.8%
Acenaphthylene	18.6%
Anthracene	15.1%
Benzo(a)anthracene	80.8%
Benzo(a)pyrene	2.2%
Benzo(b,j,k)fluoranthene	94.0%
Benzo(g,h,i)perylene	91.8%
Chrysene	95.8%
Dibenzo(a,h)anthracene	97.6%
Fluoranthene	97.3%
Fluorene	85.3%
Indeno(1,2,3-Cd)Pyrene	98.2%
Naphthalene	64.8%
Phenanthrene	69.0%
Pyrene	92.7%

Out of 32 spiked PCB congeners, average recovery from two field spike blanks was equal to or greater than 69% for 28 congeners (Table 22). Recoveries of PCB23, PCB34, and PCB54 were between 50 and 60% and recoveries of PCB104 and PCB155 were both 45%. These

five congeners were not detected in most samples and when detected were at low concentrations (<10 pg/L); thus, even a doubling of their concentration would not be significant to the total PCB concentration. Recovery of the lighter weight congeners was generally lower than that of the heavy weight congeners. However, the average recovery for all spiked congeners was 85% suggesting that on a total PCB basis, there may only be a small low bias on the PCB flux.

Table 22. Average Recovery of PCB Congeners in Two Field Spike Blanks

Congener	Average Recovery
1	72.9%
3	70.4%
4	69.4%
15	70.6%
19	69.9%
23	55.6%
34	54.5%
37	80.1%
54	60.2%
77	97.0%
81	92.7%
104	44.8%
105	94.9%
114	88.7%
118	99.6%
123	89.8%
126	104.2%
155	45.4%
156 + 157	106.8%
167	106.0%
169	111.0%
170	99.4%
180	97.1%
182	93.8%
187	98.0%
188	72.0%
189	102.9%
202	85.6%
205	102.5%
206	99.2%
208	88.6%
209	89.8%

The average recoveries of dioxin/furan congeners in two field spike blanks were all over 92% indicating little volatilization is occurring for these compounds (Table 23). On a total dioxin/furan congener basis, the average percent recovery for the two spike blanks was 102%.

Table 23. Average Recovery of Dioxin/Furan Congeners in Two Field Spike Blanks

Congener	Average Recovery
2,3,7,8-TCDD	101.6%
1,2,3,7,8-PECDD	108.5%
1,2,3,4,7,8-HXCDD	102.0%
1,2,3,6,7,8-HXCDD	103.8%
1,2,3,7,8,9-HXCDD	104.9%
1,2,3,4,6,7,8-HPCDD	98.2%
OCDD	100.3%
2,3,7,8 TCDF	106.9%
1,2,3,7,8-PECDF	107.4%
2,3,4,7,8-PECDF	110.3%
1,2,3,4,7,8-HXCDF	100.4%
1,2,3,6,7,8-HXCDF	101.5%
1,2,3,7,8,9-HXCDF	103.5%
2,3,4,6,7,8-HXCDF	102.3%
1,2,3,4,6,7,8-HPCDF	98.8%
1,2,3,4,7,8,9-HPCDF	92.8%
OCDF	96.6%

5.8.3 Field Wipe Samples

A solvent-soaked wipe was used to clean the surface of the funnels for PAH samplers and PCB and dioxin/furan samplers to measure the efficiency of the funnel-cleaning protocol. Wipes could not be tested for metals because of background contamination found on the pre-used wipe. Two wipes were tested for PAHs, one at Kent station and one at Duwamish station. Chrysene was detected above the RDL in both wipe samples and benzo(g,h,i)perylene was detected above the RDL in one wipe sample. All other PAHs were either nondetect or detected at low mass between the MDL and RDL. Efficiency of the funnel-cleaning protocol can be calculated as the ratio of the LPAH and HPAH masses measured on the wipe compared to these masses measured in the associated samples. For LPAHs, this ratio as a percentage is 0.9% and 3.5% for the two wipes. For HPAHs, this ratio is 0.6% and 1.6%. Thus, a very low percentage of PAH mass remains on the funnel after cleaning.

One wipe was tested for PCBs and dioxin/furan congeners; this wipe was collected from the Kent station. Similar ratios were calculated for PCB and dioxin/furan congeners as a measure of the efficiency of the funnel-cleaning protocol. For total PCBs, 0.1% of the mass measured in the associated sample was detected on the wipe. For total dioxins/furans, the residual mass on the wipe was 1.3% of the mass in the associated sample. Thus, the funnel-cleaning protocol efficiency was close to 100% for total PCBs and 99% for total dioxins/furans.

5.8.4 Equipment Blank Samples

As specified in the SAP, one field equipment blank was collected for each analytical method: metals, mercury, PAHs, PCB congeners and total dioxin/furan congeners. The mass in the equipment blank was calculated (i.e., concentration X volume) and compared to the masses in all detected samples to estimate the potential contribution of the equipment blank to samples. When there was no detected concentration in the equipment blank, its contribution to the sample was considered 0%. Similarly, when a sample result was not detected, the equipment blank contribution to the sample was assumed to be 0%. The range of equipment blank contribution to detected sample masses for metals and mercury is summarized in Table 24. The median contributions for most metals are below 3% indicating small contributions from equipment contamination. The maximum potential equipment blank contribution for copper was 61% indicating that equipment contamination may occasionally contribute more substantially for this metal.

Table 24. Potential Equipment Blank Contribution to Sample Masses of Metals

Parameter	Mass in Equipment Blank	Range of Equipment Blank Contribution	Median Equipment Blank Contribution
Arsenic	0.0032	0.33 – 21%	2.19%
Cadmium	0.001	0.28 – 20%	2.27%
Chromium	0.0055	0.15 – 7.4%	0.92%
Copper	0.0964	0.53 – 61%	2.76%
Lead	0.0145	0.02 – 7.5%	0.71%
Mercury	0.00002 U ^a	0% ^b	0% ^b
Nickel	0.0062 U ^a	0% ^b	0% ^b
Silver, Total	0.001	0.66 – 24%	6.61%
Vanadium	0.0056	0.12 – 12%	0.90%
Zinc	0.16	0.12 – 8.0%	0.83%

^a Equipment blank mass for an undetected result was calculated using the MDL.

^b When a metal was not detected in the equipment blank, its contribution to any samples was considered 0%.

The post-sample equipment blank for metals was intended to determine if additional metals were mobilized after the funnel was brushed and rinsed for sample collection (i.e., the combined contribution from equipment contamination and sample remainder). Greater masses of metals were measured in the post-sample equipment blank than the regular

equipment blank. The maximum mass contribution to samples was 21% or less except for copper, which had a maximum mass contribution of 61% (Table 25). However, the median mass contribution from the post-sample equipment blank was 2.6% or less for all metals indicating typically small contributions to sample masses.

Table 25. Potential Post-Sample Equipment Blank Contribution to Sample Masses of Metals

Parameter	Mass in Equipment Blank	Range of Equipment Blank Contribution	Median Equipment Blank Contribution
Arsenic	0.0068	0.7-21.3%	1.3%
Cadmium	0.0014	0.4-19.9%	1.1%
Chromium	0.0458	1.2-7.4%	2.0%
Copper	0.173	0.9-60.6%	1.3%
Lead	0.0993	0.1-7.5%	1.3%
Mercury	0.000115	0.05-2.4%	1.0%
Nickel	0.0411	0.2-10.4%	2.2%
Silver, Total	0.0001 U ^a	0.00%	0.0%
Vanadium	0.0558	1.2-12.0%	2.6%
Zinc	0.876	0.6-8.0%	1.2%

^a Equipment blank mass for an undetected result was calculated using the MDL.

The median contributions of most PAHs in the equipment blank to detected samples were less than 12% (Table 26). However, the median contributions of phenanthrene (16%), acenaphthene (24%), and naphthalene (74%) were higher; the range of contribution for detected naphthalene is particularly high (52-92%) and suggests equipment contamination of this low molecular weight PAH is substantial. However, considering only 8 of the 124 naphthalene results were detected, the high contribution of equipment contamination to these samples is less significant than it seems to the LPAH sums.

For total PCBs, the potential contribution of equipment contamination to detected samples ranged from 0.18 to 116% with a median of 3.5%. For total dioxins/furans the potential contribution of equipment contamination to detected samples ranged from 0.03 to 21% with a median of 0.9%.

Overall, small potential contributions of metals and most PAHs were estimated from the equipment blank and higher potential contributions were estimated for PCBs and dioxins/furans. The contribution of the equipment contamination to sample masses varied substantially for any given analyte. However, the median contributions were low except for a few PAHs indicating the frequency that equipment contamination contributed substantially to sample mass was low. Because few equipment blanks were collected, the variability between equipment blanks is not well known. Further collection and analysis of equipment blanks is recommended in the future to characterize this variability.

Table 26. Potential Equipment Blank Contribution to Sample Masses of PAHs

Parameter	Mass in Equipment Blank	Range of Equipment Blank Contribution	Median Equipment Blank Contribution
Acenaphthene	0.00126	1.1 – 119%	24.0%
Acenaphthylene	0.00297 U ^a	0% ^b	0% ^b
Anthracene	0.0015 U ^a	0% ^b	0% ^b
Benzo(a)anthracene	0.0015 U ^a	0% ^b	0% ^b
Benzo(a)pyrene	0.00051	0.1 – 22%	2.4%
Benzo(b,j,k)fluoranthene	0.0014	0.1 - 40%	2.6%
Benzo(g,h,i)perylene	0.0014	0.2 - 129%	5.1%
Chrysene	0.0014	0.1 - 126%	3.2%
Dibenzo(a,h)anthracene	0.00153 U ^a	0% ^b	0% ^b
Fluoranthene	0.0065	0.3 - 98%	7.9%
Fluorene	0.0012	0.6 - 49%	11.7%
Indeno(1,2,3-Cd)Pyrene	0.00048	0.1 - 44%	2.9%
Naphthalene	0.040	52.3 - 92%	74.2%
Phenanthrene	0.010	0.6 - 66%	16.3%
Pyrene	0.0050	0.3 - 121%	6.9%

^a Equipment blank mass for an undetected result was calculated using the MDL.

^b When a PAH was not detected in the equipment blank, its contribution to any samples was considered 0%.

5.9 Chemistry Data Validation

Metals, mercury, and PAH data were validated by King County using EPA National Functional Guidelines for Superfund data (EPA 2008 and 2010) and the project SAP. Details of this validation are described in a data validation technical memorandum (Appendix D). Validation of PCBs and dioxin/furan congener data was completed by Laboratory Data Consultants, Inc. (LDC) in accordance with EPA Superfund guidance (EPA 2009). PCB and dioxin/furan congener validation reports are provided in E. This section summarizes the major findings of the chemistry data validations.

5.9.1 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 and mercury results did not receive qualification. Sample bottles for metals and mercury overflowed slightly before the deployment ended on May 2, 2012 at

the Enumclaw location. These results received a validation qualifier of “J” or estimated with unknown bias.

Between one and nine PAH compounds were detected in every method blank associated with the PAHs samples. 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 the 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 spike blank and spike blank duplicate recoveries as well as their relative percent differences (RPD) for PAHs were outside of QC limits in several sample batches. Most often this occurred for benzo(a)pyrene. Out of 126 associated samples, spike blank and spike blank duplicate recoveries were outside of QC limits affecting benzo(a)pyrene in 15 samples, benzo(a)anthracene in 5 samples, pyrene in 5 samples, and fluorene in 4 samples. RPDs exceeded QC limits affecting benzo(a)pyrene in 38 samples, anthracene in 17 samples, for acenaphthalene in 12 samples, and for acenaphthene, fluorene, 2-methylnaphthalene, naphthalene, and phenanthrene in 7 samples each. All of the affected PAHs in samples received a “J” validation qualifier with one exception; three undetected results were rejected for benzo(a)pyrene when the associated spike blank and duplicate recoveries were 0 and 1%.

KCEL observed sporadically poor recovery (<10%) of benzo(a)pyrene in spike blanks and spike blank duplicates over the course of the study. This is suspected to be related to the analytical extraction method which uses a solid-phase extraction (SPE) disc. The spike recoveries of benzo(a)pyrene using a comparable analytical method, which differs only by using liquid-liquid instead of SPE extraction, are consistently high. Thus, some unknown aspect of the SPE extraction procedure appears to result in sporadically poor recovery. Each sample is extracted on its own SPE disc. Therefore, the performance of the blank spike or its duplicate is no indication of the performance of benzo(a)pyrene in samples of the same analytical batch. Because of this uncertainty in the recovery of benzo(a)pyrene, it was decided during validation that all detected results should be flagged with a J as an estimate with low bias. All undetected results which were not rejected should be flagged UJ with low bias. Therefore, all benzo(a)pyrene data may be biased low and this bias should be weighed during interpretation of HPAH results. In the future, King County will consider collecting an additional sample to allow analysis of a matrix spike (MS) and matrix spike duplicate (MSD) and provide an additional QC metric for this method. Blank spike recoveries can differ significantly from MS/MSD samples. MS/MSD samples could not be analyzed in this study because the entire sample volume collected is extracted for the primary sample.

Recovery of surrogate 2-fluorobiphenyl in one spike blank duplicate was lower than QC limits and also resulted in RPDs outside QC limits for the seven LPAH compounds associated with this surrogate. This affected LPAHs in seven samples. LPAHs for the seven

samples received a “J” validation qualifier and are considered estimated. Recovery of 2-fluorobiphenyl were also below QC limits for four samples. Therefore, LPAH results for these samples received “J” validation qualifiers.

Sample bottles for PAHs overflowed slightly before the deployment ended on January 11, 2012 at the Kent station and May 16, 2012 at the Enumclaw station. These results received a validation qualifier of “J” (i.e., estimated) with unknown bias.

5.9.2 PCBs and Dioxins/Furans

PCBs and dioxin/furan data were validated to Level III by Laboratory Data Consultants (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 for 2,3,7,8-TCDF quantitation of all samples. Therefore, this performance issue did not result in unusable data for this compound; results from the second column were used.

For dioxins and furans, method blanks were below method performance criteria except for workgroup DPWG38582 where OCDD was found in blanks at 6.8 pg/L, which is low. Results within five times the blank concentrations were re-qualified as non-detect (U qualifier).

For PCBs, method blank contamination above method specifications was found in all batches. Most method blanks had one or more mono or di-chlorinated PCB congeners detected. Several method blanks had detections across the entire PCB homolog range. Method blanks had as few as none and as many as 50 detected PCB congeners. Under this high resolution method that quantifies 209 PCB congeners with several coelutions, it is common to have some congeners detected in method blanks. Environmental sample detections were qualified as non-detect by the contract validator whenever sample concentrations were less than five times the method blank concentration. This potentially resulted in some low bias for congeners detected above the method blank concentration but below five times the method blank.

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.

5.10 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 27). This section summarizes the data for these parameters during the study period and discusses potential relationships to the measured chemical fluxes. Potential relationships were evaluated between metals, including mercury, HPAHs, PCBs and total dioxin/furan fluxes and weather and particle parameters. Relationships between weather parameters and fluxes at Kent SC station were not tested because of the short time frame in which samples were collected at this location.

Table 27. Weather and particle data available by station.

Parameter	Beacon Hill	Duwamish	South Park	Kent	Enumclaw
Air Temp.	X	X		X	X ^d
Temperature Inversion	X ^b	X	X	X	X
Rainfall ^a		X	X	X	X
PM 2.5	X	X	X	X	
Wind Rose	X	X		X	X
Wind Speed	X ^c	X		X	X ^c

^a There are no rainfall meters at PSCAA stations. Rainfall data was acquired from King County's Hydrological Information Center database at rainfall stations closest to the air sampling stations (See Section 5.10.2). For Duwamish and South Park stations, just one rainfall gage was available to represent them (the one closest to South Park).

^b Temperature inversion days were calculated based on temperature from two different altitudes monitored at Sand Point. These were considered locally representative of the five sampling stations.

^c Wind data available measured by propeller. Other wind data for Duwamish and Kent stations were measured using sonic methods.

^d A data gap exists for the Enumclaw station resulting in a lack of temperature data to cover the last sample deployed in the study period. The flux for this last sample was therefore not included in statistical testing with temperature data.

5.10.1 Air Temperature

Historical air temperature data were available at the Puget Sound Clean Air Agency (PSCAA) air quality graphing tool website (<http://airgraphing.pscleanair.org/>) only for their Beacon Hill, Duwamish Valley, Kent and Enumclaw air monitoring stations. These monitoring stations are co-located with the locations sampled for this King County study. Hourly air temperature data were downloaded for these stations and overlaid for the study period (Figure 51). More extreme temperatures occurred in Kent than Duwamish or Beacon Hill stations but overall temperature was similar between locations over time.

To prepare the temperature data for correlation testing, average daily temperature was calculated for each deployment period for which chemical flux was sampled. Because of the

proximity of Duwamish to South Park, temperature data for Duwamish were also paired with South Park fluxes for correlation testing.

A potentially positive relationship between air temperature and metals flux was identified and examined using Spearman's rank order correlation. Temperature and flux data for all four locations were pooled for testing. The correlations for all metals except silver were significant ($p < 0.05$) in a positive relationship; however, the correlation coefficients were 0.5 or less indicating that temperature is not very predictive of chemical fluxes. The strongest correlation was seen for vanadium with an $r_s = 0.50$ (Figure 52). Metals showing a positive relationship include heavy metals such as lead, which are predominately in particulate phase at ambient temperatures (Murphy et al. 2007). The positive association between temperature and metals flux may be more directly related to the frequency of rainfall and less to temperature. The study locations experience sustained periods without precipitation. A process called coagulation produces larger particles from fine particles through collision and adhesion (NARSTO 2004). These larger particles have greater mass and are more likely to settle on surfaces. It is possible that the infrequency of precipitation during the dry season results in higher particle atmospheric concentrations and subsequently greater deposition rates. See Section 5.7.2 for an evaluation of dry period compared to wet period fluxes.

Correlations between PCBs or dioxin/furan flux and temperature were not significant ($p > 0.05$). Because individual PAHs span an array of molecular weights which affects their affinity for the gaseous or particulate phase, statistical testing of multiple PAHs as HPAHs may preclude the ability to detect significant differences. Thus, correlation with temperature was examined for indeno(g,h,i)perylene, an HPAH with a high affinity for particulates. Temperature data were prepared for correlation testing the same way as for metals: average daily temperature was calculated for each deployment period for which chemical flux was sampled. Temperature and flux data for all four locations (Beacon Hill, Duwamish, South Park and Kent) were pooled for testing. The relationship between temperature and indeno(g,h,i)perylene flux was not significant ($p > 0.05$) according to Spearman's rank order correlation.

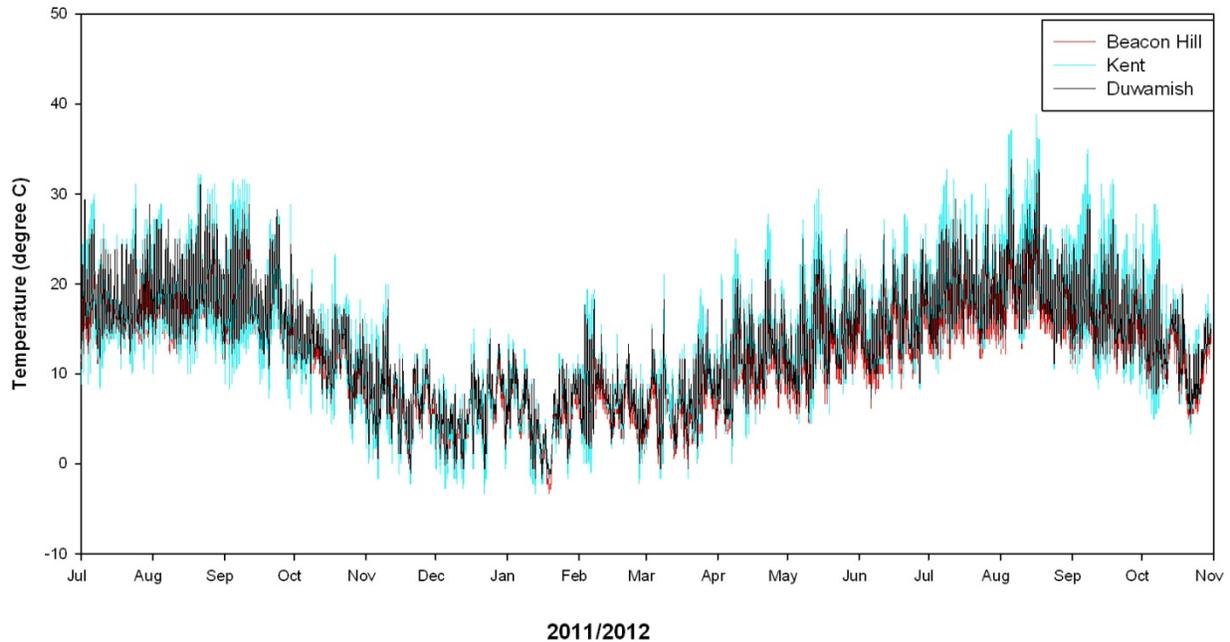


Figure 51. Hourly Temperature Over the 2011/2012 Study Period at Beacon Hill, Kent and Duwamish Stations.

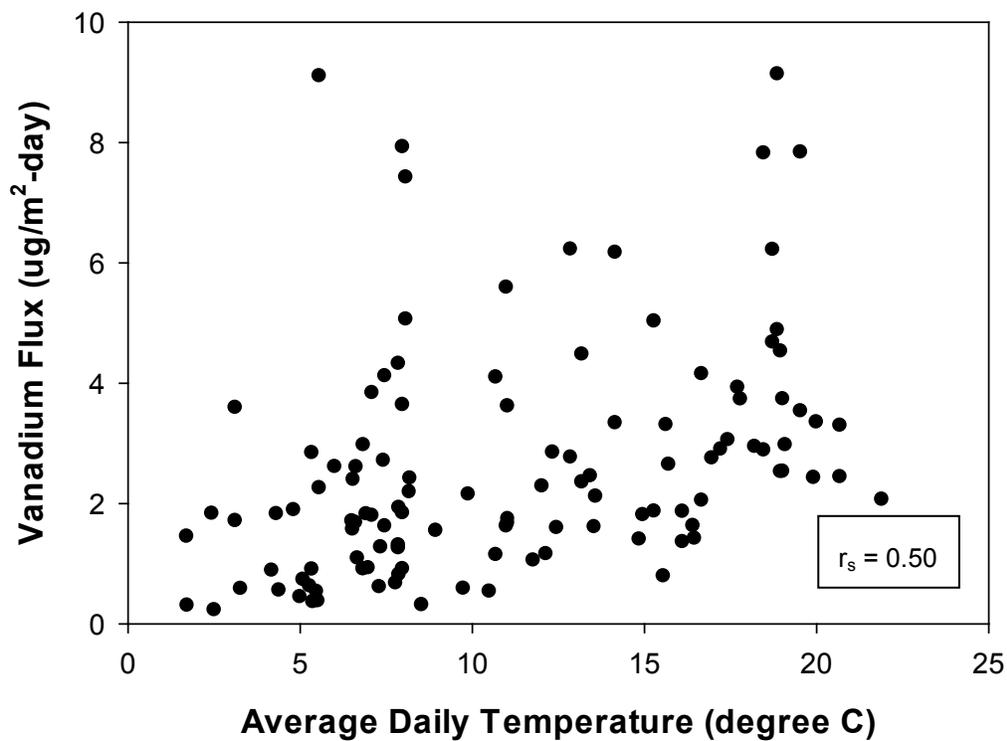


Figure 52. Relationship Between Temperature and Vanadium Flux

5.10.2 Temperature Inversion

Temperature inversions occur frequently in the Puget Sound area and are known to cause poor air quality. To investigate the potential influence of inversions on air fluxes, correlations were conducted with metals and HPAH contaminant fluxes against number of inversion days per deployment period. Temperature data collected at two elevations were used to estimate how many days of inversion occurred during each sampling period. The historical temperature measurements were taken every 30 minutes using a vertical profile instrument at Sand Point and provided by PSCAA (Erik Saganić, personal communication). PSCAA calculated the percent of day with temperature inversion using the lowest two altitude measurements, typically 115 and 240 meters. Two definitions of inversion days were tested: days with greater than 50% inversion hours and days with greater than 75% inversion hours. The temperature data at Sand Point were assumed to represent inversion conditions at all the stations and, therefore, the number of inversion days per deployment period were paired with Beacon Hill, Duwamish, South Park, Kent and Enumclaw flux data for analysis. The analysis was repeated excluding Enumclaw in case this station was too far from Sand Point to be represented well by the inversion data.

Based on testing data for all five stations, temperature inversion was significantly and negatively correlated with arsenic, copper, nickel, vanadium only when inversion was defined as days with greater than 75% inversion hours. However, the correlation coefficient was -0.333 or less showing a very weakly predictive relationship. Only mercury was significantly correlated when inversion was defined as days with greater than 50% inversion hours ($r_s = -0.186$). Without the Enumclaw station included, correlation analysis showed a significant and negative relationship between inversion (with >75% inversion hours) and all metals except cadmium and silver. The correlation coefficients were similarly weak as those from the correlations including Enumclaw data.

5.10.3 Rainfall

PSCAA does not provide downloadable precipitation data for their monitoring stations. Therefore, daily rainfall data were downloaded from the King County Hydrological Information Center database (<http://green.kingcounty.gov/WLR/Waterres/hydrology/GaugeTextSearch.aspx>) for gages (Hamm Creek-hau, Sequoia Jr. HS, Kent -SEQU, and Enumclaw-44u) in the areas of the Duwamish River Valley, Kent, and Enumclaw. No gages were located at Beacon Hill. Daily rainfall maxima were similar between locations with a large storm occurring in late November 2011 and distinctive dry periods in August and September of both years (Figures 53-55). July 2011 and 2012 were also relatively dry with fewer than three rain events. The total rainfall for the first 12 months of the study period¹² was compared to the

¹² The complete study period was more than a year. The original study period was scheduled for one year (August 2011-July 2012). It was extended to replace samples missed during the first year and collect more paired data in Kent. Rainfall data for the first twelve months was selected to encompass the core sampling period and avoid overestimating total annual rainfall.

total annual rainfall over the last 15 years at Enumclaw (Figure 56). Total rainfall for the first 12 months of the study falls above the median and below the 75th percentile of the total annual rainfall over the last 15 years (Figure 56) indicating precipitation over the study period was representative of recent years.

A negative relationship between rainfall and chemical flux for metals, including mercury, and PAHs was suspected upon visual examination of scatterplots. To prepare the rainfall data for correlation testing, total rainfall was calculated for each deployment period for which chemical flux was sampled. Rainfall data from the King County Hamm Creek rain gage (hau) near South Park was used to pair with South Park and Duwamish fluxes because of the proximity of these two stations and their location in the Duwamish River Valley. Beacon Hill fluxes were not included in this analysis because of the lack of a rainfall gage and its substantially greater altitude than the Duwamish River Valley. Rainfall and flux data for all four locations (Duwamish, South Park, Kent and Enumclaw) were pooled for testing. Correlation testing found significant negative relationship between rainfall and fluxes of six metals: arsenic, chromium, copper, nickel, vanadium and zinc. The relationship between rainfall and fluxes of these metals showed a weaker relationship than between temperature and metals flux with coefficients (r_s) less than -0.4. The highest coefficient was for zinc ($r_s = -0.35$). No significant correlations were found between rainfall and HPAH, total PCBs or total dioxin/furan fluxes.

To examine a potential relationship between wet and dry periods, the flux data for each station were combined then divided into two groups. The wet period group was defined as samples deployed during months of October through May. The dry period group was defined as samples deployed during months of June through September. Nonparametric testing determined that fluxes were significantly higher ($p < 0.05$) in the dry period for all metals except cadmium, mercury and silver. However, the weak relationships between rainfall and chemical flux indicate that rain is not the primary factor determining the seasonal difference observed in this study. HPAH, total PCBs and dioxins/furan fluxes were not significantly different during wet compared to dry periods.

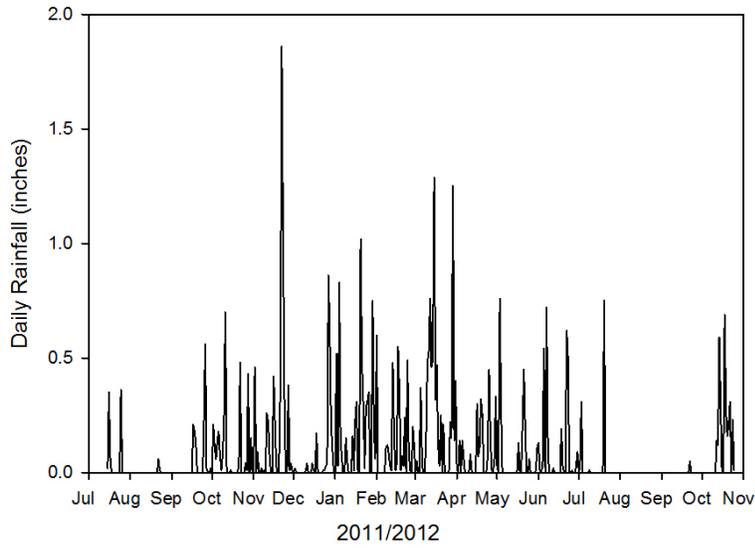


Figure 53. Average Daily Rainfall During the 2011/2012 Study Period at South Park.

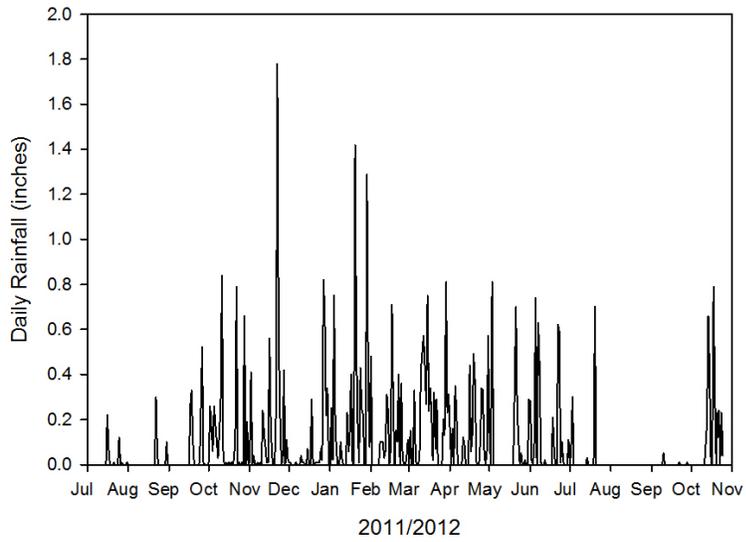


Figure 54. Average Daily Rainfall During the 2011/2012 Study Period at Kent

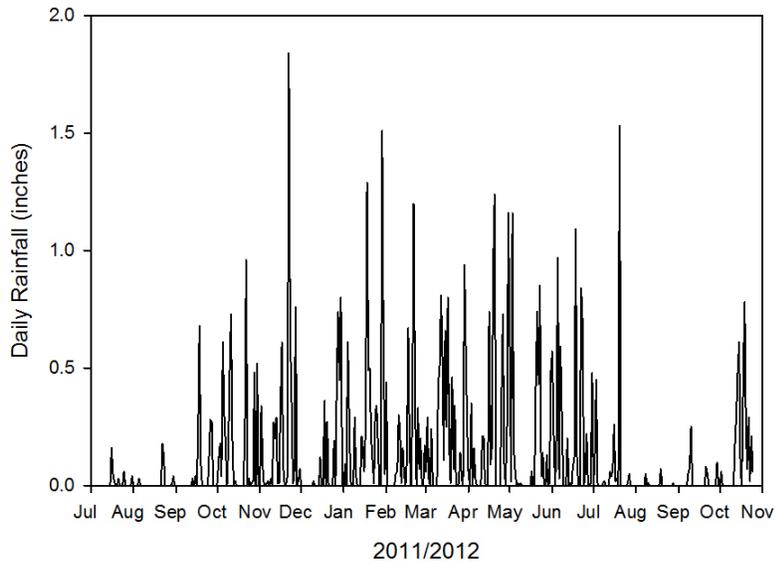


Figure 55. Average Daily Rainfall During the 2011/2012 Study Period at Enumclaw

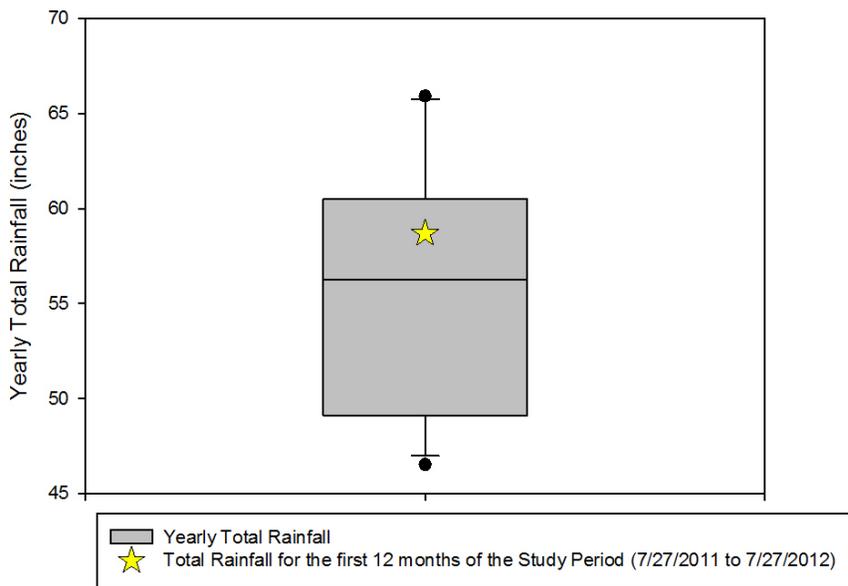


Figure 56. Total Rainfall for First Twelve Months of Study Compared to 15 Yr - Yearly Total Rainfall at Enumclaw

5.10.4 Fine Particles (PM 2.5)

Air concentrations of fine particles ($<2.5 \mu\text{m}^3$ or PM 2.5) are monitored at all PSCAA air monitoring stations except Enumclaw. Daily PM 2.5 data measured by nephelometer or partisol¹³ were downloaded from the PSCAA air quality graphing tool for Beacon Hill, Duwamish, South Park, and Kent stations. Washington Department of Ecology no longer monitors the larger size fraction of particle size concentrations (PM 10) at any of the corresponding air quality monitoring stations for this project. Therefore, historical data were only available for fine particulates. Average daily concentrations of fine particulates were lowest at Beacon Hill and reached the highest levels at Kent station (Figures 57-60). The average daily concentrations of fine particulates reached values approximately twice as high at Kent compared to the Beacon Hill station. Although the magnitudes of peaks vary by site, the pattern of PM 2.5 peaks and valleys generally agree across stations. Greater particle concentrations are often seen at times of greater home-heating needs. In winter months, the largest source of particulates is wood-stove and fireplace burning (PSCAA 2013). Other, minor sources include mobile sources, outdoor fires and industry. Residential land use in the vicinity of South Park station, industrial and mobile sources near Duwamish and mobile sources at Kent stations may all elevate fine particulates in these areas. Comparatively lower PM 2.5 levels at Beacon Hill may be due to the higher elevation at this station and lack of industrial and intense mobile sources.

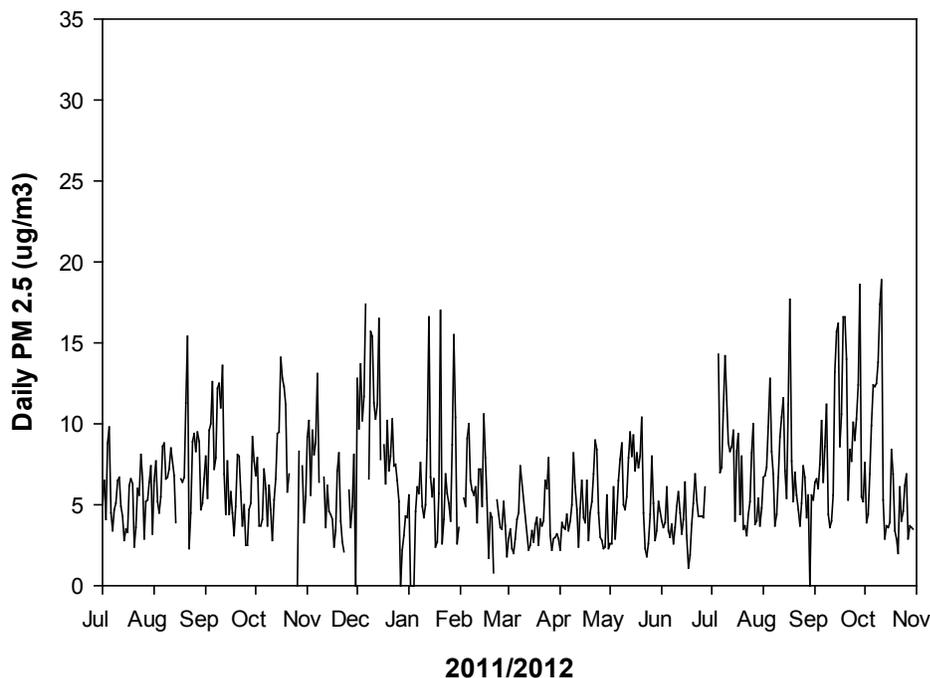


Figure 57. Average Daily Fine Particulate Concentration at Beacon Hill

¹³ Nephelometer data was preferred to partisol data. Where only partisol data were available, Teom FEM data were used to fill in time gaps.

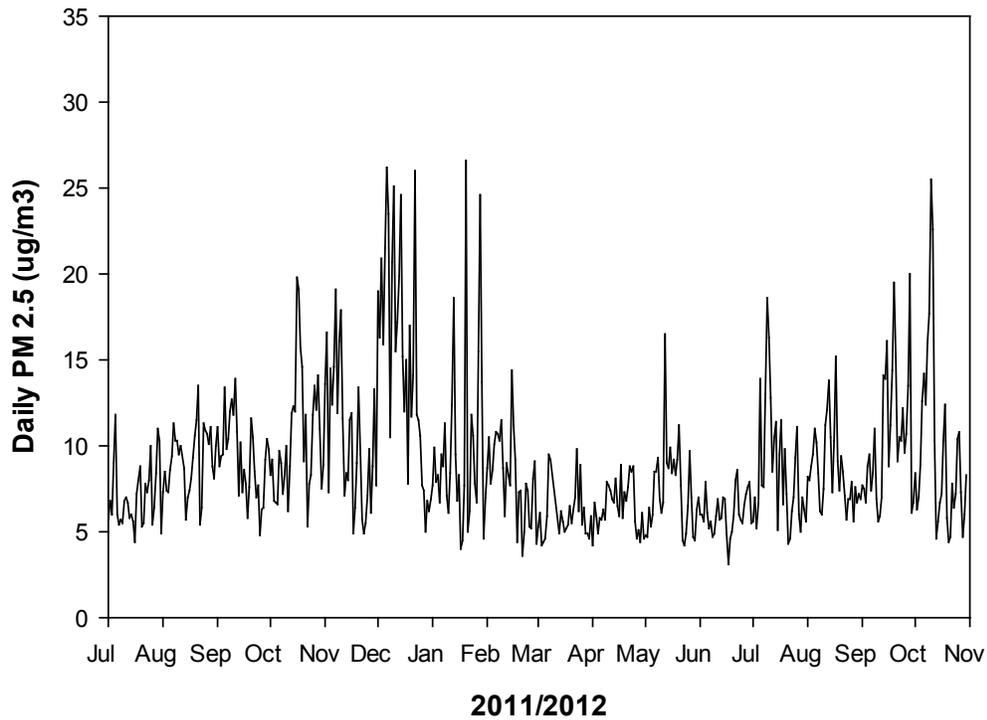


Figure 58. Average Daily Fine Particulate Concentration at Duwamish

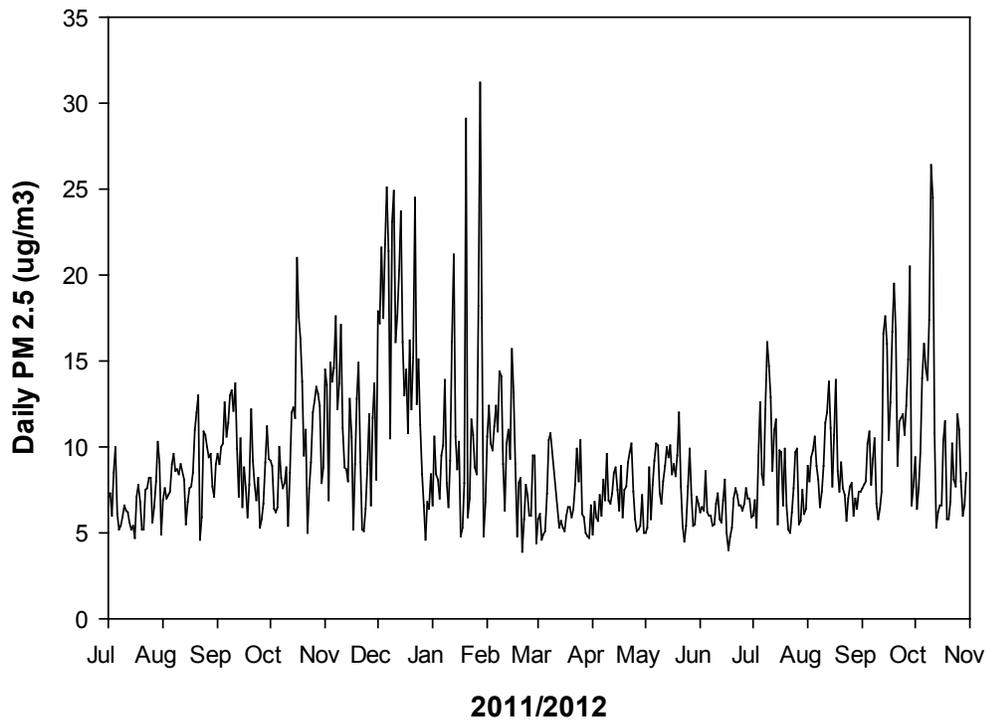


Figure 59. Average Daily Fine Particulate Concentration at South Park

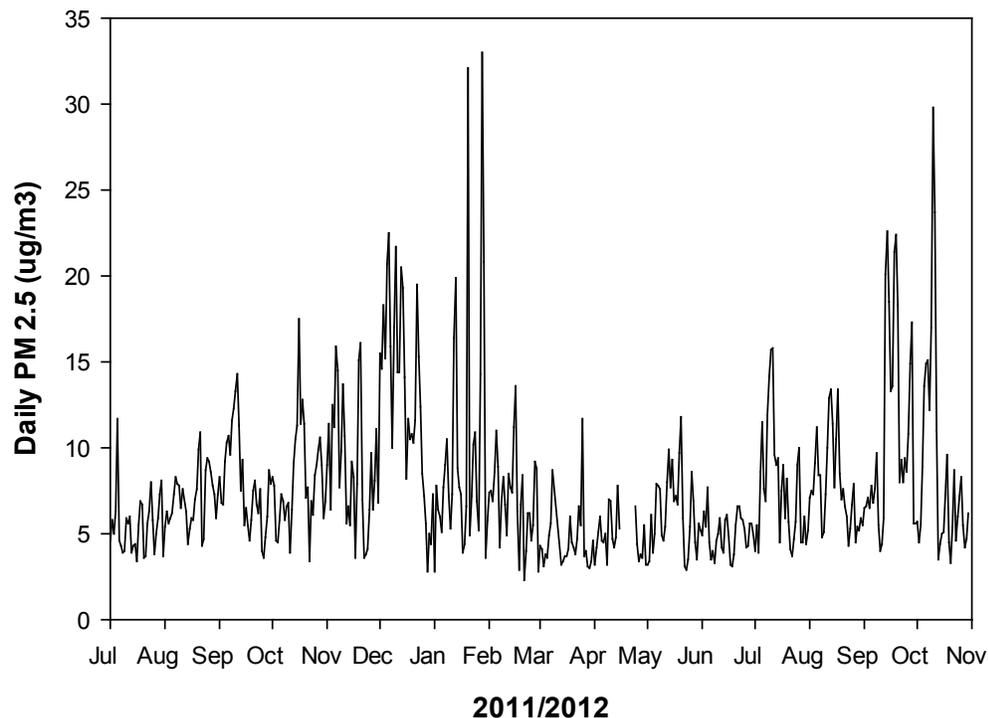


Figure 60. Average Daily Fine Particulate Concentration at Kent

The average daily PM 2.5 was calculated for each deployment period that flux was sampled. PM 2.5 data from all four stations were pooled and correlations were conducted with metals and HPAHs fluxes. Fluxes of most metals (arsenic, cadmium, chromium, copper, nickel and lead) were found to be significantly and positively correlated with PM 2.5. Mercury flux was also significantly correlated with PM 2.5 but in a negative relationship. Correlation coefficients indicated the predictive power of all metals correlations was weak (<0.4). A relationship between particulate concentrations and HPAHs fluxes was expected because multiple sources of PAHs emit particulates such as diesel exhaust and wood smoke. However, HPAH flux and PM 2.5 were not significantly correlated ($p>0.05$).

This same correlation analysis was conducted for total PCBs and total dioxin/furan flux data. A significant ($p<0.05$) and moderately strong ($r^2 = 0.53$) positive relationship was found between total PCBs flux and PM 2.5 concentrations (Figure 61). However, the correlation between PM 2.5 and total dioxin/furan flux was not significant.

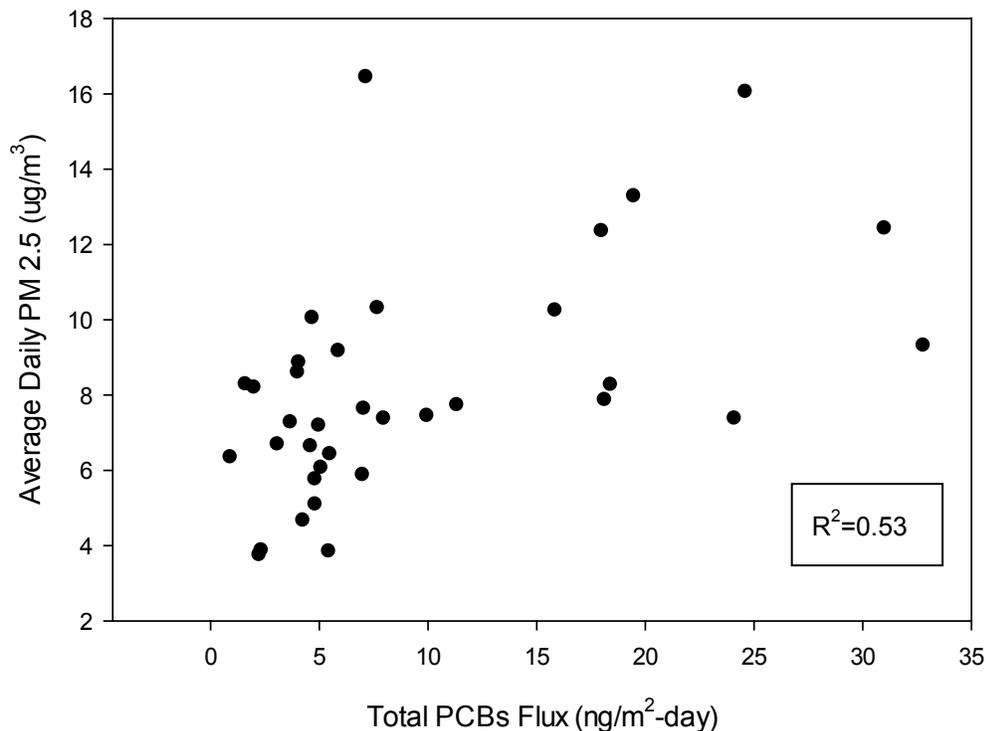


Figure 61. Relationship Between PCBs Flux and Fine Particulates (PM 2.5)

5.10.5 Wind

As a transport mechanism, wind may play a role in the deposition rates of contaminants. The potential influence of wind speed on chemistry fluxes was tested using the following approach. Wind speed data were downloaded from the PSCAA air quality graphing tool website for Beacon Hill, Duwamish, Kent and Enumclaw; wind speed data for the South Park station were not available. The average wind speeds were calculated for each deployment period and tested for correlations with flux data for all metals, HPAHs, PCBs, and dioxins/furans. Correlation testing showed a significant and positive relationship with average wind speed for cadmium, mercury, and lead. Correlation coefficients showed low predictive power for cadmium and mercury (<0.4) and moderate predictive power for lead (0.6). No significant correlations were found between wind speed and other metals, HPAHs, PCBs or dioxins/furans fluxes.

The available wind roses for the study period are provided here. The PSCAA website tool for creating wind roses was used to download and summarize wind data from the four air monitoring stations where data were available: Beacon Hill, Duwamish, Kent and Enumclaw (<http://www.pscleanair.org/airq/windrose/default.aspx>). Over the study period, the prevailing winds at Beacon Hill mainly came from the SE/S/SW or the NW (Figure 62). At Duwamish, the prevailing winds during the study period came from the S and NW (Figure 63). The prevailing winds at Kent came from the SE/S/SW (Figure 64). At Enumclaw, the prevailing winds came from the SW or ENE/NE (Figure 65).

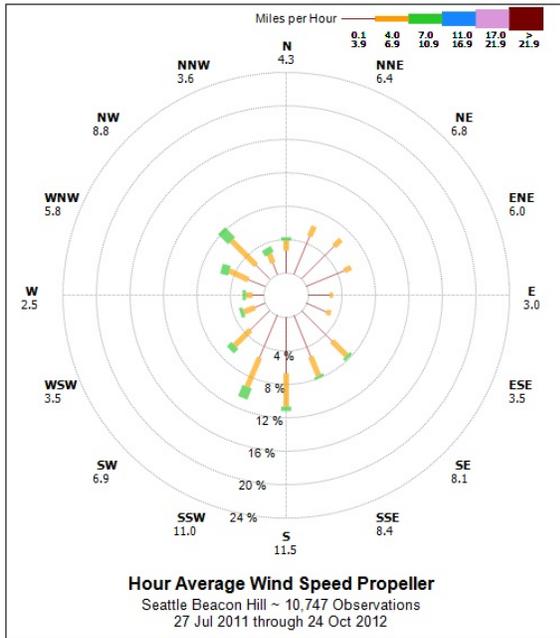


Figure 62. PSCAA Wind Rose for Beacon Hill During the 2011/2012 Study Period.

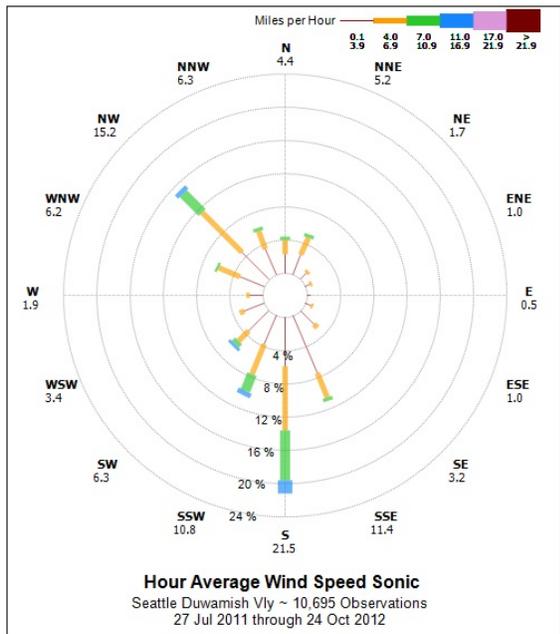


Figure 63. PSCAA Wind Rose for Duwamish During the 2011/2012 Study Period

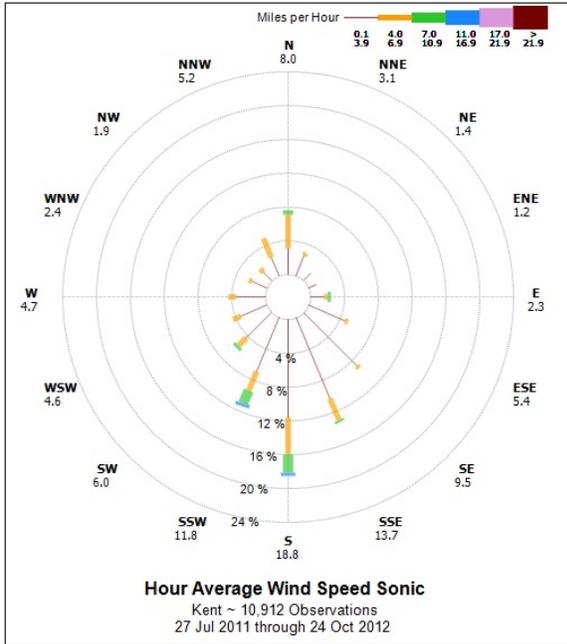


Figure 64. PSCAA Wind Rose for Kent During the 2011/2012 Study Period

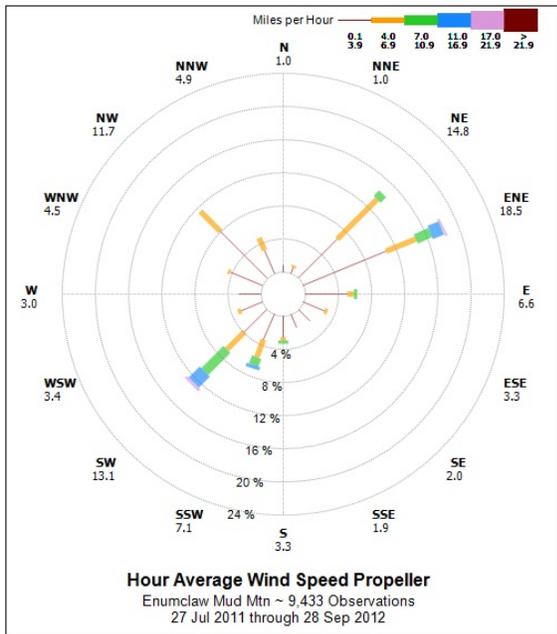


Figure 65. PSCAA Wind Rose for Enumclaw During the 2011/2012 Study Period.

5.10.6 Multivariate Analysis of Environmental Variables with Metals Flux

PCA analysis conducted on metals flux data for all stations except Kent SC 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 station and fluxes at South Park, Kent, and Beacon Hill were in between (Figure 66). Only the first axis was statistically significant by Monte Carlo permutation tests and used for interpretation. Correlation loadings analysis found that nickel accounted for most of the variation in metals fluxes, followed by vanadium, zinc, and chromium/copper (Table 28). PerMANOVA revealed similar metal deposition among most stations; metals fluxes at Enumclaw were significantly different from the rest of the stations (Figure 67; stations that do not share letters are significantly different).

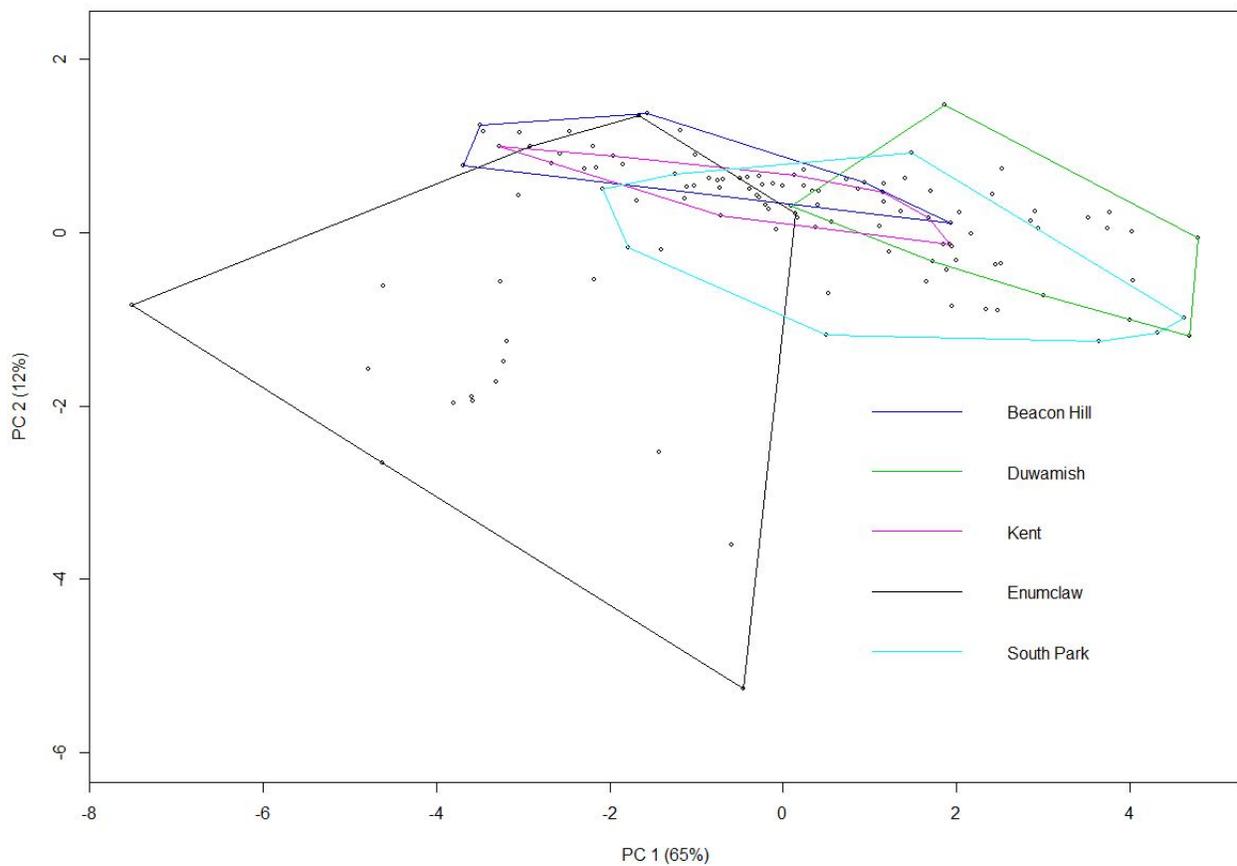


Figure 66. PCA of metal flux data at five King County sites.

Table 28. Metal variable correlation loadings of each principal component (PC).

	PC1	PC2
Arsenic	0.806	
Cadmium	0.787	
Chromium	0.863	
Copper	0.863	0.421
Lead	0.583	-0.725
Mercury	0.598	0.708
Nickel	0.913	
Vanadium	0.879	
Zinc	0.878	

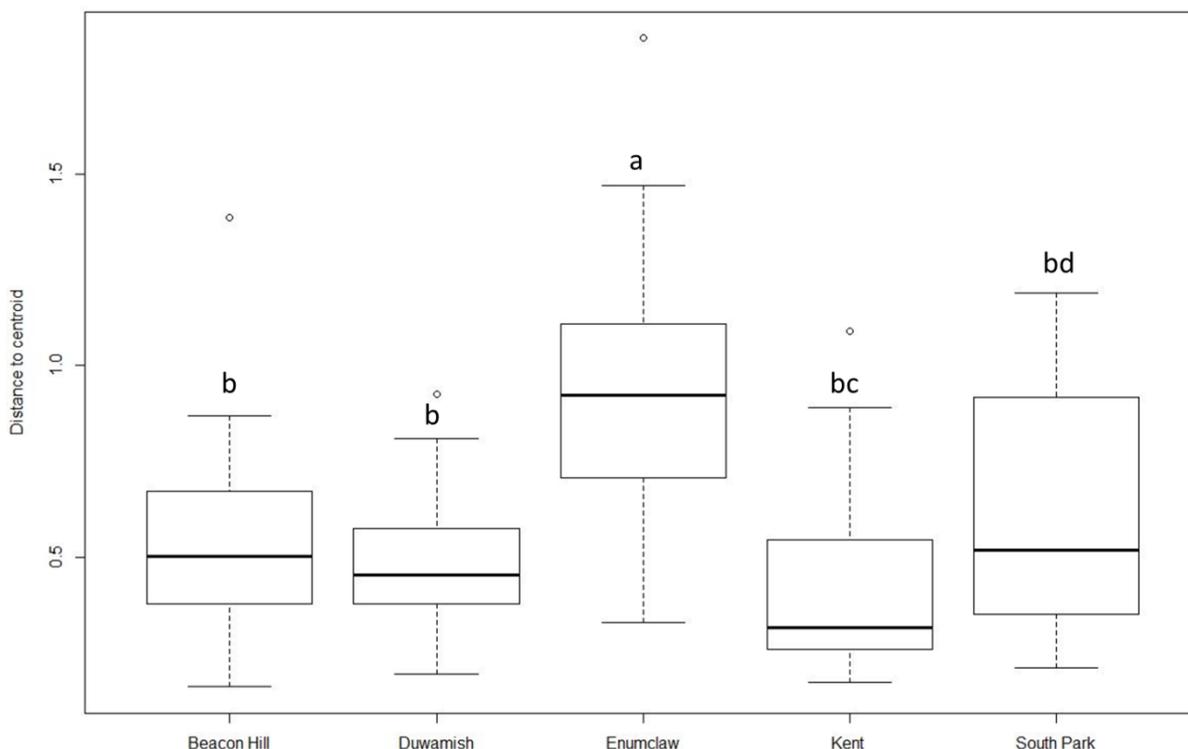


Figure 67. Boxplot of perMANOVA site variation using the Euclidean dissimilarity coefficient calculated to the centroid of the group.

Redundancy analysis was conducted using Beacon Hill, Duwamish, and Kent station metals flux data and average temperature, temperature inversion days, total rainfall, and PM 2.5 (For parameter selection rationale see Section 4.1.5). To maximize the number of environmental variables in the redundancy analysis, the average temperature data for Duwamish was assumed to be representative for South Park. Preliminary redundancy analysis determined that temperature inversion days was an insignificant factor. Thus, it was excluded in the final analysis.

The variance captured by the environmental variables explains 48% of the total variance in metals deposition. F-statistics from ANOVA showed that PM 2.5 ($F=22.85$, $p = 0.01$) is the most important contributing factor followed by wind speed ($F=19.51$, $p = 0.01$), temperature ($F=16.45$, $p = 0.01$) and rainfall ($F=3.42$, $p = 0.07$). The redundancy analysis ordination determined wind speed is a strong driver of cadmium and mercury presence (Figure 67). Copper was strongly influenced by fine particulate concentrations. High temperatures drive chromium, lead and zinc fluxes. Vanadium, zinc, and nickel deposition were associated with both particulate size and increased temperature. Total rainfall did not significantly influence metals deposition. Multivariate analyses were not conducted on PCB or dioxin/furan flux data because of the small sample sizes.

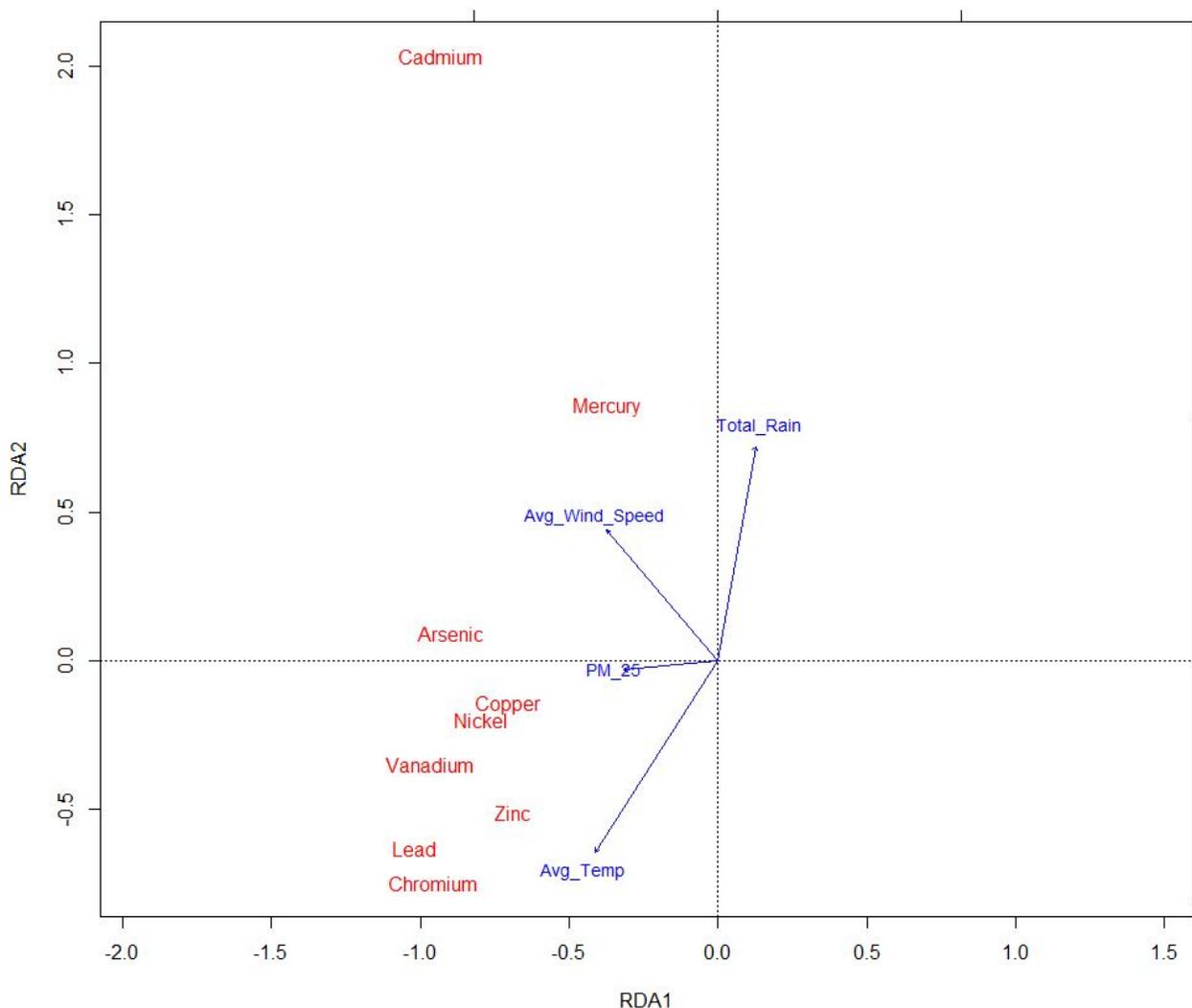


Figure 68. RDA graph of metal deposition and environmental variables at Beacon Hill, Duwamish, and Kent sites.

The stepwise multiple regression of individual metals and HPAH fluxes at Beacon Hill, Duwamish and Kent stations found that PM 2.5 significantly influenced HPAH flux (Table 29). The regression results also verified that PM 2.5, wind speed and temperature significantly influenced deposition of most metals at these stations.

Table 29. Significant ($p < 0.05$) contributing environmental variables to metal and total HPAH deposition at Beacon Hill, Duwamish, and Kent sites.

	Temperature	Total Rain	Wind Speed	PM 2.5	Inversion Days
Arsenic	x		x	x	
Cadmium			x		
Chromium	x		x	x	
Copper				x	
Lead	x		x	x	
Mercury			x		
Nickel	x			x	
Vanadium	x		x	x	
Zinc	x		x	x	
HPAHs				x	

6.0. DISCUSSION AND CONCLUSION

This section presents general overview of comparisons among sampling locations in this study as well as comparison to another regional study. Finally, overall findings are summarized followed by recommendations for further work.

6.1 Comparisons between Stations

In this study, chemical fluxes varied with location, sometimes significantly. Overall, fluxes for the two stations located in the Duwamish Valley (Duwamish and South Park) proved to be higher than stations outside the Valley. For metals, the Duwamish station median flux ranked highest of all stations for seven of ten metals analyzed (Table 30). The median flux at South Park ranked highest for the remaining three metals analyzed. In addition, fluxes at the Duwamish and South Park stations were often found to be statistically significantly higher than one or more other stations. For example, arsenic, cadmium, copper, lead, nickel and vanadium fluxes were significantly higher at Duwamish than Beacon Hill or Kent stations. In contrast, the median flux at Enumclaw ranked lowest of all stations for most metals. The ratios of each station's median flux to the lowest station median flux for each metal demonstrate the magnitude of difference in median flux between locations (Figure 68). The largest differences between stations occur for copper, nickel, vanadium and zinc. The median copper flux at Duwamish is over thirteen 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.

Table 30. Station Rankings Relative to Median Flux

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

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

Rankings for organics median fluxes were somewhat different mainly because of microscale effects on HPAHs and dioxins/furans at Kent. Ranked second after Kent for HPAHs is the Duwamish station and for dioxins/furans is the South Park station. HPAH fluxes also tested significantly higher at Kent and Duwamish stations compared to all other stations except Kent_SC. Dioxin/furan fluxes were significantly higher at Kent and South Park than Enumclaw and those at Kent were also significantly higher than Duwamish station. PCB fluxes did not appear affected by microscale effects at the Kent station and PCB fluxes at South Park and Duwamish were higher than at other stations. HPAHs, PCBs, and dioxin/furan fluxes at Enumclaw were consistently lower than any other station. Notably,

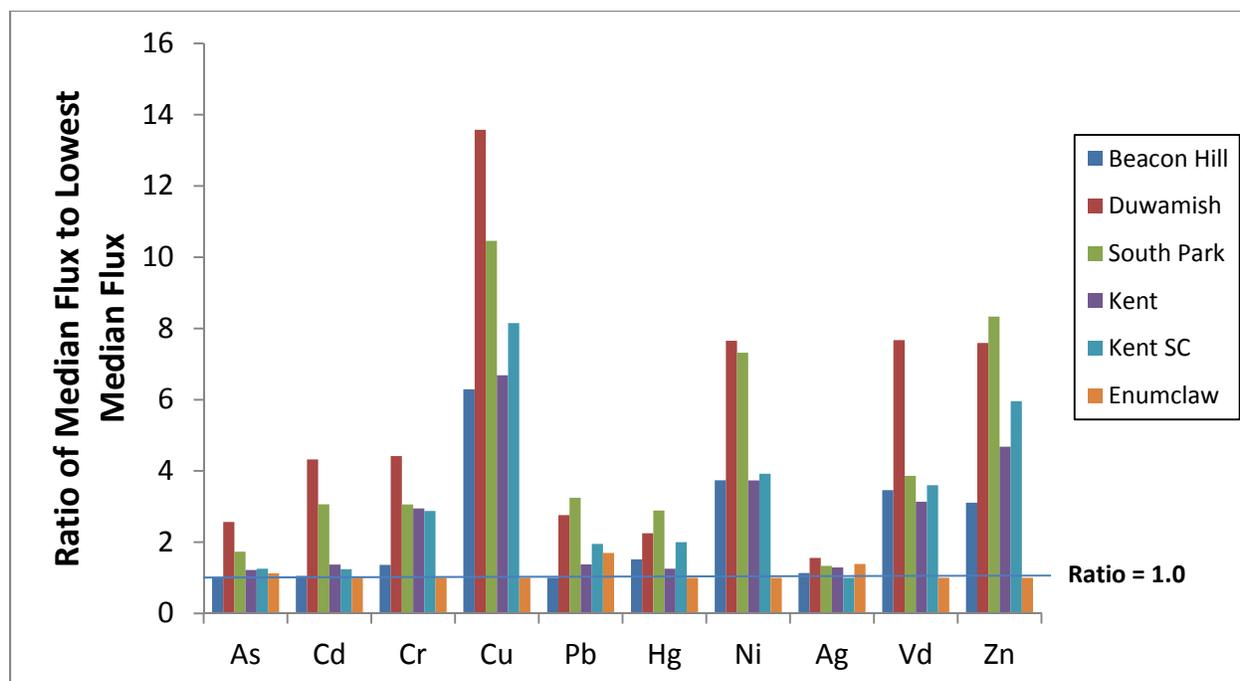


Figure 69. Ratios of Median Flux to Lowest Median Flux For Metals

organics fluxes measured at the Beacon Hill station were usually lower than both stations in Kent. 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 dioxin/furan totals. The median fluxes at Kent station are approximately 50 times higher than at Enumclaw, the station with the lowest median dioxin/furan totals. Other than Kent, much smaller differences exist between stations for dioxin/furan totals – within a factor of five. 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). The median PCB flux at South Park was more than double the median flux at Duwamish and almost 25 times higher than at Enumclaw. Both Duwamish and South Park are characterized by industrial land use; South Park also contains residential land use. It is unknown why PCB flux would be higher at South Park.

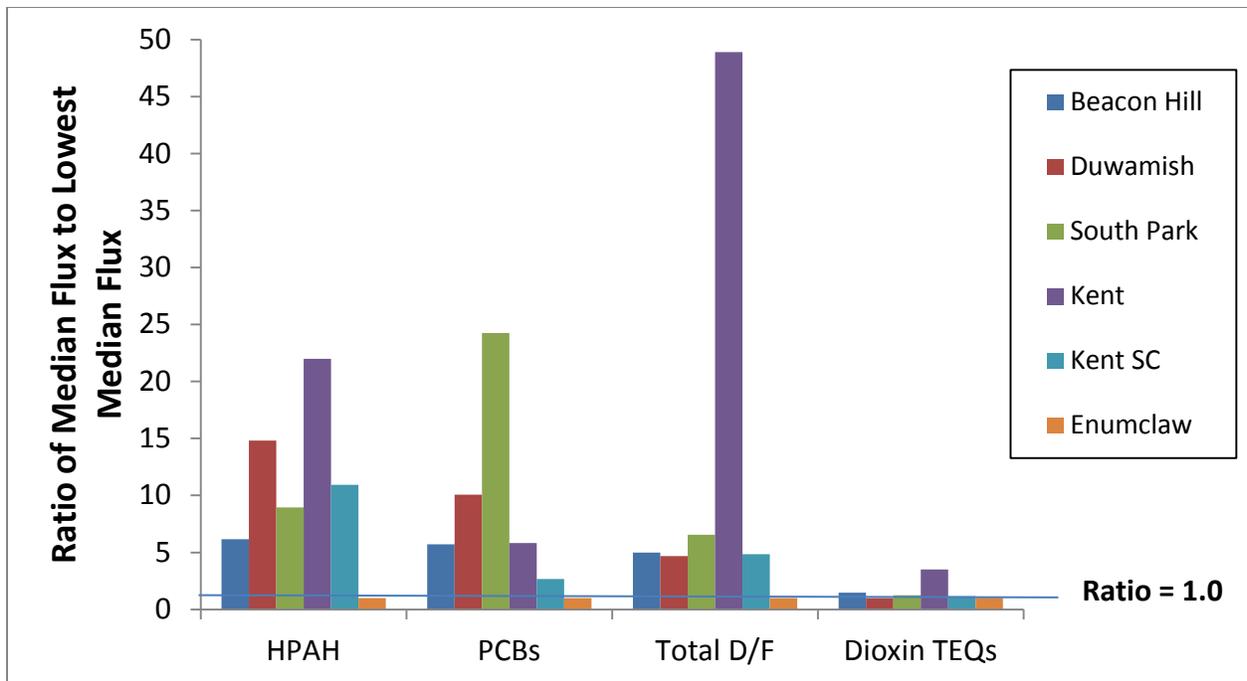


Figure 70. Ratios of Median Flux to Lowest Median Flux for Organics

6.2 Congener Profiles

The relative contribution of PCB congeners to the total flux varied between samples but PCB-129 dominated in samples at Beacon Hill, Duwamish, South Park, and Kent SC. PCB-110 dominated 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 all stations except Kent SC, where other homologues contribute nearly the same amount, and Enumclaw, where Tri- and Penta-CBs are the dominant homologues. 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. In general, the contributions of low-chlorinated PCB congeners increase and those of high-chlorinated PCB congener decrease with distance from the Duwamish and Beacon Hill stations.

The OCDD congener consistently comprised at least 60% of total dioxin/furan flux. Average dioxin/furan congener contributions are generally consistent between Beacon Hill, Duwamish, 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 contributions from dioxins and less from OCDF. The opposite pattern was seen at Kent station.

6.3 Comparison to Other Regional Studies

Overall, chemical fluxes were generally higher in areas with greater urban development. This pattern was also observed in the Puget Sound region by EPA (1991) and Brandenberger et al. (2010). Brandenberger et al. (2010) measured bulk air deposition

during three periods (Fall 2008, winter and spring 2009, and summer 2009) at eight locations in the Puget Sound region using a passive sampling method similar to this King County study. The objective of the Brandenberger et al. (2010) study was to collect data to calculate atmospheric deposition loading to Puget Sound. Therefore, all but one station, Tacoma Commencement Bay (TCB), was located on the Puget Sound shoreline. TCB was located further from the water at the University of Washington campus in the Port of Tacoma.

Between 17 and 19 events were sampled at each location over the study except for Tyee Marina which was only sampled six times. Median fluxes of total PCBs (based on 18 congeners) and metals from Brandenberger et al. (2010) were significantly higher at the industrial location in Tacoma (TCB) compared to a second station on the shore in Tacoma (Tyee Marina) and the study's other locations on shorelines in urban, suburban and rural areas (Table 31). EPA (1991) also measured higher metals fluxes in urban industrial areas than at less industrial and suburban areas of Tacoma. Although the King County study also observed higher metals and PCB fluxes in industrial areas, the calculated fluxes are substantially higher than those calculated by Brandenberger et al. (2010). This may be related to the more inland location and highly developed nature of King County study's stations. In addition, slightly lower total PCB fluxes would be expected from Brandenberger et al. (2010) because of the abbreviated list of congeners analyzed contrasted with the full congener list analyzed in this King County study. However, this is not likely to fully account for the magnitude of difference observed.

Table 31. Median Fluxes for Metals and PCBs from Brandenberger et al. (2010) and this King County Study

	Location	ng/m2-day	µg/m2-day						
		PCBs	Arsenic	Cadmium	Chromium	Copper	Nickel	Lead	Zinc
Puget Sound Shoreline Study Brandenberger et al. (2010)	Hood Canal ^a	0.24	0.11	0.017	0.19	0.61	0.29	0.3	4.8
	Nisqually River ^a	0.64	0.22	0.023	0.33	1.8	0.5	0.75	8.8
	Padilla Bay ^b	0.4	0.14	0.017	0.41	1.3	0.74	0.43	6.9
	Port Orchard ^a	0.39	0.15	0.015	0.23	1.1	0.48	0.38	4.7
	Sequim Bay ^a	0.32	0.13	0.018	0.63	1.6	1.6	0.53	5.5
	Tacoma Commencement Bay ^c	1.81	0.45	0.068	1.4	12	1.9	5.9	49
	Tyee Marina (Tacoma) ^c	0.45	0.2	0.021	0.24	2.7	0.7	1.1	11
	West Point ^c	0.57	0.15	0.017	0.35	1.4	0.81	0.57	6.8
King County Study	Beacon Hill	4.26	0.36	0.084	1.22	11	1.7	4.03	45.7
	Duwamish	7.51	0.93	0.34	3.94	23.7	3.48	11.1	112
	South Park	18.1	0.63	0.24	2.57	18.3	3.33	13.1	122
	Kent	4.35	0.44	0.11	2.61	11.7	1.7	5.54	68.8
	Kent SC	1.99	0.46	0.1	2.53	14.2	1.78	7.87	87.5
	Enumclaw	0.75	0.41	0.059	0.89	1.75	0.46	6.85	14.7

^a Dominated by rural and suburban land use

^b Dominated by rural and industrial land use

^c Dominated by urban and industrial land use

Note: PCBs in Brandenberger et al. (2010) were a total of 18 congeners; PCBs in the King County Study were a total of the full 209 congener list.

Median fluxes at the most rural station, Enumclaw, are between the two Tacoma stations (TCB and Tyee Marina) for PCBs, arsenic, cadmium, chromium, and zinc (Table 31). Copper and nickel median fluxes at Enumclaw are similar to the Tacoma shoreline station (Tyee Marina) and lead median flux at Enumclaw is just above the inland Tacoma station (TCB). Median fluxes of these chemicals at the most industrial stations in this King County study, Duwamish and South Park, were up to ten times higher than any stations in Brandenberger et al. (2010).

6.4 Additional Findings

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. Because of the high percentage (60%) of samples where results were not detected, any significant differences that may exist between stations could not be discerned.

An important conclusion from evaluation of the field blank spike samples for LPAHs was that the fluxes measured for acenaphthylene and anthracene were biased low due to loss during field deployment. As mentioned in Section 5.2, the passive sampling method used is not able to capture deposition from the gaseous phase as absorption. In addition, poor recovery of benzo(a)pyrene was observed sporadically in laboratory spike blanks resulting in a low bias for HPAH totals. These low biases should be considered when interpreting the LPAH and HPAH results from this study.

Multiple factors (i.e., temperature, inversion days, rainfall, wind speed, particle size, dry vs. wet periods) were examined which could influence the temporal variability of metals, including mercury, HPAHs, PCBs and dioxin/furan flux. Positive and significant correlations were found between cadmium, mercury, and lead fluxes and wind speed with lead having the strongest predictive power. While positive correlations were found between metals flux and temperature, the predictive power of that relationship was weak. A negative and significant relationship was found between total inversion days and most metals but the predictive power was weaker than temperature. Similarly, the significant relationship between rainfall and metals or HPAHs flux was weaker than temperature. However, dry period metals fluxes were significantly higher than wet period fluxes indicating a seasonal relationship. Higher metals fluxes in the dry season have been observed in the Puget Sound region in the past (EPA 1991). Also, fluxes of most metals (arsenic, cadmium, chromium, copper, nickel and lead) were found to be significantly and positively correlated with PM 2.5 but with low predictive power. HPAH flux was not found to be significantly correlated to PM 2.5. The relationship between PCBs and temperature and rainfall was not significant. However, there was a significant and positive correlation between PCBs and fine particle size. Correlations between dioxin/furan flux and temperature, rainfall and particle size were all insignificant.

Another general temporal trend indicated by the metals flux data is a decline in chemical flux over the fall wet period. This study only covered one fall season; however, a

precipitation scavenging process may be occurring whereby particles with adhered metals, having been suspended in the atmosphere during the dry summer season, are “flushed” out by a series of rainfall events in the fall. These rainfall events successively reduce the atmospheric particle concentrations. 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). This could explain the observed steady decrease in many trace metals fluxes from summer into early winter. This decrease can be more apparent at some stations compared to others and this may be due to the number or severity of local trace metals sources resulting in more visible changes. For example, copper fluxes at Enumclaw remained relatively low and varied little over the study period with an exception in one January sample. Cadmium fluxes at South Park were more than four times higher than Enumclaw and the early wet season decline in flux at South Park was very apparent.

Fine particles (PM 2.5) were observed to be up to twice as high at Kent than Beacon Hill and found to be significantly although weakly associated with PCBs and most metals fluxes. These findings suggest that although these two stations are less than two miles apart, there are substantial differences in conditions, perhaps related to wind circulation, altitude, and local sources (e.g., truck traffic), that impact fine particulate concentrations. Kim and Hopke (2008) 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. These results support the idea that impacts from local sources can differ substantially over short distances.

Lastly, multivariate analysis on Beacon Hill, Duwamish and Kent station metals and HPAH flux and environmental data determined that 48% of the variance in metals fluxes was explained by PM 2.5, wind speed, temperature, and rainfall. PM 2.5, wind speed, temperature were found to significantly influence metals flux but rainfall did not. The number of inversion days was found to be an insignificant factor for metals flux. PM 2.5 was found to be the only factor significant influencing HPAH flux.

6.5 Key Findings and Recommendations

The main findings of this bulk air deposition study are:

- Metals and organics fluxes generally relate positively to the degree of urbanization at stations with Enumclaw usually having the lowest fluxes and Duwamish or South Park often having the highest fluxes.
- Metals fluxes at Duwamish and South Park stations were often statistically significantly higher than other stations. For example, arsenic, cadmium, copper, lead, nickel and vanadium fluxes were significantly higher at Duwamish than Beacon Hill or Kent stations.
- Microscale effects can explain substantial differences between local stations as seen at the Kent station where significantly higher PAH and dioxin/furan fluxes were measured than another station in Kent located 0.3 miles away.

- 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.
- PCB fluxes at South Park were more than two times higher than Duwamish. The reasons for this difference are unknown.
- The PCB congener profile at Duwamish station was most similar to Beacon Hill; however, profiles at all stations but Enumclaw were generally similar. The PCB congener profile at Enumclaw was the most unique. Lower-chlorinated PCB congeners contributed more to total PCB flux in Enumclaw samples compared to other stations.
- Mean relative contributions of dioxin/furan congeners to the total flux were similar between Beacon Hill, Duwamish, South Park and Kent SC stations; there were some notable differences at Kent and Enumclaw stations.
- Metals fluxes generally decreased during the fall months into early winter, potentially due to precipitation scavenging.
- Metals fluxes are significantly higher in the dry season (July through September) than the wet season (October through June).
- Fine particulates (PM 2.5) concentrations were significantly correlated with most metals and PCBs fluxes but the correlations were only weakly to moderately predictive. Fine particulates concentrations were highest at Kent and lowest at Beacon Hill stations.
- Multivariate analysis found that PM 2.5, wind speed and temperature significantly influenced metals fluxes at Beacon Hill, Duwamish and Kent stations but rainfall did not. Also, PM 2.5 was the only environmental factor to significantly influence HPAH flux at these three stations.
- Based on the laboratory spike blank results, there is a potential for significantly low bias for all benzo(a)pyrene results in this study.
- LPAH results are biased low due to the sampling method and measured volatilization during field spike deployment, and are only provided for relative spatial comparison.

Additional data collection is recommended to supplement this study's PCB and dioxin/furan congener data and increase the likelihood of discerning seasonal trends and relationships with weather parameters and PM 2.5. Also, a third location, such as Georgetown, in the Duwamish River Valley using the same study design could help determine how much chemical fluxes differ with location inside the Duwamish River Valley.

7.0. REFERENCES

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