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# **Estimating PCB and PBDE Loadings to the Lake Washington Watershed: Final Data Report**

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**September 2013**



**King County**

Department of Natural Resources and Parks  
Water and Land Resources Division

**Science and Technical Support Section**

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

206-296-6519 TTY Relay: 711

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# Estimating PCB and PBDE Loading Reductions to the Lake Washington Watershed: Final Data Report

## Prepared for:

U.S. Environmental Protection Agency Region 10

## Submitted by:

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

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**King County**

Department of  
Natural Resources and Parks  
**Water and Land Resources Division**

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# Table of Contents

---

Executive Summary.....	viii
1.0. Introduction.....	1
1.1 Field Study Objectives.....	1
2.0. Methods.....	3
2.1 Sampling Station Locations.....	3
2.1.1 Ambient Waters.....	8
2.1.2 Stormwater Runoff.....	8
2.1.3 Combined Sewer Overflow.....	17
2.1.4 Highway Bridge Runoff.....	21
2.1.5 Atmospheric Deposition.....	21
2.2 Field Methods.....	22
2.2.1 Ambient Waters.....	23
2.2.2 Stormwater and Highway Bridge Runoff.....	26
2.2.3 Combined Sewer Overflow.....	29
2.2.4 Atmospheric Deposition.....	30
2.3 Measurement of Flow.....	33
2.4 Analytical Methods.....	33
2.4.1 PCBs.....	33
2.4.2 PBDEs.....	34
2.4.3 TOC, DOC and TSS.....	34
2.5 QAPP Modifications and Deviations.....	34
2.5.1 Decontamination Procedure for Autosamplers.....	34
2.5.2 PBDEs in Equipment Blanks.....	35
2.5.3 Scope Changes Due to Budget Restrictions.....	35
2.5.4 Change in CSO Station Location.....	36
2.5.5 Less Than Minimum Duration for a Stormwater Sample.....	36
2.6 Data Validation and Corrective Actions.....	36
2.7 Total PCB and PBDE Reporting.....	37
3.0. Results.....	39
3.1 Data Quality Objectives and Usability.....	39
3.1.1 Precision.....	39
3.1.2 Accuracy.....	41

3.1.3	Sensitivity .....	41
3.1.4	Bias .....	41
3.1.5	Completeness.....	41
3.1.6	Conventionals .....	44
3.1.7	Summary.....	44
3.2	Chemistry Results.....	44
3.2.1	Ambient Waters.....	45
3.2.2	Stormwater Runoff.....	54
3.2.3	Combined Sewer Overflow.....	57
3.2.4	Highway Bridge Runoff.....	59
3.2.5	Atmospheric Deposition.....	59
3.3	Flow.....	65
4.0.	Discussion.....	66
4.1	Comparison of Water Pathway Concentrations .....	66
4.2	Comparison with Other Studies .....	67
4.2.1	Ambient Waters.....	68
4.2.2	Stormwater Runoff.....	69
4.2.3	Highway Bridge Runoff.....	70
4.2.4	Combined Sewer Overflow.....	70
4.2.5	Atmospheric Deposition.....	71
5.0.	Summary .....	73
6.0.	References .....	76

## Figures

---

Figure 1.	Sampling stations for field study.....	7
Figure 2.	Kirkland stormwater station vicinity map. ....	9
Figure 3.	Stormwater station in Kirkland during base flow conditions. ....	10
Figure 4.	Renton stormwater station vicinity map. ....	11
Figure 5.	Stormwater station in Renton during base flow conditions. ....	12
Figure 6.	Mercer Island stormwater station vicinity map.....	13
Figure 7.	Stormwater station in Mercer Island during base flow conditions.....	14
Figure 8.	Seattle, Seward Park stormwater and CSO sampling locations. ....	15
Figure 9.	Seattle, Madrona stormwater sampling location.....	16

Figure 10.	Seattle, Fremont stormwater sampling location.....	17
Figure 11.	Seattle, Ballard 150/151 CSO sampling location. ....	19
Figure 12.	Seattle, Dexter CSO sampling location with local sewer piping.....	20
Figure 13.	Downspouts and settling basin under I-90 Bridge.....	21
Figure 14.	Prevailing winds at the Beacon Hill weather station during the study period (data from Puget Sound Clean Air Agency).....	22
Figure 15.	Stormwater sampling dates relative to Sea-Tac airport rainfall gage.....	28
Figure 16.	Stormwater outflow pipe with sampler inflow tubing under I-90 Bridge.....	29
Figure 17.	Atmospheric deposition sampler exterior.....	31
Figure 18.	Atmospheric deposition sampler interior with collection jar.....	32
Figure 19.	tPCB results for stream samples by date (2011-2012), replicates shown.....	46
Figure 20.	tPBDE results for stream samples by date (2011-2012), replicates shown.....	47
Figure 21.	tPCB results for river samples by date (2011-2012), replicates shown.....	49
Figure 22.	tPBDE results for river samples by date (2011-2012), replicates shown.....	50
Figure 23.	tPCB results for lake and ship canal samples by date (2011-2012), replicates shown.....	51
Figure 24.	tPBDE results for lake and ship canal samples by date (2011-2012), replicates shown.....	52
Figure 25.	t PCB results for stormwater samples including bridge runoff by date (2011-2012), replicates shown.....	55
Figure 26.	tPBDE results for stormwater samples including highway bridge runoff by date (2011-2012), replicates shown.....	56
Figure 27.	tPCB results for CSO samples by date (2011-2012), replicate shown.....	57
Figure 28.	tPBDE results for CSO samples by date (2011-2012), replicate shown.....	58
Figure 29.	tPCB results for atmospheric deposition samples by date (2011-2012), replicates shown.....	60
Figure 30.	tPBDE results for atmospheric deposition samples by date (2011-2012), replicates shown.....	61
Figure 31.	Average and standard deviation concentrations of tPCBs in major water pathways. ...	66
Figure 32.	Average and standard deviation concentrations of PBDEs in major water pathways...	67

## Tables

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Table 1.	Sampling station selection criteria (King County, 2011a) .....	3
Table 2.	Sampling station coordinates.....	5

Table 3.	River sampling events.....	23
Table 4.	Lake Washington composite sample aliquot collection depths by sampling date and sub-sampling locator.....	25
Table 5.	Montlake Cut and Locks Station composite sample aliquot collection depths by sampling date and locator.....	26
Table 6.	Stormwater sampling event dates, durations and flow volumes.....	27
Table 7.	CSO sampling event dates, durations, and overflow volumes.....	30
Table 8.	Atmospheric deposition sample deployment periods and duration.....	33
Table 9.	Precision of field replicates by sample type.....	40
Table 10.	Sampling stations and counts relative to completeness goals.....	43
Table 11.	QA/QC Frequency and laboratory acceptance criteria for conventionals.....	44
Table 12.	tPCB and tPBDE summary statistics for tributary samples combined in pg/L.....	47
Table 13.	Summary statistics for tributary sample conventionals results by flow regime in mg/L.....	48
Table 14.	tPCB and tPBDE summary statistics for river samples in pg/L.....	50
Table 15.	Summary statistics for river conventional parameter concentrations in mg/L.....	51
Table 16.	Lake Washington stratified and mixed lake composite tPCB and tPBDE summary statistics in pg/L.....	52
Table 17.	Lake Washington Ship Canal at Montlake and the Ballard Locks tPCB and tPBDE summary statistics in pg/L.....	53
Table 18.	Lake Washington stratified and mixed lake composite tPCB and tPBDE paired filtrate and solids results.....	53
Table 19.	Lake Washington stratified and mixed lake composite conventionals results in mg/L.....	54
Table 20.	Lake Washington Ship Canal at Montlake Cut and the Ballard Locks conventionals summary statistics in mg/L.....	54
Table 21.	tPCB and tPBDE concentrations in pg/L, all stormwater locations combined.....	56
Table 22.	Conventionals concentrations in mg/L, all stormwater locations combined by flow regime.....	57
Table 23.	tPCB and tPBDE concentrations in pg/L for all CSO locations combined.....	58
Table 24.	Conventionals concentrations in mg/L for all CSO locations combined.....	59
Table 25.	tPCB and tPBDE concentrations for highway bridge runoff in pg/L.....	59
Table 26.	Conventional results for highway bridge runoff in mg/L.....	59
Table 27.	Atmospheric deposition measured concentrations in primary samples with calculated deposition rates.....	62
Table 28.	Atmospheric deposition measured concentrations in replicate samples with calculated deposition rates.....	63
Table 29.	Air deposition rate (ng/m <sup>2</sup> /day) summary statistics by parameter and location.....	64

Table 30.	Post rinse air deposition funnel residual tPCB and tPBDEs .....	65
Table 31.	Lake Washington water concentrations of total PCBs and total PBDEs as back calculated from SPMD measurements (Sandvik, 2010) compared to current study.....	69
Table 32.	tPCB concentrations in pg/L for Lake Washington and Lower Duwamish Waterway locations combined.....	71
Table 33.	Daily atmospheric deposition fluxes of tPCBs and tPBDEs at Puget Sound urban air deposition stations (ng/m <sup>2</sup> /d) .....	71

## Appendices

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Appendix A	Data Validation memo
Appendix B	Electronic summary of all chemistry results

## EXECUTIVE SUMMARY

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This project collected and analyzed samples from receiving waters and five different pathways to support the development of mass loadings estimates of total polychlorinated biphenyls (tPCBs) and total polybrominated diphenylethers (tPBDEs) to Lake Washington and subsequently Puget Sound in Seattle, Washington. The receiving waters and pathways evaluated were: (1) ambient Lake Washington water, (2) waters from the Ship Canal, (3) three streams during both base flow and storm conditions, (3) the Cedar and Sammamish Rivers, (4) three combined sewer overflow (CSO) discharges, (5) six stormwater discharges and, (6) combined wet and dry atmospheric deposition. The data in this report fill data gaps for low level concentrations of PCBs and PBDEs in the watershed, while future reports will use this information to develop additional reports and modeling tools to answer three management questions:

1. Which types of import pathways are the highest priorities for tPCB/tPBDE load reduction?
2. How long might the system take to respond to these hypothetical loading reductions?
3. How will potential loading reductions from these pathways reduce the magnitude of fish PCB concentrations and the need for a fish consumption advisory on Lake Washington?

The lowest concentrations of tPCBs and tPBDEs were detected in Lake Washington and river samples. Comparison of the Lake Washington and two Ship Canal stations showed the highest detected concentrations at the Ballard Locks station, indicating significant inputs of tPCBs into the Ship Canal. Analytical challenges for low level tPBDE analysis in lake waters limit comparisons between these stations for tPBDEs.

In the Cedar and Sammamish Rivers, tPCB and tPBDE concentrations were similar although river waters were often close to method blank concentrations limiting also this study's ability to quantify them. tPCB and tPBDE concentrations measured in tributaries differed by location, with Thornton Creek consistently exhibiting the highest concentrations. tPCB and tPBDE concentrations varied widely in stormwater runoff. tPCB concentrations at Fremont were over two times higher than the next highest tPCB concentrations in highway bridge runoff. tPBDE concentrations were highest in highway bridge runoff. The highest tPCB and tPBDE concentrations at CSO locations were consistently observed at the Dexter CSO. Higher variability was observed in samples from the Dexter CSO station compared to the Seward Park and Ballard 150 CSOs.

tPCB and tPBDE air deposition rates calculated for Beacon Hill were consistently higher than at Sand Point. The difference in tPCB air deposition rate between sites does not appear significant, but tPBDE deposition rates appeared about four times higher at Beacon Hill. tPBDEs were detected at higher concentrations than tPCBs in all pathways with the exception of CSOs.

The conventional parameter concentrations indicated relatively low total organic carbon (TOC) content in ambient water samples with the lowest average concentration observed in Lake Washington and highest in streams during storm conditions. As would be expected from these pathways, dissolved organic carbon (DOC) and TOC content was highest and most variable in stormwater runoff, highway bridge runoff and CSOs. As expected, Total Suspended Solids (TSS) was highest in tributaries during storm events and CSOs and lowest in the lake samples.

The data presented in this report provide the first extensive measurements of low level tPCB and tPBDE concentrations in whole water from Lake Washington and the Ship Canal, as well as a variety of other input pathways. The tPCB and tPBDE data have been used to estimate loadings to Lakes Washington and Union and subsequently from the watershed to Puget Sound, which addressed the first question above (King County 2013). The PCB data will also be used to develop both fate and

bioaccumulation models for Lake Washington. These models will be developed to help inform, in combination with the loadings information: a) where management should invest resources to decrease PCB residues in Lake Washington fish, b) the magnitude of loadings reductions needed to reduce PCB levels in Lake Washington fish, c) next steps to better understand sources and bioaccumulation in Lake Washington and the Ship Canal, and inputs to Puget Sound.

## 1.0. INTRODUCTION

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In 2010, King County was awarded a grant by the U.S. Environmental Protection Agency (EPA) to investigate total polychlorinated biphenyl (tPCB) bioaccumulation in fish, and estimate tPCB and total polybrominated diphenylether (tPBDE) loadings to Lake Washington and from the Lake and Ship Canal to Puget Sound. The project goals were to quantify inputs from key pathways for these two persistent compounds and estimate (1) the magnitude of decline in fish tissue concentrations that would result if tPCB loading reductions were successfully implemented and (2) the response time to hypothetical loadings reductions. This data report covers the field study component of the project which was intended to fill data gaps. One specific goal of the field study was to measure concentrations of tPCBs and tPBDEs in key import pathways (rivers, streams, stormwater, combined sewer overflows, and air deposition) to Lake Washington and the Ship Canal. The second goal of the study was to measure the concentrations leaving Lake Washington through the Ship Canal to Puget Sound. These data enable calculation of the first known estimates of current tPCBs and tPBDEs loadings to Lakes Washington and Union and the Ship Canal. The project also estimates relative contributions from each pathway type, as well as total loadings of these contaminants to Puget Sound from the Greater Lake Washington watershed.

This project will fill data gaps and develop modeling tools to answer three management questions:

1. Which types of import pathways are the highest priorities for tPCB/tPBDE load reduction?
2. How long might the system take to respond to these hypothetical loading reductions?
3. How may potential loading reductions from these pathways reduce the magnitude of fish tPCB concentrations and the need for a fish consumption advisory on Lake Washington?

The field study was designed to provide data to answer Question #1 and provide data to assist in addressing Questions 2 and 3.

### 1.1 Field Study Objectives

The field study component to this project was designed to fulfill multiple data needs and objectives, including:

- To collect whole water samples from potential major pathways into Lake Washington or Lake Union and the Ship Canal, as well as water exiting the Ship Canal to Puget Sound.
- To analyze the whole water samples for PCB and PBDE congeners at low detection limits, using standard methods to produce data of sufficient quality for use in loadings calculations, fate and transport, and bioaccumulation models.
- To measure the fractions of tPCBs and tPBDEs partitioned between the particulate and dissolved water phases in a subset of whole water samples. Measurement of partitioning is needed to calibrate fate and transport models describing the movement of tPCBs and tPBDEs between media.
- Analyze total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) in all whole water samples for use in loadings calculations, fate and transport, and bioaccumulation models.
- Where possible, collect flow measurements for use in loading calculations.

This report describes the methods used to collect and analyze samples in the field study, summarizes the data validation, presents the resulting data, and summarizes the major findings. These data are used to estimate tPCB and tPBDE loadings to Lake Washington, Lake Union, and to Puget Sound. The loadings analysis can be found in a separate report: PCB/PBDE Loading Estimates for the Greater Lake Washington Watershed (King County 2013). The next step of this project is the development of tPCB fate and bioaccumulation models of Lake Washington to describe the response of the lake to external tPCB loading and uptake of tPCBs into fish from lake water, sediments and via the food web respectively.

## 2.0. METHODS

The study design and sampling methods for this field study were followed in accordance with the QAPP (King County 2011a), except where noted below in Section 2.5. This section summarizes the sampling and analytical methods used in this field study.

### 2.1 Sampling Station Locations

Sampling stations were selected as described in the QAPP (King County 2011a) (reproduced in Table 1). The descriptions of sampling locations discussed later will refer to these selection criteria as appropriate.

**Table 1. Sampling station selection criteria (King County, 2011a)**

Ship Canal and Locks	Location represents water flowing toward Puget Sound Not influenced by Locks operation
Lake	Location represents Lake Washington water not directly influenced by nearshore drainage (e.g., streams, rivers, streams or pipe discharges)
Major Rivers	Flow into Lake Washington Location is just upstream of confluence of river with Lake Washington Location is minimally impacted by lake backwater
Tributaries	Drains into Lake Washington (no tributaries drain into the Ship Canal) Reasonable accessibility for sampling Increased flows during storm events Drains a relatively large watershed compared to other tributaries
Municipal Stormwater	Drains into Lake Washington or Lake Union/the Ship Canal Average to large drainage basin for the jurisdiction Drains land use or land use mix that is representative of the shoreline municipalities Reasonable accessibility for sampling Ability to secure field equipment on-site Minimally influenced by backwater conditions from lake or Ship Canal
CSOs	Drains into Lake Washington or Lake Union/the Ship Canal Average to large drainage basin for the jurisdiction Drains land use or land use mix that is representative for the jurisdiction where site is located Reasonable accessibility for sampling Ability to secure field equipment on-site Considered an uncontrolled CSO (overflow frequency greater than once per year) Overflow frequency is relatively high

Highway Bridge Runoff

Location can capture runoff from a major road not co-mingled with other land uses.

Reasonable accessibility for sampling

Ability to secure field equipment on-site

Location is accessible by vehicle instead of by boat

Air Deposition

Located away from trees and substantial buildings

Located to capture prevailing winds toward Lake Washington

Preferable to have weather station nearby for other collocated data (precipitation, wind patterns, etc.)

Accessible yet within a secure area

All sampling station locations presented in the QAPP were sampled with some exceptions which are detailed in Section 2.5. The coordinates for each station are presented in Table 2. All the stations sampled for chemistry are mapped in Figure 1.

**Table 2. Sampling station coordinates.**

Location	Sample Type	Locator	Site Description	X plan	Y plan	Latitude	Longitude
Thornton Creek mouth	Tributary	0434	Thornton Creek one block south of Mathews Beach at the mouth	1285010	257324	47°41'46.7"	122°16'36"
May Creek mouth	Tributary	0440	May Creek at gaging station on Lake Washington Blvd and SE 80 <sup>th</sup>	1302480	196322	47°31'47.9"	122°12'05"
Juanita Creek mouth	Tributary	0446	Juanita Creek at USGS gaging station north of Juanita Park	1299808	260356	47°42'19.3"	122°13'00"
Cedar River at USGS gage	River	0438	Cedar River in Renton at the Bronson Way bridge near the library	1301804	178939	47°28'56.3"	122°12'10"
Cedar River mouth	River	X438	Cedar river near mouth from Cedar River Trail. Southwest of Boeing hangers.	1299193	183733	47°29'43.1"	122°12'49"
Sammamish River	River	B472	Sammamish River at 96 <sup>th</sup> Ave NE Bridge/Wayne Golf Course.	1300905	275948	47°44'53.4"	122°12'48"
Madrona Seattle drainage	Stormwater	MADRONASPU81	Manhole in pullout along Lake Washington Blvd at Madrona Dr	1283209	226702	47°36'44.2"	122°16'54"
North Mercer Island drainage	Stormwater	MERCERISL10-EPA	Creek adjacent to N. Mercer Island King County sewage pump station	1294378	218752	47°35'27.8"	122°14'09"
Seward Park Seattle drainage	Stormwater	SEWARDSPU173	Lake Washington Blvd S. at Seward Park	1288913	203489	47°32'56.2"	122°15'24"
Fremont Seattle drainage	Stormwater	FREMONTSPU102	Manhole at 3 <sup>rd</sup> Ave NW and NW 36 <sup>th</sup> St. Northwest of power line fencing	1263929	242005	47°39'11.5"	122°21'40"
Central Way drainage	Stormwater	CENTRALWYKIRK	Culvert outlet at south end of 7 <sup>th</sup> St. North of 85 <sup>th</sup>	1305319	250904	47°40'47"	122°11'37"
North Renton drainage	Stormwater	0828JC7SB	Roadside tributary ditch to John's Creek along East side of Lake Washington Blvd. Sampler deployed in SE culvert	1302565	185988	47°30'05.9"	122°12'01"

Location	Sample Type	Locator	Site Description	X plan	Y plan	Latitude	Longitude
Lake north	Lake Washington	0826	Depth aliquots from these three locations were composited and the resulting samples are epilimnion, hypolimnion, or mixed composites	1295117	253655	47°41'12.3"	122°14'07"
Lake mid	Lake Washington	0852		1286567	235474	47°38'11.4"	122°16'07"
Lake south	Lake Washington	0890		1286489	213199	47°34'31.6"	122°16'02"
Montlake Cut	Ship Canal	0540	Ship Canal at Montlake Bridge	1277624	239584	47°38'50.3"	122°18'19"
Locks Station	Ship Canal/outlet	0580	Salmon Bay ~200m upstream from the locks	1257176	246277	47°39'52.4"	122°23'19"
I-90 Bridge	Bridge Runoff	I-90_E_HIGHRISE	East high-rise of I-90 floating bridge	1289394	218374	47°35'23.2"	122°15'21"
Sandpoint	Atmospheric deposition	SAND_POINT	In field north of Magnuson Park	1289345	252853	47°41'03.4"	122°15'31"
Beacon Hill Ecology weather station	Atmospheric deposition	BWR	Ecology air monitoring station immediately west of golf driving range	1276200	210777	47°34'05.8"	122°18'32"
Seattle CSO 150	CSO	BALLARDSPU150	Manhole near south end of 24 <sup>th</sup> Ave NW	1257450	247279	47°40'02.3"	122°23'16"
Seward Park Seattle CSO	CSO	SEWARDSPU44	Seward Park parking lot south of Lake Washington Blvd S. and S. Juneau St.	1288685	203392	47°32'55.2"	122°15'28"
King County Dexter CSO	CSO	S035026	King County CSO at 1418 Dexter Ave N.	1268382	234141	47°37'54.8"	122°20'32"

Notes: X and Y plan are Washington State Plane North coordinates in feet (horizontal datum: NAD 1983 HARN). Latitude and longitude use the WGS 1984 datum.

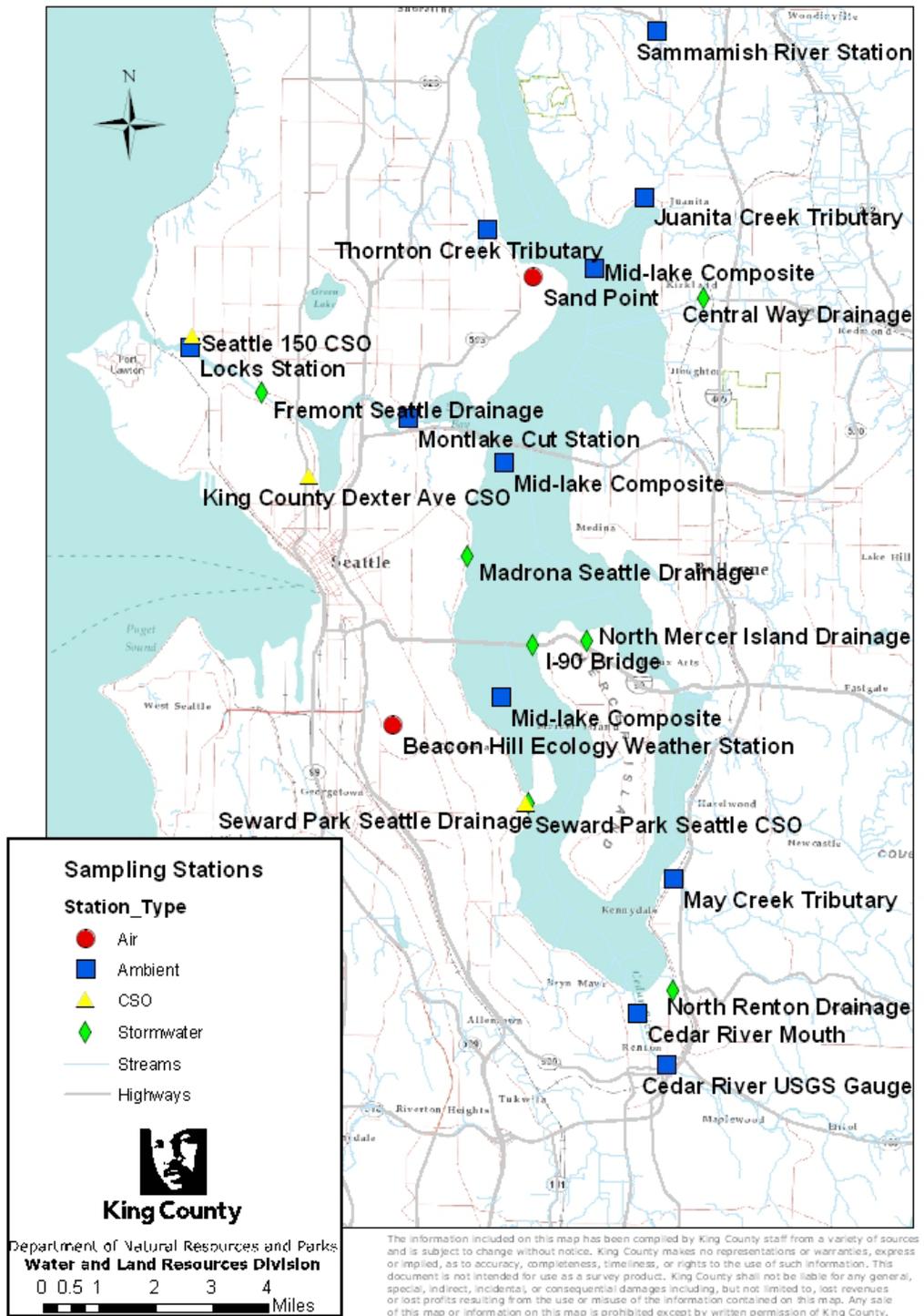


Figure 1. Sampling stations for field study.

## 2.1.1 Ambient Waters

The primary objective for ambient water samples was to measure chemical concentrations in Lake Washington away from localized inputs. River and tributary samples were to measure those inputs themselves as close to the Lake as practicable. Thus, river and stream sampling stations were generally located near the mouths of these water bodies adjacent to flow gages.

### 2.1.1.1 Tributaries

Three tributary sampling sites were identified at the mouths of Thornton (0434), Juanita (0446), and May (0440) Creeks (Figure 1). These creeks were selected because they drain large basins, have continuous flow gages, and are located in areas of variable development density. Each basin represents a gradient of type and density of development from low density, mostly suburban residential development in May Creek to high density residential and commercial development in Thornton Creek.

### 2.1.1.2 Rivers

The Sammamish and Cedar Rivers are the primary rivers that drain to Lake Washington. The Sammamish River station (B472) is located above the backwater influence of Lake Washington just below the confluence with North Creek (Figure 1). Two sampling locations were selected on the Cedar River. The primary upstream Cedar River station (0438) located in the City of Renton was selected to avoid potential backwater influences of Lake Washington (Figure 1). This site is also adjacent to a USGS gage. A second Cedar River station (X438), located closer to the mouth below station 0438, was also chosen (Figure 1). This station was included to evaluate the potential influence of downstream industrial property inputs from the highly developed urban area in Renton downstream of Station 0438. The downstream Cedar location is likely influenced by backwater effects from Lake Washington; no flow gage is available at this site.

### 2.1.1.3 Lake Washington and Ship Canal

Water samples were collected and composited from three mid-lake locations on Lake Washington; one in the north end (0826), central portion (0852) and southern portion (0890) (Figure 1). These lake locations are away from nearshore influences. Two stations were located in the Ship Canal, one at the Montlake Cut (0540) and another near the Hiram Chittenden Locks (0580). These stations were selected to measure concentrations at the outlet of Lake Washington and at the up and downstream ends of the Ship Canal.

## 2.1.2 Stormwater Runoff

Stormwater runoff enters Lakes Washington, Union and the Ship Canal directly from pipes, bridges, and overwater roadways. It also enters indirectly via streams and tributaries. The following subsections only address direct stormwater inputs to Lake Washington via ditches and pipes. Stormwaters entering via tributary streams and highway bridges are addressed in Sections 2.1.1.1 and 2.1.4.

Six stormwater sampling locations were identified in Kirkland, Renton, Mercer Island and Seattle. Sites were selected based primarily on accessibility, draining land uses representative of lake shore jurisdictions, and average to large basin sizes. Basin sizes were estimated in ESRI ArcGIS and confirmed through consultation with relevant jurisdictions.

### 2.1.2.1 Kirkland

The Kirkland stormwater station (CENTRALWYKIRK) is located north of NE 85<sup>th</sup> Street, east of downtown Kirkland. This discharge drains a 216 acre basin that is characterized by urban residential and some commercial land use (Figure 2).

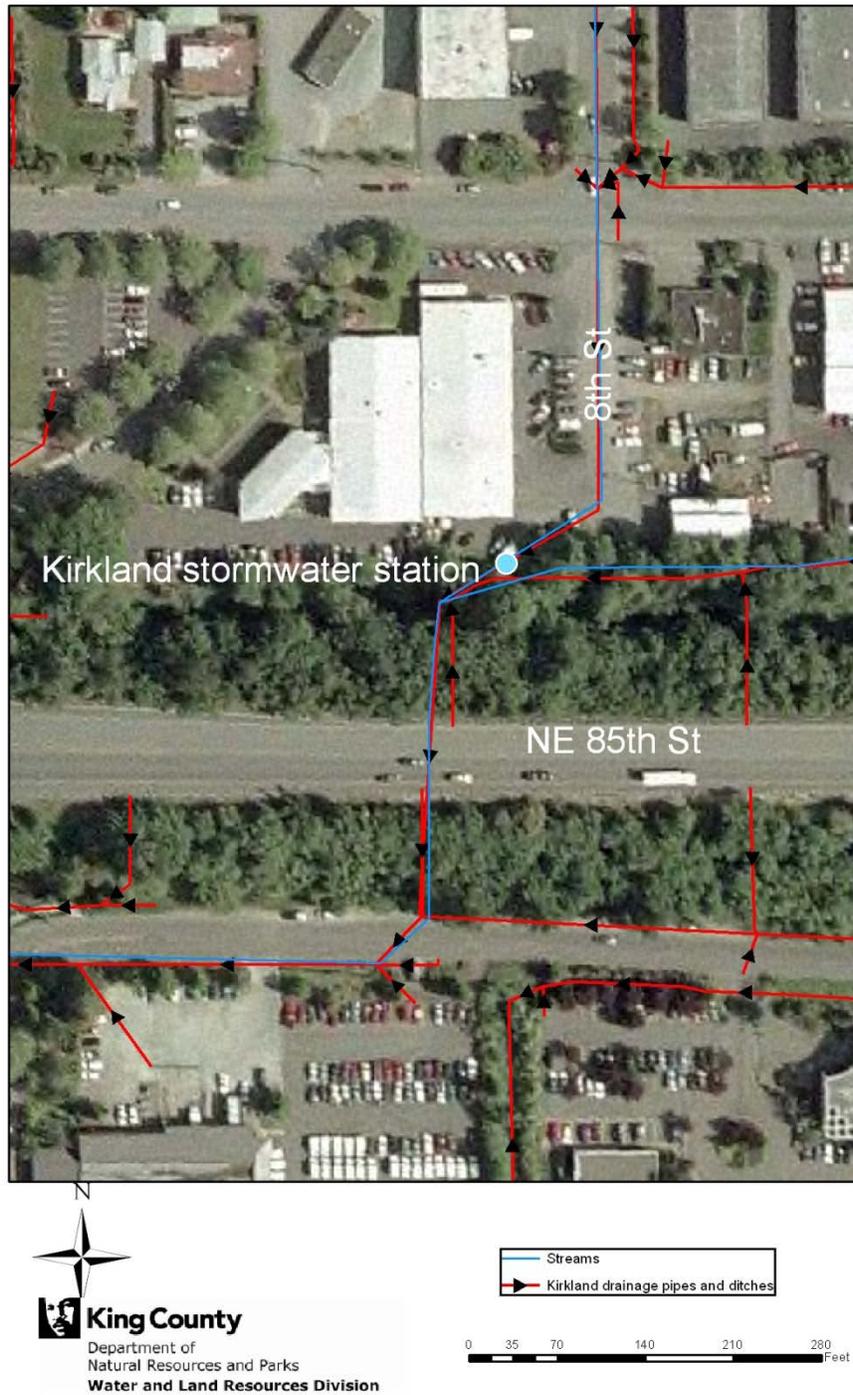


Figure 2. Kirkland stormwater station vicinity map.

The sampling site is located in a cement pipe between NE 85<sup>th</sup> St. and the terminus of 8<sup>th</sup> St (Figure 3). Stormwater at this station flows along NE 85<sup>th</sup> St. through downtown Kirkland and is ultimately discharged into Lake Washington.



**Figure 3. Stormwater station in Kirkland during base flow conditions.**

#### 2.1.2.2 Renton

The Renton stormwater station (0828JC7SB) is located near two major roadways, Interstate 405 and NE Park Drive. The sampling station was located at the downstream end of the northernmost of two paired pipes that carry stormwater from a 706 acre drainage basin (Figure 4). The drainage basin is characterized by a mix of commercial and urban residential land use. Stormwater was sampled from a corrugated metal pipe (Figure 5). The discharge from the paired pipes empties into a stormwater pond which also receives stormwater from a second, different basin. Water exits the stormwater pond via a pipe that travels beneath Lake Washington Blvd. N and briefly becomes an open stream that flows into Lake Washington from within Gene Coulon Park (Figure 4).

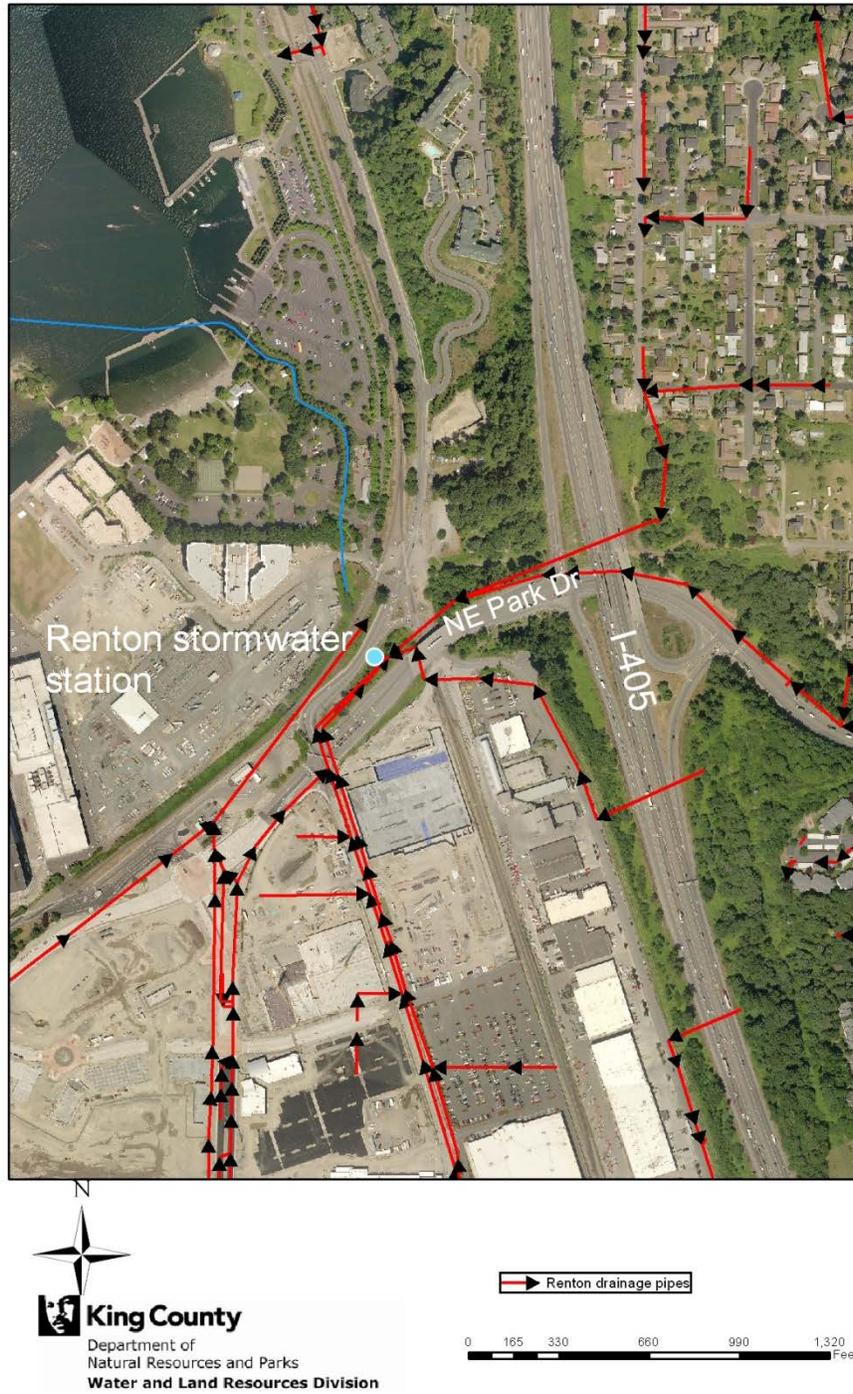


Figure 4. Renton stormwater station vicinity map.



**Figure 5. Stormwater station in Renton during base flow conditions.**

### 2.1.2.3 Mercer Island

The Mercer Island stormwater station (MERCERISL10-EPA) is located on the North end of the island (Figure 1). This station is just north of I-90 and adjacent to a King County pump station. Like all stormwater conveyance systems on the island, stormwater at this station is carried by a combination of pipes and open ditches to its terminal discharge into Lake Washington (Figures 6 and 7). This stream drains the most commercially developed area and largest drainage basin on the island (231 acres).

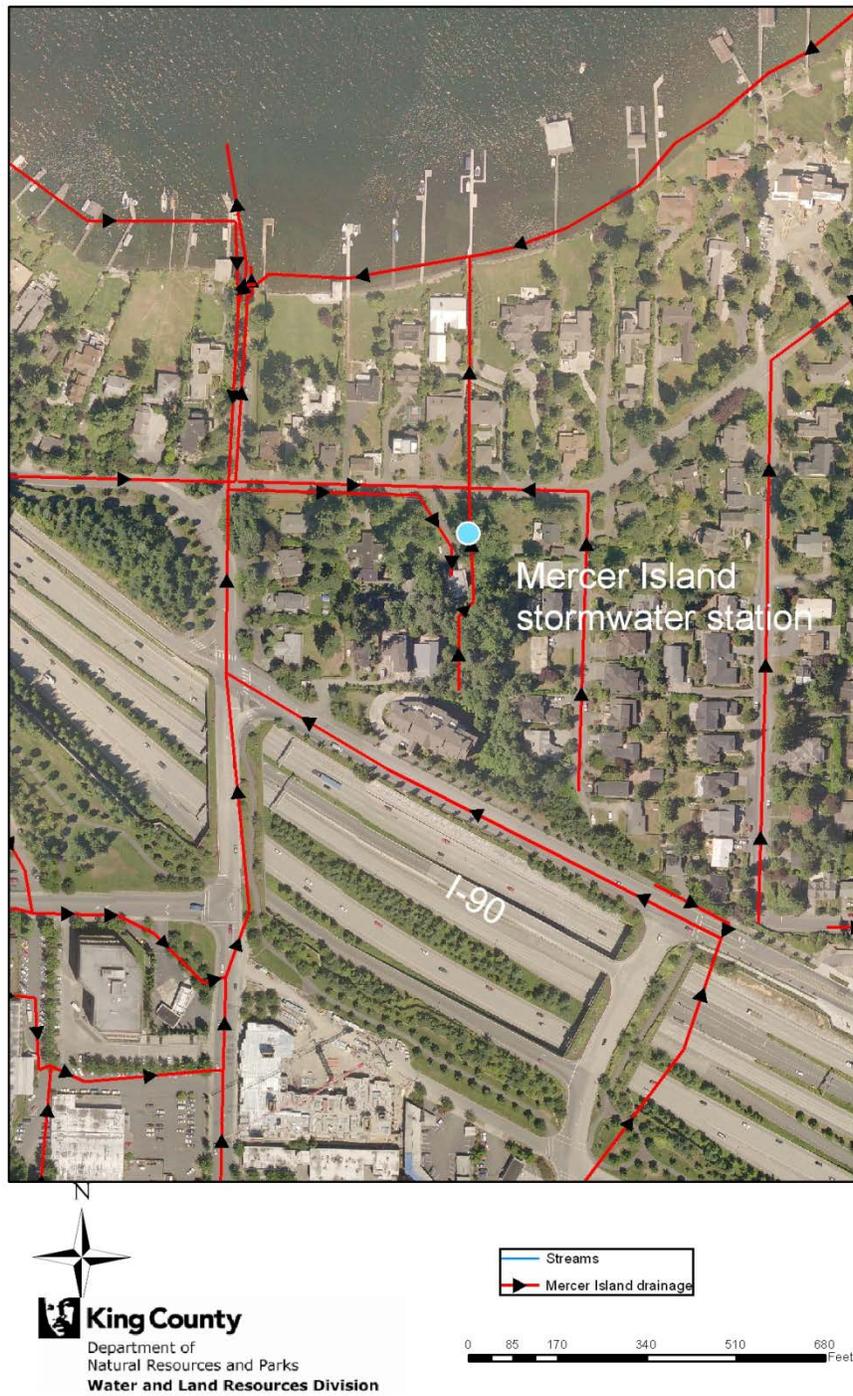


Figure 6. Mercer Island stormwater station vicinity map.



**Figure 7. Stormwater station in Mercer Island during base flow conditions.**

#### 2.1.2.4 Seattle

Three stormwater sampling sites were located in Seattle. Two stations, Seward Park (SEWARDSPU173) and Madrona (MADRONASPU81), discharge to Lake Washington and a third, in the Fremont neighborhood (FREMONTSPU102, Table 2), discharges to the Ship Canal. Seattle's stormwater stations were all located in conveyance pipes generally one or two manholes upstream from their terminal discharge. The Seward Park stormwater station is located on the Lake Washington shoreline at the southern entrance to the park (Figure 8). The area that drains to Lake Washington is 111 acres and characterized by urban residential and recreational land uses.



**Figure 8. Seattle, Seward Park stormwater and CSO sampling locations.**

The Madrona stormwater station is located on the Lake Washington shoreline near the intersection of Lake Washington Blvd and Madrona Drive (Figure 9). The area that drains to Lake Washington is 115 acres and characterized mainly by urban residential land uses.



**Figure 9. Seattle, Madrona stormwater sampling location.**

The Fremont stormwater station is located on the shoreline of the Ship Canal at 3<sup>rd</sup> Ave NW and NW 36<sup>th</sup> Street (Figure 10). The drainage area is 200 acres and is characterized by urban residential and commercial land uses.



Figure 10. Seattle, Fremont stormwater sampling location.

### 2.1.3 Combined Sewer Overflow

CSO sampling sites were selected because they discharge directly to Lake Washington, Lake Union or the Ship Canal, were not controlled to one or fewer overflow events per year, and were

accessible for sampling. Three CSO sampling locations were identified. The Ballard 150 CSO (BALLARDSPU150, Table 2) is a City of Seattle owned pipe located on the northern side of the Ship Canal about 150 m upstream of Ballard Locks (Figure 11). It drains 392 acres which is much larger than the average Seattle CSO basin size of approximately 117 acres. The Dexter CSO (S035026, Figure 1) is a large King County owned CSO point along the southwest shore of Lake Union (Figure 12) with a drainage area of 952 acres. While this drainage area is smaller than some other King County CSOs, which on average drain approximately 3,300 acres, the Dexter site has a 20-year average overflow frequency of 12.1 events per year. This relatively high overflow frequency allowed for efficient sampling of actual overflow events.

The conveyance system of the Henderson Street CSO, which was originally planned for sampling in the QAPP, proved to be too complex. Due to variations in pump station status and service area over time, it was determined that the representativeness of this location would vary excessively. Therefore, an alternative City of Seattle CSO location (SEWARDSPU44, Table 2), approximately 2.8 km north near Seward Park, was chosen for sampling (Figure 8). The Seward CSO serves an area of 169 acres which is also larger than the average Seattle CSO basin.



**King County**  
Department of  
Natural Resources and Parks  
Water and Land Resources Division

Combined  
Partially separated - stormwater  
Fully separated

0 55 110 220 330 440 Feet

Figure 11. Seattle, Ballard 150/151 CSO sampling location.

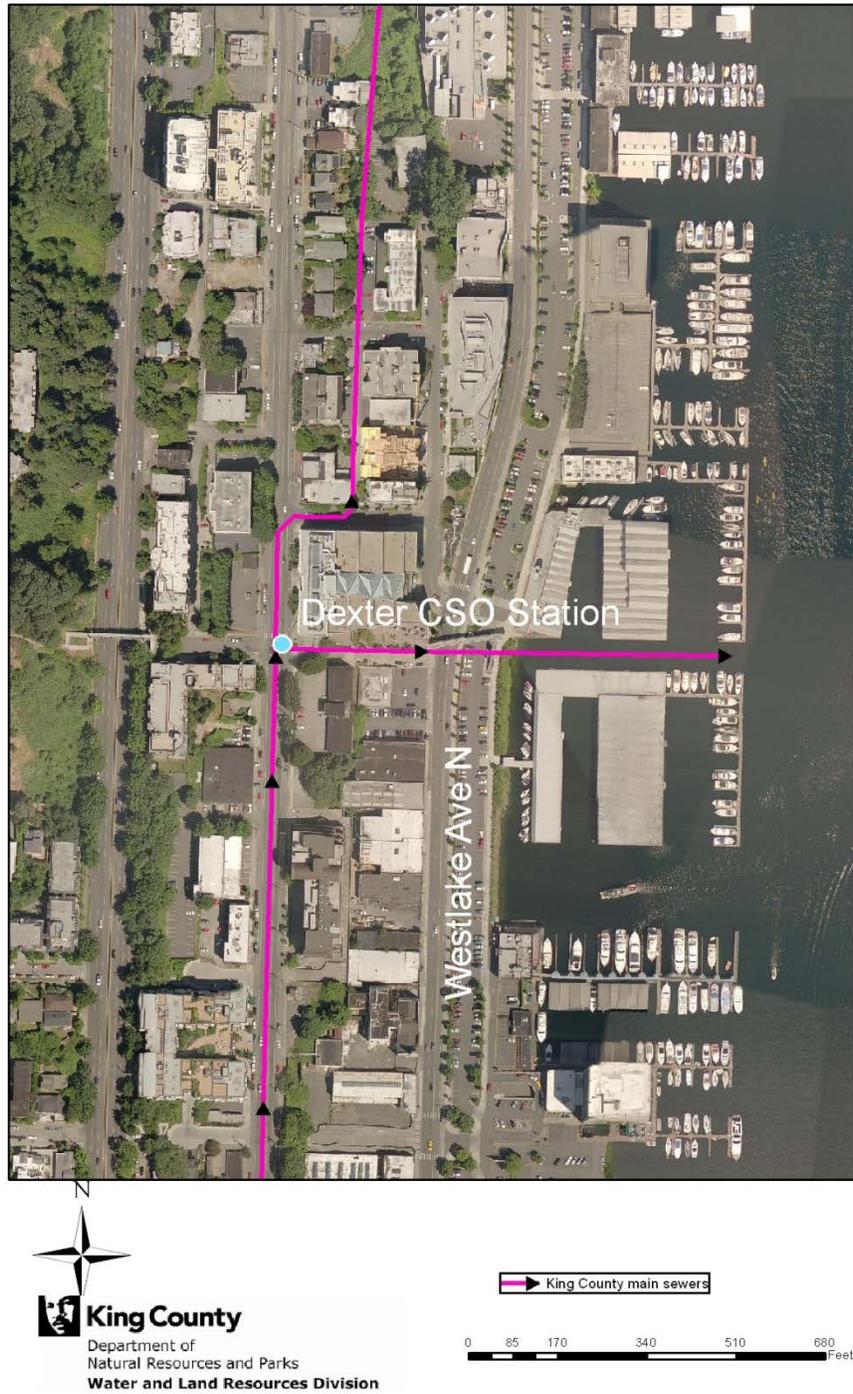


Figure 12. Seattle, Dexter CSO sampling location with local sewer piping.

## 2.1.4 Highway Bridge Runoff

One sampling station was identified for collection of highway runoff. The I-90 Bridge runoff station (I-90\_E\_HIGHRISE, Table 2) was located under the eastbound lanes just west of Mercer Island. At this station, stormwater flows directly off the bridge deck through two vertical downspouts to a settling basin (Figure 13). A horizontal outflow carries the stormwater to another down spout that drops runoff into Lake Washington. The flow meter and autosampler inflow tubing were placed inside the horizontal outflow pipe.



**Figure 13. Downspouts and settling basin under I-90 Bridge.**

## 2.1.5 Atmospheric Deposition

Atmospheric deposition was sampled to evaluate the potential loadings of tPCBs and tPBDEs directly to the lake as dry particulate and rainfall combined. Two atmospheric deposition stations were selected for this purpose: the Washington Department of Ecology (Ecology) Beacon Hill weather station (BWR) and a site on Sand Point Way (SAND\_POINT) near Magnuson Park (Figure 1). The Beacon Hill station was selected because it has been used to represent regional atmospheric conditions (King County, 2011b) and can provide co-located weather parameters such as rainfall, wind direction, and temperature. The Sand Point Way station was selected because it provided secure atmospheric deposition collection close to lake level elevation and at the shoreline. The Sand Point Way station is expected to represent the air mass that would impact direct atmospheric deposition on Lake Washington and the Ship Canal. It is located on the Lake Washington shoreline but less than 5 km from the Montlake Cut. A weather station is also located less than 800 m from this site. Both stations are upwind of Lake Washington based on average prevailing winds (Figure 14).

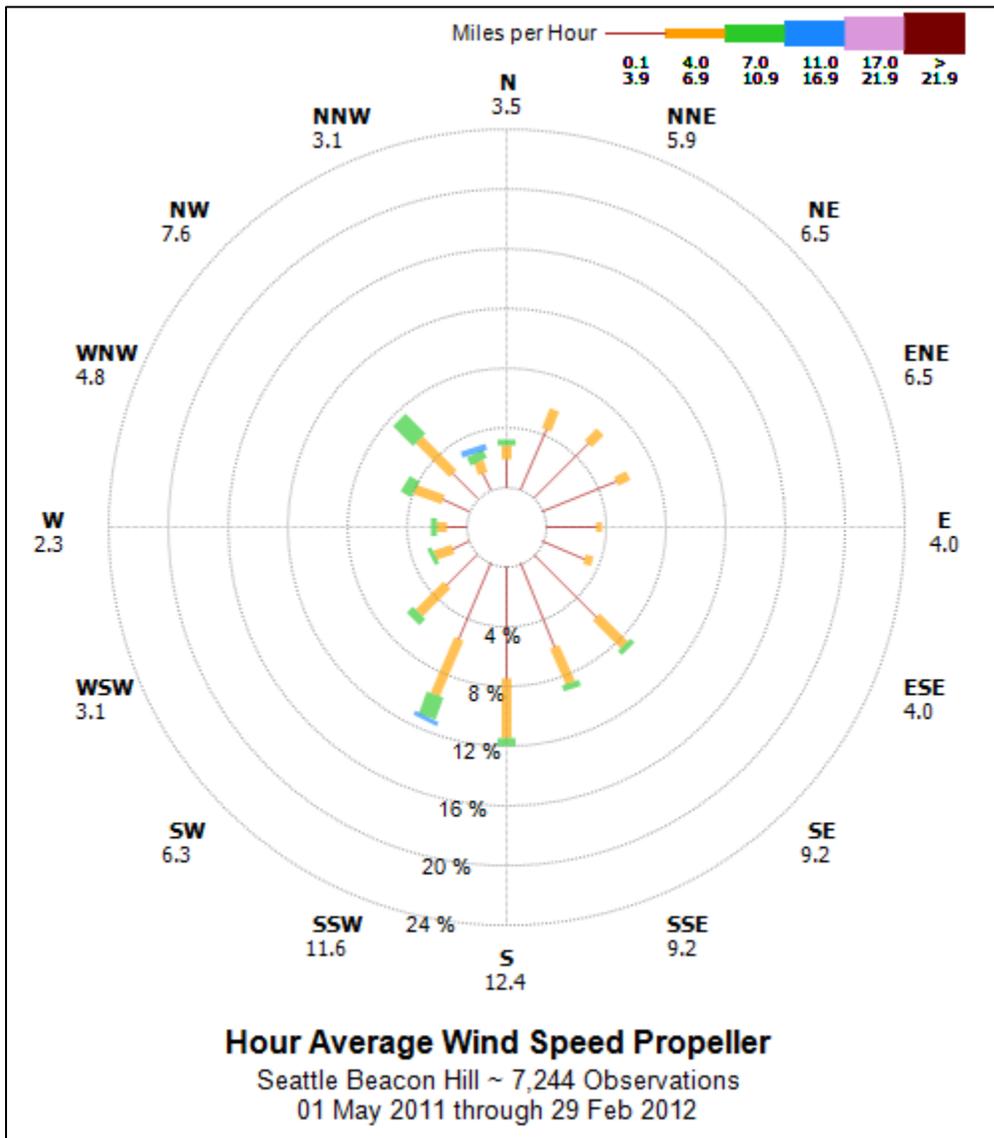


Figure 14. Prevailing winds at the Beacon Hill weather station during the study period (data from Puget Sound Clean Air Agency).

## 2.2 Field Methods

This section describes the various methods used for collection of ambient water, stormwater runoff, CSOs, highway bridge runoff, and bulk atmospheric deposition samples. Total PCBs and tPBDEs were measured in all samples with a few exceptions described in Section 2.5. TOC, DOC, and TSS were measured in all water samples, but not in bulk deposition samples.

All samples submitted to AXYS for PCB and PBDE analysis were collected directly with proofed sample jars or decanted from sample collection devices (e.g., carboys or Scott bottles) into proofed sample jars. AXYS takes jar samples from each lot delivered from the manufacturer and documents their cleanliness and suitability for low level PCB and PBDE congener analysis. These jars are not otherwise cleaned, but, hereafter, will be referred to as proofed sampling jars or containers. All

samples were stored on ice or refrigerated at 4°C under chain of custody protocols until shipped or analyzed.

## 2.2.1 Ambient Waters

The following sections describe the methods used to collect water samples from the tributary, river, Lake and Ship Canal locations.

### 2.2.1.1 Tributaries and Rivers

Grab samples were collected from the tributaries and the Cedar River sampling locations. A Scott bottle was used to collect samples from the Sammamish River due to the steep, inaccessible banks at this site. The Scott bottle allowed for sampling from the NE 96<sup>th</sup> Ave NE/Bothell Way Bridge.

Tributary stations were sampled quarterly. At these stations, proofed glass sampling jars were dipped while facing upstream in the thalweg of the channel. At the three tributaries, samples were collected once under base flow conditions and again during three storm events:

- 1) June 1, 2011 (storm flow)
- 2) September 6, 2011 (base flow)
- 3) November 17, 2011 (storm flow)
- 4) January 4, 2012 (storm flow)

For the Cedar River stations, grab samples were collected by wading to waist deep (~1.2 m) water along the bank and hand dipping the proofed sampling jars.

The Sammamish River was sampled with a Scott bottle which was laboratory-cleaned using Alconox® detergent and rinsed with deionized (DI) water. A final rinse with on-site water was conducted prior to sample collection. The Scott bottle was lowered to the ~1 m depth three times and approximately 1L of water was decanted into the proofed sampling jars until a total of 3-3.5L was collected. Attempting to sample deeper in the water column presented too great a risk of having the Scott bottle stir up sediment from the bottom and compromise the sample. To minimize the risk of introducing additional laboratory contamination, the glass compositing carboy proposed in the QAPP was not used.

River stations were sampled bimonthly except for the Cedar River Mouth station (X438) which was sampled quarterly. Table 3 outlines the collection dates for the river samples. Specific river flows were not targeted for sampling.

**Table 3. River sampling events.**

Location Name and Locator	Collection Date
Cedar River, downstream (X438)	4/18/2011
	8/1/2011
	10/3/2011
	2/6/2012
Cedar River, upstream (0438)	4/18/2011
	6/6/2011
	8/1/2011

Location Name and Locator	Collection Date
	10/3/2011
	12/5/2011
	2/6/2012
Sammamish River at golf course (B472)	4/18/2011
	6/6/2011
	8/1/2011
	10/3/2011
	12/5/2011
	2/6/2012

### 2.2.1.2 Lake Washington and the Ship Canal

Samples were collected from Lake Washington by remotely triggering Niskin bottles mounted on a conductivity, temperature and depth (CTD) instrument rosette. The CTD rosette was rinsed with on-site water during descent and samples were collected during ascent. Sample aliquots were decanted from the Niskin bottles into proofed sample containers.

The King County-operated in-situ YSI profiling buoy in Lake Washington was used to confirm the stratification status prior to a sampling event. A hydrolab instrument was used to record real-time water quality data at the time of sample collection to corroborate the YSI data on the depth of the thermocline in Lake Washington. During periods of mixing and absence of clear stratification, aliquots were collected from three depths, divided approximately evenly from 2-3 m above the lake bottom to 1 m below the lake surface. During periods of stratification, three aliquots were collected from the hypolimnion: 1 m above the lake bottom, middle and top of the hypolimnion. Three aliquots were also collected from the epilimnion: 1 m below the surface, the middle, and the bottom of the epilimnion. The three aliquot grabs collected from the epilimnion at each of the three mid-lake stations were composited to create one (epilimnetic) composite sample. The three aliquots collected from the hypolimnion were combined in an identical fashion to create one (hypolimnetic) composite sample.

Maximum water depth at each of the three Lake Washington stations was 47 to 60 m. During stratified periods, the thermocline was found at approximately 20 m. The specific depth aliquots taken to form the mixed composite samples are listed below in Table 4. Six field replicates were also collected from Lake Washington.

**Table 4. Lake Washington composite sample aliquot collection depths by sampling date and sub-sampling locator.**

Collect Date	Sample ID <sup>a</sup> and field replicate ID	Aliquot Collection Depths by Locator
<b>Mixed conditions</b>		
4/11/2011	L52966-5 and 6	0826 and 0890: 1, 20 and 47m. 0852: 1, 25 and 60m
12/12/2011	L54746-4 and 5	0826 and 0890: 1, 20 and 47m. 0852: 1, 20 and 60m.
2/13/2012	L55097-4 <sup>a</sup> and 5	0826 and 0890: 1, 20 and 47m. 0852: 1, 20 and 60m.
<b>Stratified conditions</b>		
<b>Epilimnion</b>		
6/15/2011	L53423-4 and 5	0826, 0852 and 0890: 1, 10 and 15m.
8/9/2011	L53757-4	0826, 0852 and 0890: 1, 5 and 10m.
10/12/2011	L54359-4 and 5 <sup>b</sup>	0826, 0852 and 0890: 1, 5 and 10m.
<b>Hypolimnion</b>		
6/15/2011	L53423-6	0826 and 0890: 25, 40 and 47m. 0852: 25, 50 and 60m
8/9/2011	L53757-5 and 6	0826 and 0890: 20, 40 and 47m. 0852: 20, 50 and 60m.
10/12/2011	L54359-6 <sup>b</sup>	0826 and 0890: 20, 40 and 47m. 0852: 20, 50 and 60m.

<sup>a</sup> Sample was analyzed for dissolved and particulate PCBs.

<sup>b</sup> Sample was analyzed for dissolved and particulate PCBs and PBDEs.

A subset of ambient lake samples were filtered by the contract laboratory using a 1.1 µm filter. The liquid and solid fractions were then both analyzed and reported separately. This was done to better understand partitioning and assist with future bioaccumulation model development. While this pore size will not capture some small bacteria<sup>1</sup>, it will collect plankton of all sizes. TOC, DOC and TSS were not analyzed in these filtered waters or the particulate fractions.

The Ship Canal stations at the Locks (0580) and Montlake (0540) were sampled on the same days as Lake Washington using a Scott bottle washed with Alconox® detergent and rinsed with de-ionized water. The bottle was given a final on-site rinse with lake water prior to sample collection. Three aliquots were collected with the Scott bottle and each was used to fill approximately one-third of the analytical sampling containers. One grab was taken 1 m above the bottom of the Ship Canal, one from the middle of the water column and one from 1 m below the surface. Table 5 documents the depths at which the Montlake Cut (0540) and Locks Station (0580) aliquots were collected by sample. Seven field replicates were collected; three for the Montlake Cut station (0540) and four at the Ballard Locks (0580). None of the Ship Canal stations were filtered.

<sup>1</sup> Bacteria are in the 0.2 to 2.0 µm (Lalli and Parsons 1993). Thus, filtration to remove this biological fraction would typically be conducted using a 0.2 µm filter. Due to an oversight, the filter size was not confirmed with AXYS before samples were filtered for the filtrate and solids analysis. Thus, samples were filtered with their standard 1.1 µm filter size

**Table 5. Montlake Cut and Locks Station composite sample aliquot collection depths by sampling date and locator.**

Locator	Collect date	Sample ID and field replicate ID	Aliquot collection depths (m)
0540	4/11/2011	L52966-3 and 4	1, 4, 8
	6/15/2011	L53423-3	1, 4, 8
	8/9/2011	L53757-2 and 3	1, 4, 8
	10/12/2011	L54359-3	1, 4, 8
	12/12/2011	L54746-2 and 3	1, 4, 8
	2/13/2012	L55097-3	1, 4, 8
0580	4/11/2011	L52966-1 and 2	1, 4, 7
	6/15/2011	L53423-1 and 2	1, 4, 7
	8/9/2011	L53757-1	1, 2.5, 6
	10/12/2011	L54359-1 and 2	1, 3, 6
	12/12/2011	L54746-1	1, 3, 6
	2/13/2012	L55097-1 and 2	1, 3, 6

## 2.2.2 Stormwater and Highway Bridge Runoff

Stormwater samples were collected using autosamplers (Isco® 3700, Isco® 3700C, Isco® GLS or, Isco® 3780 Intrinsic [Zone-1 rated]) with liquid level actuators. Sampler collection jars were proofed clean by AXYS. To minimize the risks of cross contamination, sampler tubing was dedicated to each location. Tubing was initially cleaned using Alconox detergent and rinsed with acetone. However these PCB/PBDE decontamination protocols contaminated the tubing with organic solvents which then contaminated the TOC and DOC blanks. Section 2.5 discusses this issue further and the resulting collection protocol changes from the QAPP (King County, 2011a).

Before sampling, flow data were collected at each site (see methods under Section 2.3) to determine the range of stormwater heights in the selected pipes during several storm events. These flow data were used to select a sampling trigger based on water height in the pipe. Base flow was present at the Kirkland (CENTRALWYKIRK), Renton (0828JC7SB) and Mercer Island (MERCERISL10-EPA) stormwater sites and they were each grab sampled once during the dry season. The trigger height for storm sampling was then set above base flow. Sample collection was initiated when flow exceeded the trigger height and continued until flow decreased below the trigger height. The sampler was programmed to collect an aliquot every 10 minutes and where possible, the sampling duration was set for two hours. Thus, stormwater and highway bridge runoff samples are considered time-paced, not flow-weighted.

The sample flow volume and duration for each storm can be found in Table 6. Flow volume at each site was recorded to document the range of storm events sampled and to assist with setting autosampler trigger heights. Continuous monitoring of flow at all stormwater and highway runoff sampling locations was impractical, and thus these volumes only represent the flow during sampling and not the total volume discharged.

Field replicates were collected at sampling stations where there was space to place a second autosampler in a secure location. The field replicate sampler was set up to collect a sample on the same aliquot time schedule as its paired primary sample (Table 6).

**Table 6. Stormwater sampling event dates, durations and flow volumes.**

Site	Sample ID and replicate	Date	Duration (hrs)	Aliquots collected	Volume (gallons)
Renton	L53463-3	6/16/2011	3.18	14	9,720
	L54176-2	9/26/2011	2.02	13	39,760
	L54326-2	10/10/2011	2.17	14	42,900
	L54894-1	1/4/2012	2.17	14	est. 78,000
Fremont	L54692-1	11/22/2011	2.00	12	9,400
	L55115-2	2/17/2012	2.17	14	73,960
	L55231-1 & -5	3/12/2012	2.02	13	54,800
Seward Park	L55309-1	3/14/2012	2.00	14	4,872
	L55391-1	3/29/2012	2.17	14	7,478
	L55450-5	4/3/2012	2.00	13	1,838
Madrona	L54692-2	11/22/2011	2.00	12	69,964
	L55115-4	2/17/2012	2.02	14	Meter Failed
	L55175-2 & -6	2/24/2012	2.00	14	51,180
	L55231-2 & -6	3/12/2012	2.02	13	16,285
I-90	L54326-4	10/10/2011	2.17	6*	7,118
	L54326-11	11/2/2011	1.02	14	5,010
	L55115-1 & -8	2/13/2012	2.33	14	8,922
	L55115-9	2/14 - 17/2012**	74.00	14	12,575
Kirkland	L53463-1	6/16/2011	2.00	12	2,286
	L54176-1	9/26/2011	2.00	13	11,250
	L54326-1	11/2/2011	2.17	14	10,800
	L54894-3	1/4/2012	2.10	14	est. 9,050
Mercer Island	L53463-2	6/16/2011	2.00	12	26,083
	L54176-3	9/26/2011	2.22	13	123,750
	L54326-3	10/10/2011	2.17	14	102,300
	L54894-2	1/4/2012	2.17	14	135,106

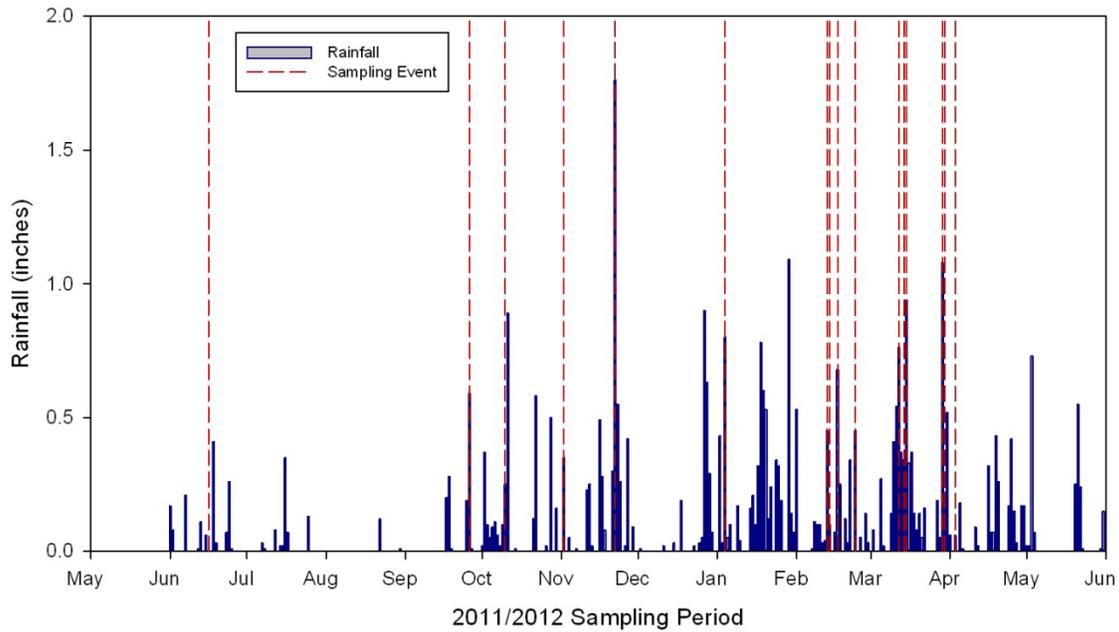
Notes: Where there are two sample IDs, a field replicate was collected.

est. = the flow volume had to be estimated. At Kirkland, this was due to a malfunction of the date/time recorder. At Renton, the flow is likely estimated low because of backwaters flowing into the pipe from the other subbasins discharging near this location.

\*Eight of the fourteen aliquots were not collected due to equipment malfunction.

\*\*This sample was collected intermittently over 74 hours due to variability in precipitation.

Figure 15 illustrates the dates of stormwater and I-90 sampling events compared to rainfall events as measured by the Sea-Tac airport rainfall gage. For each sampling event, not all stations were sampled; however, the range of storm sizes sampled by the project is illustrated in Figure 15.



**Figure 15. Stormwater sampling dates relative to Sea-Tac airport rainfall gage.**

As shown below (Figure 16), the bridge runoff sample collection tubing was potentially impacted by debris in the pipe. Also, during some storms, the flow meters were unable to document the runoff volume of a sampling event. However, as previously mentioned the flow meters and resulting volumes were only used to aid in setting and refining autosampler trigger heights.



**Figure 16. Stormwater outflow pipe with sampler inflow tubing under I-90 Bridge.**

### 2.2.3 Combined Sewer Overflow

CSO samples were collected from the Ballard150 (BALLARDSPU150), Dexter (S035026) and Seward Park (SEWARDSPU44) CSOs. The autosamplers used to collect stormwater samples were also used to collect CSO samples. Minimum water depth to initiate CSO sampling was based on professional judgment, weir height, and for Dexter, prior consultations with King County wastewater engineers. The samplers were set to collect higher flow waters which may under certain pipe or pump status conditions lead to overflow events. The samplers were programmed to collect an aliquot of sample every 10 minutes and sampling continued as long as water depths remained above the trigger level for a maximum of 2 hours; however, during some events the storm duration was less than 2 hours. Unlike the other two CSO stations where space was more limited, the Dexter location allowed for parallel deployment of two carboys; the replicate was collected simultaneously with the primary sample using a “Y” in the pump tubing. No other replicate CSO samples were able to be collected.

Autosamplers could not be deployed in manholes where the City of Seattle maintains flow meters that monitor CSO overflow volumes due to limited space. Therefore, manholes immediately up or downstream from the flow monitoring station were used for sampling access. The sampling manholes were within 50-m of the flow monitoring manholes and within the same pipe with no or limited side sewer connections between them. Although sampling trigger heights were set to capture actual overflows, in two cases the sampler was triggered, but the City of Seattle flow data indicate that an overflow event never occurred. The two samples collected on days without actual overflows represent “higher combined flows” which may have overflowed under different pipe conditions. Because they are considered similar to actual overflow events, they were analyzed for the purposes of this project as if an actual overflow event had occurred on that day.

**Table 7. CSO sampling event dates, durations, and overflow volumes.**

Location	Sample ID and replicate	Collection Date and Time	Sampling Duration in Hours	Total Overflow Volume (gallons)
Ballard 150	L55309-2	3/15/2012 10:20	0.17	205,591
	L55391-2	3/30/2012 13:03	2	No overflow this day
Dexter	L54692-3	11/22/2011 9:54	2	164,400
	L55115-7	2/17/2012 16:35	2	473,000
	L55319-1 & 2	3/15/2012 9:55	2	1,166,000
Seward Park CSO	L54692-4	11/22/2011 15:19	2	1,874
	L55175-3	2/24/2012 17:49	1.75	No overflow this day
	L55231-7	3/12/2012 13:38	2	14,156

### 2.2.4 Atmospheric Deposition

Samplers to collect atmospheric deposition were designed to collect both rainwater and dry particulates. The sampler design is a modification of the design used by Pacific Northwest National Laboratories (PNNL) (Brandenberger et al. 2010) (Figure 17).

Primary and field replicate samplers were constructed side-by-side on the same structure (Figure 17). The collection pan consisted of a 20 inch diameter (0.1642 m<sup>2</sup>) stainless steel basin with a stainless funnel welded to the bottom. The basin/funnel design was constructed by King County Environmental Lab (KCEL) field staff because large diameter stainless steel funnels were not commercially available. During the wet season, smaller 9 inch diameter (0.0366 m<sup>2</sup>) funnels were used to avoid overflowing the collection bottles. Silicon/vinyl pump tubing was attached to the funnel spout which was then attached to ½-inch ID Teflon® tubing leading to the 4 L amber, glass collection vessel (Figure 18). The collection vessel was capped with a Teflon® coated lid through which the Teflon® tubing led. A second piece of Teflon® tubing was placed in the lid leading outward to prevent backpressure and downward to avoid incidental collection of particles (Figure 18).

The pan/funnel was attached to the top of a wooden structure approximately 6 feet off the ground. The glass collection bottle was inside the wooden structure to shield the deposition sample from light exposure and prevent photo-oxidation. The wooden structure was built of unfinished, untreated plywood and 2x4 inch beams. Wooden bird-repellant “spikes” were placed around the edge of the pan/funnel (Figure 17).



**Figure 17. Atmospheric deposition sampler exterior.**



**Figure 18. Atmospheric deposition sampler interior with collection jar.**

The collection basins were decontaminated using (1) Alconox® laboratory grade detergent, (2) a DI water rinse, followed by (3) an acetone rinse. The Teflon® tubing and natural bristle brush received this same cleaning protocol. The 4-liter glass collection vessels were proofed by AXYS as clean for PCB and PBDE congener analysis. Samplers were deployed for approximately two weeks. Rainfall was monitored during the deployment to ensure that collection jars didn't overflow; if necessary, the two week deployment was abbreviated to avoid overflows. To save analysis costs, two planned two-week sampler deployments were combined into one four-week deployment.

Wet deposition collected in the basin/funnel and drained passively into the glass collection vessel. Dry deposition collected on the basin/funnel and, at the end of the deployment period, was brushed and rinsed into the collection vessel using a natural bristle brush and KCEL DI water from a Teflon® rinse bottle.

**Table 8. Atmospheric deposition sample deployment periods and duration.**

Location	Sample & Replicate ID	Deployment Date and Time	Collection Date and Time	Deployment Duration (days)
Beacon Hill	L53194-2 & 3	5/2/2011 10:47	5/12/2011 09:35	9.95
	L53296-2 & 3	5/18/2011 09:57	6/1/2011 09:15	13.97
	L53784-2 & 4	8/1/2011 09:45	8/17/2011 09:30	15.99
	L53968-2 & 4	8/17/2011 09:35	9/1/2011 15:05	15.23
	L54416-2 & 4	10/26/2011 11:33	11/9/2011 08:45	13.88
	L54608-2 & 4	11/9/2011 08:45	11/22/2011 13:00	13.18
	L55024-2 & 4	2/1/2012 09:15	2/29/2012 10:20	28.05
Sand Point	L53194-1 <sup>a</sup>	5/2/2011 10:00	5/12/2011 10:30	10.02
	L53296-1 & 4	5/18/2011 09:14	6/1/2011 08:20	13.96
	L53784-1 & 3	8/1/2011 09:00	8/17/2011 08:30	15.98
	L53968-1 & 3	8/17/2011 08:32	9/1/2011 13:20	15.20
	L54416-1 & 3	10/26/2011 10:00	11/9/2011 08:00	13.92
	L54608-1 & 3	11/9/2011 07:59	11/22/2011 13:40	13.24
	L55024-1 & 3	2/1/2012 08:30	2/29/2012 09:45	28.05

<sup>a</sup> Replicate not collected due to spike blank collection.

## 2.3 Measurement of Flow

Two types of flow meters were used to record flow data at stormwater stations during sample collection; an Isco® 4230 bubbler meter and an Isco® 4250 or Sigma® 930 T area/velocity meter. These types of flow meters have a mechanism for measuring water pressure as depth of water which is converted into flow volume using an algorithm, programmed by the user. As previously indicated, stormwater and CSO flow measurements were only used to establish sampling trigger heights and provide some understanding of the magnitude of the flows sampled. To estimate loadings, flow gauge measurements from CSOs, rivers and streams were collated from published sources. Annual stormwater flows were estimated using rainfall and other data. Annual flow through the Ship Canal was estimated using a water balance approach. Details about these flow data and how they are used in loadings estimates are outlined in King County (2013).

## 2.4 Analytical Methods

All samples were analyzed for PCB congeners and most for PBDEs; one lake sample was not analyzed for PBDEs to save on analytical costs. All samples except air deposition samples were analyzed for TOC, DOC, and TSS. A brief review of analytical methods is included below.

### 2.4.1 PCBs

PCB congener analysis followed EPA Method 1668A Revision A, which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. Beginning with samples analyzed on December 5, 2011, AXYS switched to Revision C of Method 1668 during this project. Method 1668C (EPA 2010) 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.

AXYS performed the analysis according to their Standard Operating Procedure (SOP) MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668. Whenever possible, 1 L samples were extracted followed by standard method clean-up, which included layered Acid/Base Silica, Florisil, and Alumina. Some bulk deposition samples were less than 1 L in size and in these cases the entire aliquot was extracted and analyzed. Analysis was performed with an SPB Octyl column and a secondary DB1 column used to resolve the co-eluting congeners PCB156 and PCB157. No samples contained more than 1 percent solids, so solids and liquids were always co-extracted.

#### 2.4.2 PBDEs

All samples were analyzed for PBDE congeners following EPA Method 1614 (EPA 2003), which is a HRGC/HRMS method using an isotope dilution internal standard quantification similar to Method 1668A/C for PCBs. This method provides reliable analyte identification and very low detection limits. An extensive suite of labeled surrogate standards were added before samples were extracted. Data were “recovery-corrected” for losses in extraction and cleanup, and analytes quantified against their labeled analogues or a related labeled compound.

AXYS performed this analysis according to their SOP MLA-033 Analytical Method for the Determination of 46 PBDE Congeners by EPA Method 1614. However, to minimize analytical costs through limited use of standards and calibration, only the nine most commonly found PBDE congeners were reported by AXYS. Approximately 1 L samples were extracted followed by standard method clean-up, which included layered Acid/Base Silica, Florisil, and Alumina.

#### 2.4.3 TOC, DOC and TSS

Conventional analyses followed Standard Methods (SM) protocols (American Public Health Association [APHA] 1998). DOC and TOC were analyzed according to SM5310-B, which is high-temperature combustion with infrared spectroscopy. TSS analysis was performed according to SM2540-D, which is a gravimetric determination.

### 2.5 QAPP Modifications and Deviations

Several implementation issues required deviations from the methods presented in the QAPP (King County 2011a). This section describes the rationale for these changes and their impacts on the project.

#### 2.5.1 Decontamination Procedure for Autosamplers

Isco® autosamplers with level actuators were used to collect stormwater and CSO samples. The autosamplers require several lengths of Teflon® tubing and some shorter lengths of more flexible silicon tubing for the peristaltic pump to function. The QAPP originally proposed that the tubing

would be cleaned using Alconox® detergent, acetone, and de-ionized water. However, analysis of blank samples conducted during the first stormwater sampling (September 26, 2011) event demonstrated that the acetone rinse was contaminating the TOC and DOC analyses with organic carbon residues. Laboratory testing confirmed that multiple de-ionized water rinses were inadequate to remove the residual acetone from inside the Teflon® and silicon tubing. The initial stormwater samples were analyzed for PCBs and PBDEs and these results are valid; however, TOC and DOC results associated with these samples were rejected due to the acetone contamination (Appendix A). Thus, three stormwater samples do not have DOC and TOC results due to acetone contamination of the autosampler tubing.

To address this issue and obtain unbiased TOC and DOC data for stormwater collected by autosamplers, the original cleaning protocol in the QAPP was altered. Site-specific dedicated Teflon® tubing was used at each sampling location. Prior to sampling, this tubing was washed with Alconox detergent and rinsed with de-ionized water; but no organic solvents were used. These tubing use changes provided minimal opportunity for different stormwater or CSO sampling locations to bias each other's PCB and PBDE results. Eliminating the organic solvent rinse from the autosampler cleaning protocol allowed for uncontaminated TOC and DOC samples as demonstrated by subsequent equipment blank results.

### 2.5.2 PBDEs in Equipment Blanks

Initial results raised some concerns about equipment blanks - notably, equipment blanks conducted with King County laboratory water. This water was used for Niskin, Scott bottle, air deposition samplers and Isco® autosampler equipment blanks. After blank results were reviewed, it was apparent that a significant concentration of tPBDEs was present in blanks and project scientists suspected King County laboratory water may have been the source. Niskin and Scott bottle blanks were especially concerning relative to ambient Lake Washington and Ship Canal tPBDE concentrations. Therefore, two additional blanks were analyzed using laboratory grade water shipped to King County by AXYS. The tPBDEs in equipment blanks using AXYS supplied water had approximately four times lower tPBDE concentrations. This confirmed suspicions that King County laboratory waters were a source of PBDEs to equipment blanks.

These laboratory waters are not suspected to have contaminated actual samples collected with Niskin or Scott bottles since these samplers were rinsed with site waters prior to collection. The potential impacts of KCEL laboratory water contamination on air deposition results and on stormwater and CSO samples collected with autosamplers are addressed in those results sections.

### 2.5.3 Scope Changes Due to Budget Restrictions

Collection of storm and CSO water samples proved to be more time consuming and challenging than originally anticipated. To provide enough time and staff resources to collect stormwater samples at the remaining locations, the Kirkland Moss Bay stormwater site was dropped from the site list. Land use and anticipated loadings at the Moss Bay site were considered similar to the Kirkland Central Way location. Therefore, the lack of stormwater concentration data from the Moss Bay site is not considered to impact the overall ability of the project to estimate stormwater loadings.

Another change related to the additional resources required for stormwater sampling was elimination of the filtration and filtrate/solids analysis for PBDE's for a composite lake sample. Filtration and filtrate/solids analysis for PCBs was conducted on epilimnion and hypolimnion samples as well as a mixed lake sample. To help recover the unanticipated costs of stormwater sampling, the filtrate/solids analysis for PBDEs of a mixed lake sample was eliminated. This is not

expected to impact the objectives of the project as these analyses were conducted to acquire data for the modeling phase which will only be conducted for PCBs.

The last budgetary scope modification required changing two, two-week sampling events into one four-week sampling event. This change is not expected to impact the air deposition data analysis because deposition was measured over the equivalent time period as originally planned.

#### 2.5.4 Change in CSO Station Location

Within the Henderson Street CSO basin, both the area and pipe configuration proved to be variable and highly dependent on pump station status and volume of waste and stormwater from pipes outside of the basin. To address this issue, the Henderson Street CSO station was moved approximately 2.8 km north along the Lake Washington shoreline to a more defined and predictable basin at the southwest boundary of Seward Park. The Seward Park CSO basin is smaller than the Henderson CSO basin, 111 vs. 488 acres respectively, and it is characterized by greater residential land use with less light commercial uses.

#### 2.5.5 Less Than Minimum Duration for a Stormwater Sample

The last modification to the QAPP concerns the sampling duration for a storm event at the Ballard 150 CSO. One of the sampled overflow events was quite intense and the force of the flow in the pipe moved the inlet of the sampler tubing. This movement, combined with the apparent short duration of the overflow event, prevented the autosampler from collecting over the 2 hour time period targeted by the QAPP. The autosampler was only able to collect for approximately 20 minutes. Initially, the project team was uncertain if this sample would be needed, so the sample was preserved and held in the laboratory. Once it became clear that the target number of CSO samples would not be met, this sample was sent for analysis. At this point, holding times for TOC, DOC and TSS had expired and these analyses were not conducted. PCB and PBDE analyses were well within their 1-year holding time. Although the flow was violent enough to dislodge the intake tubing, little else is known about the ~20 minutes of the storm which were collected. Thus, bias in this short duration sampling event cannot be predicted.

## 2.6 Data Validation and Corrective Actions

Data were validated according to method specifications and to ensure they met the project data quality objectives (DQOs) as described in the QAPP. This generally meant that methods and their respective results were validated to level “2A” (EPA, 2009) and all data were assessed for usability. A detailed memo describing the verification, validation, and usability examinations conducted is provided in Appendix A.

The most significant issue affecting data usability was unacceptable method blank contamination experienced in some PCB samples. After discussions with AXYS, the contract laboratory, this contamination was traced to laboratory construction conducted at the time certain sample batches were extracted and/or analyzed. Per EPA direction (G. Grepo-Grove, pers. comm.) select PCB-7 results were consequently considered to be non-detect at elevated detection limits equal to the method blank concentration. Depending on the sample, the affected congener results were either a trivial or a substantive (>20%) portion of the tPCBs in the affected samples.

In response to this issue, AXYS re-extracted and re-analyzed 9 samples for PCB-7. The 9 samples were selected because PCB-7 was greater than 20% of the total PCB sum and enough sample

volume remained for re-extraction. PCB-7 was either non-detect at <3.6 pg/L or only detected in the reanalyzed samples at between 2 and 7 pg/L. These results demonstrate that the PCB-7 detections were generally a product of laboratory contamination and not native to any of the sampled waters. Thus, those samples which were not re-extracted and re-analyzed are considered valid and complete despite their non-detect PCB-7 results. Only the revised data are graphed, tabulated and presented in the results section below.

Another significant issue was PBDE contamination discovered in laboratory water. The use of King County laboratory water for cleaning and decontamination is not suspected to have significantly contaminated most environmental samples. Select air deposition and stormwater samples for tPBDEs were exceptions to this pattern. The mass of PCBs and PBDEs in air deposition has been compared to the mass of tPCBs/tPBDEs potentially introduced by the funnel rinse water, but the reported sample masses have not been corrected for this potential contamination. The potentially contaminated stormwater samples have elevated detection limits set based on the highest detected congener in their associated equipment blanks. Thus, equipment and method blank contamination functions as a “lower limit” on result reporting.

The data usability portions of this review are discussed in the next section with reference to the DQOs.

## 2.7 Total PCB and PBDE Reporting

The following subsections will present PCB and PBDE concentrations in picograms per liter (pg/L), the original units reported for each congener by the laboratory. tPCB and tPBDE sums were rounded to the nearest picogram. These totals were calculated by the following rules as prescribed by EPA Region 10 (G. Greppo-Grove, personal communication):

- Non-detect congeners were not included in sums.
- Congeners which did not meet all method identification criteria, estimated maximum potential concentrations, and thus “K” flagged by the analytical laboratory were re-qualified as non-detect at the reported concentration.
- When more than one method blank was conducted for an analytical batch, the average method blank concentration was used.
- Detected congeners less than five times their respective method blank concentrations were not included in the sums except when none of the detected congeners were greater than five times the method blank (EPA, 1995). In these cases, the congener detection limit was set at the reported method blank value.
- For stormwater and CSO samples collected using autosamplers, congener results were also compared to equipment blank results in the same manner as the method blank comparison. Thus, any congeners that remained detected after the method blank comparison were compared to five times the concentration found in the autosampler blank. Only those PCB and PBDE congeners greater than five times the concentrations found in the equipment blank were summed. Detected congeners less than five times their respective equipment blank concentrations were thereafter considered non-detect at the reported equipment blank value.
- For data presentation purposes, the single largest congener detection limit was used as a surrogate value for entirely non-detect samples. This was the largest value of the detection limit, average method blank concentration for the batch, “K” flagged value, or for

stormwater and CSO samples collected with autosamplers, the concentration detected in the autosampler equipment blank.

- For samples collected with Niskin or Scott bottles, samples were not directly compared with the associated equipment blanks because both of these sampling devices were rinsed with site water prior to collecting samples.
- For bulk deposition samples, the mass of tPBDEs or tPCBs in the rinse water was estimated by multiplying the detected equipment blank concentration by the sample specific rinse volume. The rinse water tPCB and tPBDE mass was then compared as a percentage with the environmental sample's tPCB or tPBDE result mass respectively.

For reporting and summary statistics purposes, laboratory duplicates were averaged when applicable. The resulting value was then averaged with any field replicates.

Atmospheric deposition rates were calculated using the deposited mass of tPCBs or tPBDEs. These masses were normalized to the cross-section area of the funnel opening along with the deployment duration. The atmospheric deposition tables below (Section 3.0) report duration to the nearest 1/100<sup>th</sup> of a day (14.4 minutes), although deployment normalization was conducted to the nearest minute. Because sample concentration, sample volume, funnel size, and duration are all key variables influencing the calculated deposition rate, they have been presented alongside each sample tPCB and tPBDE result to document the final calculated deposition rates.

For statistical tabulation purposes, one value is reported per sampling event. Summary statistics were prepared to describe the range of results and other characteristics of the sample set mathematically. Unlike the statistics tables, on the figures in Section 3.0, field replicates were not averaged to help visually illustrate sampling event heterogeneity. Following the result presentations, tPCB and tPBDE results have been compared to selected regional data to illustrate and describe similarities and differences with previous studies.

## 3.0. RESULTS

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The results section first evaluates data usability and in particular caveats data accuracy and precision. Specific chemistry results follow in section 3.2.

### 3.1 Data Quality Objectives and Usability

The DQOs were to collect data of known and sufficient quality to meet the project goals. The data validation and usability assessment of project data determined whether the data collected were of sufficient quality to meet project goals. A discussion of data validation for PCB and PBDE congener data is provided in Appendix A. A data usability assessment addressing the precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity DQOs is described in this section.

#### 3.1.1 Precision

Precision is an estimate of the repeatability of measured concentrations and was measured through the use of field replicates. Contaminant concentrations in some of the targeted pathways are known to be highly variable (e.g., stormwater), while others are thought to be relatively consistent (e.g., rivers); on average, precision was expected to be relatively low. The planned field replicate precision for sampled matrices was expected to meet the goals in Table 9. However, many of these pathways had not been sampled and analyzed by high resolution PCB/PBDE methods in the Lake Washington watershed before, so the precision goals were merely presumptive goals. It's notable that the precision goals for stormwater, tributaries, direct road runoff and atmospheric deposition were more reliably met than Lake Washington outflow waters at the locks and inflow waters from the Sammamish and Cedar Rivers which the poorest precision and did not meet QAPP goals 50 to 66% of the time.

Only those congeners which were detected at concentrations greater than five times the average concentration in the batch's method blank were summed to create the tPCB or tPBDE value (EPA, 1995). Particularly in ambient lake and river waters, detected congeners were frequently close to five times the average batch method blank. Thus, some of the high analytical variability between lake and river replicates is a product of the sample having particular congeners at for example, 5.2 times the method blanks, while the replicate might only have the same congener at 4.7 times the method blank. In this situation, this congener would have contributed to the sum for the primary sample but would not have contributed to the tPCB or tPBDE sums in the replicate. These slight differences were accentuated by the blank qualification rules utilized for this project and the RSDs in excess of the lake and river DQOs are partially due to this issue. Thus, samples with higher tPCB and tPBDE concentrations met the precision goals more reliably, in part, because of better analytical precision at elevated concentrations above the laboratory background.

Despite the overly ambitious precision DQOs, the resulting dataset and the variability therein are still useful to develop loading estimates, and plan future study questions and analyses even when precision objectives were not met. This dataset will assist future projects with similar sample matrices in establishing better precision targets.

**Table 9. Precision of field replicates by sample type.**

Sample Type	tPCB		tPBDE		TOC and DOC			TSS	
	Precision Goal (RSD)	Met RSD Goal <sup>1</sup>	Precision Goal (RSD)	Met RSD Goal <sup>1</sup>	Precision Goal (RSD)	Met TOC Goal <sup>1</sup>	Met DOC Goal	Goal (RSD)	Met Goal <sup>1</sup>
Lake Washington and Ship Canal ambient water	±20%	4/8, 50%	±40%	3/7, 43%	±20%	8/8, 100%	8/8, 100%	25%	8/8, 100%
Lake Washington/H. Chittenden Locks outflow water	±25%	2/4, 50%	±40%	0/4, 0%	±20%	4/4, 100%	4/4, 100%	25%	4/4, 100%
Cedar and Sammamish River water	±25%	2/6, 33%	±40%	1/6, 17%	±20%	6/6, 100%	6/6, 100%	25%	6/6, 100%
Stormwater discharge outfalls	±50%	3/3, 100%	±50%	3/3, 100%	±20%	3/3, 100%	3/3, 100%	25%	3/3, 100%
Tributaries	±50%	9/12, 75%	±50%	9/12, 75%	±20%	12/12, 100%	12/12, 100%	25%	12/12, 100%
CSO <sup>2</sup>	none	RPD 105%	none	RPD 54.1%	none	RPD 1%	RPD 1.7%	none	RPD 1.7%
Direct road runoff	±50%	1/1, 100%	±50%	1/1, 100%	±20%	- <sup>2</sup>	- <sup>2</sup>	25%	- <sup>2</sup>
Atmospheric deposition	±50%	12/13, 92%	±50%	5/13, 38%	None <sup>3</sup>	-	-	-	-

RSD = relative standard deviation

<sup>1</sup> Number of replicate pairs meeting goal/total samples, percent meeting goal

<sup>2</sup> No replicates were planned for CSO locations, however, one field replicate pair was opportunistically collected and those RPDs are reported here.

<sup>3</sup> Conventional parameters were not applicable nor measured in atmospheric deposition samples

### 3.1.2 Accuracy

Accuracy of PCB congener data is not directly quantifiable since certified reference materials (CRMs) do not exist for the concentration ranges in natural waters. The isotopic dilution methods chosen for this study are the most rigorous methods for PCB and PBDE congener analysis. These methods use isotopically-labeled PCBs or PBDEs to track the recovery performance of the range of congener homologues. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample. Therefore, the PCB and PBDE congener concentrations are believed to be as accurate as current analytical capabilities allow.

### 3.1.3 Sensitivity

The high sensitivity of these analytical methods also allowed for detections of individual PCB and PBDE congeners in the 1-10 pg/L range depending on the water matrix of interest. For instance, lake and river water samples were frequently sensitive enough to be close to the contract laboratory's ability to distinguish from background concentrations in blanks.

### 3.1.4 Bias

Bias is defined as a systematic deviation from the true value and is closely tied to what each sample is intended to represent. Grab samples were meant to represent the concentration of the parameter of interest at that moment in time. Rivers and streams were assumed to be well mixed and grab samples represent the whole water concentration entering Lake Washington at that time. Composite samples of Lake Washington water were intended to represent the entire lake's water concentration under mixed conditions, or the epilimnion or hypolimnion respectively. Various contaminant concentrations in CSOs and stormwaters are known to vary both by overflow event and within an overflow event. While tPCB and tPBDE concentrations had not been previously measured in Lake Washington or Ship Canal CSOs, concentrations in their discharges were suspected to vary similarly. Thus, composite samples were collected over two hours during CSO events to try to account for variation in contaminant concentrations throughout a CSO event and obtain a value representative of the average concentration for the entire CSO event. The 2-hour interval was selected for practical reasons and probably represents a bias relative to much longer CSO events which are rare and particularly challenging to sample.

For atmospheric deposition, no standardized methods quantifying combined wet and dry deposition exist. The methods chosen for this project were modeled after another local regional study of bulk deposition (Brandenberger et al., 2010). They were adapted to this project and similar approaches have been successfully implemented by King County for other source control projects (King County 2011b). The samples are believed to represent the cumulative wet and dry deposition throughout the sampler deployment period. However, since no industry standard or certified methods for bulk deposition exist, it is difficult to document any possible systematic bias in the approach chosen.

### 3.1.5 Completeness

Completeness is defined as the percentage of samples collected and analyzed relative to what was planned in the QAPP. Table 10 below presents the sample numbers originally planned in the QAPP,

the sample numbers changed by amendments and changes to the QAPP objectives, and the numbers of samples actually collected. The completeness goal of 90% was not met for the revised stormwater and CSO sampling plans which were only 87.5% completed. However, this 2.5% completeness shortcoming is not believed to substantially alter the project's ability to meet overall objectives. Two extra quarterly samples were inadvertently collected from the downstream Cedar River station.

**Table 10. Sampling stations and counts relative to completeness goals**

Sample type	Station Locations	Locator	Planned Frequency	Total Samples In QAPP Including Replicates	Revised Plan Sample Totals	Collected Samples	Completeness Goal Met?
<b>Ambient Waterbodies</b>							
Upstream Input	Cedar River at USGS gage	0438	Bimonthly	9	9	9	Yes 100%+
	Cedar River mouth	X438	Quarter 1 & 3	2	2	4	
	Sammamish River	B472	Bimonthly	9	9	9	
Downstream Output	Montlake Cut	0540	Bimonthly	9	9	9	Yes 94%
	H. Chittenden Locks	0580	Bimonthly	9	9	9	
Lake Washington	Composite across 3 stations	0826, 0852, 0890	Bimonthly	16 <sup>1</sup>	15	15	Yes 100%
Tributaries	Juanita Creek mouth	0446	Quarterly	8	8	8	
	May Creek mouth	0440	Quarterly	8	8	8	
	Thornton Creek mouth	0434	Quarterly	8	8	8	
<b>Stormwater, CSO and Road runoff</b>							
Stormwater	Central Way west of I-405	CENTRALWYKIRK	Quarterly	4-8	4	4	No (87.5% complete vs. 90% goal)
Stormwater	Moss Bay drainage	-	Quarterly	4-8	0	0	
Stormwater	North Renton drainage near Gene Coulon Park	0828JC7SB	Quarterly	4-8	4	4	
Stormwater	N. Mercer Island drainage at KC Pump Station	MERCERISL10-EPA	Quarterly	4-8	4	4	
Stormwater	Fremont drainage	FREMONTSPU102	Quarterly	4-8	4	3	
Stormwater	West of Seward Park drainage	SEWARDSPU173	Quarterly	4-8	4	3	
Stormwater	Madrona drainage	MADRONASPU81	Quarterly	4-8	4	4	
CSO	Henderson St. CSO	-	Quarterly	4	0	0	
CSO	Seward Park CSO	SEWARDSPU44	Quarterly	0	4	3	
CSO	150 CSO	BALLARDSPU150	Quarterly	4	4	2	
CSO	Dexter Ave CSO	S0335026	Quarterly	4	4	3	
Road Runoff	I-90 bridge, east high rise	I-90_E_HIGHRISE	Quarterly	8	4	5	
<b>Atmospheric, Wet/dry Deposition</b>							
Bulk deposition	Sand Point Way, near Magnuson Park	SAND_POINT	2/quarter	15	13	13	Yes 100%
Bulk deposition	Beacon Hill WA Department of Ecology weather station	BWR	2/quarter	15	13	13	
<b>Total Samples</b>				<b>156</b>	<b>149</b>	<b>146</b>	

<sup>1</sup>Three of these mid-lake samples were filtered and the filtrate and particulate fractions analyzed separately by AXYS.

### 3.1.6 Conventionals

Table 11 describes the minimum QC required for the conventionals analyses which were met for all batches and samples. As discussed previously in Section 2.5.1, six stormwater samples were affected by acetone contamination of the Teflon tubing and these TOC and DOC results are considered un-usable. The PCB, PBDE, and TSS results from these samples were not affected. All other conventionals results met the acceptance criteria in Table 11. PCB and PBDE analyses have additional acceptance criteria which are beyond the scope of a single table such as this, but these criteria are discussed in the data validation memo (Appendix A).

**Table 11. QA/QC Frequency and laboratory acceptance criteria for conventionals**

Frequency	Method Blank 1 per Batch*	Lab Duplicate (RPD) 1 per Batch*	Spike Blank (% Recovery) 1 per Batch*	Matrix Spike (% Recovery) 1 per Batch*	LCS (% Recovery) 1 per Batch*	Met All Frequency and Acceptance Criteria?
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	Yes
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%	Yes
Total Suspended Solids	<MDL	25%	N/A	N/A	80-120%	Yes

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

### 3.1.7 Summary

Overall, the data quality objectives for accuracy, bias, representativeness, completeness, comparability, and sensitivity were met. Some particular matrices, especially those with low tPCB and tPBDE concentrations, were subject to sample-specific qualifications and caveats especially with regards to low concentrations of tPBDEs. Particularly where precision deviated from goals, data users are advised to carry forth such qualification into further analysis and reporting if possible.

## 3.2 Chemistry Results

The following subsections present tPCB and tPBDE concentrations in picograms per liter (pg/L); a picogram is  $1 \times 10^{-12}$  gram. Conventional parameters (TOC, DOC and TSS) are presented in milligrams per liter (mg/L). Data for conventional parameters were not used in the loadings estimates, but will be helpful in development of lake models in the next phase of the project. Appendix B provides the results for the conventional parameters and the individual congeners,

including laboratory and project data qualifiers, in electronic tables. This section presents summary statistics for each pathway (by station, and combined) as they are used in the loadings estimations (King County, 2013). As mentioned earlier, lab duplicates were first averaged, and the resulting values then averaged with any field replicates. For summary statistics tables, the highest reported non-detect result was used as a surrogate value for samples with no detected congeners. As described in Section 3.1, this was the higher of the equipment blank result for stormwater or CSO samples collected with autosamplers or the method blank result for samples which were re-qualified as non-detect based on blanks.

In addition, figures include individual sample results. Concentrations being reported as non-detects are shown on the figures and tables with an associated “U”. If any sample, lab duplicate or field replicate had a quantifiable tPCB or tPBDE sum, the event was tallied as a detection for frequency of detection (FOD) calculations. The number of unique sampling events comprises the FOD denominator on summary tables.

### 3.2.1 Ambient Waters

Ambient waters include the three gauged tributaries, Thornton, Juanita, and May Creeks and two rivers, Cedar and Sammamish in addition to samples collected from Lake Washington (stratified and mixed lake composites) and the Montlake and Ballard Locks outflow locations. The following subsections provide a summary of data collected at these locations.

#### 3.2.1.1 Tributaries

tPCB and tPBDE results for individual tributary samples are presented in Figures 19 and 20, respectively. As expected, the concentrations of both contaminants were lowest during base flow conditions. The base flow tPCB concentrations in Thornton Creek were an order of magnitude higher than the other two tributaries. tPCB and tPBDE concentrations in Thornton Creek storm flows were also consistently higher than levels detected in May or Juanita Creeks.

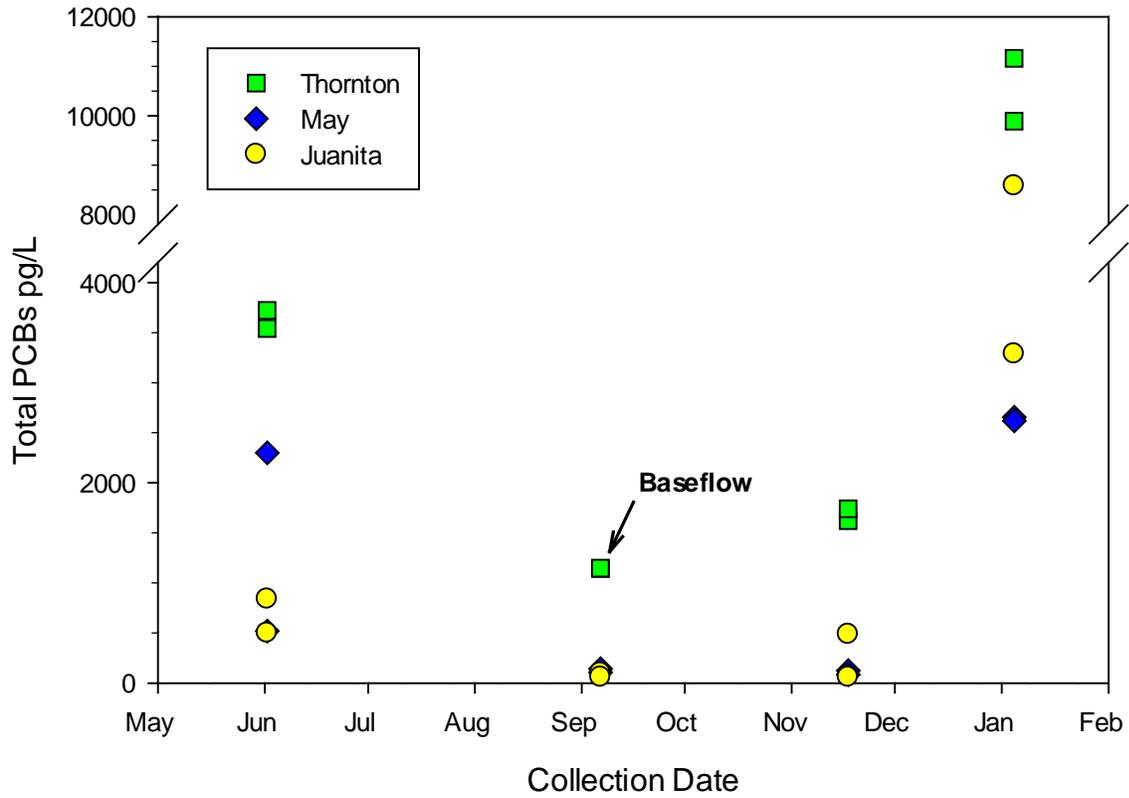


Figure 19. tPCB results for stream samples by date (2011-2012), replicates shown.

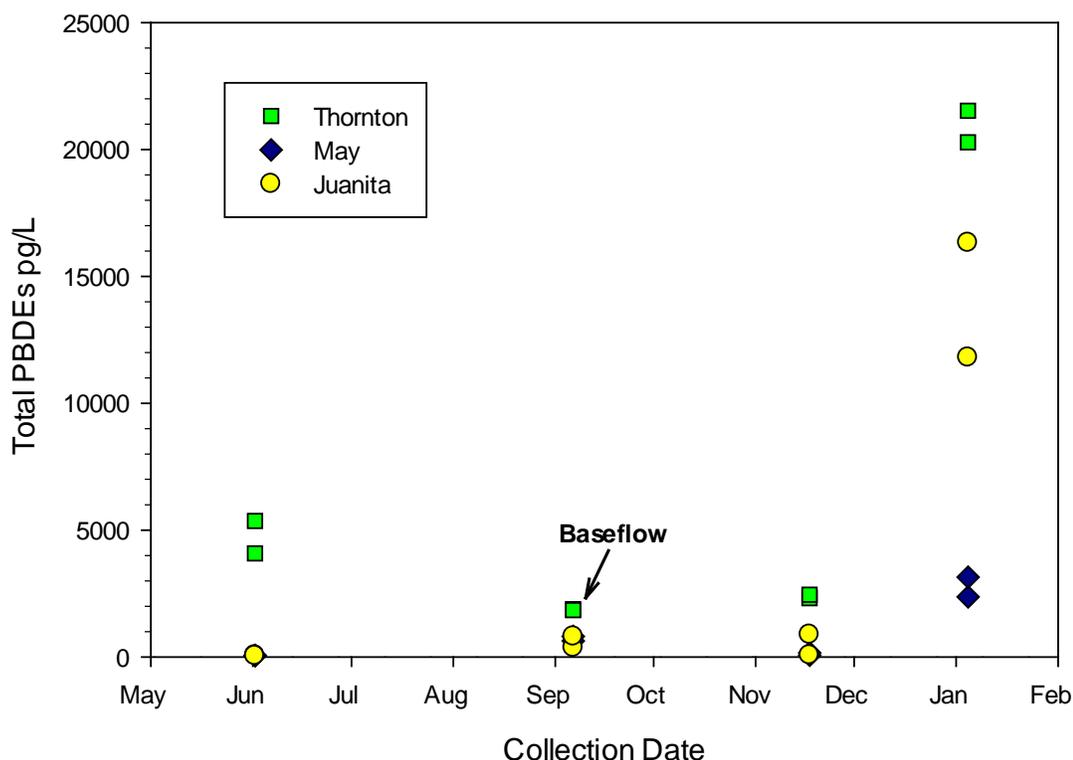


Figure 20. tPBDE results for stream samples by date (2011-2012), replicates shown.

Table 12 presents summary statistics for base and storm flow samples combined for all locations. For storm samples, the 25<sup>th</sup> percentile is approximately six times lower than the 75<sup>th</sup> percentile concentrations of tPCBs, reflecting the wide variability in tributary concentrations between storm events. Lower level tPBDE analysis was confounded by method and autosampler contamination issues, and the minimum storm flow tPBDE concentration is suspected to be biased low due to these influences. When compared to tPCBs, higher average concentrations of tPBDEs were observed in the tributaries during base flow and storm events.

Table 12. tPCB and tPBDE summary statistics for tributary samples combined in pg/L

Flow	Analysis	Detections/Events	Average	Minimum	Maximum	25th Percentile	Median	75th Percentile
Storm	tPCB	9/9	2,985	105	10,527	670	1,681	3,631
Storm	tPBDE	9/9	5,061	59	20,910	116	2,385	4,722
Base flow	tPCB	3/3	451	81	1,146	-	126	-
Base flow	tPBDE	3/3	1,058	588	1,864	-	722	-

Note: 25<sup>th</sup> and 75<sup>th</sup> percentiles are not presented when N<4.

The summary statistics for conventional parameters in tributary samples are presented in Table 13. Average DOC, TOC, and TSS are between two and 15 times higher in storm samples compared to base flow conditions. TSS exhibited the widest range with a maximum storm flow concentration two orders of magnitude higher than the minimum storm flow concentration or any of the base flow measurements.

**Table 13. Summary statistics for tributary sample conventionals results by flow regime in mg/L.**

Flow	Analysis	Detections/ Events	Average	Minimum	Maximum	25th Percentile	Median	75th Percentile
Storm	DOC	9/9	5.4	4.2	6.7	5.0	5.5	5.7
	TOC	9/9	9.5	5.8	18.5	6.5	7.9	10.6
	TSS	9/9	46.9	3.1	207.5	7.3	23.3	42
Base flow	DOC	3/3	2.7	2.4	3.3	2.5	2.5	2.0
	TOC	3/3	2.8	2.3	3.6	2.4	2.5	3.0
	TSS	3/3	2.8	1.2	5.6	1.3	1.5	3.5

### 3.2.1.2 Rivers

tPCB and tPBDE results for individual river samples are presented in Figures 21 and 22, respectively. tPCB concentrations were similar in the two rivers. tPBDE concentrations were more variable than tPCBs and overall low. One PBDE value was reported as non-detect with slightly elevated detection limits due to method blank contamination. Maximum tPBDE concentrations in the Sammamish and upstream Cedar River stations were similar. The lowest concentrations were detected in the downstream Cedar station. However, these very low detections are an artifact of the method blank qualification procedures used. Because these values are below five times the method blank concentrations, they are suspected to be biased low relative to the true concentrations.

Two locations (X438 [downstream] and 0438 [upstream]) were sampled on the Cedar River to evaluate possible industrial sources near the river mouth and the influence of inputs from the highly urban area of Renton between the upstream and downstream station. The downstream Cedar River station's tPCB concentrations were similar to or lower than those at the upstream station. The upstream Cedar River station had one tPBDE detection at 3,150 pg/L and another detected tPBDE sum of 2.5 pg/L. The downstream location had detected tPBDEs of 20 to 101 pg/L and a non-detect for tPBDEs at elevated detection limit of 232 pg/L.

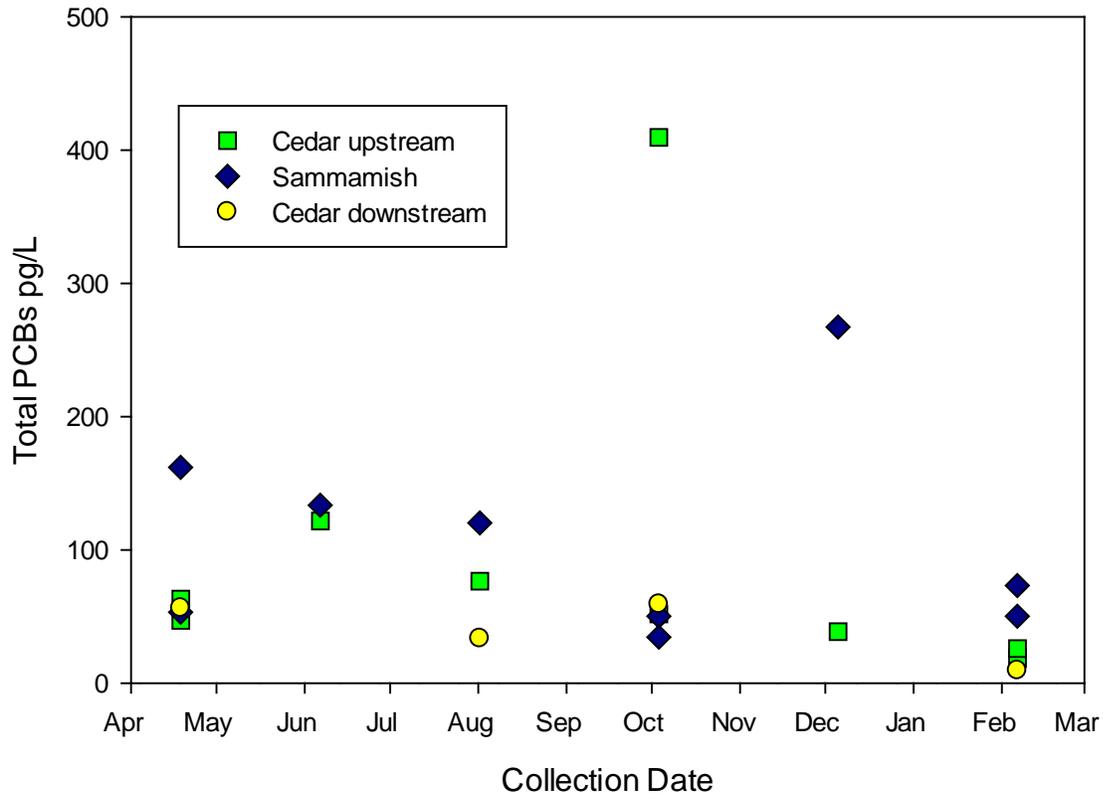


Figure 21. tPCB results for river samples by date (2011-2012), replicates shown.

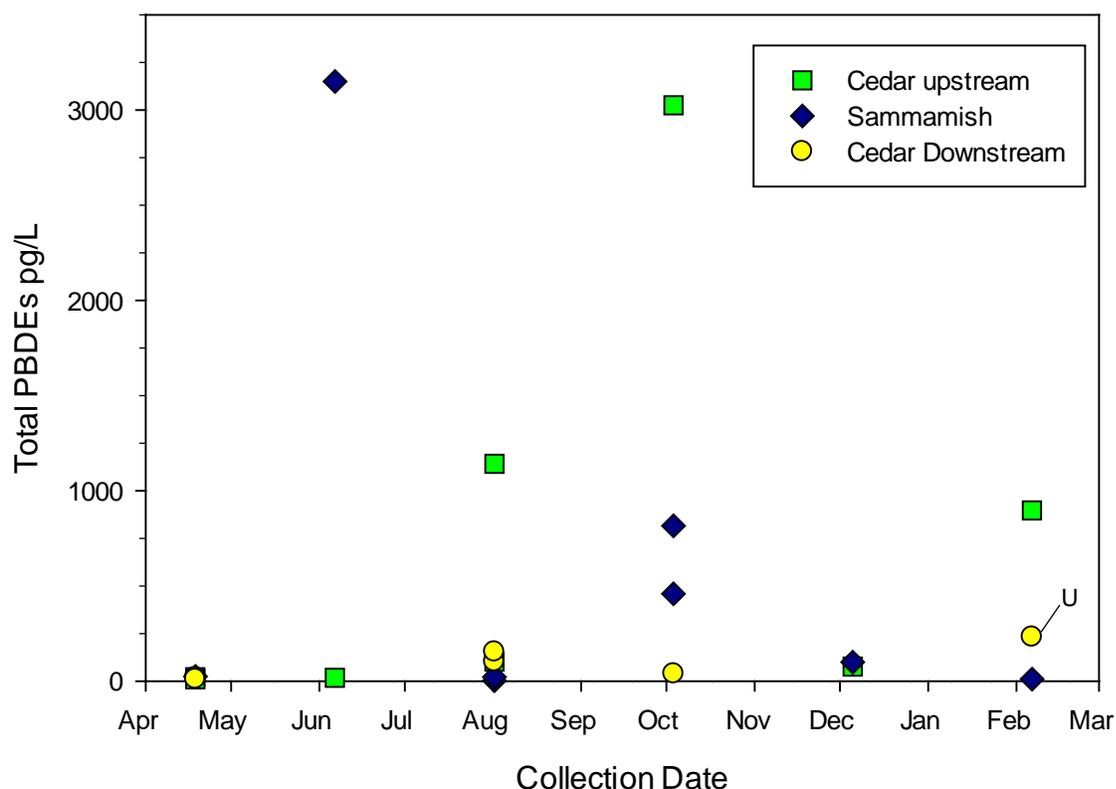


Figure 22. tPBDE results for river samples by date (2011-2012), replicates shown.

The hypothesis that concentrations of tPCB and tPBDE might increase between the upstream and downstream Cedar River stations does not appear to be supported by current data. The tPCB results are generally quite similar between the up and downstream Cedar stations and the maximum detected tPCBs were found at the upstream location. None of the four tPBDE result pairs has a higher concentration at the downstream Cedar location and both levels remain low to non-detect (with modestly elevated detection limits). The very low concentrations of tPCBs and tPBDEs detected at the upstream and downstream stations similar to and within 5 times the method blanks made detecting differences between the two Cedar stations problematic.

Table 14 presents summary statistics of tPCB and tPBDE concentrations for all samples combined. Notably, the lowest tPCB concentration detected in any sample for this project was measured in the Cedar River. The range of tPCB and tPBDE concentrations indicates tPBDE concentrations are more variable than tPCBs. Overall, tPBDE concentrations in the rivers were about five times higher than tPCB concentrations. Method blank contamination limits understanding and reporting of accurate unbiased river tPBDE concentrations.

Table 14. tPCB and tPBDE summary statistics for river samples in pg/L

Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
tPCB	16/16	90	10	267	41	60	121
tPBDE	15/16	478	3	3,150	17	88	444

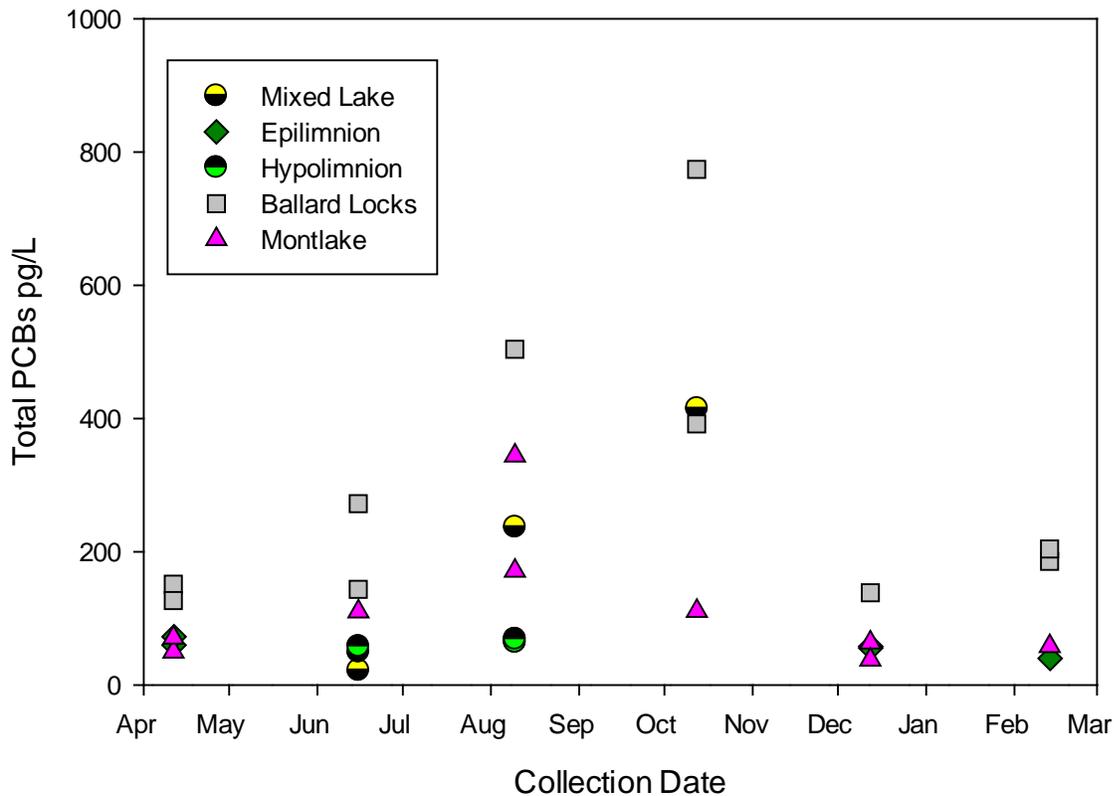
Summary statistics for conventional parameters in river samples are presented in Table 15. DOC exhibited the greatest range across river samples. However, the overall similarity of percentile values indicates low variability in all conventional parameters at all locations.

**Table 15. Summary statistics for river conventional parameter concentrations in mg/L.**

Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
DOC	16/16	2.4	0.7	5.0	1.3	1.4	4.5
TOC	16/16	2.8	1.4	5.6	1.5	1.7	4.7
TSS	16/16	3.3	1.5	4.7	2.9	3.2	3.9

### 3.2.1.3 Lake and Ship Canal

tPCB and tPBDE results for individual lake and Ship Canal samples are presented in Figures 23 and 24, respectively. The highest tPCB and tPBDE concentrations were measured at the Ballard Locks station. tPCBs in the epilimnion and the Montlake Cut stations were consistently lower than the Ballard Locks station. tPBDEs were generally 10 times higher than tPCBs and more variable as well. The highest detected tPBDE concentration of all lake and Ship Canal stations was at the Ballard Locks.



**Figure 23. tPCB results for lake and ship canal samples by date (2011-2012), replicates shown.**

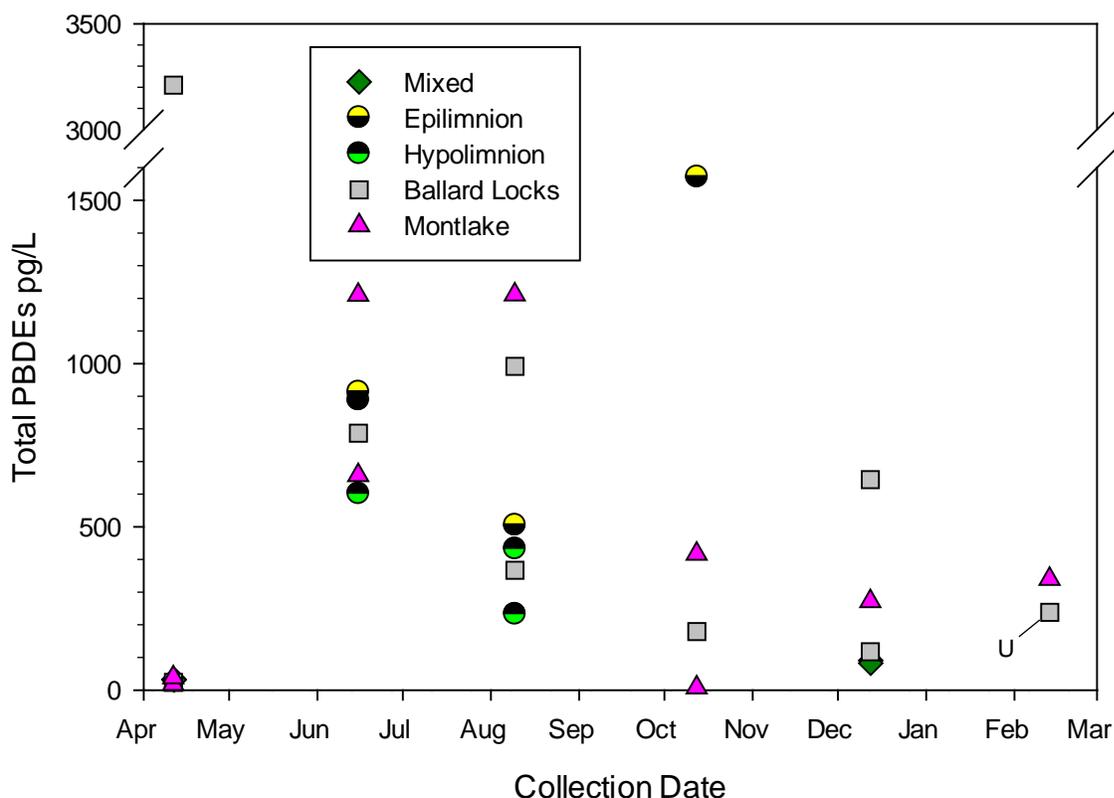


Figure 24. tPBDE results for lake and ship canal samples by date (2011-2012), replicates shown.

Tables 16 and 17 present summary statistics for tPCB and tPBDE parameters by location for the lake and Ship Canal samples. In both Lake Washington and the two Ship Canal stations, average concentrations of tPBDEs were higher than tPCBs. The tPBDE values are more uncertain due to the relatively low levels detected relative to PBDE method blanks. For tPCBs and tPBDEs, more variability was observed in the epilimnion samples than in the hypolimnion or mixed lake samples.

Table 16. Lake Washington stratified and mixed lake composite tPCB and tPBDE summary statistics in pg/L.

Lake stratification	Analysis	Detections/Events	Minimum	Maximum	Average	Median
Mixed	tPCB	3/3	40	66	54	57
Hypolimnion	tPCB	2/2	58	66	62	62
Epilimnion	tPCB	3/3	36	415	229	237
Mixed	tPBDE	2/2	32	86	59	59
Hypolimnion	tPBDE	2/2	332	601	466	466
Epilimnion	tPBDE	3/3	505	1572	993	901

Note: 25<sup>th</sup> and 75<sup>th</sup> percentiles are not presented when N<4.

**Table 17. Lake Washington Ship Canal at Montlake and the Ballard Locks tPCB and tPBDE summary statistics in pg/L.**

Ship Canal Location	Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
Montlake	tPCB	6/6	108	51	258	59	85	111
Locks	tPCB	6/6	295	138	583	153	201	430
Montlake	tPBDE	6/6	647	179	1,617	274	530	760
Locks	tPBDE	6/6	801	29	2,148	227	603	1,142

The results of the filtered samples analyses are presented in Table 18. tPCBs were overwhelmingly found associated with the dissolved phase. During the un-stratified periods of the year (October-March) approximately 71% of the PCBs in the water column appear to be in the dissolved phase, with 29% in the particulate phase. During stratified periods, this ratio appears consistent in the epilimnion with about 77.5% of the tPCBs in the dissolved phase. In the hypolimnion, a slightly higher ratio is observed; approximately 87% of the tPCBs are associated with the dissolved phase. The epilimnion tPCB filtrate plus particulate concentrations appear low relative to whole water samples (Table 16). However, it is not known if this is accurate or due to unknown biases.

Estimates of PBDE partitioning are confounded by the non-detect particulate samples with relatively elevated detection limits. Any estimate of the dissolved-particulate partitioning would depend on whatever surrogate value was used for these non-detect particulate results since all filter results were within five times the filter method blank.

The apparent lack of association between tPCBs and the particulate phase may be an artifact of how close the measured concentrations of tPCBs in filtered water and solids are to the detection limit. Precision at concentrations close to the limits of detection is lower, yet small changes in the measured values have a large impact on the calculated percentage of tPCBs in each phase.

**Table 18. Lake Washington stratified and mixed lake composite tPCB and tPBDE paired filtrate and solids results.**

Lake Stratification	Analysis	Dissolved Mass pg/L	Particulate Mass pg/sample <sup>1</sup>	Total PCBs per liter	Percent Dissolved
Mixed	tPCB	40	16	56	71.4%
Hypolimnion	tPCB	60	9	69	86.9%
Epilimnion	tPCB	62	18	80	77.5%
Hypolimnion	tPBDE	96	381 U	N/A	N/A
Epilimnion	tPBDE	554	777 U	N/A	N/A

No filtration was done for tPBDEs under mixed Lake conditions for budgetary reasons and because this analysis is to supplement PCB fate and transport modeling.

U = non-detect, J= estimated, N/A = one or more non-detect values

<sup>1</sup> pg/sample denotes analysis of solids from 1.1µm filtration of one liter of water.

Summary statistics for conventional parameters in Lake Washington and the Ship Canal are presented in Tables 20 and 21. The average DOC and TOC concentrations were slightly higher in the epilimnion of Lake Washington compared to either the hypolimnion or the mixed lake condition. Average TOC appears to decrease, while average DOC appears to increase slightly between

Montlake and the Ballard Locks, although this is unlikely to be biologically significant. TSS concentrations in lake and both Ship Canal samples were similar and low, although DOC appears to increase slightly between Montlake and the Ballard Locks. Overall, conventional parameters between stations are very similar.

**Table 19. Lake Washington stratified and mixed lake composite conventionals results in mg/L**

Lake Stratification	Analysis	Detections/Events	Average	Minimum	Maximum	Median
Mixed	DOC	3/3	2.4	2.3	2.6	2.4
	TOC	3/3	2.5	2.3	2.6	2.6
	TSS	2/3	1.0	0.6	1.7	0.7
Hypolimnion	DOC	3/3	2.7	2.5	2.9	2.7
	TOC	3/3	2.8	2.7	2.8	2.8
	TSS	3/3	1.0	0.7	1.3	0.9
Epilimnion	DOC	3/3	2.8	2.6	2.9	2.9
	TOC	3/3	3.0	2.9	3.1	3.1
	TSS	3/3	1	0.9	1.4	1.0

Note: 25<sup>th</sup> and 75<sup>th</sup> percentiles are not presented when N<4.

**Table 20. Lake Washington Ship Canal at Montlake Cut and the Ballard Locks conventionals summary statistics in mg/L.**

Ship Canal Location	Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
Montlake	DOC	6/6	2.6	2.3	3.2	2.4	2.6	2.8
	TOC	6/6	2.9	2.4	3.4	2.5	2.9	3.2
	TSS	6/6	1.1	0.5	1.9	0.7	1.1	1.6
Locks	DOC	6/6	2.8	2.3	3.5	2.5	2.7	3.0
	TOC	6/6	2.8	2.6	3.3	2.7	3	3.2
	TSS	6/6	1.4	0.7	2.6	1.0	1.4	1.6

### 3.2.2 Stormwater Runoff

Concentrations of tPCBs and tPBDEs in stormwater runoff by sampling location are presented in Figures 25 and 26, respectively. Results of the highway bridge runoff are discussed in the next section (Section 3.2.3), but are included in Figures 25 and 26 to provide context. tPCB concentrations in stormwater samples generally varied within a factor of two; although one concentration at the Fremont Seattle station was highest by nearly a factor of four. tPBDE concentrations also generally varied within a factor of two; however, Fremont was again highest by a factor of 15+. Concentrations at the Madrona and Seward Seattle locations were not particularly elevated relative to levels detected in stormwater collected from the smaller cities.

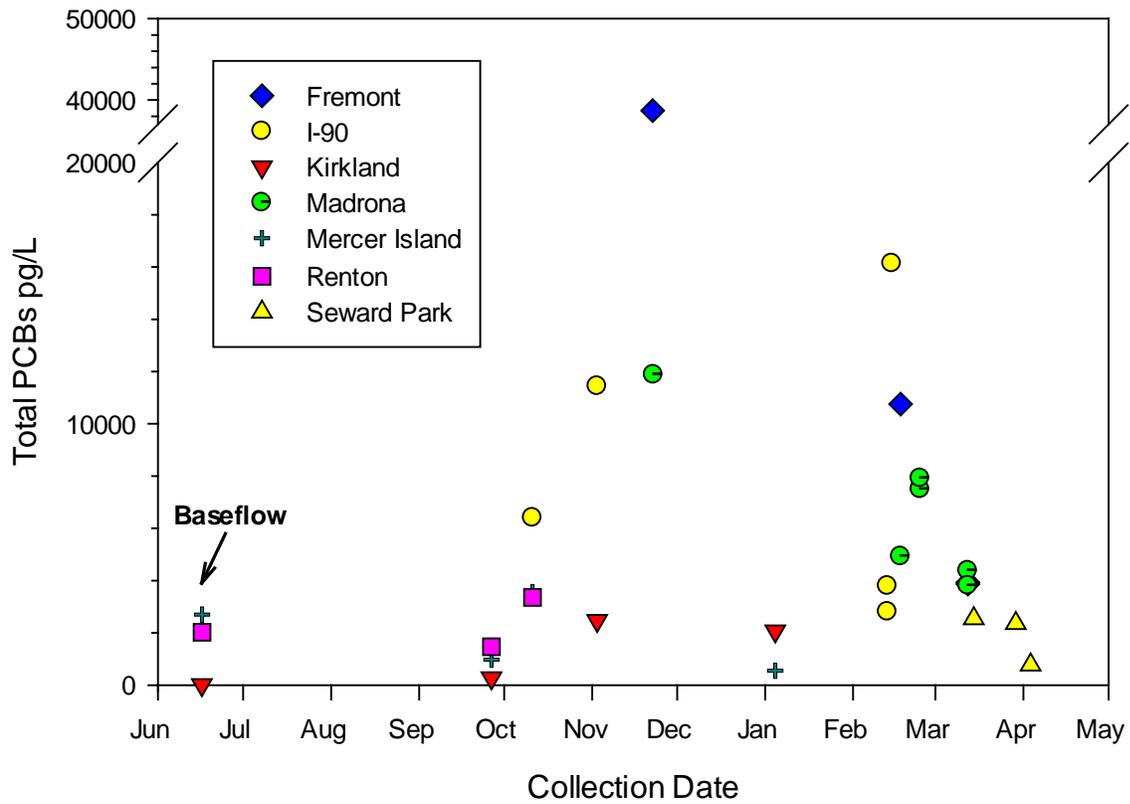


Figure 25. Total PCB results for stormwater samples including bridge runoff by date (2011-2012), replicates shown.

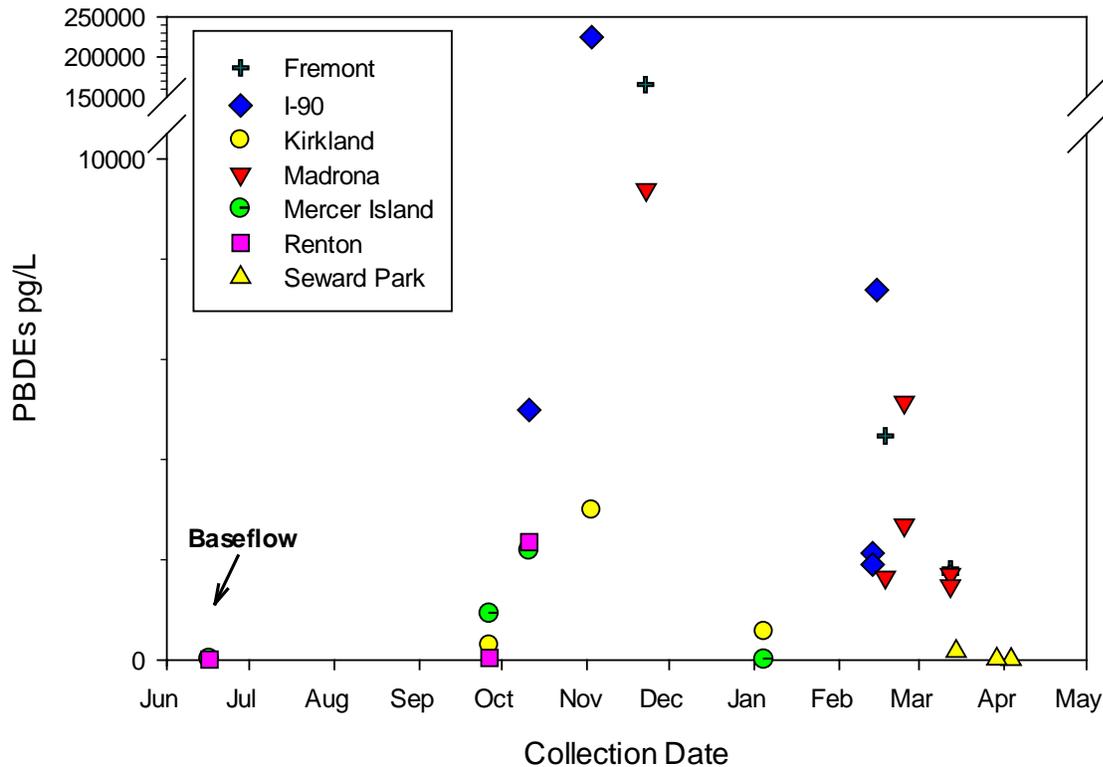


Figure 26. tPBDE results for stormwater samples including highway bridge runoff by date (2011-2012), replicates shown.

Table 21 presents summary statistics for tPCBs and tPBDEs for all stormwater locations combined. The range and percentiles of tPCB and tPBDE concentrations illustrate high variability during storm events between locations and collection date. Overall, average tPBDE concentrations in stormwater are much greater than tPCB concentrations.

Table 21. tPCB and tPBDE concentrations in pg/L, all stormwater locations combined

Flow	Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
Storm	tPCB	18/18	5,686	276	38,694	1,617	2,952	4,713
	tPBDE	18/18	11,003	8	165,685	206	1,622	2,832
Base flow	tPCB	3/3	1,576	8	2,698	-	2,022	-
	tPBDE	3/3	15	9	24	-	12	-

Note: 25<sup>th</sup> and 75<sup>th</sup> percentiles are not presented when N<4.

Summary statistics for conventional parameters at all stormwater locations are presented in Table 22. Average storm flow TOC, DOC and TSS concentrations appear higher than base flow concentrations. Compared to the variability of stormwater tPCB and tPBDE concentrations,

concentrations of DOC and TOC parameters appear to have low variability. TSS variability is higher; the maximum is almost 29 times greater than minimum TSS.

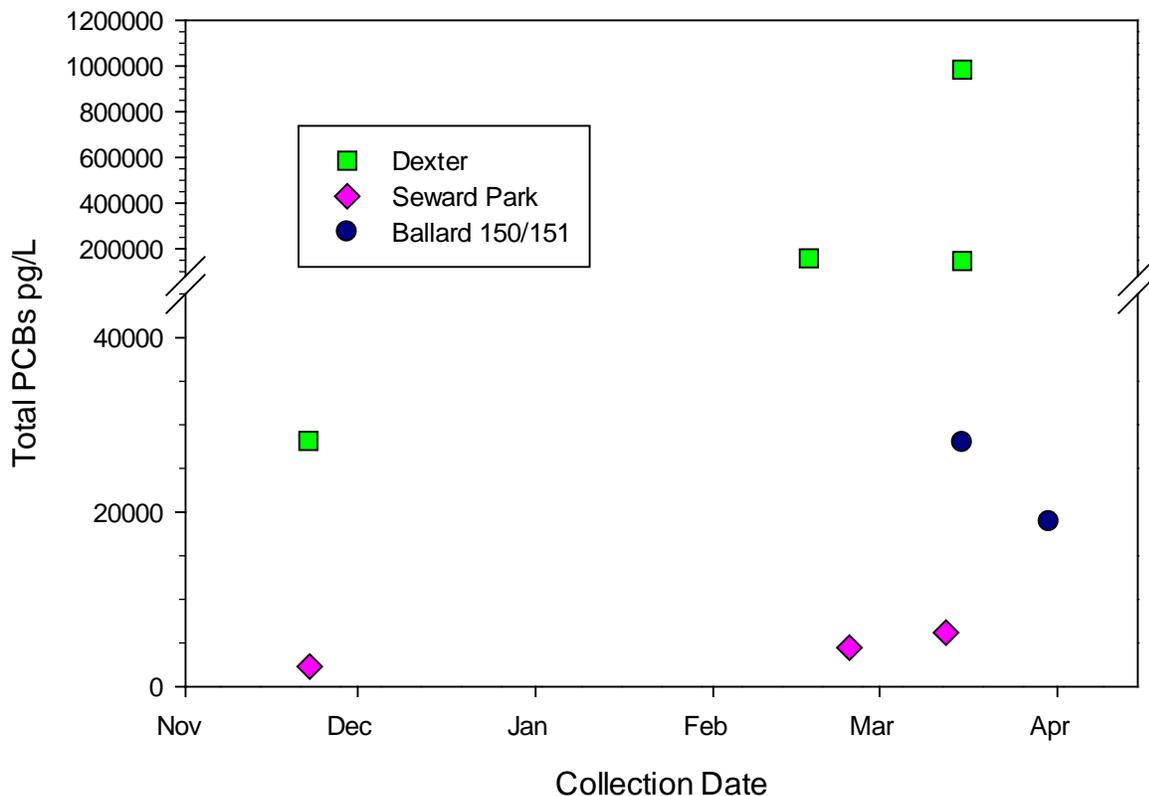
**Table 22. Conventional concentrations in mg/L, all stormwater locations combined by flow regime**

Flow	Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
Storm	DOC	15/15	6.4	2.2	16.9	4.2	5.5	7.5
	TOC	15/15	16.8	5.8	61.9	9.1	13.4	16.9
	TSS	18/18	51.3	8.3	238	20.2	34.7	68.3
Base flow	DOC	3/3	4.7	3.7	5.6	-	4.8	-
	TOC	3/3	5.1	3.5	7.4	-	4.5	-
	TSS	3/3	27.4	3	75.2	-	4	-

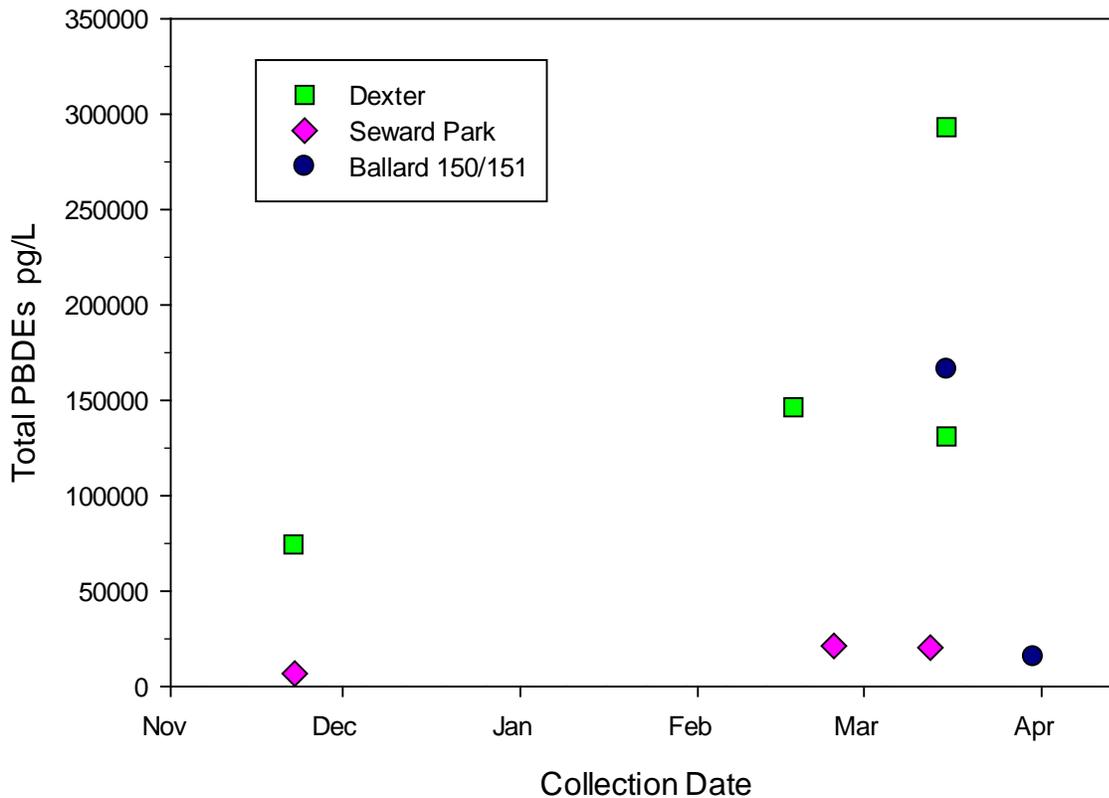
Note: 25<sup>th</sup> and 75<sup>th</sup> percentiles are not presented when N<4.

### 3.2.3 Combined Sewer Overflow

Individual tPCB and tPBDE concentrations in CSO samples are presented in Figures 27 and 28, respectively. The highest tPCB and tPBDE concentrations were measured at the Dexter CSO. The lowest tPCB and tPBDE concentrations and least variability were observed at Seward Park CSO.



**Figure 27. tPCB results for CSO samples by date (2011-2012), replicate shown.**



**Figure 28. tPBDE results for CSO samples by date (2011-2012), replicate shown.**

Summary statistics of tPCB and tPBDE concentrations for all CSO locations are presented in Table 23. The average tPCB and tPBDE concentrations are very similar; a wider range of concentrations were observed for tPCBs than tPBDEs.

**Table 23. tPCB and tPBDE concentrations in pg/L for all CSO locations combined.**

Analysis	Detections/Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
tPCB	8/8	101,426	2,301	565,108	5,751	23,438	60,700
tPBDE	8/8	82,898	6,703	212,174	19,173	47,810	151,356

Note: Maximum values are an average of replicates.

For these data, the tPCB average is much higher than the 75<sup>th</sup> percentile. 101,426 pg/L is 67% higher than 60,700 pg/L and the standard deviation is 194,243 pg/L, nearly two times the average value. This illustrates a highly skewed dataset with summary statistics strongly influenced by the maximum value.

Summary statistics of conventional parameters for all CSO locations from the current study are presented in Table 24. Total and dissolved organic carbon content varies considerably and reaches higher concentrations compared to the results seen for other pathways, such as stormwater. TSS concentrations in CSOs span a similarly wide range as that observed in stormwater.

**Table 24. Conventional concentrations in mg/L for all CSO locations combined**

Analysis	Detections/ Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
DOC	7/7	21.8	5.2	72.9	7.8	10.1	24.3
TOC	7/7	39.7	10.1	110	16.8	19.5	52.2
TSS	7/7	112.5	27.7	206	45.6	144	159.3

### 3.2.4 Highway Bridge Runoff

tPCB and tPBDE concentrations by location are plotted above in Figures 25 and 26, respectively. Samples collected from the I-90 Bridge contained some of the highest concentrations of tPCBs and tPBDEs measured in all types of stormwater runoff; summary statistics are presented in Table 25. Higher variability in concentrations was seen for tPBDEs than for tPCBs. Overall, average tPBDE concentrations were almost eight times higher than tPCB concentration in I-90 bridge runoff.

**Table 25. tPCB and tPBDE concentrations for highway bridge runoff in pg/L**

Analysis	Detections/ Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
tPCB	4/4	9,319	3,295	16,133	5,626	8,924	12,617
tPBDE	4/4	59,827	2,019	224,915	4,246	6,186	61,767

The summary statistics for conventional parameters measured in highway bridge runoff are presented in Table 26. The small ranges and similarity of percentile values indicate low variability in DOC and TOC. Variability in TSS was moderate.

**Table 26. Conventional results for highway bridge runoff in mg/L**

Analysis	Detections/ Events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
DOC	4/4	7.3	2.8	13	4.7	6.6	9.1
TOC	4/4	25.4	10.1	47.3	10.9	22	36.5
TSS	4/4	115.2	34.1	254	42.7	86.3	158.8

### 3.2.5 Atmospheric Deposition

tPCB and tPBDE deposition rates for air samples are presented in Figures 29 and 30, respectively. Generally, deposition rates were, with one exception, higher at Beacon Hill than Sand Point for both tPCBs and tPBDEs. Overall, tPBDE deposition rates were higher than those for tPCBs regardless of location.

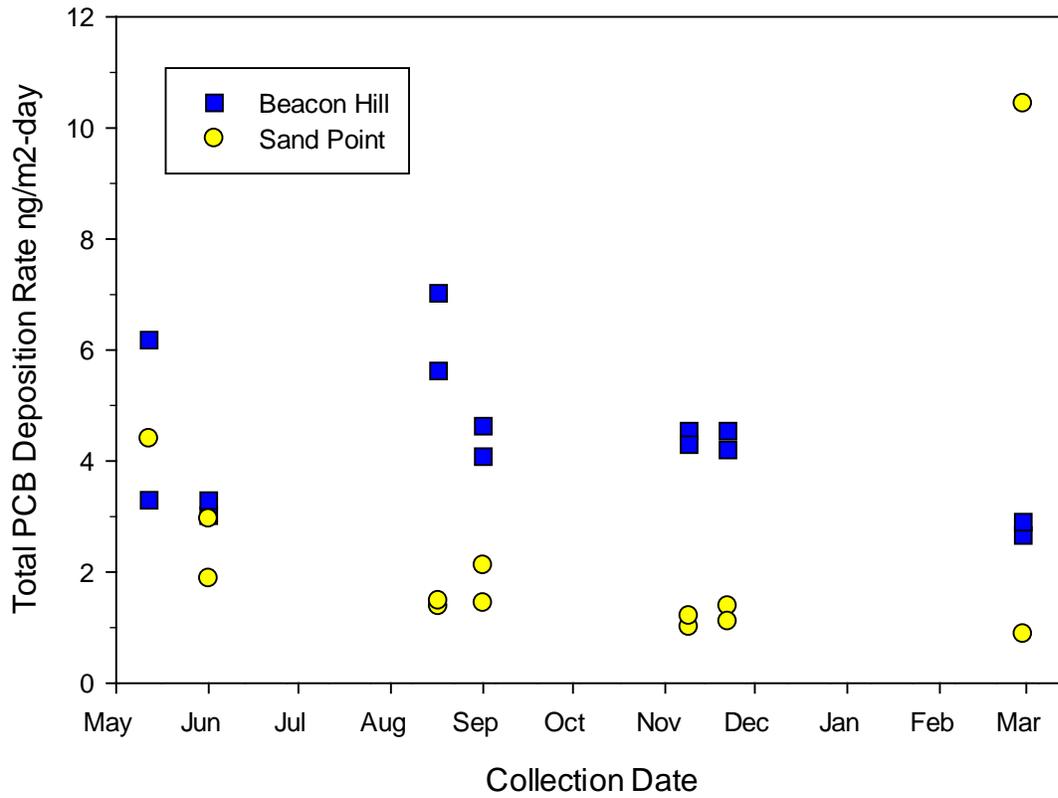
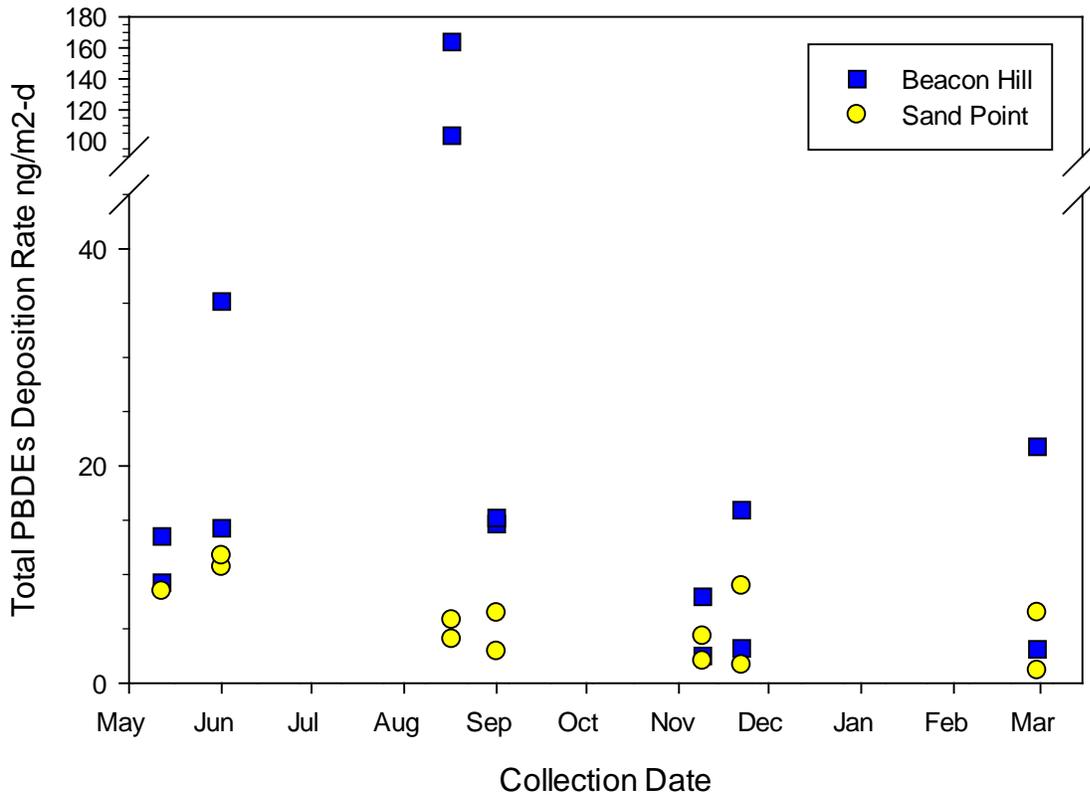


Figure 29. tPCB results for atmospheric deposition samples by date (2011-2012), replicates shown.



**Figure 30. tPBDE results for atmospheric deposition samples by date (2011-2012), replicates shown.**

tPCB and tPBDE concentrations for air deposition samples are presented for primary and replicate samples in Tables 29 and 30. These tables also show the data necessary to convert measured concentrations into deposition rate in ng/m<sup>2</sup>/day. Note that water concentrations of tPCBs and tPBDEs are reported in pg/L and 1 ng is 1000 pg. The measured concentration in pg/L was first normalized to the total volume of water (from rainfall and rinsing) in the sample to obtain the mass of tPCBs or tPBDEs per collection jar. Then, this mass was normalized to the sampling duration and funnel size to determine the mass of tPCBs or tPBDEs that deposited per square meter per day. Hence, the final rates are mass, per unit area, per day, or ng/m<sup>2</sup>/day. These rates are intended to represent direct deposition to the lake water surface.

Because the bulk deposition method is relatively new and not standardized, additional quality control samples and analyses were conducted to describe the limitations and uncertainties associated with these data. Section 3.2.5.1 discusses these additional quality control samples and references the “percent from rinse water” presented on Tables 27 and 28.

**Table 27. Atmospheric deposition measured concentrations in primary samples with calculated deposition rates.**

Location	Collection Date	Sample ID	Analysis	Total Concentration (pg/L)	Total Volume (L)	Total Mass (pg)	Days	Mass/Day (pg)	Funnel Size (m <sup>2</sup> )	Deposition Rate (Ng/day/m <sup>2</sup> )	Percent from Rinse Water
BWR	5/12/2011	L53194-2	PCB	2456.42	4.11	10.10	9.95	1.01	0.1642	6.18	0.19%
	6/1/2011	L53296-2		2882.21	2.4	6.92	13.97	0.50	0.1642	3.02	1.02%
	8/17/2011	L53784-2		46103.06	0.4	18.44	15.99	1.15	0.1642	7.02	0.38%
	9/1/2011	L53968-2		15422.76	0.75	11.57	15.23	0.76	0.1642	4.63	0.61%
	11/9/2011	L54416-2		1773.827	1.3	2.31	13.88	0.17	0.0366	4.54	3.05%
	11/22/2011	L54608-2		810.04	2.5	2.03	13.18	0.15	0.0366	4.20	3.48%
	2/29/2012	L55024-2		1030.36	2.65	2.73	28.05	0.10	0.0366	2.66	2.58%
	5/12/2011	L53194-2	PBDE	3678.28	4.11	15.12	9.95	1.52	0.1642	9.25	0.88%
	6/1/2011	L53296-2		33612.1	2.4	80.67	13.97	5.77	0.1642	35.17	0.60%
	8/17/2011	L53784-2		679053	0.4	271.62	15.99	16.99	0.1642	103.46	0.18%
	9/1/2011	L53968-2		48820.6	0.75	36.62	15.23	2.40	0.1642	14.64	1.32%
	11/9/2011	L54416-2		976.3	1.3	1.27	13.88	0.09	0.0366	2.50	38.09%
	11/22/2011	L54608-2		3072.8	2.5	7.68	13.18	0.58	0.0366	15.93	6.29%
	2/29/2012	L55024-2		8430.4	2.65	22.34	28.05	0.80	0.0366	21.76	2.16%
SAND_POINT	5/12/2011	L53194-1	PCB	2160.79	3.35	7.24	10.02	0.72	0.1642	4.40	0.97%
	6/1/2011	L53296-1		1786.26	3.8	6.79	13.96	0.49	0.1642	2.96	1.04%
	8/17/2011	L53784-1		9068.57	0.4	3.63	15.98	0.23	0.1642	1.38	1.94%
	9/1/2011	L53968-1		7052.47	0.75	5.29	15.20	0.35	0.1642	2.12	1.33%
	11/9/2011	L54416-1		428.787	1.2	0.51	13.92	0.04	0.0366	1.01	13.69%
	11/22/2011	L54608-1		268.925	2.5	0.67	13.24	0.05	0.0366	1.39	10.48%
	2/29/2012	L55024-1		317.59	2.85	0.91	28.05	0.03	0.0366	0.88	7.78%
	5/12/2011	L53194-1	PBDE	4165.03	3.35	13.95	10.02	1.39	0.1642	8.48	3.46%
	6/1/2011	L53296-1		6442.95	3.8	24.48	13.96	1.75	0.1642	10.68	1.97%
	8/17/2011	L53784-1		26478	0.4	10.59	15.98	0.66	0.1642	4.04	4.56%
	9/1/2011	L53968-1		9733.1	0.75	7.30	15.20	0.48	0.1642	2.92	6.62%
	11/9/2011	L54416-1		867.2	1.2	1.04	13.92	0.07	0.0366	2.04	46.45%
	11/22/2011	L54608-1		324.13	2.5	0.81	13.24	0.06	0.0366	1.67	59.66%
	2/29/2012	L55024-1		419.14	2.85	1.19	28.05	0.04	0.0366	1.16	40.47%

**Table 28. Atmospheric deposition measured concentrations in replicate samples with calculated deposition rates**

Location	Collection Date	Sample ID	Analysis	Total Concentration (pg/L)	Total Volume (L)	Total Mass (pg)	Days	Mass/Day (pg)	Funnel Size (m <sup>2</sup> )	Deposition Rate (Ng/day/m <sup>2</sup> )	Percent from Rinse Water
BWR	5/12/2011	L53194-3	PCB	1253.97	4.29	5.38	9.95	0.54	0.1642	3.29	0.29%
	6/1/2011	L53296-3		3142.54	2.4	7.54	13.97	0.54	0.1642	3.29	0.93%
	8/17/2011	L53784-4		36926.01	0.4	14.77	15.99	0.92	0.1642	5.63	0.48%
	9/1/2011	L53968-4		13601.31	0.75	10.20	15.23	0.67	0.1642	4.08	0.69%
	11/9/2011	L54416-4		1678.266	1.3	2.18	13.88	0.16	0.0366	4.29	3.23%
	11/22/2011	L54608-4		858.33	2.55	2.19	13.18	0.17	0.0366	4.54	3.22%
	2/29/2012	L55024-4		1122.32	2.65	2.97	28.05	0.11	0.0366	2.90	2.37%
	5/12/2011	L53194-3	PBDE	5142.8	4.29	22.06	9.95	2.22	0.1642	13.50	0.49%
	6/1/2011	L53296-3		13629.4	2.4	32.71	13.97	2.34	0.1642	14.26	1.48%
	8/17/2011	L53784-4		1075602	0.4	430.24	15.99	26.91	0.1642	163.87	0.11%
	9/1/2011	L53968-4		50713.5	0.75	38.04	15.23	2.50	0.1642	15.21	1.27%
	11/9/2011	L54416-4		3108.35	1.3	4.04	13.88	0.29	0.0366	7.95	11.96%
	11/22/2011	L54608-4		604.7	2.55	1.54	13.18	0.12	0.0366	3.20	31.35%
	2/29/2012	L55024-4		1203.6	2.65	3.19	28.05	0.11	0.0366	3.11	15.16%
SAND_POINT	6/1/2011	L53296-4	PCB	1151.809	3.75	4.32	13.96	0.31	0.1642	1.88	1.63%
	8/17/2011	L53784-3		9733.38	0.4	3.89	15.98	0.24	0.1642	1.48	1.81%
	9/1/2011	L53968-3		4795.85	0.75	3.60	15.20	0.24	0.1642	1.44	1.96%
	11/9/2011	L54416-3		513.656	1.2	0.62	13.92	0.04	0.0366	1.21	11.43%
	11/22/2011	L54608-3		214.888	2.5	0.54	13.24	0.04	0.0366	1.11	13.11%
	2/29/2012	L55024-3		3694.98	2.9	10.72	28.05	0.38	0.0366	10.44	0.66%
	6/1/2011	L53296-4	PBDE	7179.11	3.75	26.92	13.96	1.93	0.1642	11.74	1.80%
	8/17/2011	L53784-3		38101.4	0.4	15.24	15.98	0.95	0.1642	5.81	3.17%
	9/1/2011	L53968-3		21468	0.75	16.10	15.20	1.06	0.1642	6.45	3.00%
	11/9/2011	L54416-3		1831.38	1.2	2.20	13.92	0.16	0.0366	4.31	22.00%
	11/22/2011	L54608-3		1734	2.5	4.34	13.24	0.33	0.0366	8.95	11.15%
	2/29/2012	L55024-3		2300.2	2.9	6.67	28.05	0.24	0.0366	6.50	7.25%

Table 29 presents summary statistics for tPCB and tPBDE air deposition rates for all samples. The average tPBDE deposition is nearly six times higher than the average tPCB deposition. The tPBDE deposition rates exhibit more of a skewed distribution than tPCBs with sporadically high values.

**Table 29. Air deposition rate (ng/m<sup>2</sup>/day) summary statistics by parameter and location.**

Analysis	Detections/ Events	Minimum	Maximum	Average	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
tPCB	14/14	1.1	6.3	3.4	1.9	3.8	4.4
tPBDE	14/14	3.2	133.7	18.1	5.0	9.0	12.2

Note: lab duplicates and field replicates were averaged by date and location prior to calculation of summary statistics. All values in ng/m<sup>2</sup>/day.

### 3.2.5.1 Air Deposition Quality Control Samples

This study included additional quality control samples to document bulk deposition sampler performance (King County 2011a). This included analysis of an equipment blank which was used to evaluate the potential contributions of funnel rinse waters to sample masses. Two wipe tests were conducted which evaluated the mass of tPCBs and tPBDEs left on funnels after rinsing. Lastly, two spike blanks were conducted which evaluated the possible losses of PCBs or PBDEs from collection jars. Jars were deployed for 10 to 28 days and it was theorized that PCBs or PBDEs deposited earlier in the collection period might volatilize and be lost.

The QAPP (King County 2011a) dictated that 400mL of KCEL de-ionized water<sup>2</sup> and a natural bristle brush be used to rinse dry particulates and water droplets from the funnels into the underlying sample jars. An estimate of the collected tPCB or tPBDE mass which might be attributed to the tPCBs and tPBDEs in the rinse water was developed. This was based on the concentrations of PCBs and PBDEs found in the air deposition equipment blank multiplied by the sample specific rinse volume to derive a mass of each PCB and PBDE congener. These congener specific masses were compared to the measured deposition mass. These masses were summed and presented as a percent of measured deposition. For tPCBs, in some samples, as little as 0.19% of the measured deposition is estimated to have come from funnel rinse waters. For others, as much as 13.7% of the measured tPCB deposition could be attributed to the funnel rinse water. This range of potential influence is even greater for tPBDEs, 0.18 to nearly 60%. The degree of influence of the funnel rinse water is a function of both the measured concentration and the sample volume. Air deposition samples which were entirely composed of dry deposition and where the only liquid in the collection jar was the funnel rinse water were not disproportionately impacted by the potential contaminants in rinse water because the overall sample mass from dry deposition tended to be high. The samples potentially impacted the most by rinse water contaminants had moderate (e.g. 2.5L) total volumes with low reported tPCB and tPBDE concentrations.

The mass of tPCBs and tPBDEs potentially introduced to air deposition samples by funnel rinse waters is offset in part by residual PCBs and PBDEs which remained on funnels after rinsing. To measure the mass of PCBs and PBDEs left on funnels after brushing and rinsing, two wipe samples were conducted. A proofed clean laboratory wipe soaked in acetone was used to swab two different funnels after brushing and rinsing had finished. One of these funnels had been rinsed with

<sup>2</sup> This volume was chosen for practical reasons and represented a balance between rinsing as much deposition as possible into the underlying collection jar and the limited size (4L) of those jars and the likelihood of them having substantial rainfall already in them at the end of the collection period.

400 mL of de-ionized water while the other was coincidentally only able to be rinsed with 110 mL of water to avoid overflowing the underlying sampling jar. As expected, the 400 mL rinse was more effective at flushing wet and dry deposition from the funnel into the collection jar. For tPCBs, 260 pg was left on the funnel after a 400 mL rinse while 1,710 pg was left behind after a 110 mL rinse. 1,350 pg of tPBDEs remained on the funnel after a 400 mL rinse while 4,43 pg remained after a 110 mL rinse.

As can be seen from Table 30, between approximately 7 and 17% of tPCBs depositing on the funnels remained after rinsing and brushing. Similarly, between 13 and 29% of deposited tPBDEs remained on the funnels and were thus not part of the bulk deposition analysis. These low biases serve to offset some of the contaminants potentially introduced by the rinse waters themselves which are described above.

**Table 30. Post rinse air deposition funnel residual tPCB and tPBDEs**

Analysis	Collect Date	Sample Mass (pg)	Wipe Sum Of Congeners (pg/wipe)	Rinse Volume	Percent of Sample
PCB	5/12/2011	10,095	1,711	110 mL	16.90%
PCB	8/17/2011	3,627	260	400 mL	7.20%
PBDE	5/12/2011	15,118	4,427	110 mL	29.30%
PBDE	8/17/2011	10,591	1,351	400 mL	12.80%

Two spike blanks were conducted for both tPCBs and tPBDEs in air deposition samples. These were conducted to evaluate the potential loss of collected PCBs and PBDEs from the jars while the samplers remained deployed for up to 28 days. tPCB recoveries were 73-75% while tPBDE recoveries were 87 to 97% illustrating modest to low bias of air samplers due to re-volatilization or adhesion of congeners onto glassware.

### 3.3 Flow

The flow volumes measured during stormwater and CSO sampling events were summarized previously in Sections 2.2.2 and 2.2.3, respectively; continuous flow measurements are not available for these locations. Continuous flow gages are permanently installed on many of the waterbodies where flow data are needed to estimate annual PCB and PBDE loadings to Lake Washington, Lake Union/Ship Canal and through the locks to Puget Sound. Flow data were downloaded from the representative monitoring agencies (i.e., King County, Snohomish County, USGS) for use in the loadings estimation and these data are summarized within the PCB/PBDE Loading Estimates for the Greater Lake Washington Watershed report (King County 2013).

## 4.0. DISCUSSION

This section discusses similarities and differences between pathways and between this study and prior comparable investigations. This section also develops more robust and precise estimate of the CSO tPCB arithmetic average using a combined data set from this project and previous King County tPCB results sampled, analyzed, and validated identically to this project.

### 4.1 Comparison of Water Pathway Concentrations

To compare different pathways, the average and standard deviation concentrations of tPCBs and tPBDEs were plotted for visual comparison in Figures 31 and 32, respectively, using the detection limit for non-detect totals. Average CSO tPCB concentrations are approximately an order of magnitude higher than the next highest average pathway concentration, measured in highway bridge runoff. The average tPCB concentration is lowest in rivers, followed by streams during base flow conditions. Average tPCB concentrations in streams during storm events are comparable to average tPCB concentrations in stormwater runoff from smaller cities (i.e., Kirkland, Renton and Mercer Island). The average tPCB concentration in stormwater runoff from Seattle stations is similar to the average tPCB concentration in stormwater runoff from the I-90 highway bridge.

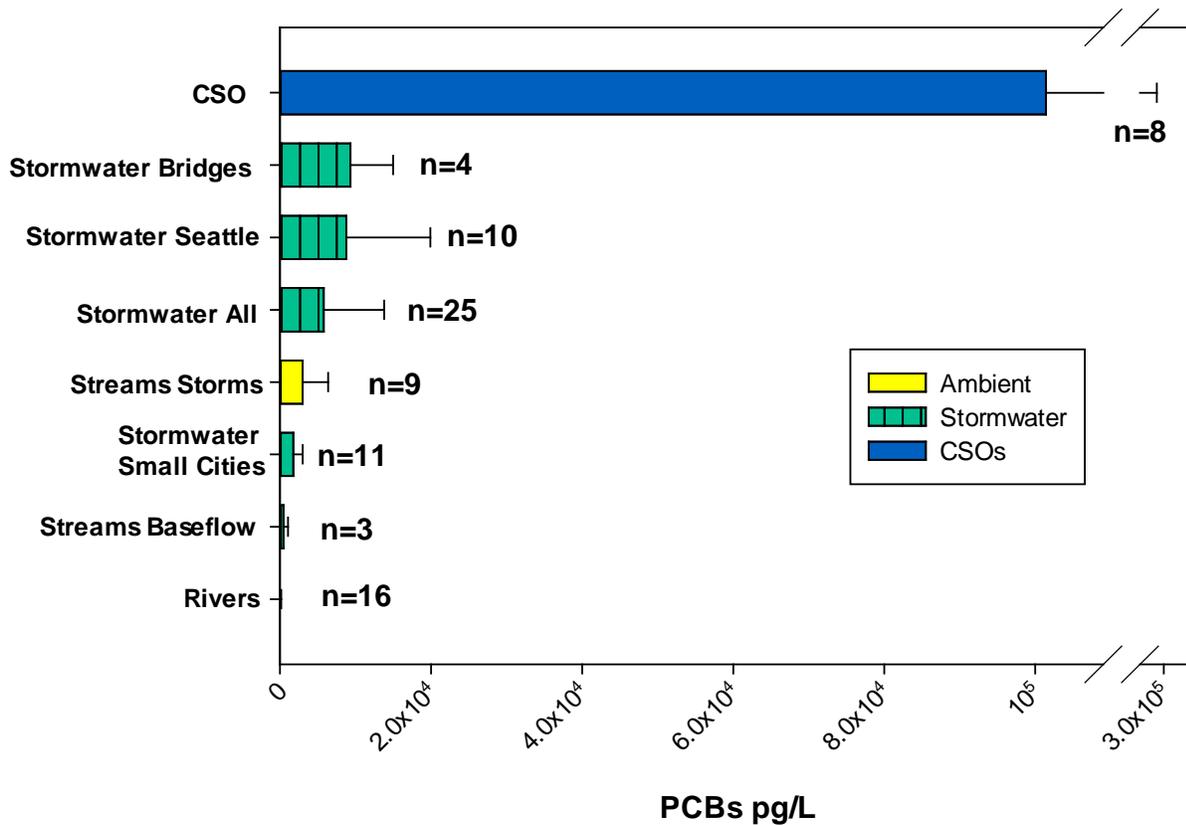


Figure 31. Average and standard deviation concentrations of tPCBs in major water pathways.

As with tPCBs, the average tPBDE concentrations in CSOs and highway bridge runoff are the highest of all pathways. Variability in the tPBDE concentrations for CSO and highway bridge runoff pathways is also high, as indicated by the large standard deviations. The average tPBDE concentrations are lowest in streams during base flow, small city stormwaters, and rivers. The average tPBDE concentration in stormwater from small cities (i.e., Kirkland, Renton, and Mercer Island) is not quite as high as average tPBDE concentration in streams during storms. The standard deviation tPBDE concentrations in the stormwater pathway (“Stormwater All” in Figure 32) indicate very high variability, although this is likely due to the high variability seen in Seattle stormwater which is much higher than that seen in the smaller city’s stormwater tPBDEs.

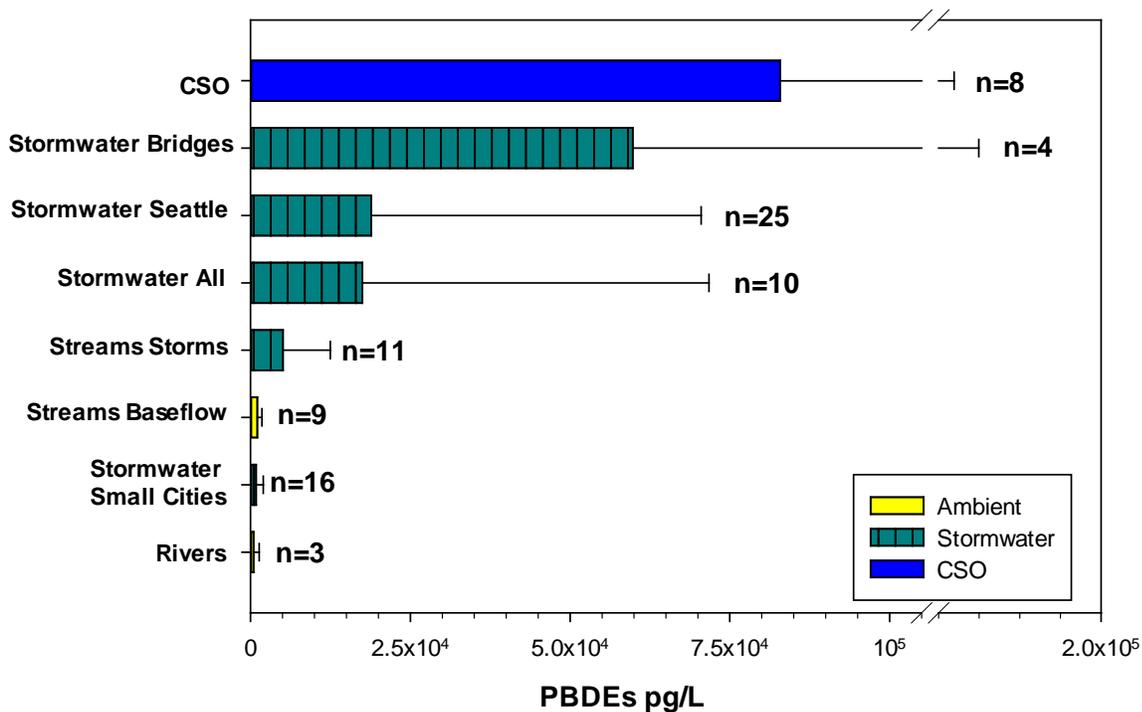


Figure 32. Average and standard deviation concentrations of PBDEs in major water pathways.

## 4.2 Comparison with Other Studies

Current project data have been compared with similar studies throughout King County and the greater Washington region. These comparisons are intended to provide a point of reference and perspective on current results. Where methods or analyses are known to deviate from the current study these are mentioned, although readers are advised to consult the referenced data sources for a complete understanding of potential differences.

#### 4.2.1 Ambient Waters

tPBDEs and tPCBs in tributaries were relatively higher in the current study compared with prior investigations for Ecology in the Snohomish and Puyallup River basins (Herrera, 2011). The Herrera (2011) study analyzed for the same number of PCB congeners, although their longer 36 PBDE congener analyte list may explain some of the differences described below. For instance, average base flow tPCB and tPBDE concentrations in the Herrera study were 301 and 525 pg/L respectively, compared to 451 and 1,058 pg/L for base flow streams in this study which are approximately 20 to 100% higher. This may in part be due to the lower minimum detected concentrations (9.5 and 10 pg/L for tPCBs and tPBDEs) found in the Herrera study which included more rural/forestry land uses. Average storm flow concentrations for PCBs in the Herrera study were 1,930 pg/L which is approximately 30% lower than found in the current investigation. However, the Herrera study's maximum storm flow PCB concentration was over twice that found in the Lake Washington basin, 27,349 compared to 10,527 pg/L. An even greater difference between these two investigations was apparent for PBDEs. The Herrera study detected a maximum of 271,499 pg/L tPBDE, while the current study detected a maximum of 20,910 pg/L. These differences are possibly due to more intensively developed commercial/industrial land uses sampled by the Herrera study in Everett and Fife, compared to the Lake Washington basin. The longer PBDE congener analyte list may also contribute to the order of magnitude tPBDE difference as well.

Fletcher (2009) measured some PCB and PBDE congeners at 14 sites throughout the Cedar River in 2007-2008. Fletcher used semi-permeable membrane devices or SPMDs which bioconcentrate lipophilic contaminants like PCBs and PBDEs. The concentrated contaminant concentrations can be converted to water concentrations using temperature and the loss rate of spiked compounds. However, Fletcher did not convert his SPMD PCB detections to water concentrations. SPMD PBDE detections were converted to water concentrations and the 72.6 pg/L average detection was over 10 times lower than the 478 pg/L average tPBDE concentration in this study. It is unknown if sampling and analytical differences account for this variation. As noted earlier, method blank contamination makes derivation of a true average river tPBDE concentration challenging. The reported average river PBDE concentration for the current study is heavily influenced by the rule that only those congeners greater than 5 times the method blank concentrations be considered detections.

The Washington Department of Ecology (Gries and Osterberg, 2011) measured 209 PCB congeners and 36 PBDE congeners in five Puget Sound Rivers: the Skagit, Stillaguamish, Nooksack, Snohomish, and Puyallup (Gries and Osterberg, 2011). The average tPCBs concentration was 16.3 pg/L, although according to the authors, concentrations would be about 60% higher if validated differently. In either case, tPCBs in the five rivers are in the similar range (2.6 to 59 pg/L) as detected in the Cedar and Sammamish (10-267 pg/L), although lower due to the more rural character of the five rivers in Ecology's study. Ecology's average tPBDE concentration of 55.6 pg/L is lower than the 478 pg/L average in the Cedar and Sammamish despite being from a longer 36 PBDE congener analyte list. Markedly higher maximum PBDE concentrations were found in this study, 3,150 pg/L versus a maximum of 265 pg/L in Gries and Osterberg (2011).

Washington State Department of Ecology has conducted a limited amount of surface water sampling for PCBs and PBDEs in Lake Washington at the entrance to the Ship Canal at the Montlake Cut (Sandvik, 2010). Similar to Fletcher (2009), this analysis was conducted using SPMDs. Ecology's calculated water concentration results are similar in magnitude to those found in the current study with the tPCB concentrations being closest and the tPBDE concentrations lower. Table 31 compares the Sandvik, (2010) SPMD data with the whole water data collected at the Montlake Cut for this

project (Table 17). Also provided are the partitioning estimates conducted in Lake Washington (Table 18) because the Sandvik (2010) study is one of the few local PCB and PBDE studies providing total and dissolved contaminant estimates. Unlike the current study which actually measured dissolved and particulate fractions, the whole water PCB and PBDE estimates in Sandvik (2010) were calculated based on the measured dissolved PCB or PBDE concentration, the TOC, and estimates of the water-organic carbon partitioning coefficient.

**Table 31. Lake Washington water concentrations of total PCBs and total PBDEs as back calculated from SPMD measurements (Sandvik, 2010) compared to current study.**

Chemical	Sandvik (2010) Average Concentration (pg/L)	Sandvik (2010) Average Dissolved Fraction, %	This Study Mixed Concentration (pg/L) sum <sup>1</sup>	This Study Mixed Dissolved Fraction. %
tPCBs	140	26.3	56	71.4
tPBDEs	220	14.5	N/A <sup>2</sup>	N/A

<sup>1</sup> Concentration is the sum of filtrate and particulate analysis, not from whole water analysis.

<sup>2</sup> Particulate PBDE concentrations were non-detect at 381 to 777 pg/sample and a whole water PBDE concentration was unable to be reliably calculated.

The current study's tPCB concentrations are about one-half those measured via SPMDs by Sandvik (2010). The dissolved fraction measured in this study appears to be about three times higher than that modeled calculated by Sandvik and this is believed to be due to the significant differences in methods between the two studies. The tPBDE concentrations and the dissolved fraction for the current study are unknown due to the method blank contamination of the particulate filters elevating the detectable concentrations.

There are no state or federal water quality standards for tPBDEs, TOC or DOC, or TSS, but tPCB measurements in ambient lake waters exceeded the 170 pg/L Washington State human health criterion based on the National Toxics Rule (40 CFR 131.36) during seven of 20 total sampling events.

#### 4.2.2 Stormwater Runoff

Few local studies of stormwater have been conducted using low level PCB or PBDE methods comparable to those used to sample stormwater outfalls in this study. A search of the Washington Department of Ecology's Environmental Information Management (EIM) system yielded no comparable studies of Western Washington stormwater. The most comparable study of urban stormwater is from the arid region of Eastern Washington in the City of Spokane (Parsons, 2007). Stormwater from 14 different outfalls was sampled during three May and June 2007 runoff events as part of a TMDL investigation. A total of 45 samples, including replicates, were analyzed for PCBs, but not PBDEs. Average tPCB concentrations were 22,500 pg/L, which is approximately four times higher than stormwater pipes discharging to Lake Washington/Ship Canal during storm events and 14 times higher than flows during base flow conditions. Minimum detected tPCB concentrations in Spokane stormwater were 620 pg/L which is very close to the minimum storm flow concentration of 276 pg/L detected in the current study. The maximum tPCBs in the Spokane TMDL investigation was 280,000 pg/L, which is approximately seven times higher than those detected in the current investigation.

Although the first storms of the rainy season were not targeted, no seasonal "first flush" phenomenon is apparent. Storms early in the rainy season (October) generally had lower tPCB and tPBDE concentrations than November-December storm concentrations (Figures 25 and 26). Late

winter and spring tPCB and tPBDE concentrations were lower, sometimes close to base flow tPCB and tPBDE concentrations. Any elevated concentrations due to first flush phenomenon within a single storm cannot be evaluated due to the single composite sampling design of this study. All but the highest tPBDE stormwater concentrations are suspected to be biased low, because only those PBDE congeners exceeding five times the equipment blank were used in these sums.

#### 4.2.3 Highway Bridge Runoff

There are no known historical direct highway or bridge runoff data using comparable methods. Based on the detected PBDE in the autosampler equipment blank, the interior of the I-90 bridge appears to have substantial PBDEs present; future PBDE studies are advised to collect equipment blanks in each unique sampling environment.

#### 4.2.4 Combined Sewer Overflow

This study was only able to collect eight of a planned 12 CSO samples due to the greater than anticipated efforts required for stormwater samples. Results from these 8 samples exhibited very high variability in flow volume (1,874 to 1,166,000 gallons, Table 7). TOC, DOC and TSS also spanned approximately a factor of 5 to 10 (Table 26). Predictably, variability of tPCB concentrations is also very high with a very high standard deviation ( $\pm 194,243$  pg/L) and uncertain average concentration. To address this high uncertainty and develop a more robust estimate of the CSO average concentration for use in subsequent tPCB loadings estimates, the current study's results have been combined with previous results from Duwamish River CSO samples collected and analyzed identically (King County, 2011c).

King County conducted a survey of Duwamish River CSOs from 2007 to 2010 (King County, 2011c). Forty-five samples including field duplicates were collected and analyzed for PCBs, but not PBDEs. Data were independently validated according to EPA protocols in a similar manner as described in Appendix A, although the Duwamish CSO samples were not validated based on autosampler equipment blanks as done for this study. These samples were taken from actual CSO overflow events and from other near-full pipe conditions which may under certain pipe or pump station conditions lead to overflows. The average tPCB concentration of all samples was 65,200 pg/L, which is lower than the 101,426 pg/L average concentration detected in the current study. The Duwamish CSO study minimum tPCB concentration of 8,010 pg/L was higher than the current study's minimum, but the maximum detected concentration of 455,000 pg/L was lower than CSO samples from the current study. Duwamish River CSOs span a narrower, and on average lower, concentration range than the limited number of CSOs sampled in Lake Washington and the Ship Canal in the current study.

Combined, these CSO data exhibit a log-normal distribution (Kolmogorov-Smirnov Goodness of Fit  $p = 0.70$ ) which is typical for environmental chemistry results. While they continue to span three orders magnitude, the average of 70,646 pg/L is less than the 75<sup>th</sup> percentile of 71,700 pg/L. The arithmetic average declined from 101,426 pg/L to 70,646 pg/L and the expanded data set has a standard deviation of 96,654 pg/L which is approximately one-half the previous standard deviation and illustrates that the expanded dataset has a much more precise arithmetic average. This larger dataset of 53 CSO results from across King County is believed to more accurately and robustly represent the arithmetic average tPCB CSO concentration.

**Table 32. tPCB concentrations in pg/L for Lake Washington and Lower Duwamish Waterway locations combined.**

Analysis	Detections/ events	Average	Minimum	Maximum	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
tPCB	53	70,646	2,301	565,108	27,800	44,400	71,700

#### 4.2.5 Atmospheric Deposition

Prior King County studies of bulk deposition in the Lower Duwamish Waterway area (King County, 2008) used Aroclor methods for PCBs which were not sensitive enough to consistently detect PCBs. Aroclor 1254 and 1260 were occasionally detected during dry periods of low rainfall with a sum of the Aroclors ranging from 11 to 64 ng/m<sup>2</sup>/day (King County, 2008). PBDEs were not analyzed prior to the current study.

Brandenberger et al. (2010) collected tPCB and tPBDE air deposition data at multiple locations around Puget Sound and these data are presented in Table 33. Brandenberger et al. (2010) only analyzed 21 PCB congeners compared to the full analytical suite of 209 PCB congeners analyzed in the current study. For PBDEs, Brandenberger et al. (2010) analyzed 14 different congeners while the current study only reported nine PBDE congeners. Thus, Brandenberger’s study is believed to underestimate PCBs and overestimate PBDEs relative to the current study’s results.

Brandenberger et al.’s (2010) closest air deposition station to Lake Washington or the Ship Canal was located at the West Point wastewater treatment plant, approximately 2 km southwest of the Ship Canal and Ballard Locks. The West Point results are similar or slightly lower than the Beacon Hill and Sand Point results from this study. This is consistent with the West Point station being adjacent to Puget Sound with a relative dearth of human development located immediately upwind. The more urban and industrial Tacoma Commencement Bay (TCB) station had higher tPBDE results than the two stations in the current study, as expected. The TCB station had tPCB results within the same range as the current study although the average was approximately 30% lower at TCB compared to the current study. Deposition results from Brandenberger, et al. (2010) are shown in Table 33.

**Table 33. Daily atmospheric deposition fluxes of tPCBs and tPBDEs at Puget Sound urban air deposition stations (ng/m<sup>2</sup>/d).**

Location	Analysis	Minimum	Maximum	Average	25 <sup>th</sup> Percentile	Median	75 <sup>th</sup> Percentile
Tacoma Commencement Bay	tPCBs	0.23	7.01	2.54	1.22	1.81	2.82
Tacoma Commencement Bay	tPBDEs	7.1	170.5	30.4	14.1	23.8	27.3
West Point	tPCBs	0.05	4.59	1.02	0.17	0.57	1.01
West Point	tPBDEs	3.7	14.6	8.2	5.4	7.8	10.6

Tables 29 and 33 illustrate that both tPCB and tPBDE depositions were consistently two to three times higher in the current study compared to West Point. This is to be expected since West Point is downwind from a large expanse of Puget Sound. As planned in the site selection criteria, both Sand Point and Beacon Hill are likely more heavily influenced by urban land uses in their immediate vicinity and those upwind. The current study's tPCB deposition spanned a smaller range than the deposition measured by Brandenberger et al (2010) and the overall average is higher. The slightly higher tPCB deposition measured in the current study might be due to the larger 209 congener analysis suite.

## 5.0. SUMMARY

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Whole water samples were successfully collected according to the study design specified in the QAPP (King County 2011a) with a few modifications; including elimination of a second Kirkland stormwater station for budgetary reasons; shifting the location of one Seattle CSO station to a site with a simpler, more consistent conveyance pattern; and eliminating the use of acetone to decontaminate autosampler tubing to avoid organic carbon residues.

Data validation identified a significant issue: PCB-7 method blank contamination in certain contract laboratory batches. This issue was addressed by re-extraction and re-analysis of nine samples for which PCB-7 represented a large portion (>20%) of the total PCB sum and additional sample volume was available. PCB-7 was detected at <10 pg/L in reanalyzed samples and these non-detect and small detected results replaced the original rejected results. PCB-7 values remain non-detect (U-flagged) in affected samples that were not re-analyzed; therefore, the PCB-7 congener was not included in the tPCB sum for these samples. Because the reanalyzed samples were non-detect or very low level detections for PCB-7 (<10 pg/L), the elevated PCB-7 detection limits in samples which were not reanalyzed are not believed to represent any significant low bias to their tPCB sums.

Some of the anticipated DQOs of precision for PCB and PBDE congeners were not met as outlined in the QAPP. However, the precision DQOs were set without the benefit of historical quality control data. The lowest reproducibility occurred in ambient waters: Lake Washington, the Ship Canal, and rivers. Concentrations measured in these samples were consistently low and impacted by lower analytical precision near the method blanks and the requirement to be greater than five times the method blank to be considered present. These EPA data validation rules (EPA, 1995) have helped avoid false positive results (i.e. detections that should be non-detect), but for very low concentrations, particularly of tPBDEs, appear to have created false negatives. PBDEs are ubiquitous and present in the cleanest laboratory waters (method blanks), and this study was in part unable to reliably measure the low to moderate tPBDE ambient lake and river concentrations because of this background contamination.

While precision DQOs provided a guideline, failure to meet the precision criteria is not considered to make the data unusable for the purposes of this project. The DQOs for accuracy, representativeness, comparability, and sensitivity for PCB and PBDE chemistry data were all met. Completeness goals were met for all matrices except stormwater/CSOs which were 87.5% complete relative to the goal of 90% completeness. Except for three stormwater samples impacted by acetone contamination of the sampler tubing, the DQOs and acceptance criteria were met for all the conventional parameters.

tPCB and tPBDE concentrations in Lake Washington and river samples were the lowest of all samples measured. This is not unexpected given that particle-associated contaminants like PCBs and PBDEs are provided a long settling time for trapping the contaminants delivered to the lake. The large lake surface also provides an output pathway through volatilization of these contaminants. Comparing data between Lake Washington and the two Ship Canal stations, the highest detected tPCB concentrations were at the Ballard Locks station, indicating inputs into Lake Union and the Ship Canal are contributing significant concentrations of tPCBs. tPBDEs in Lake and Ship Canal waters were too close to method blank concentrations to reliably measure, although the three highest measurements were at the Ballard Locks and Montlake. tPCB and tPBDE concentrations in the Cedar and Sammamish Rivers were both low and similar. River concentrations were also comparable to those measured by Herrera (2011).

tPCB and tPBDE concentrations measured in tributaries differed by location, with Thornton Creek exhibiting the highest concentrations. This may be related to the degree of urbanization in these stream drainages. As expected, tPCB and tPBDE concentrations were higher in streams during storm than base flow conditions.

tPCB and tPBDE concentrations varied widely in stormwater runoff, including highway bridge runoff. The highest tPCB concentrations in stormwater were observed in the Fremont stormwater and the second highest were in the highway bridge runoff. For tPBDEs, this pattern was reversed with the highest concentrations in the highway bridge runoff and the second highest in the Fremont stormwater. tPBDE concentrations in stormwater runoff were similar between Seattle discharges compared to small city discharges which exhibited more variability.

The highest tPCB and tPBDE concentrations at CSO locations were consistently observed at the Dexter CSO. A high degree of variability was observed in the Dexter CSO samples compared to the Seward Park and Ballard 150 CSOs. While the Dexter CSO was highest, tPCB and tPBDE concentrations from the Dexter and Ballard 150 CSOs were generally observed within the same degree of magnitude. For both tPCBs and tPBDEs, the Seward Park CSO had consistently lower concentrations. The average CSO tPCB concentration is an order of magnitude higher than the average tPCB concentration of any other aqueous input pathway. The high variability of CSO tPCB concentrations generates significant uncertainty around the arithmetic average concentration. Because an arithmetic average CSO tPCB concentration is required for modeling or loadings estimates, use of an expanded dataset including Lower Duwamish CSO samples is recommended. The combined dataset has a more reliable arithmetic average. This combined average of 53 CSO samples is 70,543 pg/L.

Among the non-CSO input pathways, tPCB concentrations in stormwater at Fremont are highest. The lowest average tPCB concentration was measured in rivers. In contrast, the average tPBDE concentration in CSOs is highest, but similar to that in detected highway bridge runoff. The lowest average tPBDE concentrations are detected in streams during base flow and rivers. Much higher variability was observed in the tPBDE concentrations in the aqueous pathways than in tPCB concentrations.

Calculated air deposition rates for Beacon Hill were consistently higher than Sand Point. However, the difference in tPCB deposition rates between sites is generally within a factor of two. tPBDE deposition rates are about four times higher at Beacon Hill than Sand Point. Average tPCB deposition rates were 3.4 ng/m<sup>2</sup>/d, whereas average tPBDE deposition rates were 18.1 ng/m<sup>2</sup>/d.

Conventional parameter concentrations indicated relatively low TOC in ambient water samples, with the lowest average concentration observed in Lake Washington and highest in streams during storm conditions. As might be expected from these pathways, DOC and TOC was highest and most variable in stormwater runoff, highway bridge runoff and CSOs. Tributary stream TSS, along with TSS concentrations in Lake Washington and the Ship Canal were low, around 1-2 mg/L. TSS concentrations were higher during storm events than base flow conditions. Consistent with the pattern seen with organic carbon, TSS concentrations were substantially higher and more variable in stormwater runoff, highway bridge runoff and CSOs.

The data presented in this report provide the first extensive measurements of low level tPCB and tPBDE concentrations in whole water from Lake Washington and the Ship Canal, as well as from the five input pathways evaluated. The tPCB and tPBDE data have been used to estimate loadings to Lakes Washington and Union in addition to their contribution to Puget Sound (King County 2013). The PCB data will also be used to develop and parameterize both a fate model and bioaccumulation model for Lake Washington. These models will be developed to help inform, in combination with the loadings information: a) where management should invest resources to decrease PCB residues

in Lake Washington fish, b) the magnitude of loadings reductions needed to reduce PCB levels in Lake Washington fish, c) next steps to better understand sources and bioaccumulation in Lake Washington and Lake Union/the Ship Canal, and inputs to Puget Sound.

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# Appendix A

## Data Validation Memo

To: Lake Washington PCB/PBDE EPA grant file

From: Richard Jack

RE: Data Validation Memorandum

This memo documents validation conducted on all project data to ensure project usability and to document any anomalies from project specifications described in the QAPP. The validation addresses most of EPA level 1 and 2A criteria. The chief deviation from EPA level 2A criteria is that sample cleanup varied at the analyst discretion and these cleanup steps were not confirmed herein. This validation memorandum adds additional information about specific samples types to assist data users and reviewers in understanding data limitations.

### **Chain of Custody**

All samples analyzed outside of King County Environmental Laboratory (KCEL) were recorded on chain of custody (COC) forms and securely shipped using a King County employee as a courier. One COC form was not signed by staff upon receipt or relinquishment. This oversight is not believed to impact data quality since King County staff transported the samples to the contract analytical laboratory (AXYS Analytical in Sydney BC [AXYS]) in a locked vehicle instead of by common carrier. Total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) data analyzed at the KCEL were not subject to COC since they were continuously in King County custody and KCEL is a secure facility.

### **Case Narratives**

All samples analyzed for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were identified in a case narrative. Case narratives are not typically produced for KCEL for conventional parameter data. The lack of case narratives is not believed to significantly impact the TOC, DOC, and TSS data as the analysts have already discussed data anomalies with the project manager (see below regarding Isco® autosampler blanks).

### **Sample Dates**

Sampling dates and times were reported correctly for all samples.

### **Results & Units**

Results were reported for all samples, although some samples were reanalyzed by the laboratory to correct method discrepancies, these results were re-reported. PCB-7 results in samples with PCB-7 method blank discrepancies were flagged as non-detect ("U") at the reported concentrations.

### **Reporting Limits**

Congener specific detection limits for some PCB and PBDE samples were elevated above those specified in the QAPP. However, the same congeners were detected in most of these samples; therefore, the elevated sample detection limits (SDLs) did not likely impact the measurement of those compounds.

Not including laboratory duplicates and other QC samples, this project analyzed 430 samples for PCBs, PBDEs, TOC, DOC, and TSS. This includes 158 PBDE and 160 PCB samples.

Four of the PBDE samples had one or more detection limits elevated above the goals specific in the QAPP.

One or more of the congener specific SDLs for the majority of the PCB samples (153 of 160) were elevated above the QAPP specifications. This is partially a consequence of the very low, 1 to 2 pg/L,

SDL goals defined in the QAPP. Of these 153 samples, only ten were significantly impacted by elevated SDLs. Detection limits greater than 10 times the QAPP goal, without a detection of the corresponding congener, were considered “significant”. Only PCB samples were found to have significantly elevated SDLs. The following are the affected samples along with a count of the number of congeners with elevated SDLs. Samples with a larger number of elevated SDLs are considered to exhibit proportionally more low bias.

**Table A-1. PCB samples with number of non-detect congeners and SDLs >10x the QAPP objectives.**

Sample ID	Location Name	Location Type	Number of congeners SDL > QAPP	Sample Type
L53784-3	Sand Point	Air Deposition	6	SA
L55319-2	Dexter	CSO	16	SA
L55319-1	Dexter	CSO	6	SA
L55319-1	Dexter	CSO	11	DUP
L55115-7	Dexter	CSO	5	SA
L54692-2	Storm drain	Stormwater	1	SA
L53784-4	Beacon Hill	Air Deposition	1	SA
L53784-2	Beacon Hill	Air Deposition	3	SA
L55391-2	Ballard 150	CSO	4	SA
L55309-2	Ballard 150	CSO	5	SA
L54190-3	Cedar River, upstream	River	1	SA

SA –Sample

DUP – Duplicate Sample

Most of the samples with significantly elevated SDLs had only one to six affected congeners. Samples L55319-1 and -2 had the highest number of elevated SDLs. For these samples, SDLs ranged from less than the QAPP objectives of 1-2 pg/L to as high as 353 pg/L. However, all of the impacted samples were collected from CSOs with a relatively more complex matrix; these samples also had the highest detected total PCB concentrations. Total detected PCBs in these two samples ranged from 113,203 pg/L up to 984,251 pg/L. When the SDLs for non-detect congeners exceeding the QAPP specifications are summed; their total represents less than 0.19% of the detected concentrations. Thus, the elevated SDLs are not considered to represent a significant low bias to these CSO samples.

Many samples had detections of either PCB or PBDE congeners which were unable to be conclusively identified and the reported concentrations are “estimated maximum potential concentrations” (EMPCs). Methods 1688 and 1614 do not allow inconclusively identified compounds to be used for regulatory purposes. Thus, all “K” flagged EMPCs were re-qualified as non-detect at elevated detection limits. Some samples were entirely composed of EMPCs. The requalification of these detections as non-detects reduces the opportunities for reporting of false positives, but increases the opportunities for reporting false negatives. The low level PBDE analysis in lake and river waters was most impacted by the requalification of EMPCs as non-detects.

### Holding times

Holding times were met for all samples and analyses.

**Analytical methods**

All results included analytical method documentation, either electronically, in writing or both.

**Method Blanks**

AXYS frequently detected various PCB and PBDE congeners in method blanks; this was expected given the very low level detection limits achieved. In six sample batches, congeners were detected in method blanks in excess of method specifications. PCB congener 7 exceeded method specifications several times. The affected sample’s specific congeners were re-qualified as non-detect. Fifty one samples and four laboratory duplicates in the following workgroups were affected. Workgroups affected by PCB method blank contamination greater than method 1668A limits are shown in Table A-2.

**Table A-2. Workgroups affected by PCB method blank contamination greater than method 1668A limits**

Workgroup	KC Sample ID	Sample Type
WG37702	L53342-3	SA
WG37702	L53667-2	SA
WG37702	L53784-5	SA
WG37702	L54036-1	SA
WG37702	L53667-3	SA
WG37702	L53667-4	SA
WG37702	L53342-2	SA
WG37702	L53342-1	SA
WG37702	L53968-4	SA
WG37702	L53968-3	SA
WG37702	L53968-2	SA
WG37702	L53667-1	SA
WG37702	L53968-1	SA
WG37702	L54036-1	DUP
WG39010	L54608-4	SA
WG39010	L54733-2	SA
WG39010	L54608-1	SA
WG39010	L54692-4	SA
WG39010	L54608-3	SA
WG39010	L54692-3	SA
WG39010	L54608-2	SA
WG39010	L54692-3	DUP
WG39375	L54808-4	SA
WG39375	L55115-8	SA
WG39375	L55115-9	SA
WG39375	L54757-6	SA

Workgroup	KC Sample ID	Sample Type
WG39375	L55115-7	SA
WG39375	L54894-2	SA
WG39375	L54808-2	SA
WG39375	L54808-3	SA
WG39376	L55097-5	SA
WG39376	L55097-1	SA
WG39376	L55027-5	SA
WG39376	L55024-1	SA
WG39376	L55097-3	SA
WG39376	L55027-3	SA
WG39376	L55024-2	SA
WG39376	L55027-4	SA
WG39376	L55097-2	SA
WG39376	L55027-1	SA
WG39376	L55027-2	SA
WG39376	L55097-3	DUP
WG39441	L55024-4	SA
WG39441	L55175-3	SA
WG40081	L55309-1	SA
WG40081	L55231-2	SA
WG40081	L55231-1	SA
WG40081	L55450-5	SA
WG40081	L55231-7	SA
WG40081	L55391-2	SA
WG40081	L55391-1	SA
WG40081	L55309-2	SA
WG40081	L55319-2	SA
WG40081	L55319-1	SA
WG40081	L55319-1	DUP

DUP – Duplicate Sample  
SA – Primary Sample

In consultation with AXYS, the source of this method blank contamination appeared to be laboratory renovations which occurred near the times of these workgroup extractions and analysis. In response, AXYS reanalyzed a portion of the affected samples, particularly where PCB-7 was a significant fraction of the total PCBs found. AXYS re-extracted and re-analyzed nine samples for PCB-7. The nine samples were selected because PCB-7 was greater than 20% of the total PCB sum and enough sample volume remained for re-extraction. PCB-7 was only found in the reanalyzed samples at non-detect or very low levels (<7 pg/L). These results demonstrate that the previous 51 PCB-7 exceedances were likely a product of laboratory contamination and not native at significant

concentrations in the sampled waters. Thus, those samples which were not re-extracted and re-analyzed are considered complete despite their PCB-7 results being re-qualified as non-detects.

One method blank slightly exceeded method specifications for PBDE congener 47 which was 130 pg/L, 30 pg greater than the minimum level in Method 1614. For PBDE congener 99; the method blank was also slightly above (136 pg/L) Method 1614 criteria of 100 pg/L. However, AXYS, the contract laboratory for this analysis, has revised PBDE 47 and 99 acceptance limits of 150 pg/L in their SOP. This SOP was adopted for this project by reference in the QAPP. Thus, for samples in this workgroup, results for congeners 47 and 99 were flagged “J” for estimated due to the exceedances of Method 1614 limits, but not the laboratory SOP. Congener results greater than 1300 pg/L for PBDE 47 and 1360 pg/L for PBDE 99 were not flagged as estimated because the method blank discrepancy was less than 1/10<sup>th</sup> the reported concentration.

In all other cases where the method blanks were within the respective limits of Method 1668A or 1614, the reported results were not flagged as estimated. Detected concentrations of PCB and PBDE congeners were compared with the average (if more than one method blank was run) method blank concentration for the samples’ laboratory workgroup batch. Those concentrations less than 5x their respective method blank were re-qualified as non-detect. See field blanks section below for further re-qualifications.

For stormwater samples, Isco® samplers were initially rinsed with acetone in an effort to clean them for PCB and PBDE congener analysis. The acetone rinse, despite subsequent rinsing with de-ionized water, contaminated the TOC and DOC blanks at levels >MDL of 0.5 mg/L. DOC in the blank was 4.62 mg/L while TOC was 2.59 mg/L. Organic carbon results in stormwater samples affected by this cleaning procedure were all less than 5 times the blank levels. Thus, these results were rejected as unusable. Three sample IDs were affected: L54176-1, L54176-2, and L54176-3. The cleaning procedure for Isco® samplers was changed due to this conflict. Later samples were collected using new tubing which was dedicated to each location, only washed with detergent, and not rinsed with acetone to avoid this contamination issue.

### **Method Recoveries**

Occasional deviations from labeled congener or surrogate recovery control specifications were observed. Because Method 1668A recovery corrects data, these deviations are not considered to significantly impact the total PCB concentrations. These congeners were considered estimates and “J” flagged due to the low surrogate recoveries.

In addition, some GC/MS peaks experienced lock mass interference; where an interfering compound of similar mass to the perfluorokerosene (PFK) reference mass causes confusion on the instrument. This leads to either a loss of accuracy in identifying the particular congener, a loss of resolution in quantifying the congener, or both. Whenever a lock mass interference was found, the affected congeners were assumed to be accurately identified. Due to the potential for the reported value to be slightly different from the true value due to the interference, these congeners were “J” flagged. These estimations are a small proportion of the overall total PCB concentration and thus additional uncertainty about the sum of PCBs is not a concern for users of the total PCB value.

### **Duplicates**

Nine laboratory duplicates were analyzed for PCBs and PBDEs. Relative standard deviations (RSD) were calculated and expressed as a percent.

**Table A-3. Water PCB laboratory duplicate results.**

Locator	Location Name	Sample Type	Sample ID	Sample (pg/L)	Duplicate (pg/L)	% RSD
0434	Thornton Creek	Creek	L54191-1	1,603	1,640	1.6
0828JC7SB	Renton storm drain	Stormwater	L53463-3	2,069	1,974	3.3
0440	May Creek	Creek	L53667-5	94	122	18.4
FIELDBLANK	--	QC	L54036-1	61	112	41.6
B472	Sammamish River at golf course	River	L54190-2	33	36	6.8
S035026	Dexter	CSO	L55319-1	113,015	178,914	31.9
S035026	Dexter	CSO	L54692-3	29,019	27,296	4.3
0540	Ship Canal, Montlake	Lake	L55097-3	98	18	97.5
I-90 E HIGHRISE	Road runoff	Stormwater	L55115-1	3,700	3,881	3.4

RSD – Relative standard deviation

PCB laboratory duplicates demonstrated modest variability. The highest RSDs are associated with the lowest reported concentrations, illustrating the increased analytical uncertainty associated with analysis near the detection limits and method blanks. Also, one relatively high RSD (31.9%) is from a CSO duplicate which is expected to be a heterogeneous matrix.

**Table A-4. Water PBDE laboratory duplicate results.**

Locator	Location Name	Sample Type	Sample ID	Sample	Duplicate	Units	% RSD
SEWARDSPU 44	Seward_CS0	CSO	L54692-4	5,929	7,477	pg/L	16.3
0540	Ship Canal, Montlake	Lake	L55097-3	277	200	pg/L	22.7
0446	Juanita Creek	Creek	L52945-4	66	32	pg/L	48.6
B472	Sammamish River at golf course	River	L54190-2	32	174	pg/L	98.0
I-90 E HIGHRISE	Road runoff	Stormwater	L55115-1	1,544	2,721	pg/L	39.0
FIELDBLANK		QC	L54036-1	10,953	5,214	pg/L	50.2
0440	May Creek	Creek	L53667-5	156	1,110	pg/L	106.6
S035026	Dexter	CSO	L55319-1	144,768	117,399	pg/L	14.8
MERCERISL1 0-EPA	Storm drain	Stormwater	L53463-2	25	23	pg/L	5.4

RSD – Relative standard deviation

RPDs for tPBDEs laboratory duplicates were generally higher than those for tPCBs, exceeding 100% once. Subsequent users of these data should be aware of their relatively high measurement variability.

## Field/Equipment Blanks

Field and equipment blank results were compared with method blanks and in most cases results were similar. There were detectable concentrations of PCBs and PBDEs in Niskin and Scott bottle blanks. Two blanks were run on this equipment because the initial blank conducted using KCEL laboratory water appeared contaminated. The subsequent blank using AXYS-supplied “Seastar” water was comparable to method blanks, illustrating that the Niskin jars and Scott bottles themselves were not significant sources of PCBs or PBDEs. Because these collection devices were subsequently rinsed with site water in the field before sample collection, these blanks have not been used to re-qualify sample results.

Some stormwater samples were collected using Isco® autosamplers. Isco® autosamplers were used to collect stormwaters at the Seattle Fremont, Seattle Madrona, Seattle Seward, Renton, Kirkland, Mercer Island, and I-90 bridge stormwaters locations.

The equipment blank for the Isco® was collected at the I-90 location inside the room housing the stormwater settling basin (Figure 13). Indoor areas are known to be more highly contaminated with PBDEs than outdoor areas and the Isco® equipment blank appears to have been contaminated by this room and/or by the use of KCEL laboratory water for the blank. It is not possible to distinguish the different potential sources of Isco® contamination from the environmental samples. Thus, detected PCBs and PBDEs congeners in all samples collected using Isco® autosamplers were re-qualified as non-detect when the reported concentration was less than five times the respective equipment blank concentration. Because the Isco® equipment blank was conducted indoors, in a potentially contaminated environment, this requalification potentially introduces some low bias to stormwater samples collected with Isco® autosamplers outdoors, away from dust and indoor air sources of PBDEs.

Sample L53784-5 was an equipment blank of the air deposition funnel, tubing and collection jar. It used KCEL laboratory water which is suspected to contain higher levels of PBDEs than AXYS “Seastar” de-ionized water. It was not possible to re-qualify the bulk deposition samples based on these blank results since a substantial portion of the mass detected is likely sourced from the laboratory water itself. To describe the potential influence of the laboratory water, which was used as a rinse to flush particulates from the funnels into the collection jars, the following analysis was conducted. The mass of each PCB and PBDE congener potentially in the rinse water of each sample was calculated using the sample specific rinse volume and the equipment blank concentration. If that congener was not found in the environmental sample, its contribution was set to zero. If each congener’s mass in the environmental sample was less than the rinse water mass, then the rinse water was considered to have contributed the environmental sample’s mass. If the mass in the environmental sample was greater than the rinse water mass then only the rinse water mass was assumed to be contributed. These rinse water masses were summed and compared to the mass of tPCBs and tPBDEs in the respective environmental sample to provide perspective on the amount of tPCBs or tPBDEs which may have been sourced from the funnel rinse water.

For both tPBDEs and tPCBs, the rinse water potentially contributed a highly variable mass to the final air deposition sample. Those samples with the greatest environmental deposition experienced the least influence from potential funnel rinse water contaminants while those samples with minimal deposition were more heavily influenced. For those air deposition samples with the highest detected tPCB and tPBDE masses, funnel rinse water contaminants contributed less than 1% of their measured fluxes. The re-qualification of laboratory EMPCs (“K” flags) to non-detects, which substantially reduced the number of congeners contributing to the tPBDE or tPCB sum, had a strong influence on the measured deposition mass and consequently the potential impact of funnel

rinse water contaminants. The PBDE sample potentially most influenced by rinse water contamination was L54608-1 for which potentially ~60% of tPBDEs were sourced from the rinse water. Closer examination of this location/date reveals that 71% of the primary sample's PBDE congeners were re-qualified as non-detect due to K flagging by the analytical laboratory or due to blank contamination greater than 5 times the sample result. In the replicate sample (L54608-3), only 7% of the reported PBDE congener mass was re-qualified as non-detect due to K flags or blank contamination issues. Thus, the estimated contribution of the funnel rinse water to the sample overall is mostly a reflection of the low detected PBDE concentrations and poor analytical performance of the primary sample. In the replicate sample, only 11% of the measured tPBDE mass is estimated to have come from the funnel rinse water.

Other tPBDE samples with high replicate RPDs and/or potentially high funnel rinse water contributions were similar. For instance, samples L54416-1 and L54416-3 had 46% and 22% of their tPBDEs potentially derived from the funnel rinse water. The large difference is almost entirely due to the requalification of the 756 pg/L detected of PBDE-209 in L54416-1 as non-detect because it was a K flagged EMPC reported by the analytical laboratory.

### Wipe method blanks and funnel wipes

To estimate the mass of PCBs and PBDEs left on funnels after brushing and rinsing, two wipe samples were conducted. The funnel wipes were used in the spring and fall to test the adherence of PBDEs and PCBs to the air deposition funnel across two different seasons. A proofed clean laboratory wipe soaked in acetone was used to swab two different funnels after brushing and rinsing were completed.

Wipe blanks (Table A-5) were within method specifications for PCBs and PBDEs. The funnel wipe concentrations were first compared with their method blank concentrations using the "5x rule". Congeners <5x their respective method blank concentration were considered non-detect and did not contribute to the tPCBs or tPBDE wipe sums. Lastly, the PCB and PBDE residues which remained after rinsing the air deposition funnels, and subsequently sampled by the wipes, were compared to the mass of tPCBs or tPBDEs collected in the air deposition sample jars.

**Table A-5. Atmospheric deposition samplers wipe method blank results.**

Sample ID	Analysis	Average Total Concentration	Units
Lab Blank	PBDE	31.7	pg/sample
Lab Blank	PCB	50.8	pg/sample

The funnel wipe results (Table A-6) indicate that the volume of water used to rinse the air/bulk deposition funnels likely had a substantial influence over the mass of PBDEs and PCBs which remained on the funnel. Samples with 400 mL rinse volumes had much less residual mass left on the funnel.

**Table A-6. Atmospheric deposition sampler funnel wipe results**

Analysis	Collect Date	Sample ID	Sum Of Congeners	Units	Rinse Volume
PCB	5/12/2011 9:45:00 AM	L53194-6	1,749	pg/sample (dry weight )	110 mL

Analysis	Collect Date	Sample ID	Sum Of Congeners	Units	Rinse Volume
PCB	8/17/2011 8:45:00 AM	L53784-6	195	pg/sample (dry weight )	400 mL
PBDE	5/12/2011 9:45:00 AM	L53194-6	6,059	pg/sample (dry weight )	110 mL
PBDE	8/17/2011 8:45:00 AM	L53784-6	1,351	pg/sample (dry weight )	400 mL

One of these funnels had been rinsed with 400 mL of de-ionized water while the other was rinsed with only 110 mL of water to avoid overfilling the underlying sampling jar. As expected, the 400 mL rinse was more effective at flushing wet and dry deposition from the funnel into the collection jar. For tPCBs, 195 pg was left on the funnel after a 400 mL rinse while 1,749 pg was left behind after a 110 mL rinse. 1,351 pg of tPBDEs remained on the funnel after a 400 mL rinse while 6,059 pg remained after a 110 mL rinse.

As can be seen from Table A-7, between approximately 7 and 17% of tPCBs depositing on the funnels remained after rinsing and brushing. Between 13 and 29% of deposited tPBDEs remained on the funnels and were thus not part of the bulk deposition analysis. These low biases offset some of the rinse water high bias described above.

**Table A-7. Post rinse air deposition funnel residual tPCB and tPBDEs**

Analysis	Collect Date	Sample mass (pg)	Wipe Sum Of Congeners (pg/wipe)	Rinse Volume	Percent of sample
PCB	5/12/2011	10,096	1,749	110 mL	17.3%
PCB	8/17/2011	3,627	195	400 mL	5.4%
PBDE	5/12/2011	15,118	6,059	110 mL	40.1%
PBDE	8/17/2011	10,591	1,351	400 mL	12.8%

For tPCBs, based on wipe blank results, there is ~5% low bias to the air deposition sampling methodology when 400 mL of rinse water was used. When the sample collection bottle was nearly full and only 110 mL of rinse water could be used to avoid overfilling the collection jar, a more substantial ~17% low bias may result. Two air deposition samples with nearly full collection jars were potentially affected by small rinse volumes. All other sample jars were rinsed with 400 mL. L53194-2 was the Beacon Hill funnel upon which the wipe test was conducted. The total mass of PCBs detected was 10,096 pg. The 1,749 pg wipe residual represents a low bias of about 17%. L53194-3, the replicate funnel also deployed at Beacon Hill was only able to be rinsed with 90 mL of de-ionized water. The 1,749 pg wipe residual potentially represents a low bias of approximately 32% of the total measured mass of 5,380 pg tPCBs in this sample. A comparable bias in PBDE mass was also likely for these 2 funnels. The 6,059 pg residual on the wipe is ~40% of the mass collected in the underlying sample jar (15,118 pg) and 20% of the unwiped replicate jar (22,063 pg). The percent of the tPCBs and tPBDEs falling on the funnel and not being rinsed into the sample collection jar for analysis is partially offset by the contaminants present in the rinse water itself. Overall, the samplers qualitatively appear to have slight to moderate low bias.

### Spike Blanks

Two air deposition spike blanks were collected. Spike blank percent recoveries illustrate that for both the May and October, 2011 air deposition sampler deployments, good recoveries were obtained. However, for some congeners, these recoveries were less than the spiked mass recovery goal of 80% specified in the QAPP. On average PCBs experienced slightly lower recoveries than PBDEs, probably due to differences in glass adhesion or volatility.

**Table A-9. Bulk deposition spike blank recoveries**

Sample ID	Collection Date	Analysis	Average % Recovery
L53194-5	12-May-11	PCB	73.7%
L54416-6	26-Oct-11	PCB	75.1%
L53194-5	12-May-11	PBDE	96.8%
L54416-6	26-Oct-11	PBDE	87.2%

**Overall Validation Summary**

Project specification deviations were found in a few batches and samples. The most significant was the presence of PCB-7 in batch method blanks which represented a significant fraction of the total PCBs in the less contaminated samples in the batch. In response to this QC discrepancy, AXYS has re-extracted and re-analyzed selected samples.

TOC and DOC results from early autosampler collected stormwater samples were rejected as unusable. The autosampler cleaning protocol was changed for future sampling and all future TOC and DOC results met acceptance criteria.

In other cases, lock-mass interference was present on the instrument, poor surrogate recovery was experienced, or slightly elevated PBDE 47 and 99 levels were found in method blanks. These data were considered usable with qualification as estimated concentrations. Various PCB and PBDE congeners were “K” flagged as EMPCs. This means that a particular peak showing on the gas chromatograph did not meet all criteria for positive identification as the congener of interest. While this investigation was not undertaken for regulatory purposes, method specifications prohibit the use of EMPCs in regulatory settings. Based on EPA Region 10 directives (G. Greppo-Grove, pers. comm.) all EMPCs were re-qualified as non-detect.

While some congeners are considered estimates, data were considered useable without particular qualification. Note that field replicate and lab duplicate results sometimes demonstrate high variability. These samples were considered acceptable, although whenever possible it is recommended to incorporate metrics of this variability into project concentration, loading, or air deposition rate calculations.

Appendix B  
Electronic Chemistry Results  
Available upon request

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