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Contact information

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

Washington State Department of Ecology https://ecology.wa.gov

Location of Ecology Office	Phone
Headquarters, Lacey	360-407-6000
Northwest Regional Office, Bellevue	425-649-7000
Southwest Regional Office, Lacey	360-407-6300
Central Regional Office, Union Gap	509-575-2490
Eastern Regional Office, Spokane	509-329-3400

Assessment of Low-Level Sampling Methods for PCBs and PBDEs in Surface Waters

by

William Hobbs, Melissa McCall and Brandee Era-Miller

Toxic Studies Unit
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

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- Snohomish River – WRIA 7 (17110011)

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Abstract

Bioaccumulative chemicals, such as polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs), are found in tissues of aquatic organisms in many Washington State waterbodies. In water samples, these contaminants are often at or near the limits of current sampling and analytical methods. Obtaining reliable surface water measurements of these bioaccumulative toxics is difficult; we are therefore limited in our ability to accurately evaluate the sources of these toxics in Washington's surface waters.

The goal of this study was to assess three approaches for actively sampling PCBs and PBDEs in surface waters. These approaches included:

- *In situ* solid phase extraction (SPE) using Continuous Low-level Aquatic Monitoring devices (CLAMs).
- Centrifugation and separation of solids and water for analysis.
- Large volume (20L) composite grab samples with filtration and extraction using XAD-2 resin at the analytical laboratory.

We found that sediments collected from the flow-through centrifuge and the *in situ* SPE (CLAM) disk were the most reliable sampling approaches based on the following factors:

1. Sensitivity (ability to measure above background contamination).
2. Bias (number of positive detections).
3. Precision (ability to replicate results).

Comparison of the results from the different sampling approaches generally did not overlap. Limited detection of some compounds and the sampling approach sensitivity are the main reasons for the lack of precision among sampling approaches.

When sampling toxics in surface waters for source identification studies, we recommend *in situ* SPE disks, discrete grab samples, and passive samplers as the most reliable approaches. When comparing samples to criteria thresholds for concentration and exposure duration, large volume composite methods can be reliable when concentrations are well above the analytical reporting limits. Following internal Quality Assurance approval, the *in situ* SPE disks would be a viable approach and represent an average concentration over a period of up to 48 hours.

Introduction

Bioaccumulative chemicals, such as polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs), are found in tissues of aquatic organisms in many Washington State waterbodies. These contaminants accumulate in higher trophic level organisms resulting in:

1. Fish consumption advisories from the Washington State Department of Health.
2. Numerous Clean Water Act 303(d) listings (for PCBs) for Washington waters.

We generally identify the presence of these contaminants in waterbodies by measuring their concentrations in fish tissues. Due to the highly bioaccumulative nature of these contaminants, concentrations in tissues have routinely been measurable with standard analytical methods (e.g., EPA Method 8082).

Measuring much lower concentrations of PCBs and PBDEs in surface waters (e.g., part-per-quadrillion range or pg/L) presents several challenges. PCBs and PBDEs, as well as many other highly bioaccumulative chemicals, are often not measurable in the water column with a grab sample, which is the sample type most commonly collected in Ecology's routine water monitoring programs. Measuring them can require a pre-concentration technique (e.g., semipermeable membrane devices or fish tissue). The cost of analysis for chemicals measured in the part-per-quadrillion range is higher, as it requires high-resolution analytical methods (e.g., EPA Method 1668C). Additionally, quality control is challenging; matrix interferences and background contamination can sometimes impact the ability to obtain quantified data. These challenges limit the ability to characterize ambient concentrations of PCBs and PBDEs in Washington's surface waters.

To help overcome many of these challenges, the Washington State Department of Ecology (Ecology) continues to investigate and improve methods for reliably measuring these contaminants. A reliable measurement is one where background contamination from the laboratory or field does not interfere with our ability to detect the contaminant in water.

Ecology has previously assessed *passive* sampling approaches for toxics in surface waters (Sandvik and Seiders, 2012). Passive samplers like semipermeable membrane devices are generally intended for longer deployments (e.g., a month), where the sampler has sufficient time to equilibrate with the surrounding environment and reflect the average concentration of toxics over the period of deployment. However, the specific uptake or rate of sampling of toxics can only be estimated with these devices; therefore, measured concentrations are considered an estimate.

Active sampling methods, on the other hand, generally have a known rate of sampling or an exact volume of sample. As a result, active sampling yields a direct measure of concentrations of toxics in the environment at a particular location and point in time.

The goal of this study was to assess select approaches for *actively* sampling PCBs and PBDEs in surface waters. These approaches include:

1. *In situ* solid phase extraction (SPE) using Continuous Low-level Aquatic Monitoring devices (CLAMs).
2. Centrifugation and separation of solids and water for analysis.
3. Large volume (20L) composite grab samples with filtration and extraction using XAD-2 resin at the analytical laboratory.

Parameters of Concern

PCBs

Polychlorinated biphenyls (PCBs) are a class of 209 compounds or congeners that contain one to ten chlorine atoms attached to two rings of biphenyl. PCBs were created to resist degradation and persist. This has made them a ubiquitous environmental contaminant despite being banned in 1979 and used in so-called closed systems (Erikson and Kaley II, 2011). They are particularly soluble in lipids (fats), leading to the accumulation and biomagnification of PCBs in biological systems (Fisk et al., 1998). PCBs are carcinogenic and can also affect the immune system, endocrine system, nervous system, and reproductive system (Longnecker et al., 1997; Brouwer et al., 1999).

PBDEs

A second group of chemicals, often present at low concentrations in surface waters, are polybrominated diphenyl ethers (PBDEs) – flame-retardants. PBDEs are also a class of 209 congeners that resemble the structure of PCBs except they contain bromine instead of chlorine. They are manufactured as flame-retardants and used in a large variety of products (e.g., plastics, furniture, upholstery, electrical equipment, and textiles) (Hale et al., 2003). There are three main homologue groups of PBDEs: penta-, octa-, and deca-brominated diphenyl ethers (BDEs). The manufacturers of PBDEs voluntarily ceased production of octa- and deca-BDEs in 2004 following human health concerns. Like PCBs, PBDEs are bioaccumulative and bind to the fats of organisms. The fate and toxicity of PBDEs varies; the heavier congeners tend to bind more readily to dust and solids, and the lighter congeners are more volatile (Hale et al., 2003). Once in the body, PBDEs can inhibit the transport of thyroid hormones affecting metabolic functions and interfering with fetal development (Birnbaum and Staskal, 2003).

Study Objectives

The objectives of this study are to measure PCBs and PBDEs using three sampling methods that could yield reliable analytical data for low concentrations in surface waters. For the purposes of this study, we define low concentrations of PCBs as those comparable to various regulatory levels currently in place in Washington State, particularly those relevant to the protection of human health (Table 1). No regulatory levels are available for PBDEs.

Table 1. Some of the water quality criteria for the protection of human health and aquatic life for total PCBs found in Washington State.

Marine Aquatic Life* (ng L^{-1})		**Freshwater Aquatic Life* (ng L^{-1})**		**Human Health**		**Spokane Tribe Human Health**
Chronic exposure	Acute exposure	Chronic exposure	Acute exposure	Consumption of water and organisms (ng L^{-1})	Consumption of organisms only (ng L^{-1})	Water and fish consumption (ng L^{-1})
30	10,000	14	2000	0.0007	0.0007	0.0013

*Chapter 173-201A-240, WAC 173-201A.

Regulatory levels of the contaminants are based on the duration of exposure. Some criteria for the protection of aquatic life are based on exposure over a 24-hour period, whereas human health exposure is typically based on a 70-year exposure. The periods of sampling for this project were dictated by our ability to accrue sufficient samples for analysis (i.e., centrifuge sediment). However, the periods of sampling represent continuous and composite sampling over 8 to 46 hours (Appendix A, Table A-1), and in the future, sampling methods could be selected to meet the representativeness of exposure periods.

Following the measurement of PCBs and PBDEs using the three sampling methods, the overall reliability of the sampling approaches will be evaluated. The evaluation of method sensitivity, bias, and precision will be compared to evaluation criteria (Table 2). In addition, sampling time and cost will be considered in the evaluation of the methods.

Table 2. Evaluation approach for the field sampling methods.

	Evaluation approach	**Evaluation criteria**
Sensitivity	Evaluated using the ratio of total PCB or PBDE in the sample to total PCB or PBDE in the corresponding lab blank.	Represents the level of blank interference and is analogous to blank censoring thresholds. Methods evaluated against USEPA thresholds for blank censoring (USEPA, 2016).
Bias	Evaluated based on the maximum number of detections among sampling approaches.	Method with the highest number of detections receives the highest rating.
Precision	Evaluated based on the sample relative standard deviation or relative percent difference.	Study QAPP method quality objectives (Hobbs and McCall, 2016).

Methods

Study Locations

The Spokane, Yakima, and Snohomish Rivers were selected for sampling to:

1. Provide data on PCBs and PBDEs that would be informative for ongoing or known contamination investigations.
2. Represent different hydrologic settings.
3. Provide some variability in the composition and concentration of suspended sediments.

The sampling sites on the rivers were selected to allow for the continuous use of equipment over an 8- to 46-hour period. The exact periods of sampling can be found in Appendix A (Table A-1).

A number of stakeholders in the Spokane River Basin in eastern Washington have ongoing efforts to control sources of PCBs to the river (LimnoTech, 2016). Fish tissues in the Spokane River have had documented PCB contamination since the early 1980s (Hopkins et al., 1985) and contamination with PBDEs since 2001 (Johnson and Olsen, 2001; Furl and Meredith, 2010). The hydrology of the river is regulated by its connection to the Spokane Valley-Rathdrum Aquifer, snowmelt, and a series of dams. The discharge peaks in April/May (~15,000 cfs) and is low in August/September (~2,000 cfs). Total suspended solids is generally low in the river, ranging from 1 to ~5 mg/L during 2008/2009, according to Ecology's River and Stream Water Quality Monitoring program[1].

The sampling site on the Spokane River is the same as the long-term monitoring site used by Era-Miller and McCall (2017). It is located downstream of the Long Lake Dam at the boundary of the Spokane Tribe of Indians' land (Figure 1). Sampling equipment was deployed off a semi-permanent dock at the Union Gospel Mission Camp. Equipment was suspended at a depth of ~ 0.5m (1.5 ft) below the water surface from the edge of the dock. Samples were collected from June 8 – 9, 2016 and February 8 – 9, 2017, and represented a sampling period of 46 and 34 hours respectively.

The Yakima River in eastern Washington has documented PCB contamination (Hopkins et al., 1984; Johnson et al., 1986; Johnson et al., 2010). PBDEs have also been investigated in a few studies of the Yakima River (Johnson et al., 2006; Seiders et al., 2016). Much of the focus on toxics in the Yakima Basin has been on legacy pesticides such as DDT (Rinella et al., 1992), which is typically measurable in surface waters using grab samples.

[1] https://fortress.wa.gov/ecy/eap/riverwq/regions/state.asp

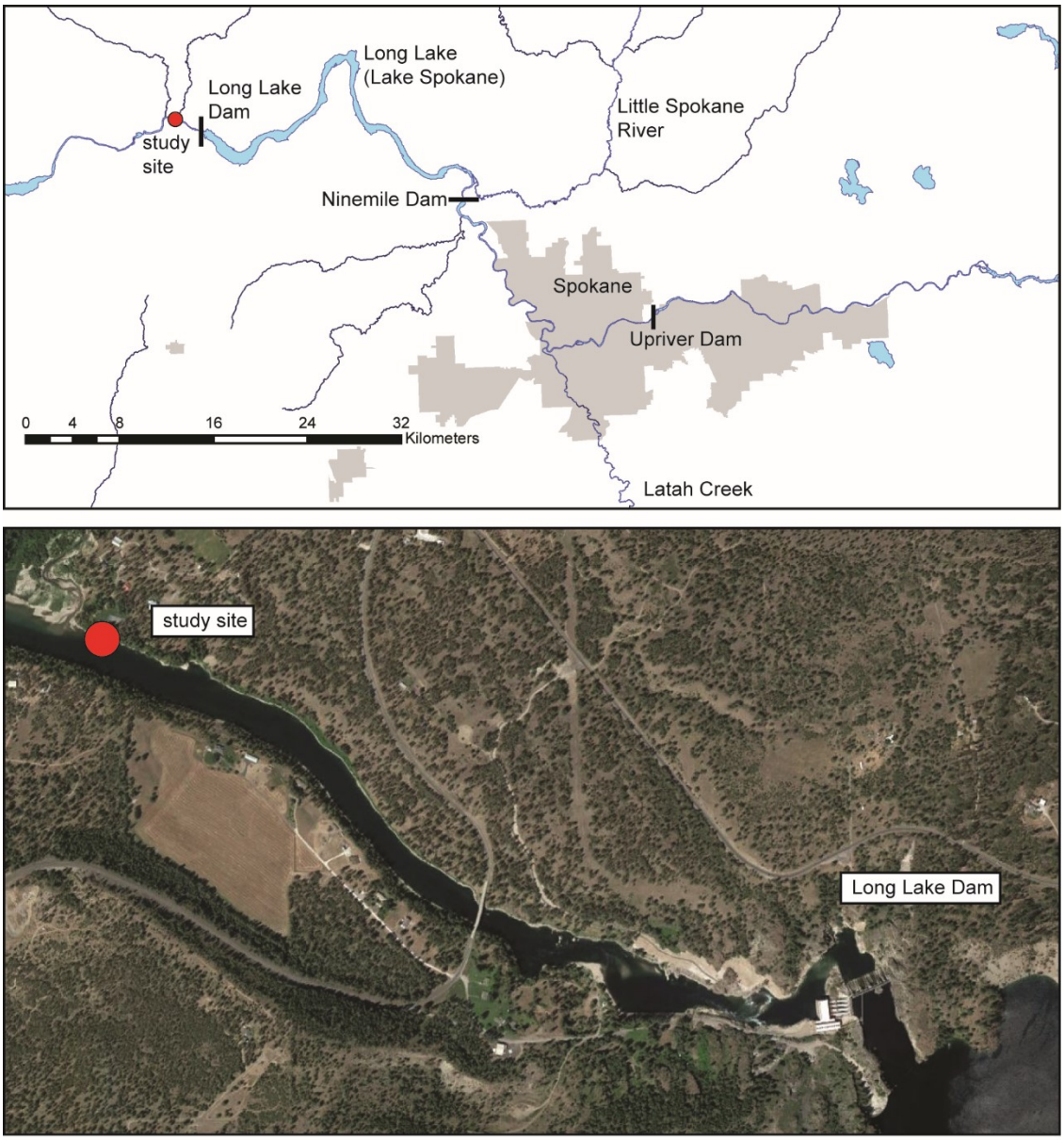

Figure 1. Location of study site on the Spokane River.

The hydrology of the Upper Yakima River is influenced by a headwater dam and the Roza Dam within the Yakima Canyon. Peak discharge in the river is in May (~6,000 cfs) and low flow is in September (~1,500 cfs). Suspended solid concentrations in the Yakima River are generally much higher than the Spokane, ranging from 2 – 39 mg/L during 2008/2009 sampling by Ecology[2]. The sampling site on the Yakima River was located just upstream of the forebay for the Roza Dam (Figure 2). Sampling equipment was deployed ~4m (13ft) from the right river bank. Equipment was suspended at a depth of ~ 0.5m (1.5ft) below the water surface from an anchored buoy. Samples were collected from August 3 – 5, 2016 over a 46-hour period.

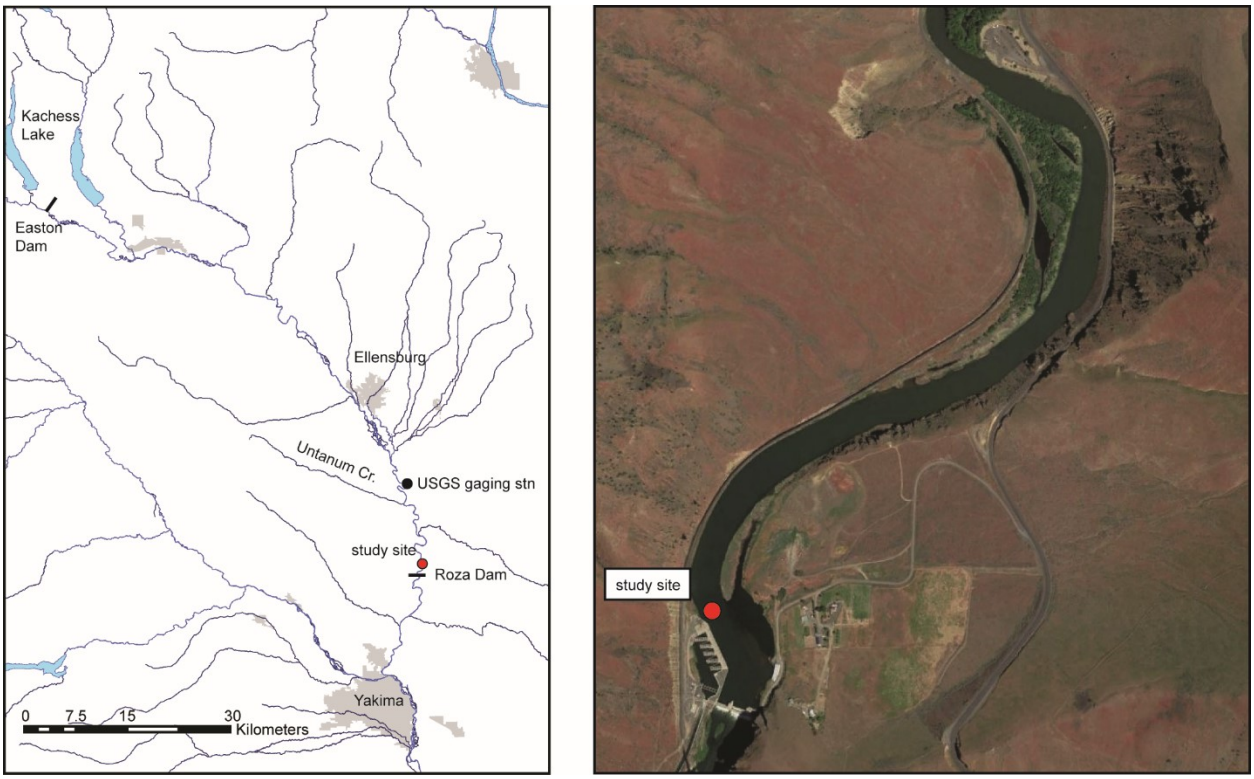

Figure 2. Study site location on the Yakima River.

The Snohomish River in western Washington was previously investigated for the presence of PCB and PBDE contamination. Studies of the suspended sediments (Gries and Osterberg, 2011), resident fish tissues (Seiders et al., 2005; Mathieu and Wong, 2016), and juvenile Chinook salmon (O'Neill et al., 2015) have all demonstrated the accumulation of PBDEs. The hydrology of the river is largely rain-dominated, unlike the Spokane and Yakima Rivers which are snow-dominated, meaning that discharge peaks in November/December (~ 40,000 cfs) in the lower Snohomish River and is at low flow in August/September (~ 2,000 cfs). The lower section of the river can be very sediment-laden with suspended solids concentrations ranging from 2 – 83 mg/L during 2015/2016 sampling by Ecology[2].

[2] https://fortress.wa.gov/ecy/eap/riverwq/regions/state.asp

The sampling site on the Snohomish River was located downstream of the town of Snohomish at the boat launch in Rotary Park (Figure 3). Sampling equipment was deployed from a permanent dock structure at a depth of ~0.5m (1.5ft) below the water surface. This section of the lower Snohomish River is tidally influenced and possibly impacted by salt water intrusion up the river depending on the strength of the tidal cycle (Yang and Khangaonkar, 2008). Samples were collected on December 15, 2016, over an 8-hour period.

Figure 3. Study site location on the Snohomish River.

Sample Media and Laboratory Methods

The three sampling methods tested in this study focused on the media of water and suspended sediments (Figure 4). Not all samples were analyzed for both PCBs and PBDEs due to budget constraints. All laboratory methods used in the study are detailed in Appendix A (Table A-2).

Both PCBs and PBDEs can bind to particulates in water. Therefore, ancillary parameters of suspended sediment concentration, total and dissolved organic carbon, total non-volatile suspended sediments, and sediment carbon and nitrogen content were also analyzed to characterize the properties of sample media that might influence dissolved and total PCB and PBDE concentrations.

Both the *in situ* solid-phase extraction (SPE) media and large volume composite samples of water are reported as total concentrations representing whole water, while the centrifugation allows us to measure the sediment-bound and dissolved/colloidal phases of the analytes. The sediment-bound concentrations (pg/g) are then multiplied by the suspended sediment concentrations of the river (g/L) and combined with the dissolved/colloidal phase to give a total concentration.

For the extraction of the large composite samples, one of two approaches were used:

1. A pre-concentration with an XAD-2 resin and then solvent (toluene) extraction of the XAD.
2. A solvent (dichloromethane; DCM) liquid-liquid extraction of the 20L sample in 2L aliquots.

Analysis of the sample media for PCBs and PBDEs was carried out using high-resolution methods for complete congener profiles.

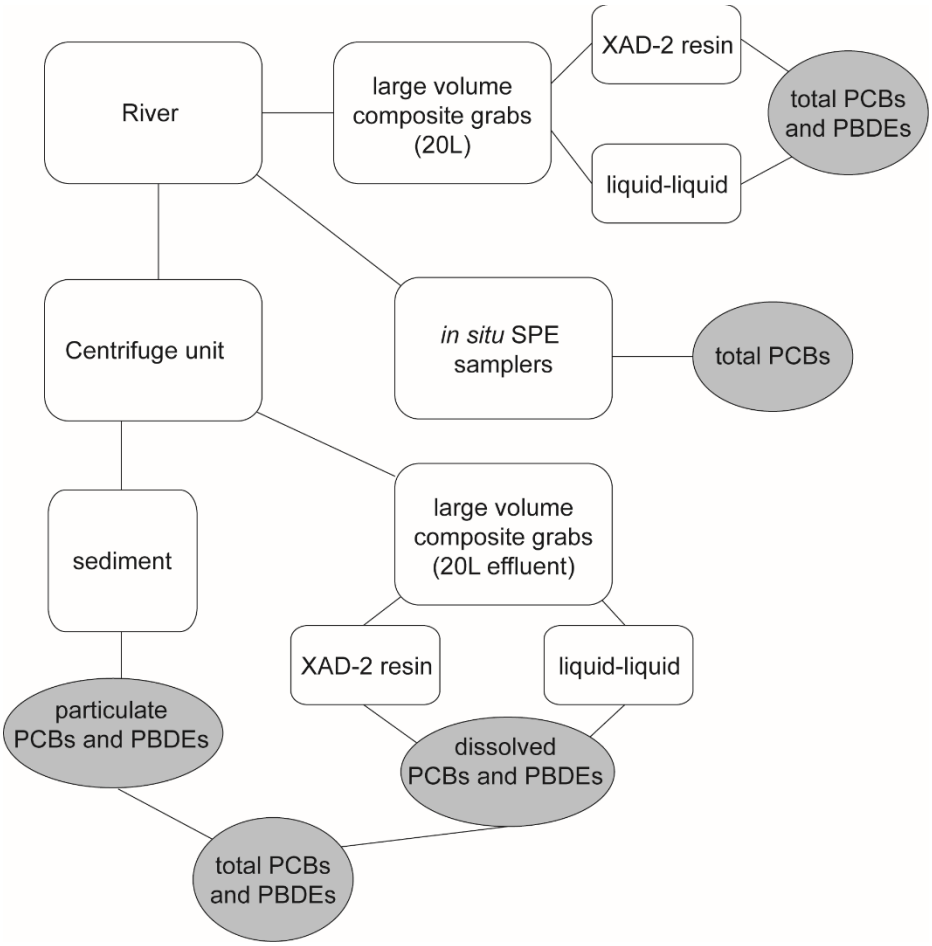

Figure 4. Flow chart of the three sampling approaches and contaminants analyzed.

Grey shaded ovals in the flow chart represent points with analytical results.

Sample Blanks and Censoring

The objectives of this project necessitate a large number of quality control blank samples to constrain possible contamination of the sample. Blanks are collected to represent different parts of the preparation, sampling, and analysis process. In Table 3, we present an overview of the blanks used in this study with which part of the process they represent.

Table 3. Summary of project blank samples.

Stage	Large-Volume Grab Samples		Centrifuge Effluent		Centrifuge Sediment	SPE-CLAM
	XAD	L-L	XAD	L-L		
Sample containers	Bottle proof		Bottle proof		Bottle proof	
Equipment decontamination	Bottle proof		Centrifuge blank		Centrifuge blank	SPE blank
Sample media preparation	XAD blank		XAD blank			
Laboratory DI	XAD-DI blank		XAD-DI blank			
Transport into the field	Transfer blank		Transfer blank			Field blank
Exposure during sampling						
Transport to the lab						
Exposure in the lab	Lab method blank		Lab method blank		Lab method blank	Lab method blank

XAD = styrene and divinylbenzene polymer
L-L = liquid-liquid extraction with separatory funnel
DI = deionized water
SPE-CLAM = solid phase extraction media in a continuous low-level aquatic monitoring device

All samples were censored using the laboratory batch method blank quality control samples. A threshold of five times the blank concentration was used to adjust the result data qualifiers. Additional blank samples (e.g., equipment and transfer samples) were not used to further censor environmental samples, but were used for comparison of possible interference with the sample results. A complete presentation of the blank data can be found in the *Results* section of this report.

As described in the analytical methods for PCBs and PBDEs, a positively or tentatively identified analyte (congener) must be above 2.5 times the detection limit (DL) of the instrument; this is referred to as the signal:noise ratio (S/N). In this study, we also calculated a ratio to express the "noise" of the sampling system or approach. To do this we took the sum of the uncensored total mass (pg) of PCBs and PBDEs in the environmental sample and divided it by the sum of the uncensored total mass (pg) of PCBs and PBDEs in the corresponding laboratory batch method blank samples. This ratio of the total PCB or PBDE mass in the sample: blank (S/B) represents the sensitivity of the sampling system for a specific sample.

The S/B ratio we calculated for each sample essentially describes a level of censoring (multiples of the blank) for each type of sample. Typically, the decision on the level of blank censoring for a particular sampling event is made prior to the analysis and depends on the use of the data. In an EPA guidance document on the assessment of the relative threat of hazardous substances to the environment, three times the background concentration is used as a threshold for source identification (USEPA, 1992). If the goal is to compare contaminant concentrations to regulatory standards, then five times the blank should be used. This is the usability threshold for data under the National Functional Guidelines (USEPA, 2016). A more stringent threshold under the

National Functional Guidelines is ten times the blank and is applicable to more common laboratory contaminants (e.g., solvent preservatives and reagent contaminants).

Result flags from the contract laboratory were converted to a result qualifier during the validation of the electronic data deliverable (EDD). In the summation of PCB and PBDE congeners, data qualified as non-detect (UJ) were excluded and data qualified as tentatively identified (NJ) were included. Tentatively identified congeners were included following data validation showing that compounds above the level of quantitation were distinguishable on chromatograms. Summing procedures are outlined in the project QAPP (Hobbs and McCall, 2016).

In Situ Solid-Phase Extraction

The continuous low-level aquatic monitoring (CLAM) device is an *in situ* sampler containing a pump and solid-phase extraction disk (SPE) manufactured by Aqualytical, Louisville, KY (Figure 5). The SPE media used in this project was C-18 extraction media, which is composed of a bonded silica filter with an octadecyl functional group that binds semi-volatile and non-volatile organic compounds (e.g., organochlorine pesticides, PCBs, and PBDEs). A detailed description of the device and protocols can be found in the Quality Assurance Project Plan (QAPP) for this study (Hobbs and McCall, 2016). To reduce possible background contamination of PCBs during this project, we manufactured a stainless steel housing for the SPE disk (Figure 5).

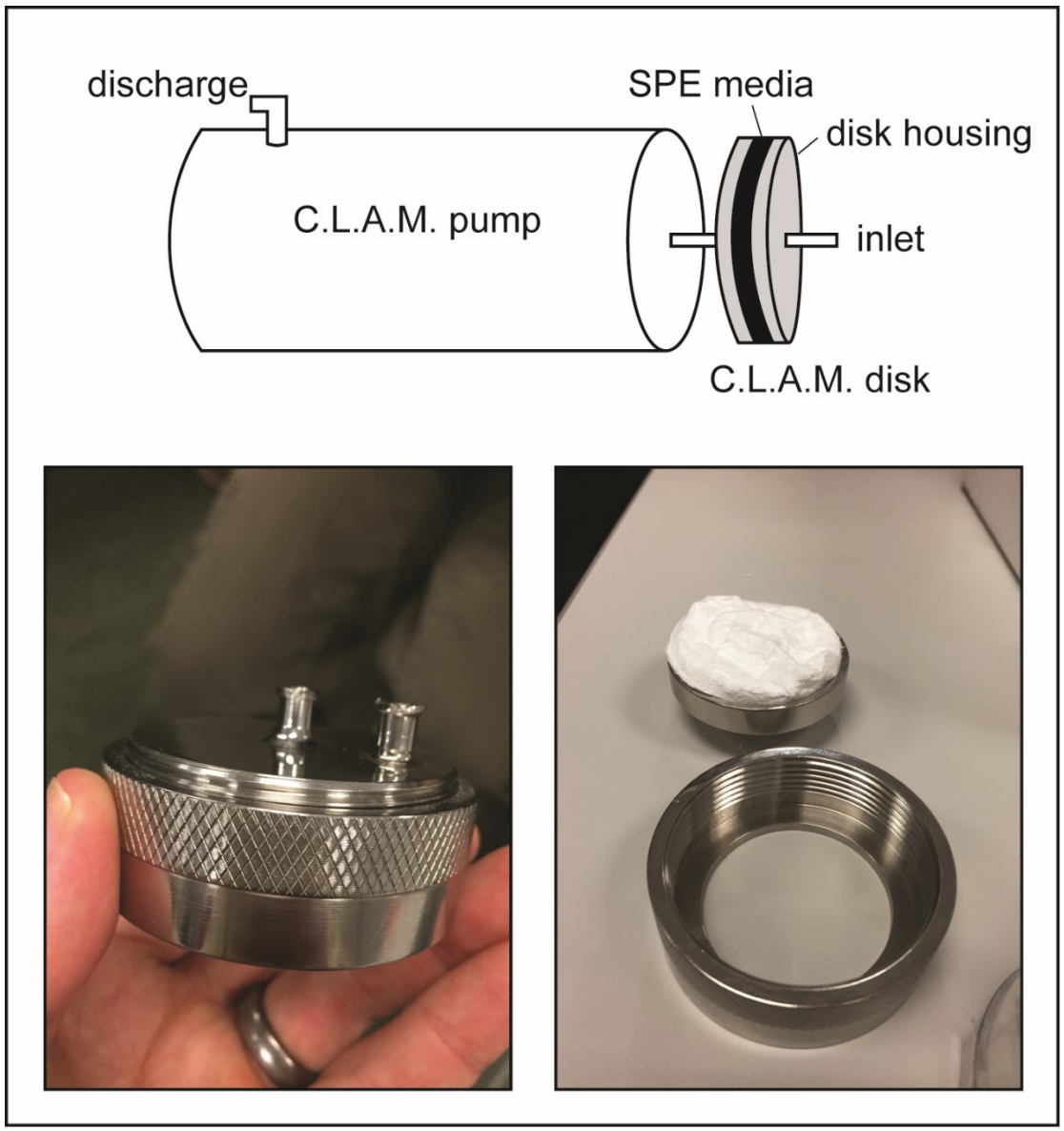

Figure 5. Parts of the CLAM sampler.
Top: Schematic of the CLAM sampler showing the position of the disk.
Bottom-right: Inside the disk housing; the white material is the SPE media.
Bottom-left: Assembled stainless steel CLAM disk housing.

Before deployment into the field, the CLAM disks were conditioned by the contract laboratory as per the manufacturer's recommendations. The assembled disk was purged with 50ml of dichloromethane (DCM), conditioned with 50ml of methanol, and rinsed with 50ml of reagent quality DI water. In the current project, isotopically-labelled PCB congeners were also added to the disk following conditioning to test for retention in the field (^{13}C-PCB-31, ^{13}C-PCB-95, and ^{13}C-PCB-153).

Before each sampling event, three conditioned SPE blanks (within the stainless steel housing) were analyzed to document background contamination. During the first three sampling events, a blank CLAM disk was transported into the field and exposed to the environment as a field blank.

Exposure of the disk entailed mimicking the time of atmospheric exposure while the CLAM disks were deployed. The field blank was then capped, stored, and shipped with the environmental samples.

The CLAMs were deployed ~0.5m below the water surface. A known volume of water was pumped through the SPE disk over an 8- to 46-hour period. Discharge water was collected at the shore or dock in a Rubbermaid container to quantify the volume. Instantaneous flow rates of the pumps were taken periodically during the sampling to monitor any changes.

The flow rates through the CLAM pumps and the SPE disks declined exponentially at all the sites (Appendix A, Figure A-2). The amount of time it took for the flow rates to decrease by 50% was shorter at the more turbid sites (Yakima and Snohomish Rivers). Over the period of pumping, the flow rates decreased by 35 – ~95%. This characteristic of exponential decline in flow rates over the course of sampling means that the sample collection is weighted more heavily to the first ~10 hours. While the objectives of this project were not necessarily to get an evenly time-weighted sample for the SPE disk, it does introduce a bias that differs from the other sampling approaches.

Centrifugation

Ecology's centrifuge unit was assembled in the late 1980s and was originally built for municipal and industrial effluent sampling and compliance (Andreasson, 1991; Yake, 1993). An informal SOP for the operation of the centrifuge trailer was written by Seiders (1990). The trailer contains flow regulators and two flow-through centrifuges (Alpha Laval, Sedisamp II, Model 101L) (Figure 6). A generator powers the unit; however, modifications made during this project allowed us to plug the unit directly into an AC outlet, when available.

External to the unit, the river water was supplied through a large groundwater pump (Grundfos SP4), which has a pump rate of approximately 20L/min. The pump was suspended off a dock or buoy, in the vicinity of the CLAM devices. Water was pumped through Teflon-lined tubing to the centrifuge unit. Prior to entering the unit, the flow was split so that approximately 30% of the flow entered the unit. Once in the unit, flow was split and regulated through a series of ball and check valves to maintain a flow of 3 L/min to each centrifuge (Figure 6). This flow rate has been determined to be the optimal flow to maximize the efficiency of solids removal (Yake, 1993; Gries and Sloan, 2009). An independent in-line optical flow meter on each inlet to the centrifuges measures flow rates and records the total volume of water sampled (Figure 6).

Figure 6. Centrifuge trailer (left) and the flow control board for each centrifuge (right).

Each centrifuge was treated as a separate sampling device, allowing for duplicate samples to be taken. The effluent from the centrifuges was periodically sampled into large volume (20L) stainless steel canisters for PCB and PBDE analysis. This eight- to ten-part composite of the centrifuge effluent represents an operationally defined dissolved and/or colloidal-bound fraction. Sediments accumulated in the centrifuges were removed as two separate samples for analysis. Depending on the suspended sediment concentrations of the water, approximately 1700 to 8500 L of water was processed over an 8- to 46-hour period.

Following sampling, the tubing and centrifuges were flushed with alconox soap and deionized water (DI). Prior to the next sampling event, all tubing and the centrifuge parts were disassembled and solvent-rinsed with acetone and hexane as per Friese (2014). The tubing on the control board of the trailer was flushed with methanol to protect the optical flow sensors. Prior to each sampling event an equipment blank sample of the centrifuge unit was taken by flushing laboratory-grade DI through and collecting it in a one-liter sample bottle for analysis by liquid-liquid extraction.

Large Volume Composite Grab Samples

Concurrent with the CLAM and centrifugation sampling, we took three large volume (20L) composite grab samples from the same sampling location. Eight to ten aliquots were collected at evenly spaced time intervals, into 20L stainless steel canisters following established protocols (Joy, 2006). A dedicated, cleaned stainless steel transfer container was used to collect the aliquot and split evenly between the three canisters. A full container of laboratory-grade DI was used during each sampling to split, transfer, and mimic sampling as a blank in a clean empty container.

At the contract laboratory, the samples were filtered through a 1µm filter and run through XAD-2 media (a polymer of styrene and divinylbenzene) to remove the organics. XAD-2 is a solid-phase extraction media that has a long history of use in the field of toxics monitoring because it efficiently binds organic chemicals from the sample water. The XAD-2 media and the 1µm filter were then eluted and the extract analyzed, representing a whole water sample.

Following the first two sampling events, it became apparent that the XAD-2 media contained background contamination high enough to overlap with concentrations from the river water. We therefore made the decision to alter how the 20L sample was being extracted. During the last two sampling events, the 20L sample was subsampled into 2L aliquots and prepared by liquid-liquid extraction using a separatory funnel. In this extraction, the river water was not filtered with a 1µm filter. The combined extract was then analyzed using EPA method 1668C (PCBs) and 1614A (PBDEs).

Results

Laboratory Quality Assurance

The QA Officer at Ecology's Manchester Environmental Laboratory (MEL) conducted a level 4 data validation for each EDD from the contract lab. The project measurement quality objectives for laboratory methods 1668C (PCBs) and 1614A (PBDEs) were generally met. Sample concentrations for these methods are reported based on isotope dilution and internal standard techniques. In some instances, poor recovery of standards and laboratory error resulted in data being qualified or rejected. In many cases, chromatographic interferences and detections in the method blank samples resulted in the raising of the reporting limits above the desired concentration outlined in the QAPP. This occurred most frequently in the water samples extracted using XAD or liquid-liquid extraction.

A complete summary of the estimated detection limits (EDL) and limits of quantitation (LOQ) are found in Appendix A (Tables A-3 and A-4). Instances of increased detection limits, low internal standard recoveries, and weak detection of the analytes due to instrument noise reflect the challenges of high-resolution mass spectrometry at low environmental concentrations among different media.

Blank Samples

Detailed results for the PCB and PBDE congeners for all the blank samples can be found in Appendix B.

Laboratory and Media Blanks

Batch laboratory method blanks are associated with each analytical batch of samples (Appendix B, Table B-1). The method blank results are presented in Appendix B (Table B-2).

Laboratory blanks were provided for the XAD-2 media and laboratory DI (Table 4). XAD media blanks were treated and extracted in the same way environmental samples were, which includes using the same volume of solvent for extraction. The XAD-DI blanks consisted of 10L of laboratory DI run through the prepared XAD-2 resin and extracted using the same methods. From the beginning of the project, it was apparent that both the XAD-2 and DI contained a background level of both PCBs and PBDEs. The XAD laboratory blank was used to censor the environmental samples that were processed and extracted using the XAD-2 resin.

Table 4. Estimated PCB and PBDE contamination in laboratory blanks of XAD and lab DI.

Sample ID		WG2329945-1	WG2329945-4	WG2368527-1	WG2368527-4
Media		XAD	XAD-DI	XAD	XAD-DI
Analysis date		8/4/16	8/4/16	10/22/16	10/22/16
t-PCBs	% detections	45	53	54	55
	pg	453 J	2498 J	540 J	1294 J
t-PBDEs	% detections	40	36	45	45
	pg	147 J	856 J	190 J	1333 J

The majority of the PCB congeners present were lighter molecular weight in the mono-, di-, and tri-chlorinated biphenyl range (Appendix B, Table B-2). The majority of the PBDE contamination can be attributed to congeners BDE-47, -99, and -209. The number of congeners detected in the XAD-2 and the XAD-DI were not that different. However, it is clear that the laboratory DI contained a significant amount of background contamination, resulting in an apparent increase of both t-PCBs and t-PBDEs by an order of magnitude (Table 4). Based on this finding, the XAD-DI blank appears to be a poor analogue for the environmental sample; therefore, the blank of solely XAD-2 media seems more reliable. Because of this, all environmental samples extracted using XAD-2 are censored to the XAD-2 laboratory method blank and not the XAD-DI blank.

Equipment Blanks

Before each sampling event, proofs of the sample containers were verified (Appendix B, Table B-3). The bottle proofs are not intended to quantify a level background contamination that could be accounted for in the environmental sample result; rather, the verification of the sample containers is to qualitatively highlight any possible major sources of contamination that might suggest a different batch or type of container is necessary. In this study, the presence of PCB-11 and PCB-31 was notable in the proofs of the Viton O-rings for the stainless steel containers. No other results suggested that sample containers would contribute to background contamination.

Sample SPE disks were acquired directly from the manufacturer and all disks for the project came from two lots (0450114 and 3060115) (Table 5). A total of 12 SPE disk blanks were analyzed over the course of the project (Appendix B, Table B-4). The disk blanks were analyzed following cleanup and preparation for the field. With the exception of two disks from the first Spokane River (2016) sampling, the background concentrations for the SPE disks ranged from 1.7 to 60.5 pg total PCBs per disk. The total PCB mass has been censored against the laboratory batch method blanks. The percent of detections was also low, ranging from 4 – 16%.

Two of the SPE blanks had 36% and 37% detection of PCB congeners, resulting in total PCB mass of 507 and 837 pg, respectively. This is well above an earlier lab blank (24.3 pg t-PCB) and the field blank (135.2 pg t-PCB) for this lot of SPE disks. It is possible that the two SPE disks with high background t-PCBs were not prepared properly by the lab or that the high concentrations reflect the variability of the background t-PCB burden in this equipment.

Table 5. Summary of the SPE disk blanks during the project.

Sample	ALS ID	Analysis Date	River	Lot #	% detections	Total PCB (pg)
EQ BLANK 3	L1771451-1	8/31/2016	Lab	0450114	12%	24.3 J
Disk blank 2	WG2329949-4	7/27/2016	Spokane	0450114	37%	507.0 J
Disk blank 3	WG2329949-5	7/27/2016	Spokane	0450114	36%	836.7 J
CLAM SPE Blank #1	L1788103-7	10/24/2016	Yakima	3060115	5%	14.2 J
CLAM SPE Blank #2	L1788103-8	10/24/2016	Yakima	3060115	16%	60.5 J
CLAM SPE Blank #3	L1788103-9	10/24/2016	Yakima	3060115	2%	1.7 J
CLAM SPE Blank #1	L1860754-19	1/17/2017	Snohomish	3060115	9%	15.5 J
CLAM SPE Blank #2	L1860754-20	1/17/2017	Snohomish	3060115	11%	19.2 J
CLAM SPE Blank #3	L1860754-21	1/17/2017	Snohomish	3060115	4%	20.8 J
CLAM BLANK #1	L1876555-19	6/2/2017	Spokane	3060115	4%	5.0 J
CLAM BLANK #2	L1876555-20	6/2/2017	Spokane	3060115	4%	4.7 J
CLAM BLANK #3	L1876555-21	6/2/2017	Spokane	3060115	13%	32.8 J

Before each use of the centrifuge system, laboratory grade DI was flushed through the entire tubing and centrifuge system and collected for analysis of PCBs and PBDEs (Table 6). Generally, the centrifuge blanks were very clean – there was no defined threshold for blank contamination for this project. There are two samples worth highlighting: the samples analyzed for PCBs from the last two sample events (1612024-1 and 1702027-1). The majority of PCBs were found in the lighter congener range (Appendix B, Table B-5). The labeled congener/internal standard recoveries were just above the lower limit for recovery (10%) for these samples (USEPA, 2010a). Some congener-specific results were rejected in sample 1702027-1 due to low recoveries. Given the potential bias in laboratory recovery and the very low concentrations observed in all the other centrifuge blanks, contamination from the centrifuge equipment was negligible.

Table 6. Estimated PCB and PBDE concentrations in centrifuge equipment blanks.

Lab ID		1606035-1	1608046-1	1612024-1	1702027-1
Sample date		6/8/2016	8/3/16	12/15/2017	2/14/17
t-PCBs	% detections	6	8	26	6
	pg/L	14 J	13 UJ	244* J	400* J
t-PBDEs	% detections	10	5	10	10
	pg/L	8 J	5 J	22 J	17 J

*likely overestimation due to very low recoveries of lighter PCB congeners

Field Blanks

Transfer blanks representing the preparation/transport of equipment and sampling of the large volume samples into the stainless steel containers were created for each sampling event. Laboratory DI was shipped to Ecology and then transferred in aliquots to a clean 20L container. The transfer blank samples were prepared and analyzed at the same time as the other large volume samples. Samples from the first two sampling events were prepared using the XAD and samples from the last two sampling events were prepared using a liquid-liquid extraction. All transfer blank samples contained measurable concentrations of PCBs and PBDEs (Table 7 and

Appendix B, Table B-6). Results of the transfer blanks were censored using the XAD laboratory method blanks.

Table 7. Estimated PCB and PBDE concentrations in large volume transfer blanks.

Lab ID		1606035-22	1608046-16	1612024-21	1702027-23
Prep method		XAD	XAD	L-L	L-L
River		Spokane	Yakima	Snohomish	Spokane
Sample date		6/8/2016	8/3/16	12/15/2017	2/14/17
t-PCBs	% detections	9	9	14	7
	pg/L	9.1 J	38.3 J	21.4 J	1.9 J
t-PBDEs	% detections	12	0	43	2
	pg/L	5.7 J	7.5 UJ	42.8* J	0.1 J

*75% of the total-PBDEs contributed by BDE-206 through BDE-209.
XAD = styrene and divinylbenzene polymer; L-L = liquid-liquid extraction with separatory funnel

The intent of the transfer blank was to capture possible contamination from the environment and equipment during sampling and shipping. However, as detailed previously, there was measurable background contamination in the XAD and laboratory DI (Table 4). In the two samples prepared using liquid-liquid extraction techniques, there were similar concentrations of PCBs to the XAD-prepared samples (Table 7). Sample 1612024-21, taken during sampling in the Snohomish Basin, had the highest concentrations of PBDEs, where 75% of the total was contributed by BDE congeners 206 to 209. Overall, laboratory materials, sampling equipment, and sampling environment likely contaminate the results of transfer blanks. These blank samples do not offer much detail of possible contamination during the sampling process.

Field blanks of the SPE media were collected during the first three sampling events (Table 8 and Appendix B, Table B-7). A single C.L.A.M disk was exposed to the atmosphere at the sample site. In general, the field blanks are similar to the blank disks analyzed in the laboratory, suggesting that the transport and exposure to the atmosphere in the field does not contribute a significant amount of PCBs.

Table 8. Estimated PCB concentrations in SPE (CLAM) field blank disks.

Lab ID		1606035-17	1608046-15	1612024-20
River		Spokane	Yakima	Snohomish
Sample date		6/9/2016	8/4/16	12/15/2017
t-PCBs	% detections	16	15	8
	pg	135.2	47.1	18.6

Conventional Parameters

During two of the four sampling events, pH, temperature, specific conductance, and dissolved oxygen were monitored periodically (Appendix B, Table B-8). All sampling quality assurance measures set by the QAPP were met for the Hydrolab sonde (Hobbs and McCall, 2016). The Snohomish River site did not show evidence of a salinity intrusion up-river from the estuary. Retrieval of measurements for all events was not possible due to a sonde malfunction.

Grab samples to characterize the dissolved organic carbon (DOC), total organic carbon (TOC), suspended sediment concentrations (SSC), and total non-volatile suspended solids (TNVSS) of the surface waters were collected at the start and end of the sampling periods on each river (Table 9). Suspended sediment concentrations were very low in the Spokane River during both sampling events, and approximately half the suspended material was organic. Both the Yakima and Snohomish Rivers had higher SSCs than the Spokane. However, the measured SSCs were below the median percentiles of the last five to ten years for the same months as sampling (Yakima – 7 mg/L; Snohomish – 10 mg/L). The suspended sediments in both the Yakima and Snohomish Rivers had a lower proportion of organic content than the Spokane River. In all rivers, the vast majority of organic carbon was present in dissolved form.

Table 9. Summary of conventional water quality parameters at the beginning and end of sampling.

River	Date	Sample ID	SSC (mg/L)	TNVSS (mg/L)	%OM	TOC (mg/L)	DOC (mg/L)
Spokane	6/8/2016	1606035-11	1	0.6	0.40	1.4	1.3
	6/9/2016	1606035-12	1	0.6	0.40	1.3	1.2
Yakima	8/3/2016	1608046-2	6	5	0.17	1.1	1.1
	8/5/2016	1608046-24	6	5	0.17	1.2	1
Snohomish	12/15/2016	1612024-03	6	5	0.17	5.85	5.68
	12/15/2016	1612024-05	7	6	0.14	5.84	5.75
Spokane	2/8/2017	1702027-2	2	1	0.50	1.5	-
	2/9/2017	1702027-3	2	1	0.50	1.48	-

%OM = % organic matter

Centrifugation Efficiency and Sediment Composition

During each sampling event, the solids removal efficiency of the centrifugation was assessed four times (Table 10). All effluent samples from the centrifuges had SSCs below detection limits. The efficiency of the centrifuges ranged from 85 – 98%. The Spokane River yielded lower centrifuge efficiencies because of the proportionally lower SSCs of the river. Efficiencies were acceptable and were similar to the earlier work of Gries and Sloan (2009).

Table 10. Centrifuge efficiency, total volume, and period of sampling.

Location	Period of Sampling	Total Volume of Water (L)	Date	Time	SSC inflow (mg/L)	SSC outflow (mg/L)		Efficiency
Spokane UGM	6/8/2016 9:35 to 6/10/2016 7:35	8323.72* 8316.59**	6/8/2016	12:19	1	0.3	U	0.85
			6/8/2016	20:20	1	0.3	U	0.85
			6/9/2016	9:30	0.9	0.3	U	0.83
			6/9/2016	18:30	1	0.3	U	0.85
Yakima Canyon	8/3/2016 9:45 to 8/5/2016 8:00	7633.02*‡ 8807.07**	8/3/2016	11:45	6	0.3	U	0.98
			8/3/2016	17:50	7	0.3	U	0.98
			8/4/2016	11:45	5	0.2	U	0.98
			8/5/2016	7:40	6.5	0.2	U	0.98
Snohomish	12/15/2016 12:10 to 12/15/2016 21:55	1772.05* 1774.53**	12/15/2016	12:50	6	0.2	U	0.98
			12/15/2016	15:35	4	0.2	U	0.98
			12/15/2016	19:05	5	0.2	U	0.98
			12/15/2016	20:45	6.5	0.2	U	0.98
Spokane UGM	2/8/2017 8:45 to 2/9/2017 19:00	6585.66* 6579.22**	2/8/2017	10:30	2	0.2	U	0.95
			2/8/2017	17:35	1	0.2	U	0.90
			2/9/2017	7:25	2	0.3	UJ	0.93
			2/9/2017	17:45	1.5	0.2	U	0.93

SSC = suspended sediment concentrations
* = centrifuge 712
** = centrifuge 713
‡ = centrifuge total volume likely underestimated due to flow meter malfunction

The organic carbon and nitrogen content of the sediment was measured during each sampling event (Table 11). As suggested previously, the suspended sediments collected from the Spokane River had a greater proportion of organic carbon. The ratio of C:N for the organic content can also give some indication of source; a higher ratio suggests that the organic matter is likely of terrestrial origin because terrestrial C is more refractory (Kaushal and Binford, 1999). The Spokane River suspended sediments had a C:N (molar) of ~7 to 8, suggesting largely an algal source for the OC, whereas the Yakima and Snohomish Rivers had a C:N of ~12, suggesting a greater proportion of terrestrial OC.

Table 11. Organic carbon and nitrogen content of the centrifuge sediment.

River	Centrifuge	Date	Sample ID	%OC	%N	C:N molar
Spokane	712	6/10/2016	1606035-20	10.8	1.74	7.2
	713	6/10/2016	1606035-21	14	2.36	6.9
Yakima Canyon	712	8/5/2016	1608046-22	5.05	0.46	12.8
	713	8/5/2016	1608046-23	4.05	0.37	12.8
Snohomish	712	12/15/2016	1612024-27	4.29	0.43	11.6
	713	12/15/2016	1612024-28	3.75	0.36	12.2
Spokane	712	2/9/2017	1702027-26	8.95	1.37	7.6
	713	2/9/2017	1702027-27	7.2	1.07	7.8

Polychlorinated Biphenyls

The recoveries by congener for polychlorinated biphenyls (PCBs) are summarized in Appendix C (Figures C-1 and C-2) for each method. The acceptable range for recovery of labeled compounds is 10 – 145% (USEPA, 2010a). In general, the lighter congeners (mono- and di-chlorobiphenyls) have lower median recoveries for all the methods (see Table C-1). The large volume 20L samples have lower recoveries across the congeners when compared to the SPE (CLAM) disks and the sediments.

The number of congeners detected for each sampling event varied across the sample media (Table 12). The large volume samples processed through the XAD media had the lowest number of detections for a given river, when compared to the other approaches. When the extraction method changed to a liquid-liquid extraction, there was a noticeable increase in the number of detections relative to the other approaches. The centrifuge sediment consistently had the highest number of detections among the sampling approaches.

Table 12. The mean percent detection of PCB congeners for each sampling approach.

River	SPE (n=3)	Sediment (n=2)	XAD (n=5)	Liquid-Liquid (n=5)
Spokane (2016)	67%	87%	7%	NA
Yakima (2016)	33%	56%	12%	NA
Snohomish (2016)	26%	54%	NA	40%
Spokane (2017)	52%	86%	NA	22%

PCB results are presented as the total or absolute mass of PCBs in the sample (pg) and the calculated concentration of PCBs in the sample based on the volume of media (pg/L or pg/g). The absolute total mass of PCBs is used when presenting the lab results relative to the laboratory blanks. This includes results for each environmental media – water (grab and centrifuge effluent), sediment (centrifuge), and SPE (CLAM). The sample PCB concentrations are then presented for each sampling approach – 20L grab samples, centrifuge (water + sediment), and *in*

situ SPE media. The complete PCB congener results for the sample blanks are detailed in Appendix B (Tables B-2 to B-7) and environmental samples are detailed in Appendix C (Tables C-2 to C-5).

The mass of PCBs found in each of the samples and in the associated blank samples are shown in Figure 7. For each sampling approach during each event, the total PCB mass in the environmental sample was above the total mass found in the method or equipment blank. Whole water samples are compared to the blank for the XAD-2 resin. The greatest difference between the samples and the blanks was found in the centrifuge sediment samples.

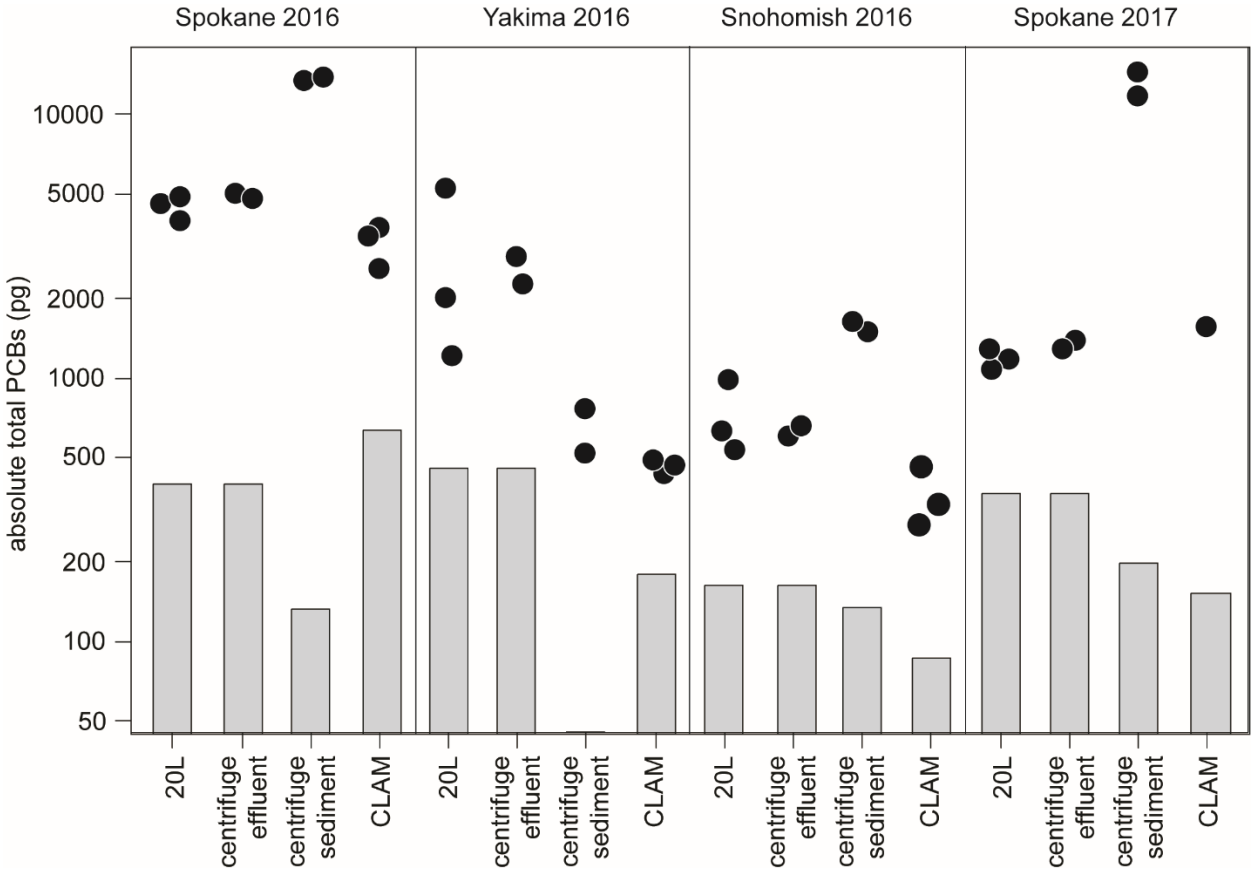

Figure 7. Absolute PCB mass in the blank (grey bars) and environmental (black dots) samples.

Note: extractions differ for the 20L samples:

- XAD – Spokane 2016 and Yakima 2016
- Liquid-liquid – Snohomish 2016 and Spokane 2017

All PCB concentrations (pg/L) for each sampling event are summarized in Table 13. All results are censored to five times the method blank. Samples with at least three replicates are summarized and a 95% confidence limit is estimated for the mean concentration. Therefore, the lower confidence limit is a conservative estimate of the concentration of PCBs at the time of sampling.

The sample-to-blank ratio (S/B) describes the absolute PCB mass of the sample (not censored) to the absolute PCB mass in the method or equipment blank (not censored) (Table 13). The S/B ratio describes the measured level of blank contamination relative to the sample. The S/B values for the Spokane River are above the five times threshold used for the lab blank censoring. None of the results for the Yakima and Snohomish River have an S/B above five.

Table 13. Statistical summary of censored total PCB results (pg/L) including uncensored absolute total PCB sample: blank (pg:pg).

	n	Mean	Median	Relative percent difference	Standard deviation	Relative standard deviation	95% CI	Lower confidence limit	Upper confidence limit	S/B*
Spokane River (2016)										
20L	3	191.04	192.24	NA	17.73	0.09	20.06	170.98	211.09	8.8
Centrifuge	2	226.84	226.84	0.05	NA	NA	NA	NA	NA	9.7/79.8
in situ SPE	3	80.31	84.70	NA	7.99	0.10	9.04	71.27	89.35	13.4
Yakima River (2016)										
20L	3	80.57	30.86	NA	102.47	1.27	115.96	<MDL	196.53	4.9
Centrifuge	2	63.41	63.41	0.60	NA	NA	NA	NA	NA	4.4/11.2
in situ SPE	3	7.82	7.26	NA	2.02	0.26	2.29	5.53	10.11	2.0
Snohomish River (2016)										
20L	3	24.22	22.09	NA	12.09	0.50	13.68	10.53	37.90	3.4
Centrifuge	2	19.13	19.13	0.01	NA	NA	NA	NA	NA	3.0/9.1
in situ SPE	3	5.18	4.58	NA	1.14	0.22	1.29	3.89	6.47	3.2
Spokane River (2017)										
20L	3	22.16	21.87	NA	2.07	0.09	2.34	19.81	24.50	2.5
Centrifuge	2	46.72	46.72	0.08	NA	NA	NA	NA	NA	2.9/51.7
in situ SPE	1	28.02	28.02	NA	NA	NA	NA	NA	NA	8.1

<MDL: less than the method detection limit.
* the S/B for the centrifuge sample is reported as the effluent sample and the sediment fraction.

In general, there is a great deal of variability in the PCB concentrations among the sampling approaches (Table 13; Figure 8). In the first two events, the 20L samples censored relative to the XAD yielded higher PCB results for the whole water (20L) and centrifuge sampling approaches. In the Spokane (2016) samples, the variability was low within each approach, but the estimated mean concentrations ranged from 80.3 ± 8.0 to 226.8 pg/L. In the Yakima River, the PCB concentrations were quite variable within the 20L (127% RSD) and centrifuge (60% RPD) approaches, while the *in situ* SPE results had a low relative standard deviation (26% RSD) and a mean concentration of 7.8 ± 2.3 pg/L.

The Snohomish River was the first sampling event where the large volume samples were processed using a liquid-liquid extraction. The variability within each sampling approach was fairly high for the whole water samples (50% RSD), but good for the centrifuge (1% RPD) and *in situ* SPE (22% RSD). Reported concentrations were 24.2 ± 13.7 pg/L (20L whole water), 19.1 pg/L (centrifuge), and 5.2 ± 1.3 pg/L (*in situ* SPE). During 2017 in the Spokane River, the sampling results for all approaches were fairly consistent and had low variability within each approach (Table 10). The reported results for the Spokane (2017) event were 22.2 ± 2.3 pg/L (20L whole water), 46.7 pg/L (centrifuge) and 28.0 pg/L (*in situ* SPE). Lab error and field malfunction caused the loss of two of the three CLAM sampler (*in situ* SPE) results.

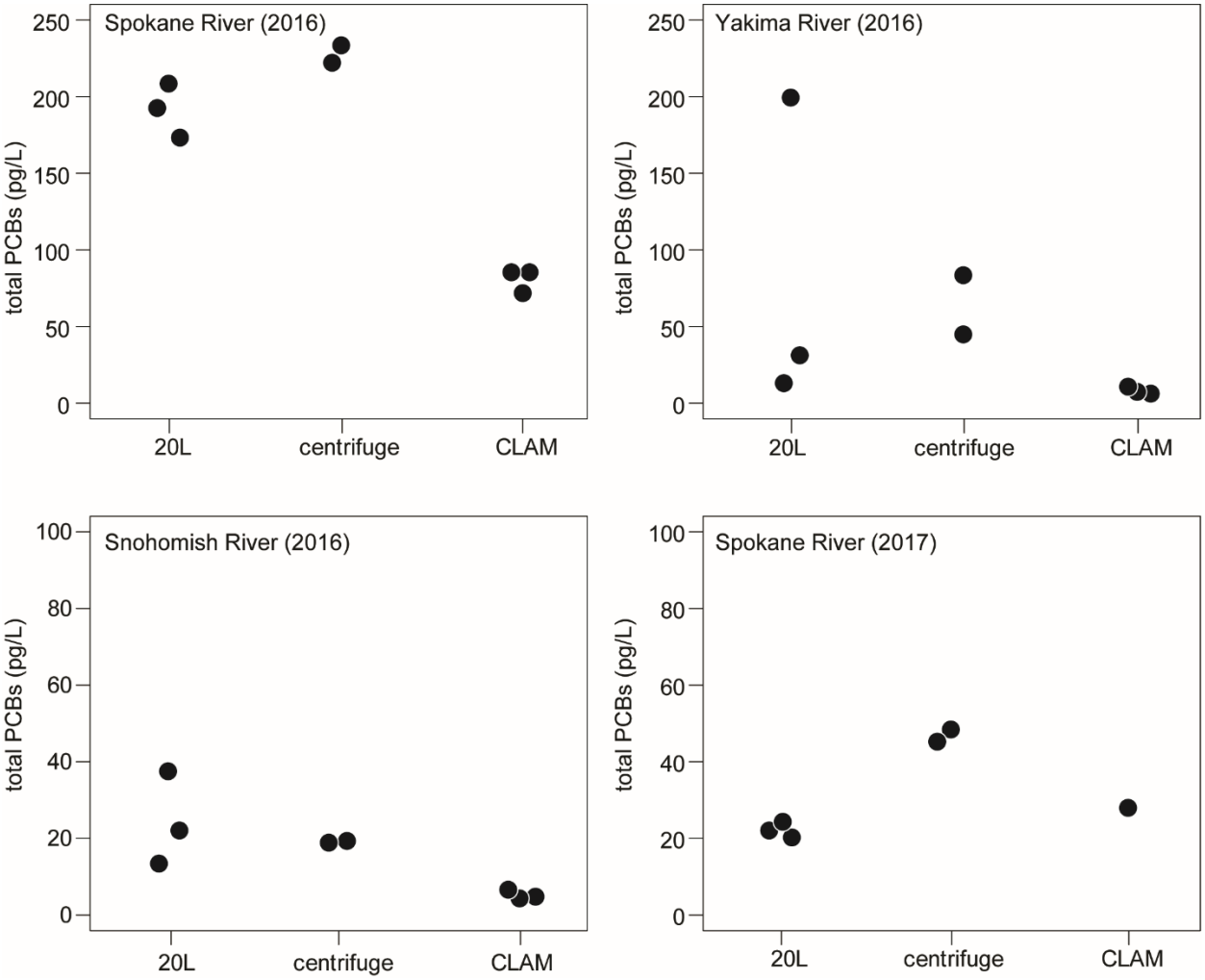

Figure 8. Blank-censored total PCB results for each sampling event.

**y-axis varies among the graphs.*

Before deployment of the CLAM samplers, the SPE media was prepared and spiked with isotopically-labelled congeners. The recovery of these labelled congeners following deployment in the field gives us some idea of the retention of PCBs by the SPE media (Table 14). The thresholds for recovery of labeled congeners as spikes within EPA method 1668C are 10 – 145%. All samples met these thresholds. With the exception of the recoveries in one sample

from the Yakima River (1608046-12) and one sample from the Spokane River (1702027-16) for ^{13}C-PCB 095, all remaining samples had recoveries between 70 – 130%. This suggests that the SPE media used in the CLAM disks has good retention of native PCB congeners.

Table 14. Summary of the recovery of PCB field spikes used in the SPE (CLAM) disks.

Sample	MEL ID	ALS ID	Sample Date	% recovery		
				^{13}C-PCB 031	^{13}C-PCB 095	^{13}C-PCB 153
CLAM 236	1606035-14	L1783722-1	6/9/2016	105	105	110
CLAM 248	1606035-15	L1783722-2	6/9/2016	78	78	82
CLAM 276	1606035-16	L1783722-3	6/9/2016	99	115	106
CLAM 236	1608046-12	L1810917-1	8/4/2016	63	44	61
CLAM 248	1608046-13	L1810917-2	8/4/2016	107	86	92
CLAM 240	1608046-14	L1810917-3	8/4/2016	100	75	80
CLAM 236	1702027-14	L1890616-1	2/10/2017	77	NQ	79
CLAM 248	1702027-16	L1890616-2	2/10/2017	78	55	73
CLAM 240	1702027-18	L1890616-3	2/10/2017	81	79	86

NQ= not quantifiable

Polybrominated Diphenyl Ethers

The recovery of labeled polybrominated diphenyl ether (PBDE) compounds is summarized for each of the sampling approaches in Appendix D (Figure D-1 and Table D-1). The acceptable recovery range for labeled compounds in EPA method 1614A is 25 – 150% (USEPA, 2010b). For many of the large volume (20L) samples, the lower limit of the recoveries is below the method thresholds. Similar to the PCB results, when we look more closely at the extraction technique data on the 20L sample, it is clear that the liquid-liquid extraction has much better recoveries, all of which meet the method limits (Appendix D, Figure D-2).

Also similar to the PCB results, the number of congeners detected for each sampling event varied across the sample media (Table 15). The centrifuge sediment consistently had the highest number of detections among the sampling approaches. The large volume samples extracted through the XAD media had the lowest number of detections for a given river, when compared to the other approaches. When the extraction method changed to a liquid-liquid extraction, there was a noticeable increase in the number of detections relative to the other approaches.

Table 15. The mean percent detection of PBDE congeners for each sampling approach.

River	Sediment (n=2)	XAD (n=5)	Liquid-Liquid (n=5)
Spokane (2016)	86%	11%	NA
Yakima (2016)	61%	8%	NA
Snohomish (2016)	74%	NA	36%
Spokane (2017)	92%	NA	78%

The PBDE results are presented as the total or absolute mass of PBDEs in the sample (pg) and the calculated concentration of PBDEs in the sample based on the volume of media (pg/L or pg/g). The absolute mass of PBDEs is used when presenting the lab results relative to the laboratory blanks, while the PBDE concentrations are used when presenting the results for the 20L grab and centrifuge sampling approach. The complete PBDE congener results for the sample blanks are detailed in Appendix B (Tables B-2, B-3, B-5, and B-6) and the environmental samples are detailed in Appendix D (Tables D-2, D-3, D-4, and D-5). PBDEs were not measured in the SPE-CLAM disks.

The mass of PBDEs found in each of the samples and in the associated blank samples are shown in Figure 9. In three of the four sampling events, the total PBDE mass in the samples were greater than the blanks. In the second Spokane (2017) sampling event, the total PBDE mass in the large volume composite sample (20L) and the centrifuge effluent was less than the blank sample. This elevated blank sample during the analysis of the large volume water samples from the Spokane River (2017) interfered with our ability to report detectable concentrations of PBDEs. During each sampling event, the total PBDEs in the centrifuge sediments were well above those in the blanks.

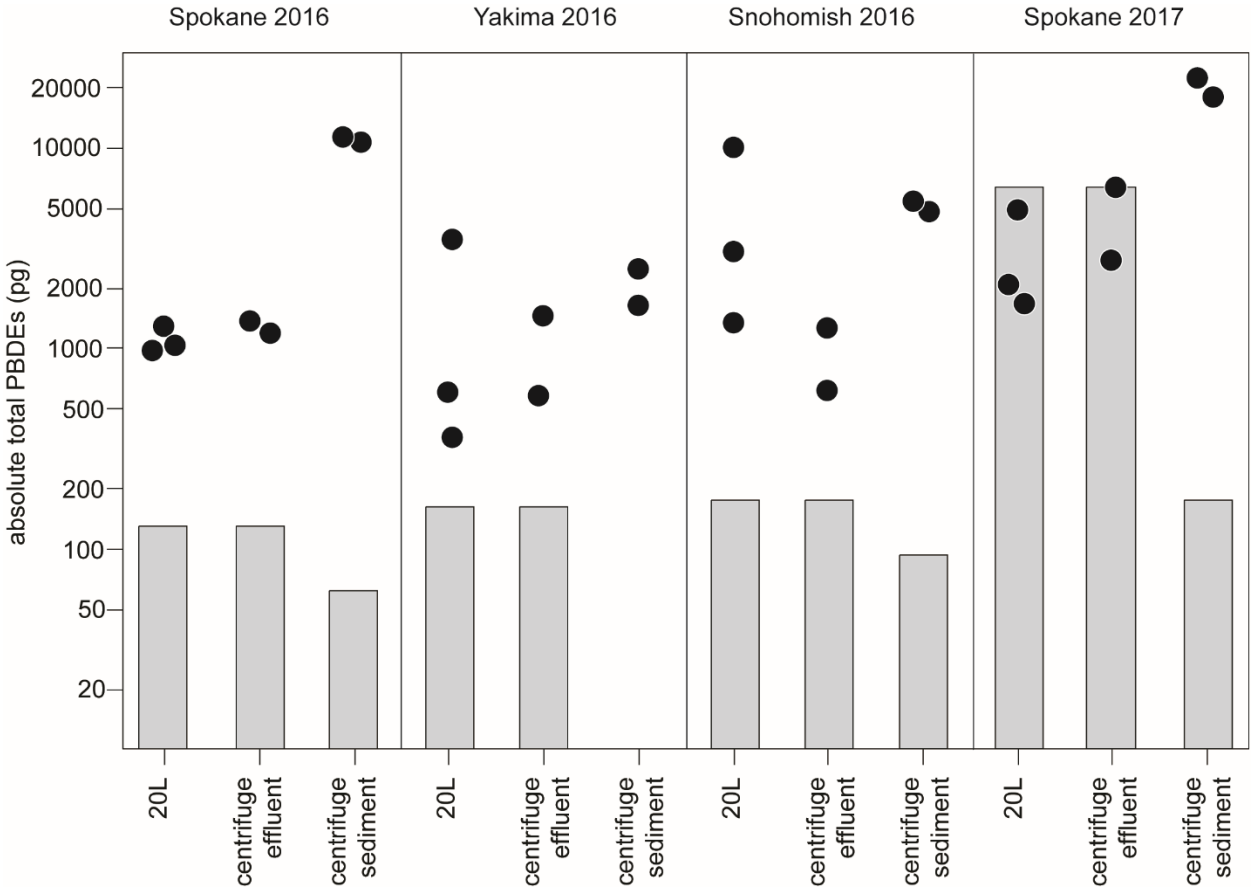

Figure 9. Absolute PBDE mass in the blank (grey bars) and environmental (black dots) samples.

The S/B for each of the sampling approaches and events were calculated and are described in Table 16, with a statistical summary of the censored total PBDE concentrations. For the Spokane (2016) and Yakima samples, the S/B was greater than five when using the XAD only. Similar to the PCB results, comparing the PBDE results to the XAD-DI blank added further background noise and lowered the S/B to around 1.0 (Table 16). The S/B in Snohomish River samples were well above five for the 20L samples and for the centrifuge sediment samples; the centrifuge effluent was less than five. In the second sampling event of the Spokane River (2017), the S/B was much less than five except for the centrifuge sediment.

Table 16. Statistical summary of total PBDE results (pg/L) including absolute total PBDE sample:blank (pg:pg).

	n	Mean	Median	Relative percent difference	Standard deviation	Relative standard deviation	95% CI	Lower confidence limit	Upper confidence limit	S/B*
Spokane River (2016)										
20L	3	38.66	33.02	NA	13.28	0.34	15.03	23.62	53.69	6.4
Centrifuge	2	53.60	53.60	0.11	NA	NA	NA	NA	NA	7.4/132.1
Yakima River (2016)										
20L	3	57.67	6.06	NA	94.37	1.64	106.79	<MDL	164.45	6.9
Centrifuge	2	37.57	37.57	1.01	NA	NA	NA	NA	NA	4.7/149.5
Snohomish River (2016)										
20L	3	225.50	145.94	NA	236.99	1.05	268.18	<MDL	493.68	20.2
Centrifuge	2	44.39	44.39	0.75	NA	NA	NA	NA	NA	4.0/40.5
Spokane River (2017)										
20L	3	62.27	1.02	NA	106.83	1.72	120.88	<MDL	183.15	0.3
Centrifuge	2	95.37	95.37	1.11	NA	NA	NA	NA	NA	0.5/85.5

<MDL: less than the method detection limit.
* the S/B for the centrifuge sample is reported as the effluent sample and the sediment fraction.

The total PBDE concentrations for the Spokane River (2016) sample had moderate variability for the 20L sample (RSD 34%) and low variability for the centrifuge sample (RPD 11%). The estimated concentrations for these sampling approaches slightly overlapped: 38.7 ± 15.0 pg/L (20L) and 53.6 pg/L (centrifuge) (Figure 10). The lower confidence limit for the 20L sample was 23.6 pg/L. The samples from the Yakima River were highly variable: 57.7 ± 106.8 pg/L (20L) and 37.6 pg/L (centrifuge).

The 20L grab samples from the Snohomish River were highly variable (105% RSD) and had a concentration of 225.5 ± 268.2 pg/L. The centrifuge sample from the Snohomish had a large RPD (75%) between samples with a mean concentration of 44.4 pg/L. The second sampling event in the Spokane River (2017) showed large variability in the 20L sample (107% RSD) with a mean of 62.3 ± 120.9 pg/L. Similarly, the centrifuge sample showed a large RPD between samples (111%) with a mean of 95.4%.

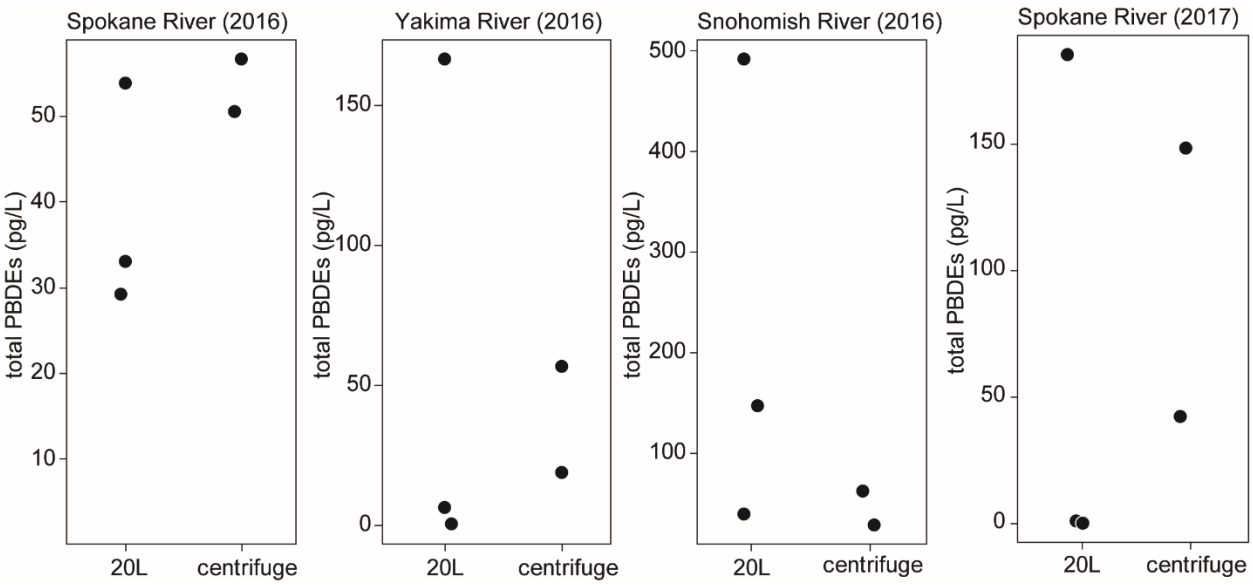

Figure 10. Blank-censored total PBDE results for each sampling event.

**y-axis varies among the graphs.*

Discussion

Sensitivity of the Sample Methods

The sensitivity of a laboratory method describes the ability of the method to detect a substance above the analytical background or noise of the system. In the evaluation of the sampling approaches, we calculated the sample-to-blank ratio (S/B) for each method over multiple sampling events (Figure 11). The calculated S/B values represent an estimate of the noise for the particular method and provide information on suitable levels of blank censoring. For example, the S/B of PCBs in the SPE (CLAM) samples from the Spokane River was 13.4 and 8.1, meaning that any level of blank censoring below ~8 times should not impact our ability to reliably measure PCBs in the environmental sample.

We found that the PCB congeners 11 and the co-elution of 44/47/65 were common laboratory contaminants and generally had higher masses in the batch method blanks. The PBDE congeners 47, 99, and 209 were also common laboratory contaminants. We did not treat background contamination of these congeners differently; however, this supports the idea that the more stringent National Functional Guideline threshold (ten times) should be applied to these congeners, while a less stringent threshold is applied to the other congeners when censoring results.

Typically, environmental samples are censored relative to the blank at an S/B of five and sometimes ten (USEPA, 2016). The only sampling method that was consistently over an S/B of ten was the centrifuge sediments. The *in situ* SPE disks (CLAM) had a wide range of S/B for PCBs and were generally above the threshold of five in the Spokane River where PCB contamination is a known issue (Serdar et al., 2011; Era-Miller and McCall, 2017).

The sampling method of collecting large volumes of water (20L) and extracting the sample using XAD proved moderately sensitive, often achieving an S/B above five for both PCBs and PBDEs. Using the laboratory XAD blank with lab-grade DI purged through to mimic a sample, reduced the S/B by an average of five, significantly lowering the sensitivity due to lab contamination. This finding brings into question whether laboratory DI is sufficiently void of contamination when used in other blanks (e.g., transfer and transport blanks) and compared to the environmental samples. Extracting the large volume sample in aliquots using a liquid-liquid extraction did not improve the sensitivity of the sampling method, especially for PBDEs (Figure 11).

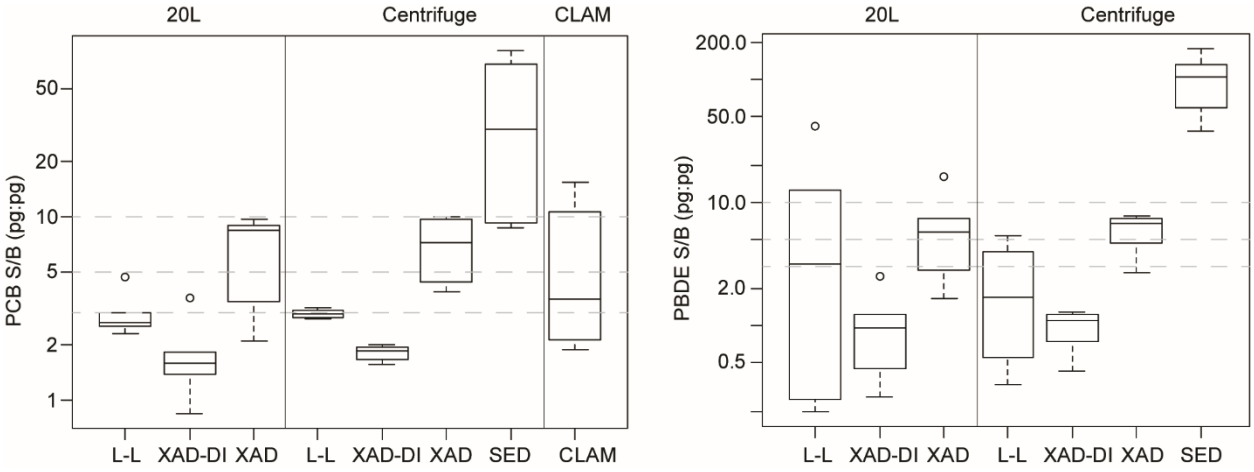

Figure 11. The range in sample:blank (S/B) of PCB (left) and PBDE (right) concentrations for all sampling approaches.

L-L: liquid-liquid extraction
XAD-DI: blank sample is lab-grade DI purged through blank XAD
XAD: blank XAD media only
SED: centrifuge sediments
CLAM: continuous low-level aquatic monitoring
*Typical thresholds of blank censoring (3, 5, and 10 times) are highlighted with dashed lines.

Differences in how the sample results are blank censored is likely to impact the total PCB and PBDE reported results. This may be particularly important if there is a regulatory context for the sampling, and if the samples are collected over time frames that appropriately reflect the durations of exposure of the threshold values. For example, depending on the blank censoring (Figure 12), the concentrations of PCBs measured in the Snohomish River using the SPE (CLAM) disks show results that are above and below the threshold of the new EPA promulgated criterion (7 pg/L) for Washington State (40 CFR 131.45). However, it must be assumed that the measured concentration reflects an average 70-year human health exposure concentration, which is unlikely to be the case. The differences in t-PCB concentrations between three and five times blank censoring are attributable to one congener, PCB-11. In general, the level of detection among the congeners does not vary greatly and there is little difference between results calculated from five and ten times blank censoring.

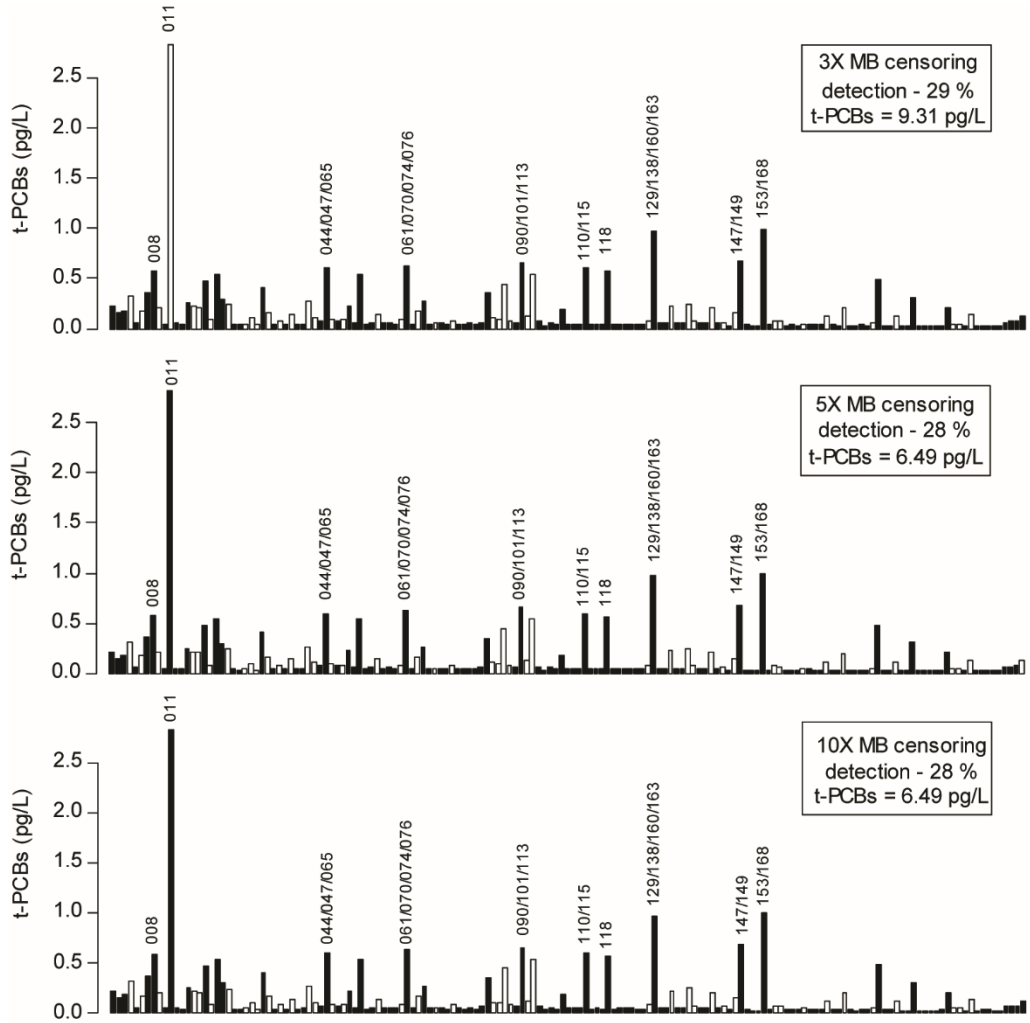

Figure 12. PCB congener profiles from an *in situ* SPE disk in the Snohomish River under different blank censoring thresholds.

PCB concentrations calculated from the PCB mass in the SPE disk and volume pumped; non-detects are shown as black bars; only the dominant congeners are labelled.

While the blank concentrations were used to censor the congener-specific results, the total PCB burden of the equipment blank was not explicitly accounted for during the calculation of the total PCB concentrations. This means that at least some proportion of the reported concentrations of PCBs and PBDEs came directly from the equipment. This may be the reason that the samples that were extracted using XAD (the first two sampling events) have total PCB concentrations that are higher than the *in situ* SPE.

To directly account for possible background contamination, blank subtraction (blank correction) is necessary (USEPA, 2010a). EPA method 1668C suggests that 10 blanks are necessary for blank corrections or subtractions to take place (USEPA, 2010a), where the mean and two standard deviations are subtracted from the measured sample concentrations (Ferrario et al., 1997; Muir and Sverko, 2006). In addition to the recommendations under EPA 1668C, congener-specific methods can be used. Dodder et al. (2002) suggest that if the PCB congener

concentrations in the blank are 10 – 30% of the environmental sample, the blank level could be subtracted from the sample. However, if the blank level is greater than 30 percent, the congener is considered non-detect.

This study generated PCB results for numerous blank SPE disks from the same lot (3060115), giving us an opportunity to test how the standard deviation of total PCBs changes with an increase in the number of blanks (Figure 13). It appears that once a sample size of six is achieved, the standard deviation is fairly stable and would likely suffice for blank subtraction. The advantage of constraining the equipment blank contamination for the SPE disks is that it is applicable to the entire lot of SPE material and does not need to be repeated for each sampling event; although, field blanks confirming a consistently low background contamination should be included in each sampling event.

The other sampling approaches would require multiple blank samples for blank subtraction each time the media (e.g., XAD) is prepared. In the case of grab samples, multiple laboratory method blank samples would constrain blank contamination for a specific batch. A simultaneous blank that accompanies each environmental sample would account for possible contamination during travel; however, given the contributions from laboratory DI, using these samples to blank censor or subtract from environmental samples might be misleading.

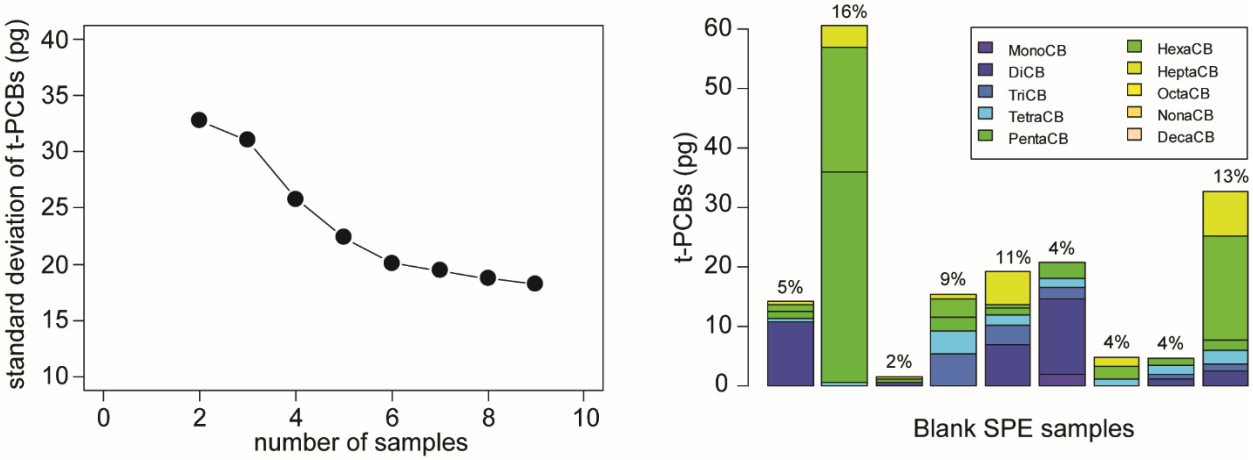

Figure 13. Standard deviation among SPE blanks (left) and PCB homologue distributions in the blanks (right).

PCB homologue distributions are measured in mass per SPE disk (pg); the percent detection level in each sample is above the stacked sample bar.

The distribution of PCB congeners present in the SPE blanks does vary and is not necessarily confined to the lighter congeners (mono- through tri-CBs) (Figure 13). This underlying variability in the blank contamination prevents us from systematically subtracting certain congeners from the environmental samples and instead focusing on the total PCB mass in the SPE disk.

Overall, the centrifuge sediment sampling method had the greatest sensitivity (i.e., highest sample:blank). The *in situ* SPE (CLAM) disk and the large volume 20L composite extracted through XAD had similar sensitivities, which were adequate for routine censoring of the data using five times the method blanks. Lastly, the large volume 20L composite extracted in aliquots

(2L) using liquid-liquid extraction had the lowest sensitivity of the methods. This low sensitivity is likely due to the combined exposure and handling of the sample in the lab.

Bias of the Sample Methods

Bias of the analytical method is typically measured through the recovery of sample spikes in the laboratory. The effect of any laboratory bias is reduced for the EPA methods used in this study because they both rely on the recovery of isotopically-labelled compounds spiked into the extracts to calculate the congener-specific result – an internal standardization method known as isotopic dilution. With the exception of a few congener recoveries, the QC range for labeled compounds was met for each method; however, there were some differences among the sample methods we tested (Appendix C and D).

If we look at the type of extraction method used for the 20L composite samples, XAD versus liquid-liquid extraction, there are differences in recoveries for both PCB and PBDE results (Appendix C, Figure C-2; Appendix D, Figure D-2). It appears that the XAD extractions have higher recoveries for the lighter congeners, but much lower recoveries for the heavier congeners. A similar finding was observed by Usenko et al. (2005) when they tested different extraction techniques for large volumes of water. The solvent used for the extraction of the XAD (toluene) is different from the solvent used for the liquid-liquid and SPE extraction (DCM). This difference in solvent may be the reason for the differences in recoveries.

As a way of further assessing bias of the sample media, we also considered the recovery of field spiked isotopically-labelled PCB congeners in the *in situ* SPE (CLAM) disks. These compounds were injected onto the SPE media during lab preparation and then measured following deployment in the field to look at retention. The recovery of the field spikes were detailed earlier in Table 14. Overall, the recovery was excellent for each labeled congener (mean ± sd):

- $^{13}C_{12}$-PCB031 – 88 ± 15%
- $^{13}C_{12}$-PCB095 – 80 ± 20%
- $^{13}C_{12}$-PCB153 – 85 ± 15%

A recent study by Era-Miller and McCall (2017) used a similar field spiking approach, but also included an additional disk to capture any loss of the field spikes. They found a similar recovery of field spikes (84 – 92%) in the first disks and found only a 0 – 1% recovery of labelled congeners in the second (additional) disk; therefore, there is very little bias using the SPE disk *in situ* and retaining the sampled PCB congeners.

We can also look at the congener profiles among the sampling approaches for samples collected at the same time as a way to assess bias inherent in the approach. In other words, we look for a sampling approach bias toward a certain range of congeners. In Figure 14, the PCB congener profiles suggest that the large volume 20L composite sample, when extracted through XAD, is biased toward the lighter congener range, but the SPE and sediment-centrifuge effluent samples seem to encompass a more complete range of congeners.

This observation of potential sampling bias is also described by the number of detections among the congeners for the different approaches. The centrifuge sediment routinely had the highest number of congeners, which is likely a function of the matrix and the volume of water processed to attain the sample (1700 to 8800 L). Generally, the SPE media had approximately 50 – 75% of the congeners found in the sediment. The large volume grab sample processed through XAD media had <25% of the congeners, while the liquid-liquid processing of the large volume sample improved the number of detections to 25 – 50% of those found in the sediment.

The congener distribution between the SPE and sediment-centrifuge effluent samples are strongly comparable, suggesting the two sampling approaches are representing a true environmental signature at the time of sampling. We would expect the sediments to bind the more chlorinated or brominated compounds because the partition coefficients of these compounds describe an affinity for soils and sediments (MacKay et al., 1997). The less brominated and chlorinated compounds with lower partition coefficients will be more prone to remaining in the water and desorbing from sediments (Figure 14).

Overall, the analysis of samples taken using all methods had low bias due to analytical methods that rely on isotope-dilution. The *in situ* SPE sample media showed no potential bias in the retention and recovery of PCB compounds from the media. There is a potential bias during sampling among the different approaches; large volume grab samples of whole water are biased toward the lighter congener range and generally have a much lower level of detection of the congeners.

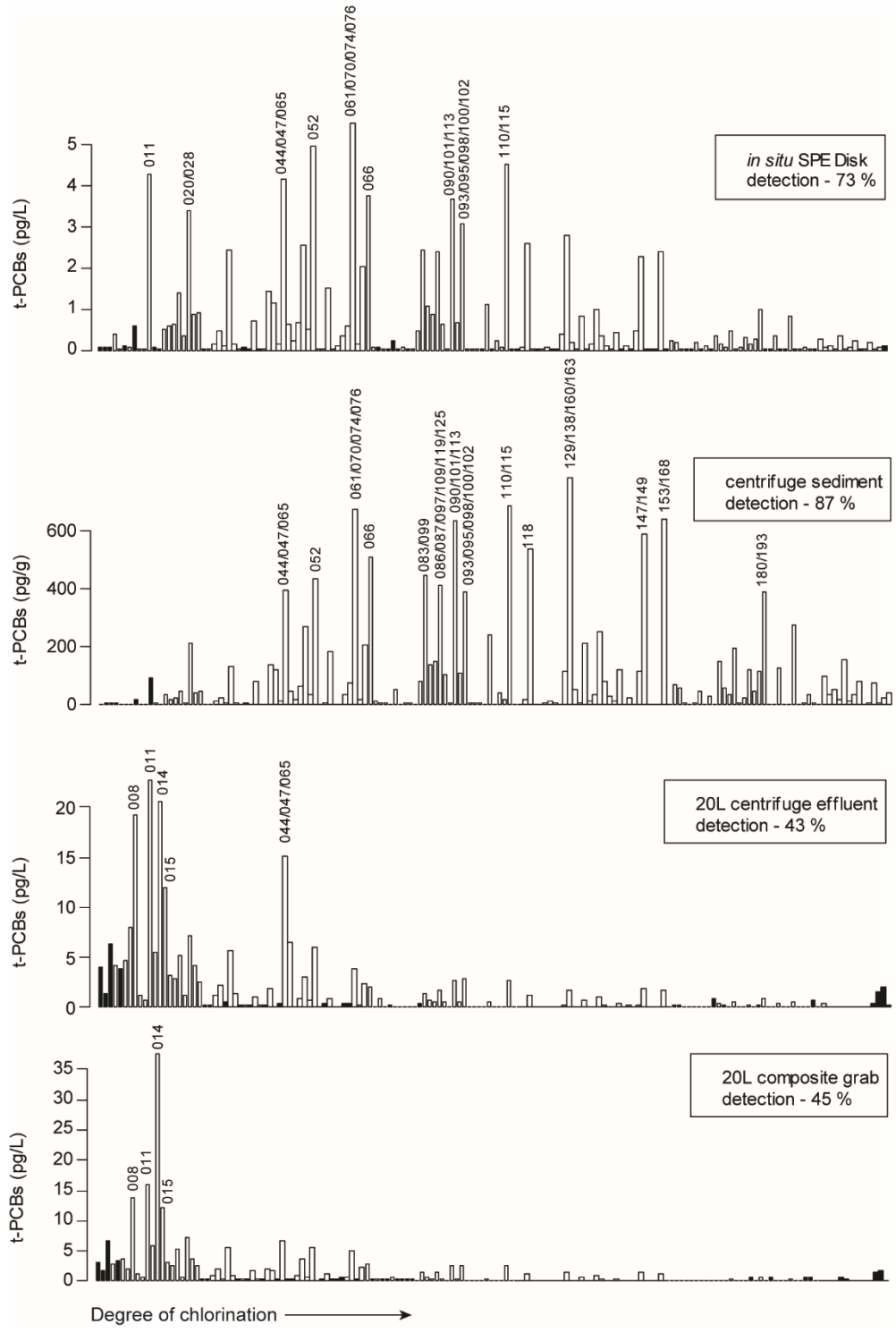

Figure 14. PCB congener profiles among the different sampling approaches from the Spokane River.

Sampling method and frequency of detection are highlighted in the legend; the degree of chlorination increases from left to right; non-detect results are shown as black bars.

Precision of the Sample Methods

Precision is a measure of the variability in the results of replicate measurements due to random error. PCBs in the Spokane River sampled by taking a large volume composite and extracted using the XAD and liquid-liquid extraction had a low relative standard deviation (RSD) of 9% among triplicate samples for both the 2016 and 2017 sampling events. The combined centrifuge samples (sediment and 20L centrifuge effluent) had a low relative percent difference between duplicate samples (5% in 2016 and 8% in 2017). Lastly, sampling PCBs using the SPE disks had a low RSD of 10% in 2016; there was no sample replication in 2017.

PCB concentrations in the Yakima and Snohomish Rivers were generally lower than the Spokane River, which can inflate the relative measures of variability among samples; however, we were able to get good precision between combined (sediment and effluent) centrifuge samples on the Snohomish River (1% RPD). Concentrations for PCBs in the SPE disks had good precision even at low concentrations: 26% RSD in the Yakima River and 22% in the Snohomish River.

The precision of the PBDE duplicate samples of the centrifuge sediment was good, ranging from 5 – 40% RPD; however, the precision of large volume composite samples of the centrifuge effluent was very poor, ranging from 25 – 180% RPD. Similarly, the precision of triplicate samples of the 20L composite was poor for most of the sampling events.

PBDEs are ubiquitous in the lab and environment, and difficulties measuring replicate samples with tight precision are common. An inter-laboratory comparison showed that precision among sediment samples varied by congener with the lighter brominated compounds having better precision and BDE-209 (the heaviest) having an RSD as high as 78% (de Boer and Cofino, 2002). This observation was not necessarily true for our dataset, where BDE-32 and BDE-79 had routinely poor precision. Interestingly, the precision for BDE-209 was very good, with an RSD ranging from 10 – 40%.

Overall, the precision of the sampling methods was good in the Spokane River where t-PCB concentrations were higher than the other rivers. The *in situ* SPE disks also had reliably good precision in the Snohomish and Yakima Rivers where PCB concentrations are lower. For t-PBDEs, only the centrifuge sediments had reliably good precision; the SPE disks were not analyzed for t-PBDEs.

Additional Sampling Methods

Grab Sample

Smaller volume grab samples are an additional approach to sampling surface waters. This approach has been used on the Spokane River to sample PCBs at the same location sampled in this study (Era-Miller and McCall, 2017). Here, a 2L 2-part grab sample was taken and extracted using liquid-liquid extraction.

The sensitivity of this approach was low with a sample-to-blank ratio of 1.9, which is similar to the large volume composite samples taken in this study. The average recovery of labelled PCB compounds was ~70% with the exception of the lighter congeners (mono- and di-chlorobiphenyls), which were < 50% recovery. This overall recovery is similar to the large volume samples from this study extracted in 2L aliquots using liquid-liquid extraction. The

number of congeners positively detected in the sample was 26%, which is comparable to the large volume sample processed using a liquid-liquid extraction. Lastly, the sampling approach had comparable precision to the composite grab samples in this study from the Spokane River; the RPD between 2L duplicate samples was 10%.

Passive Sampling

An alternative to actively sampling the water column is to passively sample by deploying a sampler that has a long period of exposure and reaches equilibrium with the surrounding environment. Passive samplers are then removed, extracted, and analyzed with the same laboratory methods. Water concentrations must be modeled based on the behavior of the compounds (i.e., partition coefficients from water to lipids/carbon).

In a recent study from the Wenatchee River in eastern Washington, Hobbs and Friese (2016) used semi-permeable membrane devices to estimate the PCB concentrations in the river water. During sampling events in 2015 and 2016, the semipermeable membrane devices had good sensitivity with an S/B ratio of ~25 at locations of suspected PCB sources and ~ 2.5 at upriver background locations. The recovery of the labelled compounds during lab analysis was good for the congeners heavier than di-chlorobiphenyls (generally > 75%). The level of detection for PCB congeners was 87% at locations of suspected PCB sources and 72% at upriver background locations. The precision of the sample blanks over two events was also good, with RSDs of 13% and 3%. The precision between duplicate samples from the field was good with an RPD of 10%.

Overall Method Assessment

The goal of this study was to assess multiple sampling methods that could yield reliable analytical data for low concentrations of PCBs and PBDEs in surface waters. To help evaluate the overall reliability of the sampling approaches, criteria were established to rate the approaches (Table 17). These evaluation criteria are modeled after the work of the EPA for the National Aquatic Resource Surveys (https://www.epa.gov/national-aquatic-resource-surveys).

Table 17. Rating scheme for evaluation of sampling approaches (good, fair, and poor).

Rating	Sensitivity (sample-to-blank ratio)[1]	Bias (number of detections)[2]	Precision (sample RSD or RPD)[3]	Overall rating
good	S:B >5	Method with the maximum # of detections	<20%	A maximum of one indicator is rated fair, and no indicators are rated poor.
fair	3<S:B<5	>50% the maximum # of detections	20-50%	One of the indicators is rated poor, or two or more indicators are rated fair.
poor	S:B<3	<50% the maximum # of detections	>50%	Two or more of the indicators are rated poor

[1] USEPA, 2016
[2] Assessed based on the maximum number of detections among sampling approaches; low bias receives a good rating.
[3] Hobbs and McCall, 2016

Sampling approaches are often dependent on the specific study design and goals. In Table 18, we assess the different sampling approaches and offer comments on when each approach might be more applicable. Pre-concentration approaches (e.g., SPE media) offer an opportunity to sample large volumes in the field. As a result, these approaches can be very sensitive, enabling the detection of low concentrations of toxics; however, they are more time consuming and more costly. Small volume grab samples are a less costly approach, but are not as sensitive, meaning that the presence of toxics in the environment can be insufficient to be above the "noise" of the sampling approach. Small volume grab samples may also have a much lower level of detection for some PCB and PBDE congeners.

A caveat to the use of the *in situ* SPE media is that it is limited by the turbidity of the water, with flow rates declining exponentially over the course of deployment. In turbid water, the disk can clog, and an insufficient volume of water is passed through the media, reducing the sensitivity of the approach. In turbid waters, small volume grab samples or flow-through centrifugation should be considered. It would be possible to sample the centrifuge effluent using the SPE-CLAM approach in a stainless steel well fed by the centrifuge(s); this approach was not tested during this study.

In general, studies focused on source identification or source tracking of toxics in a river should rely on discrete grab samples, SPE disks, or passive samplers.

Table 18. Overall assessment of low-level sampling approaches.

Method	Description	Volume Sampled (L)	Sensitivity	Bias	Precision	Overall Assessment	Sample Time	Sampling Cost	Comments
centrifuge sediment	continuous flow-through centrifuge system with a controlled flow rate of 3L/min	500 – 5,000	good	good	good	good	dependent on TSS of the water; 4 – 48 hours	high	labor-intensive; prolonged sample time can inhibit synoptic survey on a river
20L composite – XAD extraction	10 – 12 part composite sample over 24 – 48 hours into stainless steel canister; extracted in the lab using XAD-2 media	20	fair	poor	fair	fair	composite can be taken at desired frequency	low	stainless steel canisters are cumbersome in the field and lab; high shipping costs
20L composite – LL extraction	10 – 12 part composite sample over 24 – 48 hours into stainless steel canister; extracted in the lab in 2L aliquots using liquid-liquid extraction	20	poor	fair	fair	fair	composite can be taken at desired frequency	low	stainless steel canisters are cumbersome in the field and lab; high shipping costs
in situ SPE	continuous *in situ* pumping of water (5 – 75ml/minute) through an SPE media disk (C-18 media)	20 – 60	fair	good – fair*	good	good	12 – 48 hours	moderate	sampling device does not function well in turbid waters
2L composite grab	a two-part composite sample over 24 hours	~2	fair	fair	good	fair	1 – 24 hours	low	simple sampling protocols
Passive Approaches									
semipermeable membrane devices	polyethylene strips containing triolein oil deployed for 1-month in stainless steel canisters	NA	good	good	good	good	deployed for one month; three sampling trips required	moderate	not a direct measurement of water concentrations; requires a lot of data reduction and analysis

* The number of detections is lower than the maximum reported; however, the congener distribution is very similar; therefore, the rating is closer to ‘good’.

Conclusions

This study assessed three different approaches to sampling toxics at or near detection limits in surface waters. The following conclusions can be made:

- Reliable laboratory batch method blank samples that meet all project quality control criteria are an important component for any project where low-level toxics are measured.
- Laboratory deionized water (DI) can be a source of contamination, and consideration should be given as to whether field blanks using lab DI are sufficiently void of contamination to assess the sampling system (e.g., atmospheric exposure or exposure during travel) when using high-resolution analytical methods for toxics.
- Sampling approaches that rely on pre-concentration methods (e.g., SPE media) might require blank correction to account for background contaminants. Grab samples can generally rely on censoring the results using laboratory method blanks.
- Sediments collected from the flow-through centrifuge and the *in situ* SPE (CLAM) disk used to sample whole water had reliable sensitivity and precision in reported total PCB and PBDE concentrations.
- Large volume (20L) composite samples of the centrifuge effluent collected directly from the Spokane River had adequate precision and sensitivity when sampling for PCBs. The variability among sample replicates and contamination of various blanks reduced the usability of the data for other sample locations.
- Overall, the centrifuge sediment and the SPE media for the CLAM disks capture a broader range of PCB and PBDE congeners. Large volume whole water samples can be biased toward the lighter congeners. Processing the sample through XAD yielded a lower number of detected congeners compared to a liquid-liquid extraction.
- The time and cost of the centrifuge approach limits the utility of the approach during a synoptic survey or source identification study.
- Comparison of total PCB and PBDE results among the sampling approaches generally did not overlap. Limited detection of some congeners and the sampling approach sensitivity (background contamination) are the main reasons for the lack of precision among sampling approaches.
- When determining very low concentrations of PCBs and PBDEs in surface waters for source identification studies, discrete grab samples, *in situ* SPE disks, and passive samplers are likely the most reliable approaches.
- When determining very low concentrations of PCBs and PBDEs in surface waters for comparison with criteria thresholds, discrete water samples and large volume methods yield reliable data when concentrations are well above the analytical reporting limits. Following Quality Assurance (QA) approval, the *in situ* SPE disks may also be a viable approach.

Recommendations

Based on the conclusions of this study, the following recommendations can be made:

- Projects aimed at quantifying concentrations of PCBs and PBDEs at or near analytical detection limits must have a rigorous QC program capable of constraining equipment, laboratory and sampling contamination, and variability.
- Ecology's Quality Assurance personnel in both the Environmental Assessment and Water Quality Programs should evaluate the *in situ* SPE (CLAM) approach.
- A standard operating procedure (SOP) should be used for the *in situ* SPE (CLAM) approach.
- A follow-up laboratory study should be conducted to test the accuracy of the SPE-CLAM device.
- Use of the SPE disks to measure toxics in the effluent of the centrifuge trailer should be assessed; this is most applicable to the monitoring of a turbid river at a fixed sample point over time.
- Assessment of toxics under the CWA by taking discrete grab samples of surface waters requires:
    - A sufficient number of samples be taken to meet the sample size requirements for the Water Quality Assessment, as described in Ecology's Water Quality Program Policy 1-11.
    - Modifying clean hands/dirty hands sampling guidance, EPA 1669 (US EPA, 1996) and Ecology SOP EAP003 (Anderson, 2006) by using a direct immersion technique; the sample container is opened and closed below the surface of the water to avoid atmospheric contamination.

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Appendices

Appendix A. Methods

Table A-1. Period of sampling and volume of water sampled.

River	Sampling method	Date	Period of sampling (hrs)	Volume of water sampled (L)	Composite or continuous
Spokane UGM	Centrifuge (sediment)	6/8 to 6/10/16	46	8323.7 and 8316.6	Continuous
	Centrifuge (water)		46	20	Composite
	Grab		46.4	20	Composite
	CLAM (SPE)		31.7	32, 37 and 42.5	Continuous
Yakima Canyon	Centrifuge (sediment)	8/3 to 8/5/16	46.3	7633.0 and 8807.1	Continuous
	Centrifuge (water)		46.3	20	Composite
	Grab		43.2	20	Composite
	CLAM (SPE)		31.2	18.1, 28.3 and 27.5	Continuous
Snohomish	Centrifuge (sediment)	12/15 to 12/15/16	9.8	1772.1 and 1774.5	Continuous
	Centrifuge (water)		9.8	20	Composite
	Grab		8.3	20	Composite
	CLAM (SPE)		8.3	18.4, 14.4, and 14.3	Continuous
Spokane UGM	Centrifuge (sediment)	2/8 to 2/9/17	34.3	6585.7 and 6579.2	Continuous
	Centrifuge (water)		34.3	20	Composite
	Grab		29.3	20	Composite
	CLAM (SPE)		19.6	28	Continuous

Table A-2. Measurement methods (laboratory).

Analyte	Sample Matrix	QAPP Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Water samples				
Suspended sediment concentrations (mg L^{-1})	Whole Water	0.2	NA	ASTMD3977B
Total non-volatile suspended solids (mg L^{-1})	Whole Water	0.2	NA	EPA 160.4
Total Organic Carbon (mg L^{-1})	Whole Water	1	NA	SM 5310B
Dissolved Organic Carbon (mg L^{-1})	Whole Water	1	NA	SM 5310B
SPE media				
PCB congeners (HRMS) (pg $sample^{-1}$)	SPE extract	0.5 pg per congener	DCM extraction; EPA 1668C	EPA 1668C
Large Volume - XAD resin				
PCB congeners (HRMS) (pg $sample^{-1}$)	XAD extract	1	Toluene extraction; EPA 1668C	EPA 1668C
PBDE congeners (pg $sample^{-1}$)	XAD extract	10-100	Toluene extraction; EPA 1614	EPA 1614
Large Volume – Liquid – Liquid extraction				
PCB congeners (HRMS) (pg $sample^{-1}$)	Whole water	1	DCM extraction; EPA 1668C	EPA 1668C
PBDE congeners (pg $sample^{-1}$)	Whole Water	10-100	DCM extraction; EPA 1614	EPA 1614
Sediments				
PCB congeners (HRMS) (ng Kg^{-1})	Sediments	1	EPA 1668C	EPA 1668C
PBDE congeners (ng Kg^{-1})	Sediments	10-100	EPA 1614	EPA 1614
Total organic carbon and nitrogen (%)	Sediments	0.1%	EPA 440	EPA 440

HRMS = high resolution mass spectrometry
SPE = solid phase extraction media
XAD = styrene and divinylbenzene polymer
DCM = dimethyl chloride extraction as per CI Agent protocol

Table A-3. Summary of the Estimated Detection Limits (EDLs) and Limits of Quantitation (LOQ) across all sample media for PCBs by congener.

See attachment.

Table A-4. Summary of the Estimated Detection Limits (EDLs) and Limits of Quantitation (LOQ) across all sample media for PBDEs by congener.

See attachment.

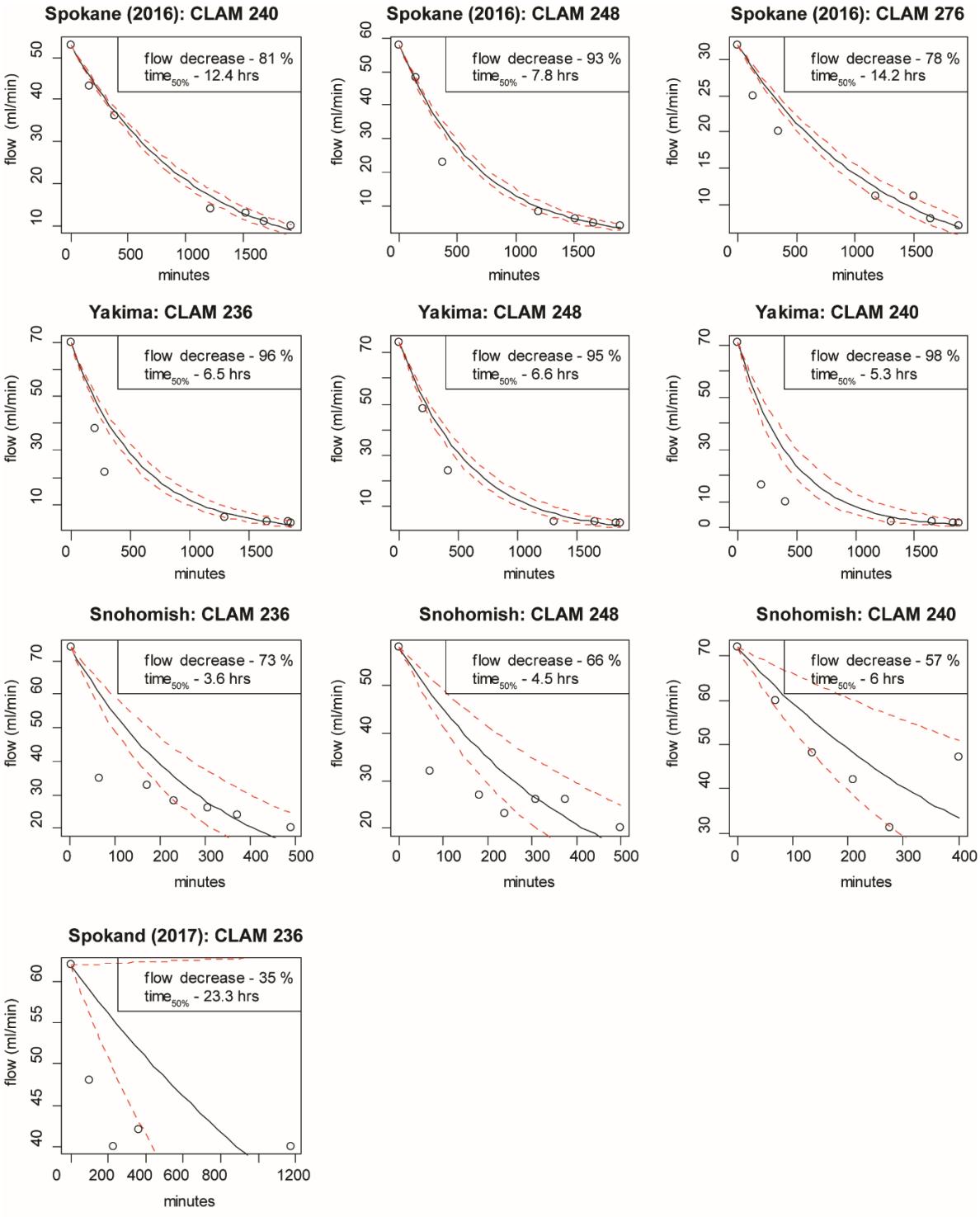

Figure A-1. Measured CLAM flow rates during deployment.

Exponential models fit to the data to describe the decline in flow over the period of deployment.
Inset box describes the decrease in flow (%) over the period of deployment and the time taken for flow to decrease by 50%.

Appendix B. Quality Assurance (Laboratory and Field Blanks)

See attachment.

Appendix C. PCB Results

See attachment for more data.

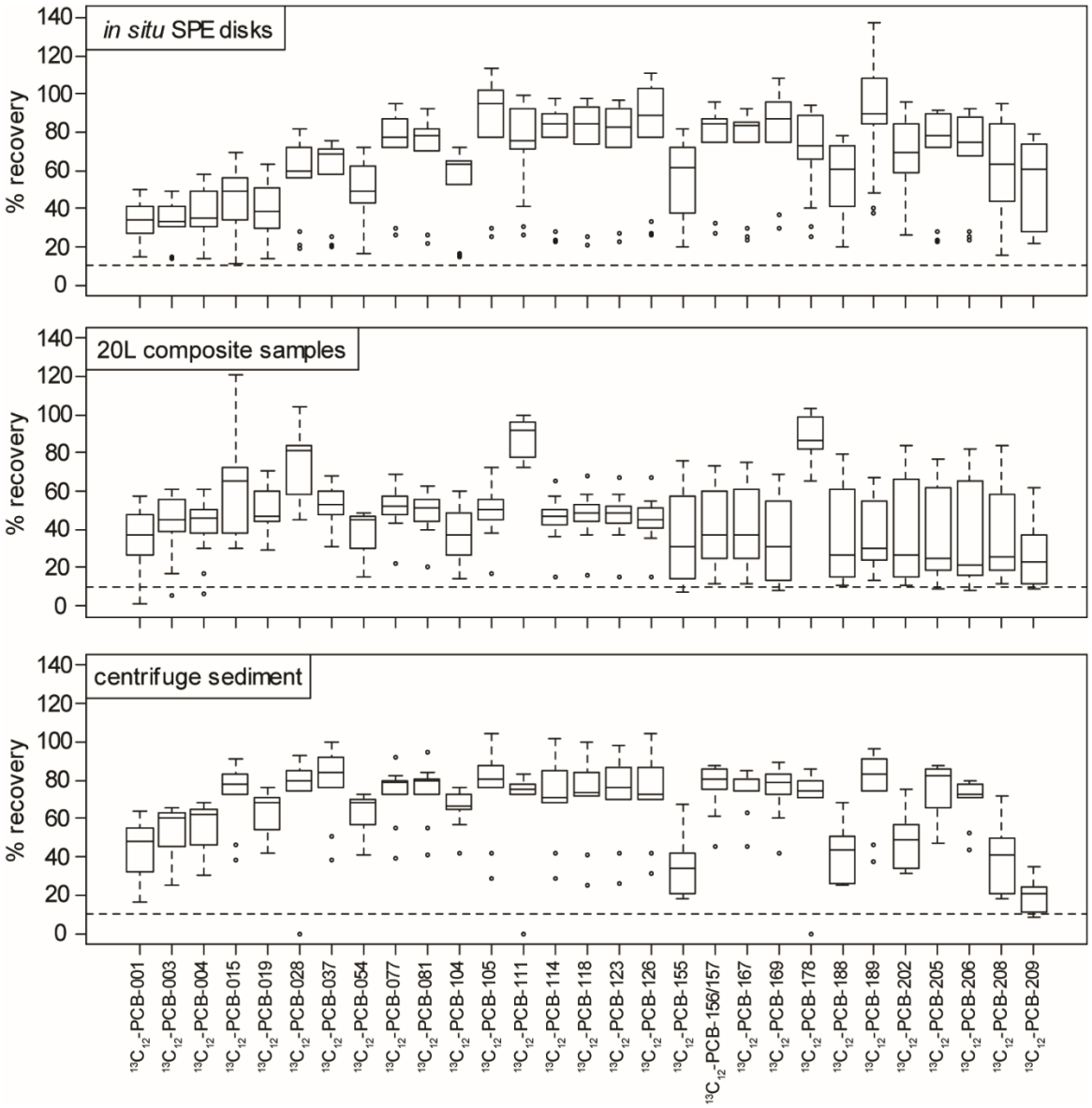

Figure C-1. Box and whiskers plot of the recoveries for the isotopically-labeled PCB congeners among sampling approaches.

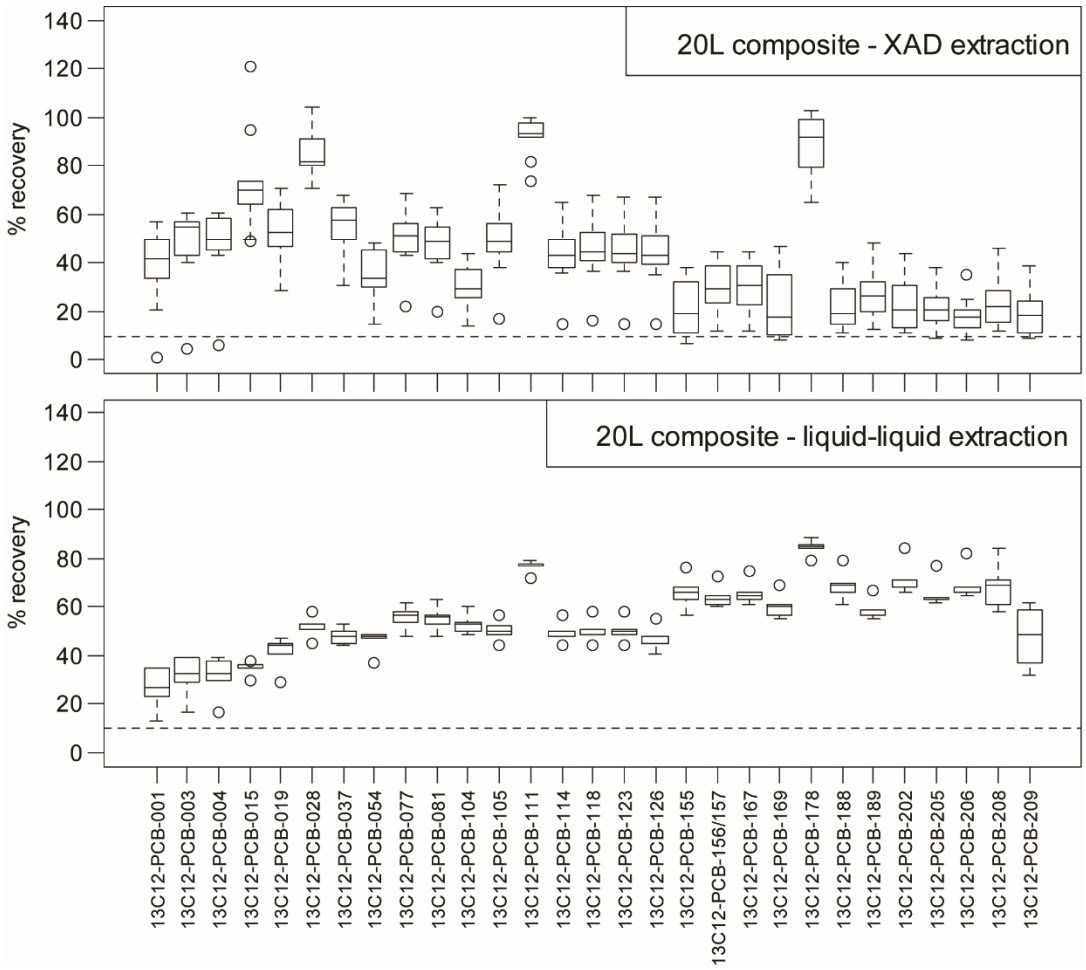

Figure C-2. Box and whiskers plot of the recoveries for the isotopically-labeled PCB congeners between large volume extraction techniques.

Appendix D. PBDE Results

See attachment for more data.

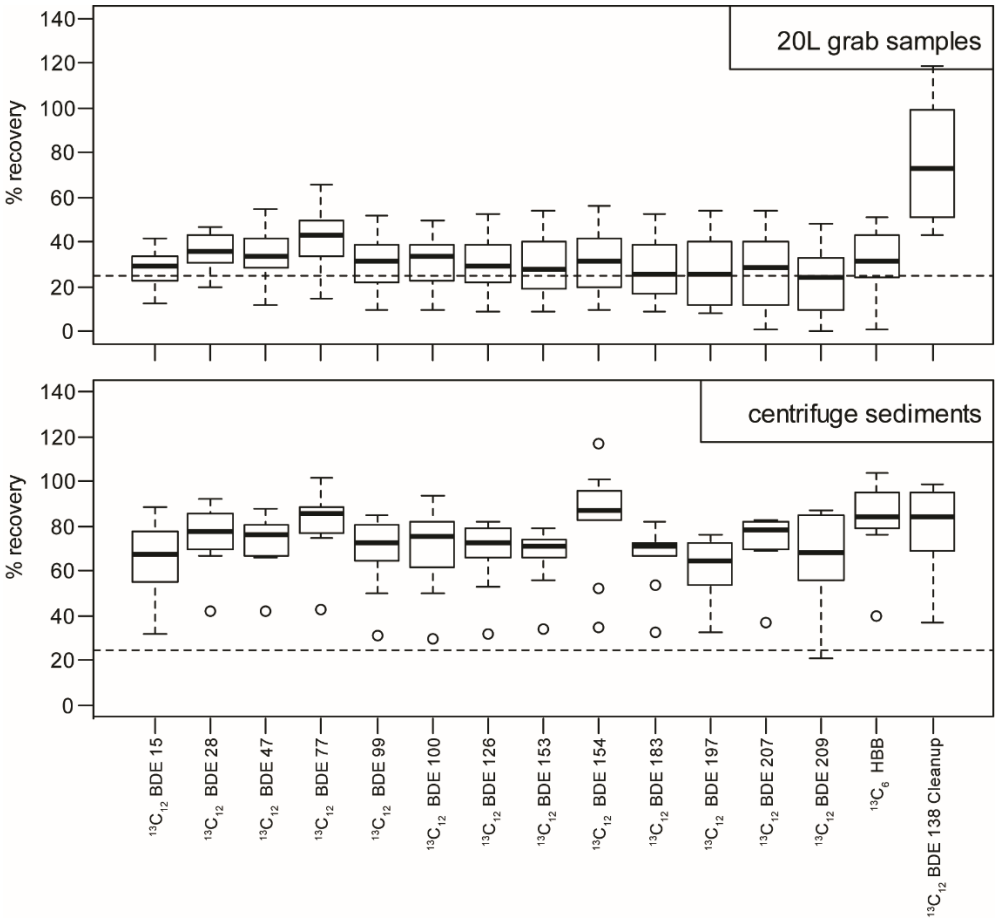

Figure D-1. Box and whiskers plot of the recoveries for the isotopically-labeled PBDE congeners between sampling approaches.

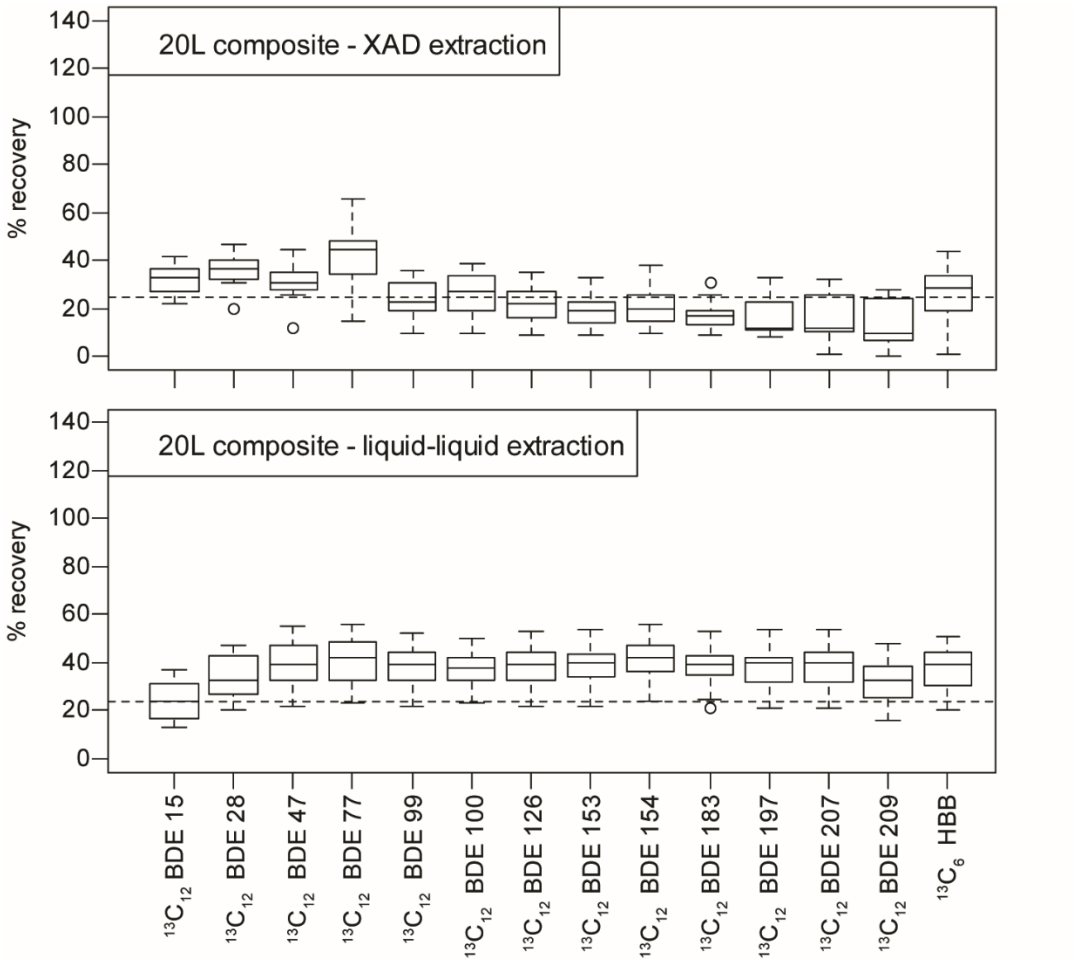

Figure D-2. Box and whiskers plot of the recoveries for the isotopically-labeled PBDE congeners between large volume extraction techniques.

Appendix E. Glossary, Acronyms, and Abbreviations

Glossary

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Congener: Similar chemical compounds related to each other by origin, structure and function, but having slightly different composition. PCB congeners all have 2 biphenyl (benzene) rings with 1 to 10 chlorine atoms; however, the chlorine and benzene rings are in different positions yielding a total of 209 possible congeners. Congeners are sometimes referred to as isomers.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Solid Phase Extraction (SPE) media: Media that is used to remove hydrophobic or hydrophilic compounds from water samples. Typically used in the laboratory to concentrate compounds of interest.

Semi-Permeable Membrane Device (SPMD): Semi-permeable membrane devices are passive sampling devices that are composed of a thin-walled, layflat polyethylene tube (91.4 cm x 2.5 cm x 70 – 95 µm thickness) filled with 1 ml of triolein, a neutral lipid compound. Semi-volatile organic compounds are taken up and retained by the oil (Alvarez, 2010).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands, and all other surface waters and water courses within the jurisdiction of Washington State.

XAD: A type of solid phase extraction media, it has a long history of use to concentrate semi-volatile compounds from large volume water samples. The media is a resin composed of a hydrophobic copolymer of styrene-divinylbenzene.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water-quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

CLAM	Continuous Low-level Aquatic Monitoring device
DI	Deionized water
DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
QA	Quality assurance
QAPP	Quality Assurance Project Plan
PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyl ethers
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
SPE	Solid phase extraction
SSC	Suspended sediment concentrations
TNVSS	Total non-volatile suspended solids
TOC	Total organic carbon
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
m	meter
mg/L	milligrams per liter (parts per million)
mL	milliliters
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
µS/cm	microsiemens per centimeter, a unit of conductivity