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State of Washington

Quality Assurance Project Plan

Assessment of Methods for Sampling Low-Level Toxics in Surface Waters

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Quality Assurance Project Plan

Assessment of Methods for Sampling Low-Level Toxics in Surface Waters

May 2016

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EAP: Environmental Assessment Program

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2.0 Abstract

The accurate assessment of toxic chemicals in surface waters is often inhibited by our ability to sample and measure very low ambient concentrations. Many of these toxic contaminants bioaccumulate and can be present in higher trophic organisms at concentrations that are detrimental to the organism and human health through consumption. To improve our ability to monitor ambient conditions and track sources, we will assess three different *active* sampling approaches to measuring low-levels of toxics in surface waters.

The approaches include: (1) *in situ* Continuous Low-level Aquatic Monitoring devices (C.L.A.M.s), (2) centrifugation and separation of solids and water for analysis, and (3) large volume (20L) composite grab samples. Sampling with each approach will occur concurrently. A total of three sampling events will be conducted in two rivers with different contaminant sources, the Spokane and Yakima Rivers, under varying flow conditions. We will focus on the sampling and measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs).

Following the field component of the project, a reference document that describes both *passive* (e.g., semi-permeable membrane devices) and *active* sampling techniques will be produced. Establishing a reference guide for the Washington State Department of Ecology on the limitations and applicability of a number of sampling approaches will allow for consistent and reliable measurement of ambient concentrations of toxics in Washington surface waters.

3.0 Background

Many surface waters of Washington State contain toxic contaminants at very low concentrations. However, those contaminants that bioaccumulate (e.g. polychlorinated biphenyls, PCBs) can be present in higher trophic organisms at concentrations that are detrimental to the organism and to human health through consumption. Many bioaccumulative chemicals are not measurable in the water column with a grab sample. Measuring them requires some kind of pre-concentration technique (e.g., semipermeable membrane devices). This has been exemplified through the listing of waterbodies impaired for beneficial uses in Washington under the Clean Water Act section 303(d). Approximately 53% of Washington's 303(d) listings for toxics are based on fish tissue concentrations, whereas 16% are based on water concentrations (mainly heavy metals) (Hobbs, 2015a). Our ability to reliably measure low concentrations of toxics in surface waters is what limits a more thorough assessment of ambient concentrations of toxics in Washington's surface waters.

Analysis is also challenging when chemicals are measured at such low concentrations. The cost of analysis of chemicals measured in the part-per-quadrillion range is considerably higher than conventional parameters. Additionally, quality control is challenging. Matrix interferences and background contamination can sometimes impact a sampling program. Therefore, reliable methods are necessary to constrain background noise (i.e., contamination) from the laboratory and the field.

The Washington State Department of Ecology (Ecology) has previously assessed *passive* sampling approaches for toxics in surface waters (Sandvik and Seiders, 2012). Here, we propose to assess select approaches for *actively* sampling toxics in surface waters. These approaches include: (1) *in situ* Continuous Low-level Aquatic Monitoring devices (C.L.A.M.s), (2) centrifugation and separation of solids and water for analysis, and (3) large volume (20L) composite grab samples with filtration and extraction using XAD-2 resin at the analytical laboratory. We will focus on the sampling and measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) – flame retardants.

The results of this study will aid in establishing a reference guide for Ecology on the limitations and applicability of a number of approaches will allow for consistent and reliable measurement of ambient concentrations of toxics in Washington surface waters.

3.1 Study area and surroundings

We will sample two rivers that have been previously monitored for toxics: the Spokane River and Yakima River (Figure 1). These rivers are both major tributaries to the Columbia River. The Spokane River watershed encompasses over 6,000 square miles in Washington and Idaho. The river flows through Post Falls and Coeur d'Alene in Idaho and large urban and industrial areas in the Spokane Valley and Spokane in Washington. Spokane has a continental climate, with warm summers (temperatures ranging from 63 to 70 ºF) and cold winters (temperatures ranging from 27 to 33 ºF). Spokane receives an annual total of 16.5 inches of precipitation. Land use within the Lower Spokane River basin is mainly forested (24%) and agricultural (rangeland – 40% and cropland – 22%), with urban lands and lakes and wetlands occupying the remaining 9% and 5%

respectively (Spokane County, 2011). Much of the land in the lower Spokane River Basin is occupied by the Spokane Tribe.

The Spokane region is a mixture of volcanic, sedimentary and metamorphic bedrock with Quaternary glacial deposits and sediments overlying in some areas. The surficial geology of the area was shaped by glaciation, the most recent culminating about 14,000 years ago and leaving the formations such as channel scablands behind.

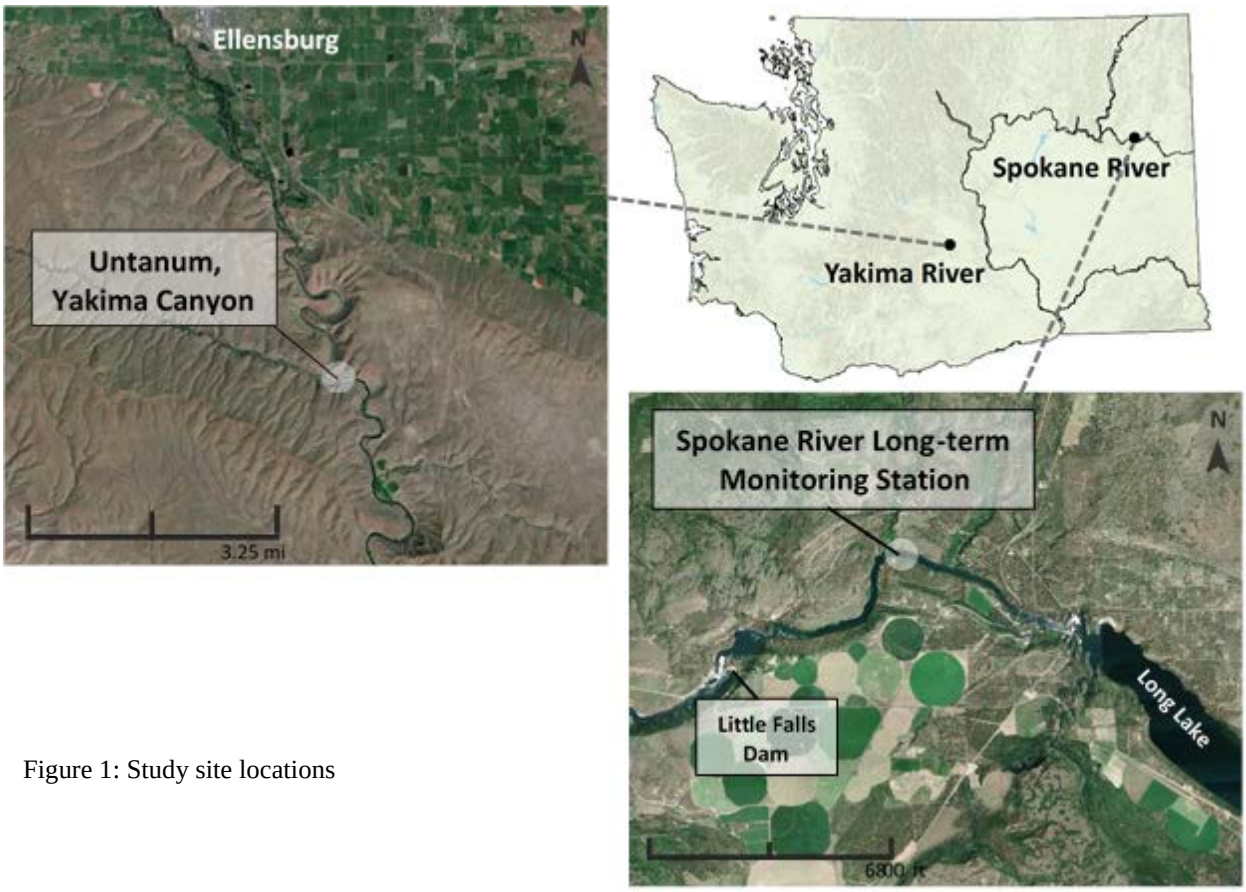

Figure 1: Study site locations

The Yakima River basin encompasses an area of 6,155 square miles. The land-use across the basin is forested (33% of the basin) in the upper reaches of the Yakima and major tributaries (e.g., Naches River), with rangeland (36%) and agriculture (28%) in the lower portions of the basin. Major urbanized areas within the basin (2% of the basin) include the towns of Ellensburg, Yakima, Toppenish, Sunnyside, and Richland. The lands of the Yakama Nation occupy approximately 15% of the basin in the southwest. There are approximately 1,900 miles of perennial streams, a number of major tributaries, and 5 lakes/reservoirs which total ~1% of the basin area (Rinella et al., 1992). There is a significant moisture gradient across the basin, with the headwaters receiving close to 140 inches of precipitation a year down to 10 inches at the mouth of the river.

The geology of the Yakima Basin is variable, comprising a number of different landforms ranging from the alpine and sub-alpine peaks of the Cascades (8,184 feet) to the low-lying Columbia plateau (340 feet). The upper basin is underlain by metamorphic, sedimentary, and intrusive and extrusive igneous rock. Basalts and unconsolidated material are present in the eastern portion of the basin. The Quaternary geology of the basin is dominated by three alpine glaciations, eroding the Yakima Valley and depositing moraines and outwash terraces with soil development during the intervening periods (Waitt Jr., 1977).

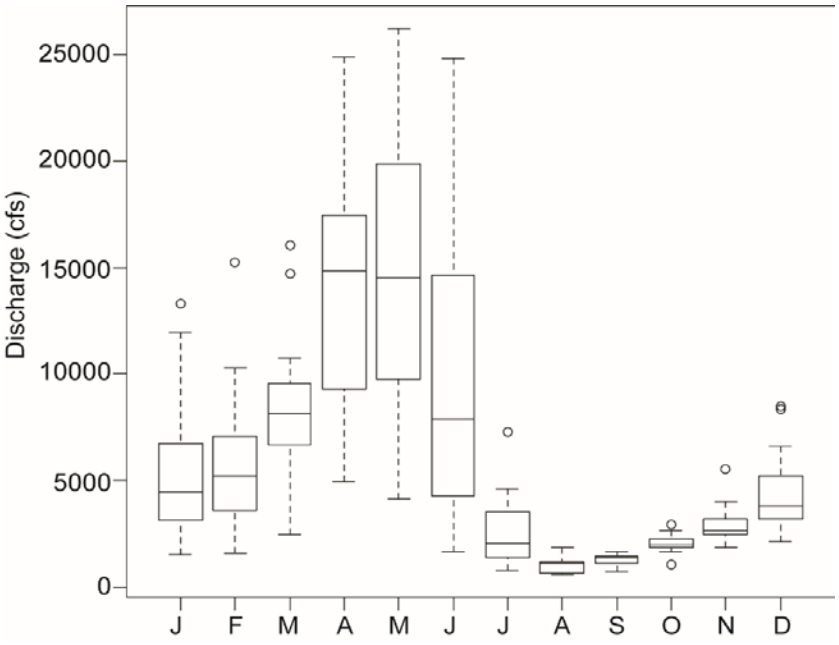

Figure 2: Discharge of the Spokane River at Spokane (USGS 12422500) from 2000-2015.

Hydrology

The hydrology of both rivers is heavily controlled for irrigation and power generation. The Spokane River is heavily influenced by the underlying Rathdrum-Spokane Aquifer which is over 370 square miles in area. The discharge of the river is snow-dominated and generally peaks in April-May (Figure 2). The Spokane River is controlled by 7 major dams that create reservoirs behind them. From upstream to downstream they are: Post Falls Dam, Upriver Dam, Upper Falls Dam, Monroe Street Dam, Nine Mile Dam, Long Lake Dam and Little Falls Dam. The study site is situated

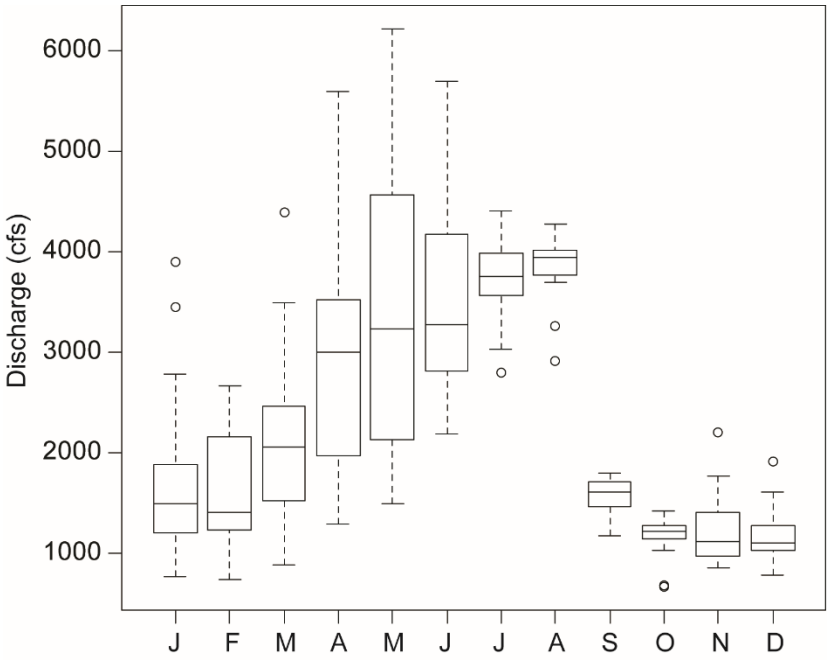

Figure 3: Discharge of the Yakima River at Umtanum (USGS 12484500) from 2000-2015.

downstream of the Long Lake dam at the eastern boundary of the Spokane Indian Reservation (Figure 1).

The headwaters of the Yakima River are in the Cascade Mountains, where the Upper Yakima flows 215 miles from Keechelus Lake to the Columbia River. Peak runoff for the Yakima River is snowmelt-dominated. The large number of reservoirs and irrigation canals control flow during the summer for agricultural lands (Figure 3). Generally there is a strong correlation between discharge and total suspended solids (TSS). However, in July and August when the discharge is heavily controlled, the TSS is often much lower than in May and June (Figure 4). Periods of low flow are variable and can occur during the summer for some reaches of the Yakima, with controlled irrigation returns experiencing low flow during the winter and other tributaries having low-flow conditions in the late summer or fall. With ~ 450,000 acres of irrigated agricultural land, the Yakima Basin is one of the most irrigated regions in the United States (Rinella et al., 1992). The study site is situated downstream of the Umtanum Creek confluence within the Yakima Canyon of the Upper Yakima Basin (Figure 1).

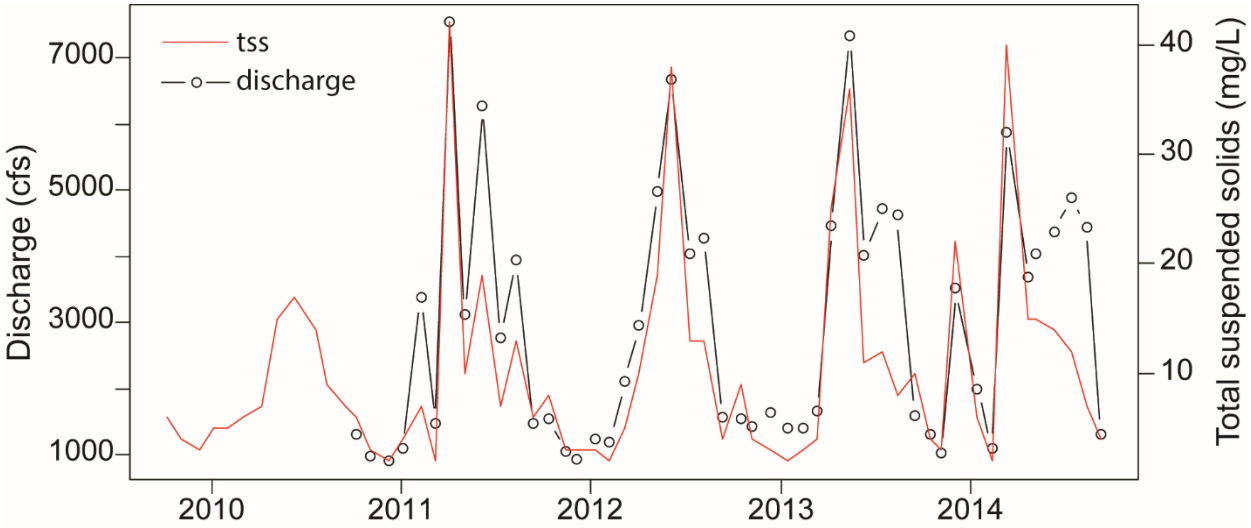

Figure 4: Records of discharge and TSS from the Yakima River at Umtanum. Data from Ecology station 39A055.

3.1.1 Logistical problems

There are no logistical issues foreseen. Both sampling sites are well-known to the project scientists. The centrifuge unit will be run off direct power from a building, but it also has a generator for powering the centrifuges.

3.1.2 History of study area

Both rivers have had a long history of human impact to the watershed and the channel morphology. As discussed earlier, both river channels have been heavily dammed in the past for irrigation and power generation. Today the Spokane River is mainly influenced by urban centers, industry, and use of the river for power generation. The development history of the region began

in the late 1800s with the Great Northern Railway and mining in the vicinity of Lake Coeur D'Alene. In the early 1900s, industry shifted towards forestry and agriculture.

The Yakima River has long been influenced by agricultural activities within the watershed. There have been many investigations into the impacts of agricultural pesticides on the aquatic communities of the Yakima River (Rinella et al., 1992; Joy and Patterson, 1997). With the establishment of major urban centers along the Yakima River, industrial contaminants such as PCBs and possibly PBDEs have become prevalent (Johnson et al., 2010). The importance of water supply to support fisheries in the river have received significant attention in recent decades with the establishment of the Yakima Basin Integrated Plan[1].

3.1.3 Parameters of interest

The contaminants of interest are polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). These compounds have proven difficult for Ecology and others to measure in surface waters.

3.1.3.1 Polychlorinated biphenyls (PCBs)

PCBs are a class of 209 compounds or congeners which contain 1 to 10 chlorine atoms attached to two rings of biphenyl. There are a number of congener groups that are defined by the degree of chlorination, ranging from monochlorobiphenyls (1 Cl atom) to decachlorobiphenyls (10 Cl atoms). They are referred to as *homolog* groups. Commercial and industrial applications of PCBs in the US relied on formulations of PCB mixtures under the trade name Aroclor. Each Aroclor is identified by a four-digit number, where the last two digits describe the % chlorine by weight (e.g., Aroclor 1254 contained 54% chlorine by weight).

PCBs were manufactured in the US from 1929-1977 and banned in 1979. However, they continue to be inadvertently and intentionally produced, because limited amounts are allowable under the 1976 Toxic Substances Control Act (Erikson and Kaley, 2011). Their primary use was as an electrical insulating fluid, and also as hydraulic, heat transfer, and lubricating fluids. The bulk of PCBs were incorporated into capacitors (~50% by mass) and transformers (~25%) (Erikson and Kaley II, 2011). Additional minor applications were blends of PCBs and other chemicals as carbonless copy paper (~4%), plasticizers, and fire retardants. These blends have been used in many products, such as sealants, caulks, and adhesives and cumulatively represent ~ 9% of the PCBs produced. The numerous applications of PCBs as plasticizers and additives represent a much smaller PCB pool, but they do have a much greater circulation in the environment.

The bioaccumulation of fat-loving or lipophilic chemicals in aquatic organisms is dependent on the physical characteristics of the chemical and the exposure pathway. The factor by which PCBs bioaccumulate will therefore vary among locations and with congener composition. PCBs are carcinogenic and can also affect the immune system, endocrine system, nervous system, and reproductive system. The most toxic have similar molecular structure to polychlorinated dibenzo-*p*-dioxins and are referred to as *dioxin-like*. To quantify the relative toxicity of these

[1] http://www.ecy.wa.gov/programs/wr/cwp/YBIP.html

dioxin-like PCBs, the concentrations are often adjusted in terms of the toxic equivalence (TEQ), which is relative to the most toxic dioxin congener (2,3,7,8-tetrachlorodibenzo-*p*-dioxin).

3.1.3.2 Polybrominated diphenyl ethers (PBDEs)

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). They began to be manufactured in the 1970s and a number of states have restricted the inclusion of them including Washington State in 2008 (RCW 70.76). 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.

The incorporation of PBDEs into products means they are released in closed systems (i.e. households) and therefore pose a large threat to indoor air quality. The release into the environment occurs through disposal and recycling of products, volatilization into local airsheds, and wastewater effluent from municipal plants. (Hale et al., 2003; Lorber and Cleverly, 2010).

Like PCBs, PBDEs are bioaccumulative and bind to the fats of organisms. The fate and toxicity of PBDEs varies, where the heavier congeners tend to bind more readily to dust and solids and the lighter congeners are more volatile. Lower brominated congeners of PBDEs tend to bioaccumulate more. Once in the body, PBDEs can inhibit the transport of thyroid hormones affecting metabolic functions and interfering with fetal development. Indeed, the impacts to mothers and infants is an active area of research. Other health impacts from PBDEs include: weight loss, toxicity to the kidney and liver, and dermal disorders. Endocrine disruption has also been observed in human and animal surveys (Birnbaum and Staskal, 2003).

3.1.4 Results of previous studies

There has been no previous study by Ecology comparing multiple sampling methods during a concurrent sampling event. There have been previous studies of PCBs and PBDEs at the study sites and these are summarized below.

Both rivers have had a long history of contamination issues from toxic chemicals. Fish tissues in the Spokane River have had documented PCB contamination since the early 1980s (Hopkins et al., 1985) and contamination with PBDEs since 2009 (Furl and Meredith, 2010). The Yakima River has not had a long history of documented PCB contamination. The first work on these contaminants in this basin is believed to be by Johnson et al. (2010), who looked at surface water concentrations using passive samplers, wastewater, and fish tissue. PBDEs have not been investigated in the Yakima River. Much of the focus on toxics in the Yakima Basin has been on legacy pesticides such as DDT (Rinella et al., 1992).

Spokane River
The proposed sampling site on the Spokane River is the same as the long-term monitoring site used by Era-Miller (2015). Results from this site, reported by Era-Miller, are summarized below.

The majority of previous sampling has taken place upriver of the sampling site proposed for this study (Figure 5).

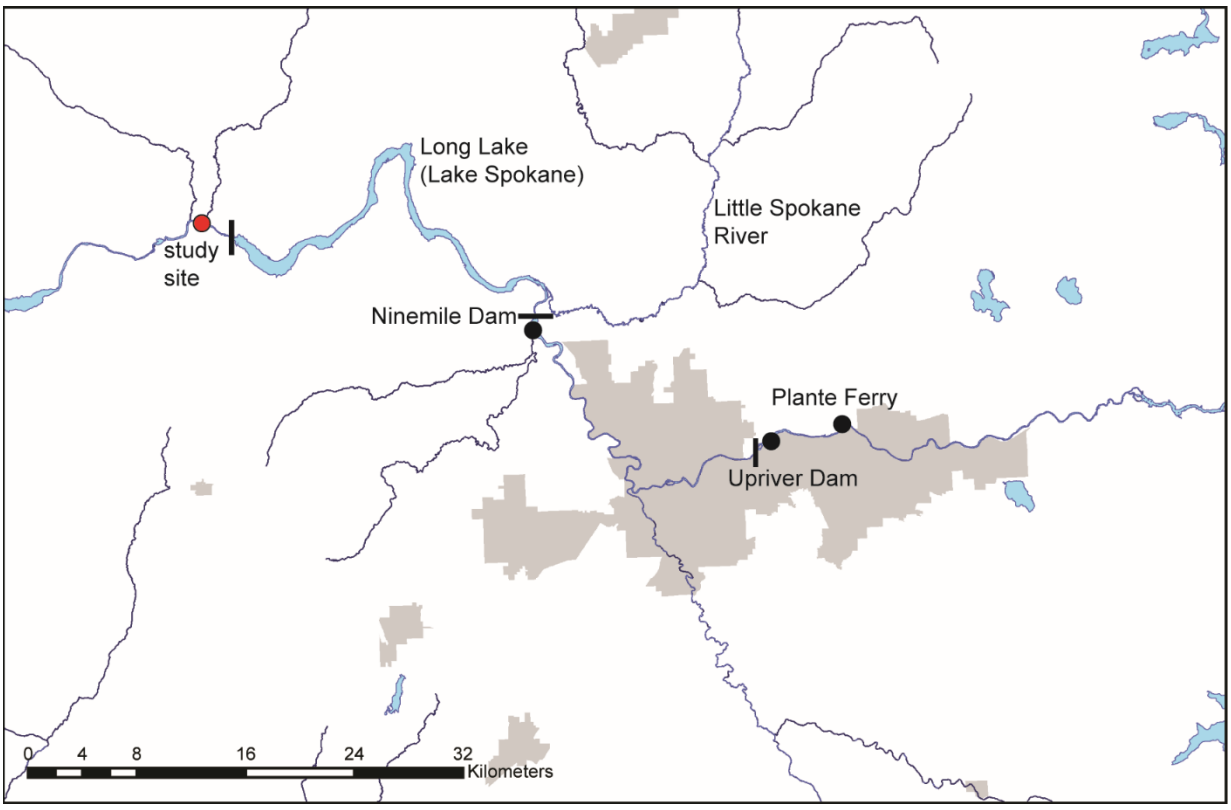

Figure 5: Map of previous sampling in the Spokane River.

In the fall of 2012, Era-Miller deployed a number of Continuous Low-level Aqueous Monitoring (C.L.A.M.) devices to estimate PCBs in water at the Upriver Dam and Ninemile Dam (Table 1). The total PCBs (t-PCBs) in the water column were much higher at the downstream, Ninemile Dam site compared with the upstream, Upriver Dam site. However, sediments collected in sediment traps show the opposite trend with the upstream site having slightly higher concentrations (Table 1). Concentrations of total PBDEs (t-PBDEs) in water were an order of magnitude greater at the Ninemile Dam site and higher in the sediments at this site (Table 1).

Table 1: Previous results of PCBs and PBDEs in C.L.A.M. and sediment samples from the Spokane River.

Site	Date	Total PCBs (pg/L)	Dissolved PCBs (pg/L)	Total PBDEs (pg/L)
C.L.A.M.				
Ninemile Dam	10/24/12	154	-	617
		151	-	714
		119	-	618
	10/25/12	108	-	-
		-	31	-
Upriver Dam	10/25/12	62	-	37
		76	-	30
		66	-	-
		-	30	-
Sediment Traps		Total PCBs (µg/Kg)		Total PBDEs (µg/Kg)
Ninemile Dam	10/10/12-2/1/13	13.7	-	65.2
		13.8	-	58.2
	2/1/13-6/13/13	17.2	-	23.6
Upriver Dam	10/9/12-1/31/13	28.5	-	22.5
	1/31/13-4/9/13	25.4	-	19.2

The amount of PCBs estimated to be in dissolved phase from the C.L.A.M. deployments (< 1.5 µm for the C.L.A.M.) is approximately 30% at Ninemile and 50% at Upriver, which is significantly less than the estimate of Serdar et al. (2011) of 94%. The estimate made by Serdar et al. (2011) was based on the theoretical partitioning of PCBs from suspended particulate matter to dissolved phase in the water. The proposed sampling will help clarify this discrepancy.

Previous sampling using the centrifuge unit has also shown higher concentrations at Ninemile Dam relative to upstream sites (Table 2). The proposed sampling site for this study is downstream of Long Lake Dam (Figure 5) and expected to have PCB concentrations lower than previously measured at Ninemile Dam.

Table 2: Suspended sediment and dissolved PCB concentrations.

Site	Date	Total PCBs (µg/Kg)	Estimated dissolved PCBs (pg/L)[a]	Dissolved PCBs (pg/L)	Reference
		Suspended sediment		SPMDs[b]	
Plante Ferry	August 1994	220	3,284	1,000 – 1,900	Ecology, 1995
	November 2003	7.09	105	<109	Serdar et al. (2011)
Ninemile Dam	November 2003	68.8	1,020	130	Serdar et al. (2011)
	October 2003	-	-	305	Serdar et al. (2011)
	April 2004	-	-	225	Serdar et al. (2011)

[a] based on the partition formula found in Serdar et al. (2011)
[b] semi-permeable membrane devices

Yakima River

Previous sampling in the Upper Yakima River for PCBs was undertaken by Johnson et al. (2010) (Figure 6). Using passive SPMD samplers, detectable low-level t-PCB concentrations of the mainstem and tributaries were measured (Table 3). No PBDEs have been analyzed for in the Yakima River. The Upper Mainstem of the Yakima River (WRIA 39) is currently listed under the Clean Water Act 303(d) list for PCBs and Dioxins in fish tissue.

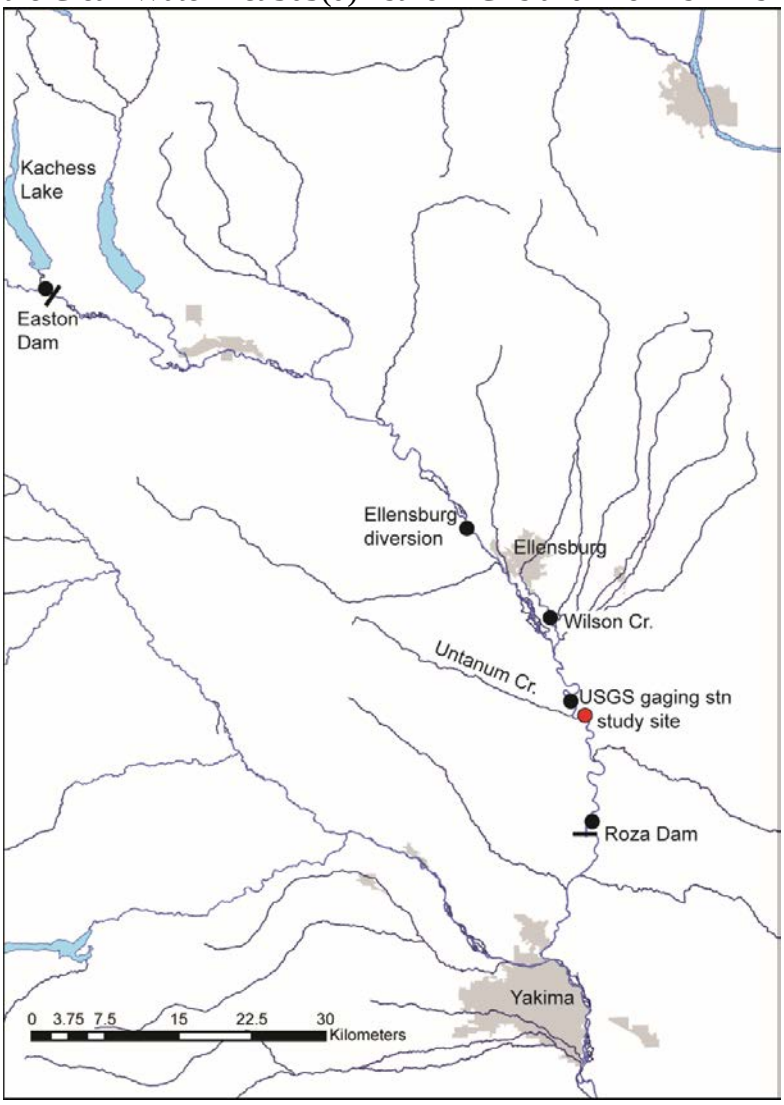

Figure 6: Map of previous sampling in Yakima River.

Table 3: Summary of SPMD data from the 2007 sampling of the Upper Yakima River.

Site	Total PCBs (pg/L)	
	May-June, 2007	Oct-Nov, 2007
Mainstem		
Easton Dam	120	34
Ellensburg Water Co. Diversion	26	57
Roza Dam	50	19
Tributary		
Wilson Creek	41	39

3.1.5 Regulatory criteria or standards

The goal of this study is not to identify compliance with regulatory standards. However, to provide context for impacts to aquatic life and human health, the results will be compared to relevant criteria and standards (Table 4). The criteria for the protection of aquatic life in the State of Washington is regulated under Chapter 173-201A of the Washington Administrative Code (WAC 173-201A). No regulatory standards are available for PBDEs.

Human health criteria for surface waters are risk-based calculations of the exposure of humans to carcinogens and non-carcinogenic illness from the consumption of fish and water. Criteria are available for fish consumption alone and fish and water consumption (Table 4). The risk and subsequent criteria calculations are based on a person of 70 kg (154 lbs) consuming 6.5 g of fish per day and drinking 2 liters of freshwater per day over the course of 70 years. For carcinogens, this full exposure information is used to calculate a water concentration (the criterion) associated with a risk level of 1 in 1,000,000. This risk level reflects the additional lifetime cancer risk based on daily consumption at the specified exposure levels. For non-carcinogens the criteria are calculated using a hazard quotient = 1, which reflects a level at which effects should not occur.

Ecology uses Fish Tissue Equivalent Concentrations (FTECs) to help assess whether the designated uses of fish/shellfish and drinking surface waters are being met in ambient waters. The FTECs are based on Washington's water quality criteria for the protection of human health (40 CFR 131.36). Fish tissue sample concentrations that are lower than the FTEC suggest that the uses of fish/shellfish and drinking surface waters are being met for that specific contaminant. The FTEC is calculated by multiplying the contaminant-specific Bioconcentration Factor (BCF) times the contaminant-specific Water Quality Criterion (40 CFR 131.36). In the Spokane River, the Spokane Tribe has established an EPA-approved water quality standard that reflects higher consumption amounts relevant to the community (Table 4).

The freshwater sediment standards for cleanup and screening are based on the protection of the benthic community and are established under the Sediment Management Standards WAC 173-204 (Table 4). Cleanup standards are expressed as dry weight and not normalized to organic carbon content (Michelson, 1992).

Table 4: Washington State water and sediment criteria for the protection of human health and aquatic life for PCBs.

Aquatic life ($ng\ L^{-1}$)†		Human health		Spokane Tribe Human Health	Freshwater sediment (µg Kg-1 dry weight) ‖	
Freshwater chronic	Freshwater acute	Consumption of water and organisms ($ng\ L^{-1}$)ǂ	Consumption of organisms only ($ng\ L^{-1}$)ǂ	Water and fish consumption ($ng\ L^{-1}$)	Sediment cleanup objective	Sediment screening level
14	2000	0.17	0.17	0.0013	110	2500

† WAC 173-201A
ǂ EPA National Toxics Rule
‖ WAC 173-204

4.0 Project Description

The measurement of toxic chemicals at low concentrations in surface waters of Washington State inhibits our ability to monitor ambient conditions and track sources. This project will assess three different *active* sampling approaches to measuring low-levels of toxics in surface waters: (1) Continuous Low-level Aquatic Monitoring devices (C.L.A.M.s), (2) centrifugation and separation of solids and water for analysis, and (3) large volume (20L) composite grab samples with filtration and XAD-2 resin extraction in the laboratory. A total of three sampling events will be conducted in two rivers with varying flow and contaminant sources. Following the field component of the project, a reference document that describes both *passive* (e.g., SPMDs) and *active* sampling techniques will be produced.

4.1 Project goals

The goal of this project is to assess different techniques of actively sampling surface waters for toxic chemicals. The study will assess these approaches based on:

- Whether the environmental signal is above background noise (i.e., blank contamination).
- Whether field replicates are sufficiently reproducible.
- Whether deployment in the field is easy and suitable for a wide variety of surface waters.
- Whether detection limits are low enough to compare with applicable water quality criteria for PCBs.

Project goals are based on characteristics of the sampling approach identified by scientists within the Toxics Studies group of EAP. As the project progresses it may become apparent that additional goals and objectives should be included.

4.2 Project objectives

Specific objectives for the project include the following activities:

- Measure total PCB concentrations in surface waters, using C.L.A.M. devices.
- Measure total and dissolved PCB and PBDE concentrations in suspended sediments and water using the centrifugation unit.
- Measure total PCB concentrations in whole water, using large-volume composite grab samples.
- Compile results with previously collected data on low concentrations of dissolved PCBs in surface waters, using passive samplers.

4.3 Information needed and sources

The passive sampling results from studies previously completed by the Toxics Studies Unit, Environmental Assessment Program, are available in a data repository on the program internal SharePoint website: http://partnerweb/sites/EAP/passive_samplers/default.aspx.

4.4 Target population

The target population is low concentrations of PCBs and PBDEs in ambient surface waters and suspended sediments of the Spokane and Yakima rivers.

Due to budgetary constraints we are only assessing PBDEs in the particulate and dissolved phase using the centrifuge unit. PCBs will be assessed across all approaches.

4.5 Study boundaries

The sampling sites for this project are situated in the Lower Spokane River Basin (WRIA 54; HUC 17010307) and the Upper Yakima River (WRIA 39; HUC 17030001) (Figure 5 and 6). The Spokane site is downstream of Long Lake dam and upstream of the Spokane Tribal boundary. The Yakima site is within the Yakima Canyon reach near the Umtanum Creek input, which is also a USGS gauging station (12484500) and an Ecology long-term freshwater monitoring station (39A055).

4.6 Tasks required

The tasks of the study depend on a field component and production of a reference report. Specific tasks include:

- Assembling the necessary equipment for concurrent sampling using (1) C.L.A.M. devices, (2) the centrifuge unit (as per Gries and Sloan, 2009), and (3) large-volume (20L) composite grab samples.
- Establishing a contract lab to analyze the samples using high-resolution gas chromatography-mass spectrometry.
- Establishing a rigorous quality assurance (QA) program to assess background or blank contamination.
- Capturing a high- and low-flow event at the long-term monitoring site on the Spokane River (Era-Miller, 2015), and a low-flow event on the Upper Yakima River, at the Ecology long-term freshwater monitoring site at Umtanum Creek.
- Analyzing all samples and validating all data through Manchester Environmental Lab's quality control (QC) process.
- Compiling all data from the active sampling events with previous data from passive sampling events (e.g., Sandvik and Seiders, 2012) to provide a reference guide for monitoring low concentrations of toxics in surface waters.

4.7 Practical constraints

The main practical constraint for this project is budgetary. When comparing multiple approaches, we improve our ability to assess reproducibility and precision by increasing the number of samples. We have limited the number of samples for budgetary reasons, but we have included enough replication to make some basic statistical comparisons.

Practical constraints for this project also pertain to the successful functioning of the centrifuge unit. This unit has not been used for the last 4 years, approximately. We have incorporated a significant refurbishment period for the unit, which includes a field trial and equipment blank prior to the first sampling event in May-June, 2016.

4.8 Systematic planning process

The preparation of this Quality Assurance Project Plan (QAPP) represents the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

This project was requested and initiated by EAP and therefore there is no client.

Table 5: Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
William Hobbs Toxic Studies Unit Statewide Coordination Section Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and reviews data in EIM. Writes the draft report and final report.
Melissa McCall Toxic Studies Unit Statewide Coordination Section Phone: 360-407-7384	Field Assistant	Assists with field preparation and centrifuge refurbishment, collects samples and records field information. Enters project data into EIM and internal repository for passive/active sampler data.
Brandee Era-Miller Toxic Studies Unit Statewide Coordination Section Phone: 360-407-6771	Project Investigator / Acting Unit Supervisor for the Project Manager	Assists with project scoping, field logistics, data analysis, and report writing. Provides internal review of the QAPP, approves the budget, and approves the final QAPP. Reviews draft reference report.
Jessica Archer Statewide Coordination Section Phone: 360-407-6596	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Tom Mackie Eastern Operations Section Phone: 509-454-4244	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
Karin Feddersen Manchester Environmental Laboratory Phone: 360-871-8829	Lab QA Officer	Manages contract with contract laboratory and provides review of contract data.
Contract Laboratory	Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan

5.2 Special training and certifications

This project will require training on the use of the centrifuge unit. Tom Gries, Statewide Coordination Section, EAP has agreed to conduct training in the lab and field, including a field trial, to ensure proper protocols are followed during sampling (Gries, pers. comm.). Tom

completed the most extensive deployment of the centrifuge unit during a project on the Lower Duwamish (Gries and Sloan, 2009).

Sampling using the C.L.A.M. devices does not have formal written guidance in an SOP, as these devices continue to be in a trial stage. The data generated in this project will further our validation of the devices. The project team has extensive use with these devices in previous projects (Hobbs, 2014, 2015b; Era-Miller, 2014, 2015).

5.3 Organization chart

See Table 5 for the description of the organization chart.

5.4 Project schedule

The schedule for the project is described in Table 6.

Table 6: Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Centrifuge refurbish and field trial	April 2016	William Hobbs/Melissa McCall
Lower Spokane	May/June 2016	William Hobbs/Melissa McCall
Lower Spokane-Upper Yakima	August/September 2016	William Hobbs/Melissa McCall
Field work completed	October 2016	William Hobbs/Melissa McCall
Laboratory analyses completed	January 2017	
Environmental Information System (EIM) database		
EIM Study ID	ID number WHOB003	
Product	Due date	Lead staff
EIM data loaded	February 2017	Melissa McCall
EIM data entry review	March 2017	William Hobbs
EIM complete	March 2017	Melissa McCall
Final report		
Author lead / Support staff	William Hobbs / Melissa McCall and Brandee Era-Miller	
Schedule		
Draft due to supervisor	March 2017	
Draft due to client/peer reviewer	April 2017	
Draft due to external reviewer(s)	May 2017	
Final (all reviews done) due to publications coordinator	June 2017	
Final report due on web	July 2017	

5.5 Limitations on schedule

There are no foreseen limitations on the project schedule.

5.6 Budget and funding

Budget for the project is detailed in Table 7.

Table 7: Project budget detail.

Blank Batch QC	Samples	QA	Cost	Subtotal	In-house	Contract
PCB Congeners (GC/ECD) - centrifuge	3	0	$115	$345	$345	0
PCB Congeners (HRMS) – C.L.A.M. SPE disk	0	3	$800	$2,400	0	$2,400
			Blank Total	$2,745	$345	$2,400
Water - 1 sampling event	**Samples**	**QA**	**Cost**	**Subtotal**	**In-house**	**Contract**
Total organic carbon	1	1	$45	$90	$90	0
Dissolved organic carbon	1	1	$45	$90	$90	0
Total suspended solids	5	2	$27	$189	$189	0
PBDEs (HRMS)	1	2	$800	$2,400	0	$2,400
PCB Congeners (HRMS)	8	5	$800	$10,400	0	$10,400
conditioning SPE disks	6	0	$50	$300	0	$300
20L canister processing	7	0	$500	$3,500	0	$3,500
			Water Total	$16,969	$369	$16,600
Sediment (centrifuge) - 1 sampling event	**Samples**	**QA**	**Cost**	**Subtotal**	**In-house**	**Contract**
TOC	1	1	$45	$90	$90	0
PBDEs (HRMS)	1	1	$800	$1,600	0	$1,600
PCB Congeners (HRMS)	1	1	$800	$1,600	0	$1,600
			Sediment Total	$3,410	$210	$3,200
					Sample Event Total (1 station, 1 event)	$20,379
					Lab Subtotal (all events + batch QC)	$63,522
					Lab Contracting	$15,881
					Lab Total	**$79,403**
					Equipment	$8,000
					Project Total	**$87,403**

GC/ECD = gas chromatography – electron capture detection
HRMS = high resolution mass spectrometry
SPE = solid phase extraction

The projected budget for FY16 is $36,669 ($28,669 laboratory and $8,000 supplies) and $50,648 (all laboratory) for FY17.

6.0 Quality Objectives

6.1 Decision quality objectives (DQOs)

The use of the C.L.A.M. devices is still under validation as an accepted sampling method. If the QA and initial sampling event in May 2016 show that the devices fail to allow for a clear environmental signal (above the blank concentrations of the device), the C.L.A.M. devices will be dropped from further assessment. We have experience using the other methods in this study and do not anticipate needing DQOs for these approaches.

6.2 Measurement quality objectives (MQOs)

The MQOs for this study are detailed in Table 8. The MQOs for the field parameters (pH, dissolved oxygen, temperature, and conductivity) are in Table 9.

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision for two replicate samples is measured as the relative percent difference (RPD) between the two results. If there are more than two replicate samples, then precision is measured as the relative standard deviation (RSD).

Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Table 8. PCBs in the C.L.A.M. solid phase extraction (SPE) media will be analyzed as field triplicates each sampling event. The suspended particulate matter (SPM) and water from the centrifuge unit will be analyzed in duplicate. The large volume (20L) composite grab samples will be analyzed in triplicate. Acceptance limits for field precision of these samples is ≤50 RPD.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this project, bias is measured as acceptable % recovery. Acceptance limits for laboratory verification standards, matrix spikes, and surrogate standards are shown in Table 8.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. For the high resolution methods being used in this study, each congener is assessed for sensitivity and qualified or censored if the sample is not above 10X the laboratory blank. The laboratory reporting limits (RLs) for the project are described in Section 9.2.

Table 8. Measurement quality objectives**.**

Parameter	Verification Standards (LCS,CRM,CCV)	Duplicate Samples	Matrix Spikes	Matrix Spike-Duplicates	Surrogate Standards	Lowest Concentrations of Interest
	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits[a]	Units of Concentration
Water samples						
TSS	80-120%	± 20%	NA	± 20%	NA	1 mg L^{-1}
Total Organic Carbon	80-120%	± 20%	75-125%	± 20%	NA	1 mg L^{-1}
Dissolved Organic Carbon	80-120%	± 20%	75-125%	± 20%	NA	1 mg L^{-1}
Conductivity	80-120%	± 20%	NA	± 20%	NA	1 µmhos cm^{-1}
PCB Congeners (blank water)	80-120%	± 50%	50-150%	± 20%	50-150%	1 ng/L
SPE media						
PCB congeners	50-150%	± 50%	50-150%	± 20%	50-150%	50 pg $sample^{-1}$
Large Volume - XAD resin						
PCB congeners	50-150%	± 50%	NA	± 20%	50-150%	0.5 pg $sample^{-1}$ per cong
PBDE congeners	50-150%	± 50%	NA	± 20%	25-150%[b]	0.5 pg $sample^{-1}$ per cong 0.10%
Sediments						
PCB congeners	50-150%	± 50%	NA	NA	50-150%	0.5 ng Kg^{-1} per cong
PBDE congeners	50-150%	± 50%	NA	NA	25-150%[b]	0.5 ng Kg^{-1} per cong
Total organic carbon	80-120%	± 20%	NA	NA	NA	1%

LCS = laboratory control sample
CRM = certified reference materials
CCV = continuing calibration verification standards
RPD = relative percent difference
[a] labeled congeners
[b] PBDE 209 recovery of 20-200%
SPE = solid phase extraction media (C.L.A.M. device)
XAD = polystyrene resin used to absorb soluble organic compounds

Table 9: Measurement quality objectives for Hydrolab calibration checks

Parameter	Units	Accept	Qualify	Reject
pH	std. units	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Conductivity*	uS/cm	< or = ± 5	> ± 5 and < or = ± 15	> ± 15
Temperature	° C	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Dissolved Oxygen	% saturation	< or = ± 5%	> ± 5% and < or = ± 15%	> ± 15%
Dissolved Oxygen**	mg/L	< or = ± 0.3	> ± 0.3 and < or = ± 0.8	> ± 0.8

* Criteria expressed as a percentage of readings; for example, buffer = 100.2 uS/cm and Hydrolab = 98.7 uS/cm; (100.2-98.7)/100.2 = 1.49% variation, which would fall into the acceptable data criteria of less than 5%.
**When Winkler data is available, it will be used to evaluate acceptability of data in lieu of % saturation criteria.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Section 8.1 lists the standardized operating procedures (SOPs) to be followed for field sampling. Appendix A and B give a summary of the field and laboratory procedures used by EAP for sample collection using C.L.A.M.s and the centrifuge unit. All analytical methods used for the project are approved methods commonly used by Ecology for monitoring of toxics.

6.2.2.2 Representativeness

Representativeness is a measure of whether the sample media reflects reality. We will ensure proper representatives by adhering to the approved SOPs and sampling protocols. Samples will be preserved and stored in conditions to ensure that holding conditions and lab holding times are met. Samples will be collected to represent high-flow and low-flow conditions in one river. Additional samples will be collected to represent high-flow conditions in a second river.

6.2.2.3 Completeness

The data for this project will be considered complete if 95% of the planned samples were collected and analyzed acceptably.

7.0 Sampling Process Design (Experimental Design)

7.1 Study design

Our inability to measure ambient concentrations of PCBs and PBDEs in surface waters of Washington State inhibits thorough assessment of many rivers and lakes. This project will assess three methods for measuring low concentrations of PCBs and PBDEs in the Spokane and Yakima Rivers. Sampling will occur during higher flow in the Spokane and at lower flow in the Spokane and Yakima. Capturing variability in flow regimes will allow us to measure differences in the particulate and dissolved phases during these periods.

We will take concurrent samples using:

1. C.L.A.M. devices with C-18 SPE media in stainless steel housing will be deployed in triplicate, each with 2 disks to assess breakthrough of the first disk. Disks will be analyzed for PCBs.
2. Centrifugation to separate the suspended particulate matter (SPM) and water and to analyze both the particulate and dissolved phase for both PCBs and PBDEs.
3. Large volume (20L) composite grab samples taken over the period of sampling. The sample will be analyzed for PCBs, using XAD-2 resin and extraction in the laboratory.

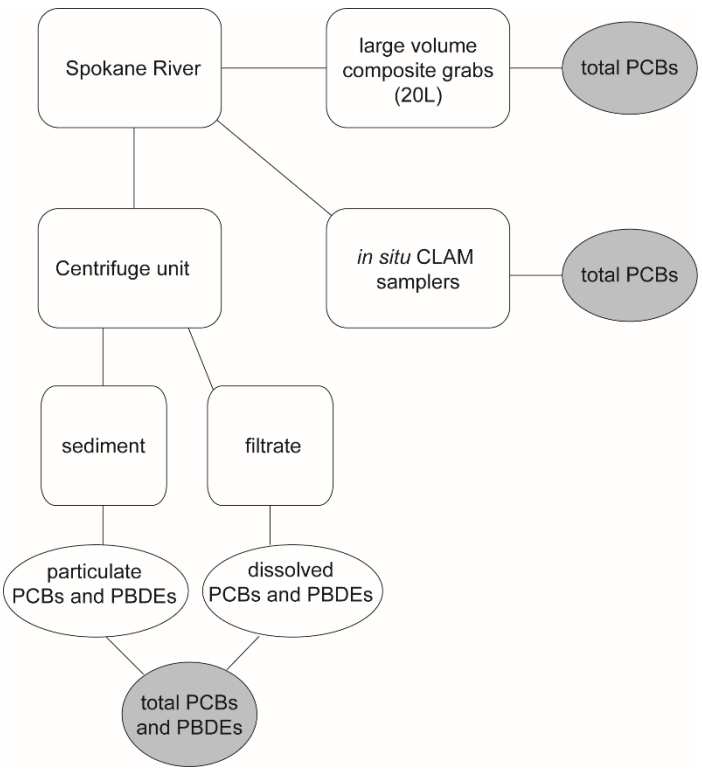

Figure 7: Flow chart of the three sampling approaches being employed this project.

The methods being used will provide information on the particulate, dissolved, and total phases of the contaminants (Figure 7). The centrifuge unit will allow us to assess the particulate and dissolved concentrations in a large volume of water and by combining these fractions we can attain a total. The C.L.A.M. devices will sample total concentrations, and dissolved phase PCBs will be attained from the large volume composite samples. Analyzing the various phases of PCBs in surface water is relevant to our understanding of the fate and transport of PCBs in this system. Previous work in the Spokane River suggests that 94% of the PCBs are dissolved phase (Serdar et al., 2011). This work will help confirm this.

High-resolution mass spectrometry will be used to quantify PCB and PBDE congeners at the required detection limits.

7.1.1 Field measurements

During the period of sampling, a calibrated hydrolab will be deployed in the area of sampling, measuring continuous temperature, dissolved oxygen, conductivity, and pH.

7.1.2 Sampling location and frequency

The sampling site on the Spokane River was selected because it is the proposed long-term monitoring site for PCBs and PBDEs on the Spokane (Era-Miller, 2015). The site typically has lower concentrations of the contaminants of concern compared to upstream sites, but both PCBs and PBDEs have been measurable in grab samples with high-resolution mass spectrometry. Furthermore, the proposed project dovetails well with the previous sampling and extends our temporal knowledge of the contaminants in Spokane River surface water. Since the main goal of this project is to assess methods for sampling low-level toxics, it is appropriate to select the site on the Spokane River with some of the lowest concentrations.

The sampling site on the Yakima River was selected to provide a comparison to surface waters with different contaminant sources. From previous sampling on the Yakima, we know that PCBs are an important contaminant of concern (Johnson et al., 2010). But we have no information on PBDEs.

Sampling will take place over a 12- to 36-hour period. Given typical total suspended sediment loads, the approximate time necessary to centrifuge a sufficient volume of water can be calculated (Table 10). The sampling strategy is designed to allow for a statistical comparison of the results among the three methods. Each method will have replication.

Table 10: Estimate of the necessary volume and time required to capture sufficient sediment mass to analyze.

Site	Date	Mean TSS (mg dw / L)	Centrifuge efficiency[a]	Water needed for 12g dry weight (L)[b]	Time (hrs)[c]
Spokane	May	8	0.95	1579	8.77
Spokane	Aug-Sept	2	0.95	6316	35.09
Yakima	Aug-Sept	8	0.95	1579	8.77

[a] taken from Gries and Sloan, 2009
[b] sample mass required for each replicate of PCBs/PBDEs and total organic carbon
[c] based on adjusted flow rate of 3 L/min to each centrifuge
TSS = total suspended solids

7.1.3 Parameters to be determined

Previously described in sections 3.1.3, 4.4, and 7.1.1.

7.2 Maps or diagram

Sample sites are shown in Figure 1.

7.3 Assumptions underlying design

We know that PCBs and PBDEs are present and can be measured at the selected study sites (Johnson et al., 2010; Era-Miller, 2015). We are assuming that the solid phase extraction disks of the C.L.A.M. device are effective in accurately binding the contaminant mass flowing through the device. While we can compare results among the approaches, it is not possible to assess the true accuracy of them.

7.4 Relation to objectives and site characteristics

The study was designed to test the stated objectives of the project and the selected sites will allow us to address the project objectives.

7.5 Characteristics of existing data

We currently have no data to assess multiple sampling methods during a concurrent sampling event. This study will directly address this data gap.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

All sampling will take place in the same general sample location to allow for comparable results among sampling approaches. In addition to the sampling outlined below, composite grab samples will also be taken from the main sample location for dissolved organic carbon (DOC), total organic carbon (TOC), and total suspended solids (TSS) (Joy, 2006).

Continuous low-level aquatic monitoring

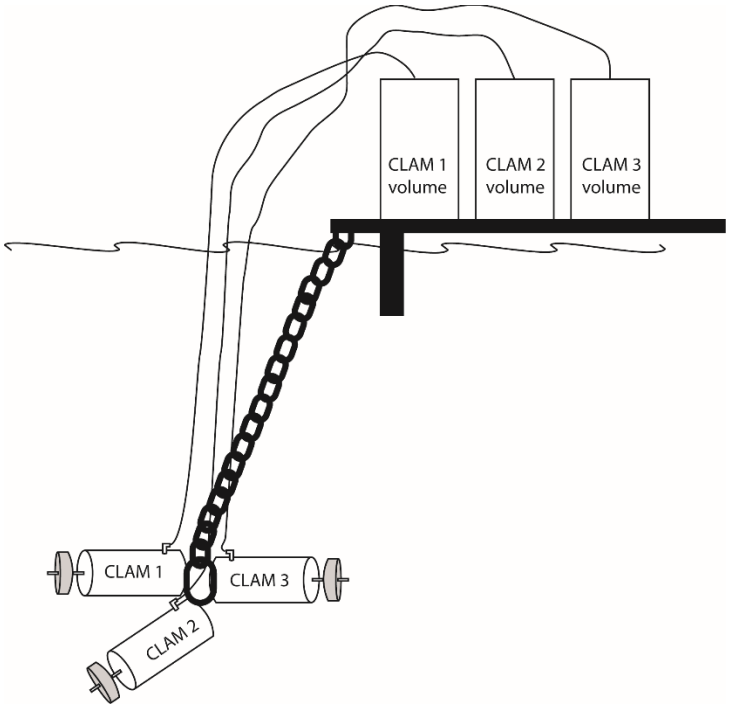

Figure 8: Schematic diagram of the deployment set-up for the C.L.A.M. devices.

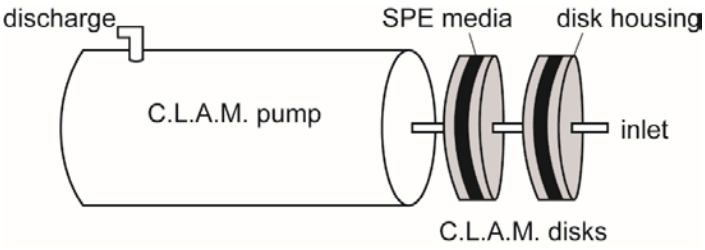

Figure 9: Schematic of the C.L.A.M. unit describing the individual parts.

The C.L.A.M.s will be deployed for a period of 24 to 36 hours. A complete description of the deployment and retrieval protocols is included in Appendix A. There is currently no SOP for these devices. The C.L.A.M. devices will be deployed in triplicate off the dock at a depth of approximately 2-3 m at the Spokane site (Figure 8). They will be deployed from the shore on concrete blocks in the Yakima River at a depth of approximately 0.5 m.

Recent work by our project team has shown that the previous housing surrounding the SPE media (C-18 media) has introduced PCBs at a concentration that interferes with detection of low-level environmental concentrations. In this project we will acquire stainless steel housing for the SPE media. Prior to the first sampling event, the housing and SPE media will be tested for blank contamination by the contract lab. In addition, recent improvements to the system also include adding a collection vessel to capture all the water sampled by the unit, which allows us to accurately measure the total volume sampled (Figure 8).

We will assess the retention and efficiency of the SPE media by using two disks back-to-back before the C.L.A.M. pump (Figure 9). The front disk will be spiked with labeled PCB congeners

(^{13}C-PCB-31, ^{13}C-PCB-95 and ^{13}C-PCB-153) at a known concentration to assess retention of PCBs. The second disk will be measured for the labeled congeners and comparison to all 209 congeners to assess the efficiency of the front disk to sample and retain PCBs. The contract lab will be responsible for cleaning the disk housing, conditioning the SPE media and shipping the disk ready for deployment into the field.

Centrifuge unit

The centrifuge unit was assembled in the late 1980s and has had limited use since that time. While there is no established SOP for the unit, Seiders (1990) compiled a detailed operations guide which is supplemental to the owner's manuals for the individual components. Furthermore, a detailed procedures list was compiled based on the work of Gries and Sloan (2009) (Lubliner, pers. comm.) (Appendix B).

The centrifuge unit is housed in a trailer and consists mainly of flow regulators and two flow-through centrifuges (Alpha Laval, Sedisamp II, Model 101L) (Figure 10). A generator powers the unit; however, modifications made during this project will allow us to plug the unit into a direct current outlet. External to the unit, the river water is supplied through a large groundwater pump (Grundfos SP4) which has a pump rate of approximately 20L/min. The pump will be deployed off the dock at the Spokane site and in the thalweg of the Yakima River, in the vicinity of the C.L.A.M. devices. Water is pumped through Teflon-lined tubing back to the centrifuge unit. Prior to entering the unit, the flow is split so that approximately 30% of the flow enters the

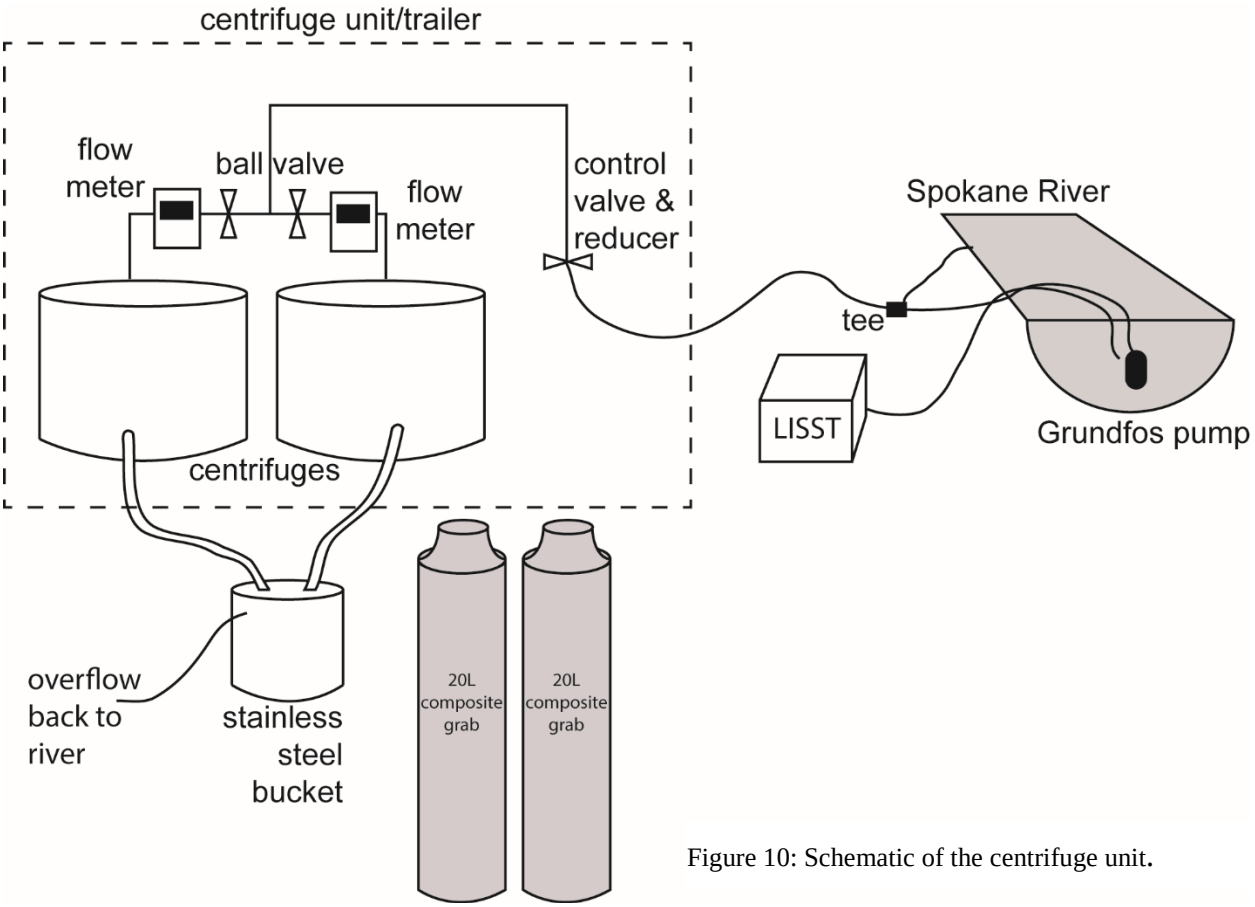

Figure 10: Schematic of the centrifuge unit.

unit. Once in the unit, flow is regulated through a series of ball and check valves to maintain a flow of 3 L/min to each centrifuge. This flow rate has been determined to be the optimal flow to maximize the efficiency of solids removal (Gries and Sloan, 2009). There will be an independent in-line optical flow meter on each inlet to the centrifuges (Figure 10). These flow meters will also record the total volume of water sampled by each centrifuge. Detailed protocols on centrifuge use and removal of solids can be found in Appendix B. Sediments accumulated in the centrifuges will be removed, combined, homogenized, and split into two replicates for analysis.

A separate pump will sample water from the same location and evaluate the sediment through a unit which uses Laser In-Situ Scattering and Transmissometry (LISST unit) to determine the grain size of suspended particles. We will run the LISST periodically throughout the sampling period to screen grain size distributions in a semi-quantitative manner over the course of the sampling. The goal of this supplementary data is to show the typical grain size being sampled in the centrifuges and to monitor any changes in grain size throughout sampling. The LISST unit will be calibrated and trialed in the lab prior to deployment in the field. No Ecology SOP exists for the LISST unit; however, we will receive guidance and training by Tom Gries (pers. comm.) who acquired the unit for Ecology and used it in a previous study (Gries and Sloan, 2009).

The filtrate water that is discharged from the centrifuges will pass through Teflon-lined tubing into a stainless steel container. Most of this water will overflow the container and be discharged back to the river. Over the period of sampling two large volume (20L) composite samples will be taken of the filtrate to be analyzed for PCBs and PBDEs. These samples will represent the 'dissolved' phase and will be processed by the lab in same way the whole water composite grab samples will be (see subsequent section).

Samples for TSS will be taken twice during the period of sampling to assess the efficiency of the centrifugation (influent and effluent samples). The efficiency is then calculated by:

$$\%\, efficiency = \frac{(TSS_{influent} - TSS_{effluent})}{TSS_{influent}} \times 100 \quad (1)$$

The decontamination of the centrifuge unit will follow guidelines already outlined by previous projects (e.g., Gries and Sloan, 2009) and the SOP for the decontamination of equipment (Friese, 2014). Prior to any field trials of the unit, the centrifuges, valves, and tubing will be thoroughly decontaminated. Following the initial decontamination, an equipment blank of laboratory-grade reagent water will be circulated through the centrifuge unit and sent to Manchester Environmental Lab (MEL) for analysis of PCB congeners. This will be repeated until no equipment contamination is confirmed. MEL's PCB congener analysis uses EPA method 8082 and has higher detection limits than EPA method 1668c which is used on the environmental samples. Budgetary constraints require us to use a less sensitive method on the initial equipment blanks, but it will provide an adequate level of detection during the initial stages of the project. After confirmation that no equipment is contaminated and before each sampling event an equipment blank will be collected using laboratory-grade reagent water from the contract lab.

Large volume composite grab samples

Concurrent with the C.L.A.M. and centrifugation sampling, we will be taking a large volume (20L) composite grab sample from the same sampling location. Three 5-part composite samples will be collected into 20L stainless steel canisters following established protocols (Joy, 2006). A dedicated cleaned and proofed transfer bottle will be used to collect the aliquot and split evenly between the three canisters. Aliquots will be collected by opening the transfer bottle under water in an effort to reduce atmospheric inputs. A transfer blank will be analyzed with the set of composites.

The canisters will be shipped to the contract lab for processing and analysis. Such large volume samples must be extracted using a pre-concentration technique. The samples will be 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 and efficiently binds organic chemicals from the sample water. The XAD-2 media is then eluted and the extract will be analyzed for PCBs, using method 1668c. This extraction procedure represents the dissolved phase PCBs.

8.2 Containers, preservation methods, holding times

Table 11: Sample containers, preservation, and holding times.

Parameter	Matrix	Container	Preservation	Holding Time
PCB congeners (GC/ECD)	Equipment Blank water	1 gallon glass jar w/ Teflon lid liner	Cool to 6°C	1 year
DOC	Surface Water	125 mL pre-acidified poly bottle	1:1 HCl to pH<2; Cool to 6°C	28 days
TOC		125 mL pre-acidified poly bottle	1:1 HCl to pH<2; Cool to 6°C	
TSS		1 L poly bottle	Cool to 6°C	7 days
PCB congeners (HRMS)		20 L canister	Cool to 6°C	1 year
PBDE congeners				
PCB congeners	C.L.A.M. SPE media	The self-contained C-18 SPE disks are sealed with luer-locks and placed in a tin foil pouch	Cool to 6°C	14 days
TOC	Suspended particulate matter	Certified 2-oz amber glass w/ Teflon lid liner	Cool to 6°C	14 days or 6 months frozen
PCB congeners (HRMS)		Certified 4-oz amber glass w/ Teflon lid liner	Transport at 6°C; can store frozen at -18°C	1 year extraction; 1 year analysis
PBDE congeners				

GC/ECD = gas chromatography / electron capture detector
HRMS = high resolution mass spectrometry
SPE = solid phase extraction media

8.3 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in SOP EAP070 (Parsons et al., 2012), *Minimizing the Spread of Invasive Species*. Our study areas are not considered to be of high concern.

8.4 Equipment decontamination

Decontamination of equipment will be particularly relevant to the centrifuge unit. Our approach to verifying decontamination was described in section 8.1. Teflon-lined tubing previously used in other projects will be used in this project. To clean the tubing properly, soapy water and solvent rinses will be carried out multiple times to ensure decontamination. This will be confirmed using an equipment blank prior to field deployment.

Proof of cleanliness of the compositing jars and 20-liter canisters for analysis of PCBs and PBDEs will be required from the contract laboratory.

C.L.A.M.s are clean and ready for use when they arrive from the contractor. Surface water is filtered through single-use SPE disks that are specifically cleaned as part of the conditioning process by the contract laboratory.

8.5 Sample ID

Laboratory sample IDs will be assigned by MEL and the contract lab.

8.6 Chain-of-custody, if required

Chain of custody will be maintained for all samples throughout the project.

8.7 Field log requirements

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date.

The following information will be recorded in the project field log:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Field instrument calibration procedures
- Field measurement results

- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

As previously described, training and field trials of the centrifuge unit and LISST particle analyzer will be carried out prior to field deployment.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

Field data will be measured using a MiniSonde multi-meter following guidance in SOP EAP033 – Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0 (Swanson, 2007).

Field parameters for the project include:

- Temperature
- pH
- Conductivity
- Dissolved Oxygen

9.2 Lab procedures table

Table 12: Measurement methods (laboratory).

Analyte	Sample Matrix	Samples	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Water samples						
Total Suspended Solids (mg L^{-1})	surface water	21	1 - 50	1	N/A	EPA 160.2
Total Organic Carbon (mg L^{-1})	surface water	6	1 - 20	1	N/A	SM 5310B
Dissolved Organic Carbon (mg L^{-1})	surface water	6	1 - 20	1	N/A	SM 5310B
PCB congeners (GC/ECD) (ng L^{-1})	blank water	3	1-2	3	EPA 8082	EPA 8082
SPE media						
PCB congeners (HRMS) (pg $sample^{-1}$)	SPE extract	24	0.5-50 per cong	0.5 pg per congener	DCM extraction; EPA 1668C	EPA 1668C
Large Volume - XAD resin						
PCB congeners (HRMS) (pg $sample^{-1}$)	XAD extract	21	0.5-50 per cong	1	EPA 1668C	EPA 1668C
PBDE congeners (pg $sample^{-1}$)	XAD extract	9	5-10,000 per cong	10-100	EPA 1614	EPA 1614
Sediments						
PCB congeners (HRMS) (ng Kg^{-1})	Sediments	6	0.5-1500 per cong	1	EPA 1668C	EPA 1668C
PBDE congeners (ng Kg^{-1})	Sediments	6	0.5-25000 per cong	10-100	EPA 1614	EPA 1614
Total organic carbon (%)	Sediments	6	1-15%	0.1%	PSEP TOC	PSEP TOC

GC/ECD = gas chromatography / electron capture detector
HRMS = high resolution mass spectrometry
SPE = solid phase extraction media
XAD = styrene and divinylbenzene polymer
DCM = dimethyl chloride extraction as per CIAgent protocol

9.3 Sample preparation method(s)

See Table 12.

9.4 Special method requirements

The selected contract lab will be required to have an in-house SOP for the extraction and quality control of the XAD-2 resin. They will be required to demonstrate experience and present previous quality control data on their setup. The lab will also be required to demonstrate they have an in-house system that can accommodate the evacuation and filtering of the 20L canisters.

The lab SOP will broadly reflect the following procedure. The evacuation of the stainless steel 20L canister should allow for almost no residual liquid or *dead volume* remaining in the vessel. The filter will be a 47mm in line quartz fiber filter and possibly a 50g sand pre-filter. A column of XAD-2 (60g) in 6" x 1" ID stainless steel trap. All of the media, including XAD-2 and quartz sand are controlled, ultra-clean materials. Following evacuation of the canister, 3-4 rinses using ultra-pure water will ensure no residual solids. This rinse water will be added to the sample. The insides of the stainless steel 20L canister and connecting tubing up to the XAD-2 trap will be rinsed three times with toluene and collected/combined with each sample.

The filter, the solids in the XAD-2 trap plus any solids from the optional sand filter are transferred for soxhlet extraction. The solids are spiked for each sample with PCB and PBDE extraction standards and a Dean-Stark soxhlet extraction is completed. A laboratory method blank and LCS are prepared and processed in the same manner as the samples using ultra-trace water. The LCS natives are spiked into the soxhlet timble at the same stage as the extraction standard spiking. The samples being analyzed for both PCBs and PBDE congeners will undergo co-extraction and then the analytes will be fractionated on cleanup columns for each method separately.

9.5 Lab(s) accredited for method(s)

Accreditation is required under the bid solicitation and request of qualifications for the laboratory contract.

10.0 Quality Control Procedures

10.1 Table of field and lab quality control (QC) required

Table 13. QC samples, types, and frequency.

Parameter	Field			Laboratory				
	Replicates	Transfer blank[a]	Equipment blank	Check Standards	Method Blanks	Matrix Spikes	OPR Standards	Duplicate
Water Samples								
TSS	1/batch	-	-	1/batch	1/batch	-	-	1/batch
TOC/DOC	1/batch	-	-	1/batch	1/batch	1/batch	-	1/batch
SPE Media								
PCB congeners	2/batch	-	3/project[c]	1/batch	1/batch	All samples	1/batch	1/batch
Large Volume - XAD resin								
PCB congeners	2/batch	1/batch	1/batch[b]	1/batch	1/batch	All samples	-	1/batch
PBDE congeners	2/batch	1/batch	1/batch[b]	1/batch	1/batch	All samples	-	1/batch
Sediments								
PCB congeners	1/batch	-	-	1/batch	1/batch	All samples	-	1/batch
PBDE congeners	1/batch	-	-	1/batch	1/batch	All samples	-	1/batch
TOC	1/batch	-	-	-	1/batch	-	-	1/batch

[a] transfer blank is relevant to the 20L composite grab sample

[b] equipment blank is run through the centrifuge trailer prior to sampling

[c] SPE media blanks are analyzed as batch QC for the media (3 total for the project)

batch = one sampling event and laboratory run

10.2 Corrective action processes

The laboratory analysts will document whether project data meets method QC criteria. Any departures from normal analytical methods will be documented by the laboratory and described in the data package from the laboratories and also in the final report for the project. If any samples do not meet QC criteria, the project manager will determine whether data should be re-analyzed, rejected, or used with appropriate qualification.

Field instruments will be checked and calibrated prior to the field. The post-field check of the instrument should be within the MQOs defined in Table 9. The appropriate qualification or rejection threshold is detailed in the MQOs.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs, initials, and date. Data will be transferred to Microsoft Excel for creating data tables. Statistical analysis will be completed in R and will consist of comparisons among the sampling approaches using an analysis of variance (ANOVA) with a Levene's test for equality of variance. Non-parametric methods, such as the Kruskal-Wallis test or one-way ANOVA on ranks, may also be used to analyze non-normally distributed data rather than transforming the data.

11.2 Laboratory data package requirements

The laboratory data package will be generated or overseen by MEL. MEL will provide a project data package that will include: a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in *Section 13.0 Data Verification*).

The following data qualifiers will be used:

- "J" – The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" – The analyte was not detected at or above the estimated reporting limit.
- "NJ" – The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" in the "Result Data Qualifier" column.
- No results are reported below the EDL.
- Only results reported are for those congeners that have a value at least FIVE times the signal-to-noise ratio, and that meet ion abundance ratios required by the method.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").
- Results that do not meet ion abundance ratio criteria are reported with "NJ". If an Estimated Maximum Possible Concentration (EMPC) value is calculated and reported, the calculation is explained in the narrative, and an example calculation used for this value is provided.
- Results that contain interference from polychlorinated diphenyl ethers (PCDEs) are qualified with "NJ".

11.3 Electronic transfer requirements

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. The contract lab will provide an electronic data deliverable (EDD) that meets the format defined by MEL.

11.4 Acceptance criteria for existing data

All existing data are stored in EIM and as such are acceptable for use as described under the data quality descriptions in EIM. Data generated by the C.L.A.M. devices continue to be viewed as estimates and are not acceptable for entry into EIM. Currently a data repository within the Ecology intranet exists for passive sampling and C.L.A.M. data.

11.5 EIM/STORET data upload procedures

All completed project data will be entered into Ecology's Environmental Information Management (EIM) database for availability to the public and interested parties, with the exception of the surface water data generated using C.L.A.M. Until standard operating procedures have been approved for the C.L.A.M., data will not be entered into EIM.

Data entered into EIM follow a formal data review process where data are reviewed by the project manager, the person entering the data, and an independent reviewer.

EIM can be accessed on Ecology's Internet homepage at www.ecy.wa.gov. The project will be searchable under Study ID WHOB003.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

No defined audit exists for the field work in this project. We will conduct a field trial with the centrifuge unit before we collect samples with the assistance of Tom Gries (pers. comm.) who has experience using the centrifuge unit. During sampling on the Spokane River, Brandee Era-Miller will be on-site to oversee the sampling protocols for grab sampling and C.L.A.M. use; she has experience in both these sampling approaches (Era-Miller, 2015).

The Ecology Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the laboratory is capable of providing accurate, defensible data. All assessments are available from Ecology upon request, including MEL's internal performance and audits.

12.2 Responsible personnel

The project manager will be responsible for all reporting.

12.3 Frequency and distribution of report

One final report will be written at the end of the project summarizing the assessment of both passive and active sampling techniques for low concentrations of toxics in surface waters. Presentation of the findings from this study will also be given to the Toxics Technical Coordination Team at one of their meetings. As part of this presentation a simple reference sheet will be compiled that summarizes the following characteristics of the sampling approach:

- Ease of deployment
- Analytical method necessary
- Analytical detection and reporting limits
- Cost of sampling and analysis
- Reproducibility
- Sensitivity (detection above background)

Accuracy is not included in the list of characteristics because we cannot reliably assess this.

12.4 Responsibility for reports

The report will be co-authored by William Hobbs and Melissa McCall.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The field assistant will review field notes once they are entered into Excel spreadsheets. Oversight will be provided by the project manager.

13.2 Lab data verification

As previously described, MEL will oversee the review and verification of all laboratory data packages. All data generated by the contract lab must be included in the final data package, including but not limited to: a text narrative; analytical result reports; analytical sequence (run) logs, chromatograms, spectra for all standards, environmental samples, batch QC samples, and preparation benchsheets. All of the necessary QA/QC documentation must be provided, including results from matrix spikes, replicates, and blanks.

13.3 Validation requirements, if necessary

It is expected that external data validation will not be necessary for this project.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

The project manager will determine if the project data are useable by assessing whether the data have met the MQOs outlined in Tables 8 and 9. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

14.2 Data analysis and presentation methods

No specific numerical analyses are necessary for this project

14.3 Treatment of non-detects

The handling of non-detects will be relevant to the summing of PCBs and PBDEs. Non-detect values (U, UJ) are assigned a value of zero for the summing process when the group of analytes being summed has both detected and non-detected results. Alternatively, for results with large numbers of non-detects, the Kaplan-Meier method can be used to compute the mean concentration that is then multiplied by the number of analytes (Helsel, 2012). This latter method was recently verified in an Ecology study on PCBs and found to give total PCB sums that were not significantly different from substitution methods (Coots, 2014). There is also a recent SOP for the analysis of non-detects using the above methods (Gries, 2016).

If qualified data comprise more than 10% of the total summed concentration, then the total concentration should be qualified. If qualified data make up less than 10% of the total summed concentration, the total should not be qualified. Data sums will be qualified with: “J” if that is the only qualifier used; with "NJ" if that is the only qualifier used; and "J" if there is a mix of "J" and "NJ" qualifiers. When all values for individual analytes in the group are reported as non-detects, and the reporting limits are different, the highest value present is assigned as the “total” value. The sum “total” will be qualified with: “U” if all values are qualified as U, “UJ” if all the values are qualified as UJ, and "U" if there is a mix of both U and UJ.

14.4 Sampling design evaluation

This study was designed to assess and compare three sampling approaches during a concurrent sampling event in two different rivers. One likely outcome of this project is to evaluate and suggest a method that best suits the needs of Ecology for assessing the ambient concentrations of toxics in surface waters of Washington State.

The number of sample replicates is the minimum required to evaluate the variability within each approach and among approaches. We will be able to test for significant difference among the results using a 3-sample one-way ANOVA. More replication would increase the power of this

comparison. However, it is likely that the results will be very similar and therefore the number of samples required to define a strong effects size will be very large, depending on the variability around each result.

If each of the approaches draw significantly different results, the current study design will not allow us to interpret the accuracy of the results. Laboratory studies would be the only way to determine true accuracy of the results.

14.5 Documentation of assessment

The final report will present the findings, interpretations, and recommendations from this study.

15.0 References

Personal Communication

Gries, Tom. Provided ongoing support on operation of the centrifuge trailer.

Lubliner, Brandi. Provided an updated detailed checklist for operation of the centrifuge trailer.

References

Birbaum, L.S. and D.F. Staskal, 2003. Brominated Flame Retardants: Cause for Concern? Environmental Health Perspectives. 112(1):9 – 17.

Coots, R., 2014. PCB Method Comparison of High and Low Resolution Sediment Analysis. Washington State Dept. of Ecology. Olympia, WA. Publication No. 14-03-009. https://fortress.wa.gov/ecy/publications/summarypages/1403009.html.

Ecology, 1995. Department of Ecology 1993-94 Investigation of PCBs in the Spokane River. Washington State Dept. of Ecology. Olympia, WA. Publication No. 95-310. https://fortress.wa.gov/ecy/publications/summarypages/95310.html.

Era-Miller, B., 2014. Technical Memo: Spokane River Toxics Sampling 2012-2013 – Surface Water, CLAM and Sediment Trap Results. Technical memo to Adriane Borgias, Washington State Department of Ecology, Water Quality Program, Eastern Regional Office, Spokane Washington from Brandee Era-Miller, Washington State Department of Ecology, Environmental Assessment Program. Memo dated May 30, 2014.

Era-Miller, B., 2015. Quality Assurance Project Plan: Spokane River PCBs and other Toxics Long Term Monitoring at the Spokane Tribal Boundary. Washington State Department of Ecology, Olympia, WA. Publication No. 15-03-111. https://fortress.wa.gov/ecy/publications/SummaryPages/1503111.html

Erickson, M., and R. Kaley, 2011. Applications of polychlorinated biphenyls. Environmental Science and Pollution Research. 18:135-151.

Friese, M., 2014. Standard Operating Procedure for Decontaminating Field Equipment for Sampling Toxics in the Environment. Washington State Department of Ecology, Olympia, WA. SOP Number EAP090. www.ecy.wa.gov/programs/eap/quality.html

Furl, C and C. Meredith, 2010. PBT Monitoring: PBDE Flame Retardants in Spokane River Fish, 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 10-03-015. https://fortress.wa.gov/ecy/publications/SummaryPages/1003015.html

Gries, T. and J. Sloan, 2009. Contaminant Loading to the Lower Duwamish Waterway from Suspended Sediment in the Green River. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-028. https://fortress.wa.gov/ecy/publications/SummaryPages/0903028.html

Gries, T., 2016. Standard Operating Procedures for Use of Non-detect Environmental Data, Version 2.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP093. www.ecy.wa.gov/programs/eap/quality.html

Hale, R.C., M. Alaee, J.B. Manchester-Neesvig, H.M. Stapleton, and M.G. Ikonomou, 2003. Polybrominated diphenyl ether flame retardants in the North American environment. Environment International. 29: 771-779

Helsel, D.R., 2012. Statistics for Censored Environmental Data Using Minitab and R, 2nd edition. John Wiley and Sons, New Jersey. p. 324.

Hobbs, W., 2014. Quality Assurance Project Plan: Pine Creek Toxaphene Source Assessment. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-107. https://fortress.wa.gov/ecy/publications/SummaryPages/1403107.html

Hobbs, W., 2015. Technical Memo: Review of National TMDL Approaches to Toxics. Technical memo to Melissa Gildersleeve, Washington State Department of Ecology, Water Quality Program. Memo dated August 21, 2015.

Hopkins, B., D. Clark, M. Schlender, and M. Stinson, 1985. Basic Water Monitoring Program Fish Tissue and Sediment Sampling for 1984. Washington State Department of Ecology, Olympia, WA. Publication No. 85-7.

Johnson, A., K. Carmack, B. Era-Miller, B. Lubliner, S. Golding, and R. Coots, 2010. Yakima River Pesticides and PCBs Total Maximum Daily Load, Volume 1: Water Quality Study Findings. Washington State Department of Ecology, Olympia, WA. Publication No. 10-03-018. https://fortress.wa.gov/ecy/publications/summarypages/1003018.html.

Joy, J., 2006. Standard Operating Procedure for Grab sampling – Fresh water, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. www.ecy.wa.gov/programs/eap/quality.html

Joy, J. and B. Patterson, 1997. A Suspended Sediment and DDT Total Maximum Daily Load Evaluation Report for the Yakima River. Washington State Department of Ecology, Olympia, WA. Publication No. 97-321. https://fortress.wa.gov/ecy/publications/SummaryPages/97321.html

Lorber, M. and D. Cleverly, 2010. An exposure assessment of polybrominated diphenyl ethers. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. EPA/600/R-08/086F.

Michelson, T., 1992. Organic Carbon Normalization of Sediment Data. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-032. https://fortress.wa.gov/ecy/publications/summarypages/0509050.html

Parsons, J., D. Hallock, K. Seiders, B. Ward, C. Coffin, E. Newell, C. Deligeannis, and K. Welch, 2012. Standard Operating Procedures to Minimize the Spread of Invasive Species. Washington State Department of Ecology, Olympia, WA. SOP Number EAP070. www.ecy.wa.gov/programs/eap/quality.html

Rinella, J.F., S.W. MacKenzie, and G.J. Fuhrer, 1992. Surface-water quality assessment of the Yakima River Basin, Washington: Analysis of available water quality data through 1985. U.S. Geological Survey Open-File Report: 91-453.

Sandvik, P. and K. Seiders, 2012. Washington State Toxics Monitoring Program: Evaluation of SPMDs for Trend Monitoring of PBTs in Washington Waters, 2010-2011. Washington State Department of Ecology, Olympia, WA. Publication No. 12-03-036. https://fortress.wa.gov/ecy/publications/SummaryPages/1203036.html

Seiders, K., 1990. Particulate Sampling System Operations Guide. Compliance Monitoring Section of Environmental Investigations and Laboratory Services Program, Washington State Department of Ecology. 39 pp.

Serdar, D., B. Lubliner, A. Johnson, and D. Norton, 2011. Spokane River PCB Source Assessment, 2003-2007. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-013. https://fortress.wa.gov/ecy/publications/summarypages/1103013.html.

Spokane County, 2011. Spokane River Watershed: Nonpoint Source Phosphorus Reduction Plan. Prepared by GeoEngineers, Hubbard Gray Consulting, and HDR Engineering Inc. 451 pp.

Swanson, T., 2007. Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/laws-rules/ecywac.html

Waitt Jr., R.B., 1977. Guidebook to the Quaternary Geology of the Columbia, Wenatchee, Peshastin, and Upper Yakima Valleys, West-Central Washington. US Geological Survey. Open-file Report 77-753.

16.0 Figures

The figures in this QAPP are inserted after they're first mentioned in the text.

17.0 Tables

The tables in this QAPP are inserted after they're first mentioned in the text.

18.0 Appendices

Appendix A. Continuous low-level aquatic monitoring

The continuous low-level aquatic monitoring (CLAM™) sampling device is a submersible, low-flow sampler that continuously and actively draws water through filtration and solid-phase extraction (SPE) media. The main supplier of the devices and the SPE disks used in this study is CIAgent (http://www.ciagent-stormwater.com). The pumps were commercially introduced in 2007, but the technology for SPE disks has been in laboratory use for the last 15 years under established EPA protocols (EPA3535A). Recent work by Coes et al. (2014) has documented the efficacy of CLAM devices when compared to both grab samples and passive samplers. Ecology has also begun using CLAM™ samplers on a more regular basis (Anderson and Sargeant, 2009; Coots, 2014; Hobbs, 2014); however, there is no established SOP and therefore the technique is still in trial.

Solid-Phase Extraction (SPE) Disks

The CLAM device is simply a vessel for the SPE disk, which binds organic contaminants as water is pumped through. The pore size of the disks is 1.5 micrometers. The SPE media is specific to the contaminant of interest. C-18 extraction media 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 PAHs). The hydrophilic/lipophilic balanced (HLB) media uses a modified styrene polymer to effectively bind polar and non-polar compounds. The HLB disk has been used to sample many different pesticides, pharmaceuticals, and emerging contaminants.

The manufacturer of the CLAM device has conducted a retention and depletion bench study of the pump and the SPE disks for non-polar compounds. They found that there was excellent retention of spiked PAH and pesticide compounds in the disks following 100L of flushing with de-ionized water (DI) (Aqualytical, 2014; available at http://www.ciagent-stormwater.com/documents/watermonitoring/RetentionandDepletionofIntegratedAnalytesintheCLAM.pdf). The manufacturers of the SPE media and the lab suppliers have also conducted many retention studies for a variety of compounds.

The disks themselves are not directly handled by the lab or the field personnel. Disks are ordered and come contained in a sealed HDPE filter case with lure-locks at either end. Before deployment, the disks require conditioning with solvent, which rids the disk of any possible residual contamination. A complete step-by-step procedure is outlined in the manufacturer's laboratory application notes available online (http://www.ciagent-stormwater.com/new-water-monitoring/). The disks are cleaned with 50ml of dichloromethane (DCM), conditioned with 50ml of methanol, and rinsed with 50ml of reagent quality DI water. Residual DI water is left in the disk to maintain the pore space in the glass pre-filter that has been established by the conditioning rinse. The disks are capped and placed back in the foil pouch for shipment to the field. Conditioned disks can be kept refrigerated for up to 30 days; unconditioned disks are stable for up to a year.

Deployment

The CLAM devices can be secured to suit the sample site. During deployment, the device must be carefully situated so that it does not obstruct the intake port. Typically in small streams the CLAM is positioned with the intake facing downstream and the device is suspended at 2/3 the channel depth. In a shallow stream U-shaped rebar can be hammered into the streambed and the device suspended horizontally. In a deeper stream or lake, a concrete block with a float attached by cable and positioned just below the water surface can be used as line to attach the CLAM to (Anderson and Sargeant, 2009).

Before deployment, the flow rate of the device is measured. The device is assembled and the battery pack is hooked up; this starts the internal pump. The device and extraction media are not compromised if the pump runs out of the water during set-up. A stainless steel bucket is filled with water from the site and the CLAM is placed in the bucket. Air is purged from the filter and then flow rate can be measured. A syringe is attached to the discharge port of the CLAM, with tubing, and the collected water volume is measured in the syringe and timed with a stopwatch. This procedure is repeated until the flow rate is consistent. The device can now be deployed and time of deployment recorded.

Recent additions to the CLAM system include a collection container in order to calculate the total volume pumped through the SPE media. This is nothing more than 30 gallon Rubbermaid container with luer-locks attaching the discharge tubing from the device.

Retrieval

The typical time of deployment for the CLAM is 12 to 36 hours. The device's battery pack limits the maximum time of deployment, and the water turbidity limits the minimum time of deployment. Suspended solids can slow flow rate by clogging the filter, ultimately stopping flow; this could result in a lost sample. Therefore, in turbid waters field personnel need to either return to the pump periodically to verify the pump is still running or deploy the pump for less time. There are no experimentally derived guidelines for time of deployment in turbid waters, since times vary dramatically with particle size and streamflow.

Before removing the device, personnel should take notes on its condition and exact time of retrieval. The flow rate of the CLAM is then measured as per the deployment. The total volume is measured from the collection container using a large graduated cylinder. This gives a precise measurement of the total volume pumped through the SPE media.

The CLAM is pulled from the water and disassembled at the site. The SPE disk is removed and placed back in the foil shipping pouch. The disks are placed in a cooler on ice until shipped directly to the lab. Refrigerated SPE disks have a holding time of 14 days.

Analysis

SPE disks are shipped directly to the lab, accompanied by a standard chain of custody form. SPE disks are generally considered "other" as a matrix description and not water samples. While there is not an established SOP for the CLAM-deployed SPEs, the contract lab should have an SOP for

large volume extraction in the lab using similar or the same media. Established preparatory procedures should be in place from previous projects using CLAM samplers.

To analyze the total contaminant concentration bound to the SPE media, the lab must completely elute the deployed disks into separatory funnels. The disks are first rinsed with acetone to remove any water from the disk and then rinsed with dichloromethane to elute the disk. Before the DCM is added, the disk is spiked with a surrogate for laboratory QC of the separatory funnel extraction. The sample is concentrated using micro-Kuderna-Danish distillation under an N2 atmosphere. The final extract volume is 1.0 mL. The extract is then run according to the methods pertaining to the contaminant of concern (e.g., GC/ECD in the case of toxaphene).

Data Calculations and Reporting

The final quantified concentration is derived from the mass of the compound per milliliter of extract. The concentration of the compound in the sampled water is then calculated, using the total volume of water pumped through the CLAM.

The following example illustrates this process. If the concentration of toxaphene in the extract is 5.05 ng ml^{-1}, and the final volume of extract was 2.0 ml, there is 10.1 ng of toxaphene in the sample. If 44.1 L of water were sampled, the concentration is therefore 0.23 ng L^{-1}. Currently, the derived water concentration is an estimate and should be qualified as such.

References

Anderson, P and D. Sargeant, 2009. Quality Assurance Project Plan: Skagit-Samish Watershed Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-120. https://fortress.wa.gov/ecy/publications/summarypages/0903120.html

Coes, A. L., Paretti, N. V., Foreman, W. T., Iverson, J. L., and Alvarez, D. A., 2014. Sampling trace organic compounds in water: A comparison of a continuous active sampler to continuous passive and discrete sampling methods. Science of the Total Environment, 473-474: 731-741.

Coots, R., 2014. PCB Method Comparison of High and Low Resolution Sediment Analysis. Washington State Department of Ecology. Olympia, WA. Publication No. 14-03-009. https://fortress.wa.gov/ecy/publications/summarypages/1403009.html

Appendix B. Details for operating flow-through centrifuge unit

This information was gathered through personal communication with Brandi Lubliner.

Pre-Use Checklists

- Check tire pressure.
- Check gas level for the generator – fill with unleaded gasoline without ethanol because ethanol gums up small engines such as generators.
- Start generator to see if it is running well.
- Clean centrifuge parts to study quality needs. This takes a whole day.

Centrifuge Generator Set-up

- At the back of the generator, turn yellow knob to vertical position to open up the gas flow to the generator engine.
- At the back of the generator, toggle the switch toward the "external fuel tank" writing. It will make a click when orientation is good (roughly 2 o'clock position).
- At the toe of the big red fuel tank by the generator, turn the white knob all the way open to allow gas flow to the generator.
- On the generator itself:
    - Pull the choke knob out.
    - Turn the start switch to turn it on.
    - Flip the toggle switch on the side of the generator that says "Fuel pump on."
    - Push choke back in after about 20 seconds.
    - Don't turn circuit breaker switch yet.

Power from the Circuit Breaker to the Trailer

- Plug in the large black plug (4-prong) into the plug below the circuit breaker box.
  Note: large black power cord coming out of the circuit breaker itself is just for extra power if needed to run instruments (3-prong one).
- Plug 4-prong plug into the face of the generator and flip the circuit breaker switch on face of generator.
- In the circuit breaker box, flip "main circuit breaker" switch to power the inside-the-trailer circuit breaker.
- Inside the centrifuge trailer, flip all the circuits up to power the lights and outlets.
- Light switch is on the wall (gray toggle).

Centrifuge bowl assembly

- Match numbers from the centrifuge spindle bases to the bowls.
- Put some of the Vaseline on the spindle.
- Brakes should be backed off to allow bowl to slide down the spindle, spin to make sure the bowl is seated (no sounds of catching) and that the bowl spins true and is not wobbly.
- Lock brakes by screwing pins (both in place).
- Put cone assembly in bowls and match the notches.
- Set the lid in next, match the notches, and place the o-ring in place.

- Screw the nut at the top of post to keep the bowls in place.
- Use crescent wrench to get it slightly snugger than "finger tight". Don't wrench it down.
- Unlock the brakes and spin bowl. Listen and look for spinning trueness.
- Relock the brakes.
- Put large locking ring on hand tight (reverse threaded), then grab large red locking ring wrench and rubber mallet.
- Align the two markings that look like this  by hitting the wrench with the mallet. They must be within a ¼ inch of alignment.
- Next set the small cone hood and small locking ring in place. It is reverse threaded also.
- Use the small red locking ring wrench (there is a small notch to grab the ring), and hand/body to tighten. Get it as tight as possible, but don't hammer.
- Unlock the brakes and spin bowl. Listen and look for spinning trueness.
- The hood manifold is next. They're interchangeable and don't need to match the numbers on the bowls. Line up the outlet tube to the hose to catch the exit water.
- Hook up the lines to plumb hoods to the incoming water. The compression fittings are fairly soft Teflon thread, so tighten carefully to not cross thread.
- Screw lug-nuts to hold down the manifold once the plumbing is connected. Hand tight is fine. You may need to check after several hours of operation to see if they've loosened.

Powering up the Centrifuges

- Once the bowls have been assembled, the centrifuge can be turned on. Plug the power cable into the outlet. Power up one bowl at a time to minimize the power draw on the generator. It takes about 3 minutes for the centrifuge to reach full power. Then turn second centrifuge on.
- Once the centrifuges are running, the oil globe will be opaque with frothy oil.
- Turn on the water source. Ideal sampling flow rate for the centrifuges is 6 liters per minute to the trailer when running both centrifuges (3L/min each).

While centrifuges are sampling

- Keep constantly aware of clogging on the plumbing board. The small diameter fittings clog easily on stormwater or highly turbid water. Flick all joints and turn on and off flow toggles to dislodge sediment. It is also a good idea to measure exit water flow rates at regular intervals or after disruptions.

Shutting down the Centrifuge

- Shut of the water source and wait until the bowls' exit water dries out.
- Pull the power plug. It takes about 5 minutes for the centrifuge to slow down.
- There is a breaking button, but just let the bowls slow down naturally.
- Unscrew all locking rings and spindle.
- Siphon off water into centrifuge jars or waste it, depending on how much sample you think you need.
- Use the "puller" to lift the bowls off the spindle.

Appendix C. Glossaries, acronyms, and abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

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.

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

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Existing uses: Those uses actually attained in fresh and marine waters on or after November 28, 1975, whether or not they are designated uses. Introduced species that are not native to Washington, and put-and-take fisheries comprised of non-self-replicating introduced native species, do not need to receive full support as an existing use.

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.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

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.

Thalweg: The deepest and fastest moving portion of a stream.

Total suspended solids (TSS): Portion of solids retained by a filter.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

C.L.A.M.	Continuous Low-level Aquatic Monitoring
DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others

MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SPE	Solid Phase Extraction
SPM	Suspended particulate matter
TOC	Total organic carbon
TSS	(See Glossary above)
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area

Units of Measurement

cfs	cubic feet per second
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
ug/Kg	micrograms per kilogram (parts per billion)
um	micrometer
ww	wet weight

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

Bias: The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean. (Kammin, 2010)

Data Integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

Data Quality Indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

Data Quality Objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.
(USEPA, 2006)

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

Measurement result: A value obtained by performing the procedure described in a method. (Ecology, 2004)

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of

an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all "parameters." (Kammin, 2010; Ecology, 2004)

Population: The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

Quality Assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

Quality Control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

Sample (statistical): A finite part or subset of a statistical population. (USEPA, 1997)

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split sample: A discrete sample that is further subdivided into portions, usually duplicates. (Kammin, 2010)

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

References for QA Glossary

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html

Kammin, B., 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia, WA.

USEPA, 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency. http://www.ecy.wa.gov/programs/eap/quality.html

USEPA, 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. U.S. Environmental Protection Agency. http://www.epa.gov/quality/qs-docs/g4-final.pdf

USGS, 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf