

### **Quality Assurance Project Plan**

Spokane River Toxics Fish Tissue and Preliminary Monitoring in Fiscal Year 2013 in Support of the Long-term Toxics Monitoring Strategy

January 2013 Publication No. 13-03-103

#### **Publication Information**

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

The plan for this study is available on Ecology's website at <u>https://fortress.wa.gov/ecy/publications/summarypages/1303103.html</u>

Ecology's Activity Tracker Code for this study is 12-027.

#### **Author and Contact Information**

Brandee Era-Miller P.O. Box 47600 Environmental Assessment Program Washington State Department of Ecology Olympia, WA 98504-7710

For more information contact: Communications Consultant, phone 360-407-6834.

Washington State Department of Ecology - <u>www.ecy.wa.gov/</u>

0	Headquarters, Olympia	360-407-6000
0	Northwest Regional Office, Bellevue	425-649-7000
0	Southwest Regional Office, Olympia	360-407-6300
0	Central Regional Office, Yakima	509-575-2490
0	Eastern Regional Office, Spokane	509-329-3400

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

If you need this document in a format for the visually impaired, call 360-407-6834. Persons with hearing loss can call 711 for Washington Relay Service. Persons with a speech disability can call 877- 833-6341.

### **Quality Assurance Project Plan**

### Spokane River Toxics Fish Tissue and Preliminary Monitoring in Fiscal Year 2013 in Support of the Long-term Toxics Monitoring Strategy

January 2013

#### Approved by:

Signature:	Date: January 2013
Adriane Borgias, Client, Water Quality Program, Eastern Regional Office	
Signature:	Date: January 2013
David T. Knight, Client's Unit Supervisor, Water Quality Program, Eastern Regional Office	
Signature:	Date: January 2013
Jim Bellatty, Client's Section Manager, Water Quality Program, Eastern Regional Office	
Signature:	Date: January 2013
Brandee Era-Miller, Author / Project Manager, EAP	
Signature:	Date: January 2013
Dale Norton, Author's Unit Supervisor, EAP	
Signature:	Date: January 2013
Will Kendra, Author's Section Manager, EAP	
Signature:	Date: January 2013
Thomas Mackie, Section Manager for Project Study Area, EAP	
Signature:	Date: January 2013
Joel Bird, Director, Manchester Environmental Laboratory	
Signature:	Date: January 2013
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

## **Table of Contents**

Pag	<u>se</u>
List of Figures and Tables	.3
Abstract	.4
Background Study Area	
Project Description	.6
Organization and Schedule	.7
Quality Objectives	.8
Sampling Process Design (Experimental Design)1 Surface Water	11 11 12
Sampling Procedures	14 16 17
Measurement Procedures	
Quality Control Procedures	24
Data Management Procedures	26
Audits and Reports	26
Data Verification	27
Data Quality (Usability) Assessment	27
References	27
Appendices	30

# List of Figures and Tables

### Figures

Figure 1.	CLAM Monitoring Plan for Spokane River, October 201216
Figure 2.	Schematic of Sediment Trap Design and Deployment Configuration (Norton,
	1996)

#### **Tables**

Table 1.	WRIA and HUC Numbers for the Spokane River Study Area	5
Table 2.	Organization of Project Staff and Responsibilities	7
Table 3.	Proposed Schedule for Completing Field and Laboratory Work and Reports	8
Table 4.	Measurement Quality Objectives for Toxics Parameters.	9
Table 5.	Sampling Design for Spokane Toxics in FY13.	10
Table 6.	Fish Composite Samples for PCB Aroclor Analysis	13
Table 7.	Sample Containers, Preservations, and Holding Times	15
Table 8.	Parameters, Reporting Limits, Expected Concentrations and Analytical Methods.	21
Table 9.	Funding for the Spokane River Toxics FY13 Project	22
Table 10	. Estimated Laboratory Analysis Budget for the Spokane River Toxics FY13 Project <sup>†</sup>	23
Table 11	. Field Quality Control Samples.	24
Table 12	. Laboratory Quality Control Samples.	25

### Abstract

The Department of Ecology's Environmental Assessment Program, Toxics Studies Unit (TSU) will conduct a comprehensive survey of toxics in fish tissue and limited preliminary sampling of toxics in surface water and suspended particulates in the Spokane River. The study will take place during the fall of 2012 and spring of 2013. The purpose of the fish tissue survey will be to assess for long-term trends in toxics chemicals present in the river. Preliminary sampling will aid in the development of a long-term monitoring plan for toxics the Spokane River.

Toxic chemicals to be sampled include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans (PCDD/Fs) and metals (arsenic, cadmium, lead, mercury and zinc).

### Background

The Spokane River contains elevated levels of a number of toxic chemicals including: polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans and metals. These contaminants are prevalent in water, sediment, and fish tissue. Numerous studies and clean-up activities to address contamination are ongoing in the Spokane River watershed.

The Washington State Department of Ecology (Ecology) recently entered into a Memorandum of Understanding to establish a Spokane River Regional Toxics Task Force (SRRTTF). Participants on the task force include representatives of Ecology, Spokane Regional Health District, Washington State Department of Health, Spokane County, the City of Spokane, the Liberty Lake Sewer and Water District, Inland Empire Paper Co., Kaiser Aluminum Washington, the Spokane Riverkeeper, the Lands Council, and the Lake Spokane Association. The US Environmental Protection Agency and Avista Corporation have signed letters of support and have an advisory role. The Idaho Department of Environmental Quality, Spokane Tribe of Indians, and Coeur d'Alene Tribe are also advisors to the Task Force.

The mission of this regional task force is to work collaboratively to characterize the sources of toxics in the Spokane River and identify and implement appropriate actions needed to make measurable progress towards meeting applicable water quality standards. Applicable standards include those promulgated by the State of Washington, State of Idaho, and the Spokane Tribe of Indians.

To assist the regional task force in accomplishing their mission, Ecology's Environmental Assessment (EA) Program – Toxics Studies Unit (TSU) recently drafted recommendations for a long-term monitoring plan for toxics in the Spokane River (Era-Miller, 2012). These recommendations describe a multiple line of evidence approach to long-term monitoring that focuses on several different environmental matrices including surface water, bottom sediments, suspended particulates, fish tissue and osprey eggs.

Recommendations also include a plan for some preliminary monitoring to be conducted during the fall of 2012 and spring of 2013 to aid in designing a long-term monitoring program for the mainstem Spokane River. The preliminary monitoring does not include all the environmental matrices recommended for the long-term plan, but focuses on limited monitoring of surface water and suspended particulates. Also included is a comprehensive survey of fish tissue.

Monitoring to be conducted in 2012 and 2013 is described in this Quality Assurance (QA) Project Plan.

### **Study Area**

The Spokane River begins in northern Idaho at the outlet of Lake Coeur d'Alene and flows west 112 miles to the Columbia River. Major tributaries to the river include the Little Spokane River, Latah Creek, Deep Creek, and Chamokane Creek. The current study will focus on the mainstem Spokane River from the state boundary with Idaho (river mile 96) to just downstream of the last dam on the Spokane River, Little Falls Dam (river mile 20). The mainstem of a river is the primary segment of the river, excluding any tributaries.

A map of the study area is shown in Appendix A, Figure A-1.

# Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area

The WRIAs and HUCs for the Spokane River study area are listed in Table 1. The Little Spokane River and Latah Creek have their own WRIAs and HUCs; however these tributaries are not a part of the current study.

WRIA Number	HUC Code	Description				
54	17010307	Lower Spokane River – mouth to the City of Spokane				
57	17010305	Upper Spokane River – upstream of the City of Spokane				
WRIAs as	WRIAs and HUCs bordering the study area					
55	17010308	Little Spokane River				
56	17010306	Latah Creek				

Table 1.	WRIA an	d HUC Numbe	rs for the Spol	kane River Study	y Area.
----------	---------	-------------	-----------------	------------------	---------

### **Project Description**

Long-term environmental toxics monitoring in the Spokane River will focus on the mainstem of the river, while at the same time numerous other efforts will focus on source identification and control. Toxics monitoring to be conducted during the fall of 2012 and spring of 2013 will aid in designing a long-term monitoring program for the mainstem Spokane River. The mainstem is the primary segment of the Spokane River, excluding any tributaries.

Toxics monitoring during the fall of 2012 and spring of 2013 will include a comprehensive survey of toxics in fish tissue and some limited preliminary sampling of toxics in surface water and suspended particulates. A new sampling technology called Continuous Low-Level Aquatic Monitoring (CLAM) will be used in addition to direct surface water sampling. The CLAM is a pre-concentration collection method for water that should allow for much lower (up to 100 times lower) detection limits than with direct analysis of surface water. Suspended particulates will be collected with sediment traps deployed in the water column for several months.

The fish tissue monitoring will be included as part of the Washington State Toxics Monitoring Program (WSTMP) Long Term Trends effort. The WSTMP will lead the fish tissue monitoring with the goal of developing a baseline program for detecting long-term trends for toxics in fish in the Spokane River. The fish tissue monitoring will also meet the needs of the Washington State Department of Health (DOH) to review and potentially update the current fish consumption advisories on the Spokane River.

Preliminary sampling of toxics in surface water and suspended particulates is not intended to represent comprehensive monitoring. Instead, it is designed to test different sample collection methods and analytical reporting limits. The goal of collecting this preliminary data is to help Ecology, SRRTTF, and other entities design future monitoring plans for toxic chemicals in the Spokane River. A separate Quality Assurance (QA) Project Plan will be prepared to describe Ecology's long-term monitoring effort in the mainstem of the Spokane River.

For purposes of this study, "toxics" is defined as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins/furans (PCDD/Fs) and metals (arsenic, cadmium, lead, and zinc) unless otherwise specified.

# **Organization and Schedule**

Table 2 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 3 presents the proposed schedule for this project.

Staff (all are EAP except client)	Title	Responsibilities			
Adriane Borgias Water Quality Program Eastern Regional Office Phone: 509-329-3515	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.			
Brandee Era-Miller Toxics Studies Unit Statewide Coordination Section Phone: 360-407-6771	Project Manager/Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft technical memo and final technical memo.			
Dale Norton Toxics Studies Unit Statewide Coordination Section Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.			
Will Kendra Statewide Coordination Section Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.			
Thomas Mackie Eastern Operations Section Phone: 509-454-4244	EAP 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	Approves the final QAPP.			
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Approves the draft QAPP and the final QAPP.			

Table 2.	Organization	of Project Staff and Responsibilit	ies.
10010 -			

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

Field and laboratory work	Due date	Lead staff	
Field work completed	May 2013	Brandee Era-Miller	
Laboratory analyses completed	July 2013		
Environmental Information System (EIM)	database		
EIM user study ID*	BERA0009 (surface	water & particulates only)	
Product	Due date	Lead staff	
EIM data loaded	September 2013	Brandee Era-Miller	
EIM quality assurance	October 2013	Paul Anderson	
EIM complete	November 2013 Brandee Era-Miller		
Final Technical Memo			
Author lead / Support staff	Brandee Era-Miller		
Schedule			
Draft due to supervisor	August 2013		
Draft due to client/peer reviewer	September 2013		
Draft due to external reviewer(s)	October 2013		
Final due	December 2013		

Table 3. Proposed Schedule for Completing Field and Laboratory Work and Reports.

\*Fish tissue data will be entered into EIM under the Washington State Toxics Monitoring Program (WSTMP). The EIM user study ID for the fish tissue data will be WSTMP12. Continuous Low-Level Aquatic Monitoring (CLAM) data will not be entered into EIM.

## **Quality Objectives**

Quality objectives for this project are to obtain data of sufficient quality to minimize uncertainty. For fish tissue data, the objective is to produce results comparable to data from past, present, and future studies on the Spokane River. For preliminary monitoring using continuous low-level aquatic monitoring (CLAM) samplers, the objective is also to produce enough field duplicate data and laboratory quality assurance (QA) data to evaluate the precision and accuracy of the collection method and analytical methods for this new technology.

These quality objectives will be achieved by carefully following the *Sampling Procedures* and *Quality Control Procedures* described in this QA Project Plan. This plan was written following the guidance document: *Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies* (Lombard, S. and C. Kirchmer, 2004).

Ecology's Manchester Environmental Laboratory (MEL) and laboratories contracted by MEL for analysis of project samples are expected to meet the measurement quality objectives (MQOs) selected for the project. The MQOs that will be used for the project are shown in Table 4.

Parameter	Analytical Method	Lab Control Samples (% Recovery)	Duplicate samples (RPD)	Matrix Spike (% Recovery)	Matrix Spike Duplicates (RPD)	Surrogate Recoveries (% Recovery)
Water						
TOC & DOC	SM 5310B	80 - 120	≤20%	75 – 125	20%	NA
TSS	SM 2540D	80 - 120	≤20%	NA	NA	NA
PCB congeners	EPA 1668C	$50 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a}$
PBDEs – HR	EPA 1614	$50 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a,b}$
CLAM						
PCB congeners	EPA 1668C	$50 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a}$
PCB Aroclors	EPA 8082	50 - 150	≤40%	50 - 150	40%	50 - 150
PBDEs – HR	EPA 1614	$50 - 150^{\dagger}$	≤50%	NA	NA	25 - 150 <sup>a,b</sup>
PBDEs – LR	EPA 8270	$40 - 175^{\circ}$	≤40%	$40 - 175^{\circ}$	≤40%	10 - 130
PCDD/Fs	EPA 1613	$25 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a}$
Particulates						
% Solids	SM 2540G	NA	≤20%	NA	NA	NA
TOC	PSEP – TOC	80 - 120	≤20%	NA	NA	NA
Cd, Pb, & Zn	EPA 200.7/8	85 - 115	≤20%	75 – 125	20%	NA
PCB congeners	EPA 1668C	$50 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a}$
PBDEs – HR	EPA 1614	$50 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a,b}$
PCDD/Fs	EPA 1613	$25 - 150^{\dagger}$	≤50%	NA	NA	$25 - 150^{a}$
Fish						
	MEL SOP 730009	NA	≤20%	NA	NA	NA
As, Cd, Pb, & Zn	EPA 200.7/8	85 - 115	≤20%	75 – 125	20%	NA
Hg	EPA 245.6	80 - 120	≤20%	75 – 125	20%	NA
PCB Aroclors	EPA 8082	50 - 150	≤40%	50 - 150	40%	50 - 150
PCB congeners	EPA 1668C	compound specific <sup><math>\dagger</math></sup>	≤50%	NA	NA	$25 - 150^{a}$
PBDEs – LR	EPA 8270	50 - 150	≤40%	50 - 150	40%	50 - 150
PCDD/Fs	EPA 1613	compound specific <sup>†</sup>	≤50%	NA	NA	$25 - 150^{a}$

Table 4. Measurement Quality Objectives for Toxics Parameters.

CLAM: Continuous Low-Level Aquatic Monitoring device

HR: high resolution (isotopic dilution) methods

LR: low resolution methods

EPA: the Environmental Protection Agency

SM: Standard Methods

PSEP: Puget Sound Estuary Protocols

MEL SOP: Manchester Environmental Laboratory Standard Operating Procedure

RPD: relative percent difference

TOC: total organic carbon

DOC: dissolved organic carbon

PCDD/Fs: dioxins and furans

<sup>†</sup> Per Method for Ongoing Precision and Recovery (OPR), internal standards, and labeled compounds

<sup>a</sup> labeled congeners; <sup>b</sup> BDE 209 recovery of 20 – 200%;

<sup>c</sup> BDE 191 and 209 LCS recovery of 40 – 225%

# **Sampling Process Design (Experimental Design)**

The design for toxics monitoring in the Spokane River is shown in Table 5. Monitoring includes a comprehensive fish tissue study and preliminary sampling of surface water and particulates using several collection methods.

Monitoring Component	Toxics Parameters Analyzed	Analytical Method	Monitoring Sites	Collection Dates	
Surface	PCB Congeners	EPA 1668C	Stateline, Upriver Dam, Above Latah,	October 23-25, 2012 and again	
Water	PBDEs (high resolution)	EPA 1614	Ninemile Dam, and Above Chamokane	in May 2013	
	PCBs Aroclors	EPA 8082			
	PCB Congeners	EPA 1668C			
CLAM	PBDEs (low resolution)	EPA 8270	Upriver Dam and Ninemile Dam	October 23-25, 2012	
	PBDEs (high resolution)	EPA 1614			
	PCDD/Fs	EPA 1613B			
	PCB Congeners	EPA 1668C		October 2012 – April 2013 (deployment period)	
Dentionaleter	PBDEs (high resolution)	EPA 1614	Upriver Dam and		
Particulates	PCDD/Fs	EPA 1613B	Ninemile Dam		
	Cadmium, Lead, and Zinc	EPA 200.7/8			
	PCBs Aroclors	EPA 8082	a		
	PCB Congeners	EPA 1668C	Stateline, Upriver, Mission Park,		
	PBDEs (low resolution)	EPA 8270	Ninemile, Upper Lake	September 17 –	
Fish	PCDD/Fs	EPA 1613	Spokane, Little Falls Pool, and below Little	October 12, 2012	
	Arsenic, Cadmium, Lead, and Zinc	EPA 200.7/8	Falls	2012	
	Mercury	EPA 245.6			

Table 5. Sampling Design for Spokane Toxics in FY13.

CLAM: Continuous Low-Level Aquatic Monitoring device EPA: Environmental Protection Agency

Figures showing the Washington portion of the Spokane River (from the state border with Idaho to the confluence with the Columbia River) and select river sections for the FY13 toxics monitoring effort are located in Appendix A.

#### **Surface Water**

Surface water from the Spokane River will be collected at 5 locations from the Idaho-Washington border downstream to below Little Falls Dam. Surface water samples will be collected once during the low-flow season and again during spring high flows. Seasonal sampling will attempt to represent differences in water quality conditions between low and high flows.

The main objective of the surface water sampling is to test the detection limits of current high resolution methods for PBDEs (EPA 1614) and PCBs (EPA 1668C). Very little direct surface water data exists for toxics in the Spokane River. Some data does exist for calculated methods such as through semi-permeable membrane devices (SPMDs), but this data represents modeled estimates of dissolved concentrations only. The reason that very little direct water data exists for the Spokane River is that historically the concentrations of many organic toxic chemicals such as PCBs have been too low in surface water to detect with available analytical methods.

Detection limits have greatly improved for high resolution methods in recent years. One recent example of detecting organics in surface water is the Puget Sound Toxics Loading Analysis where, as part of the loading analysis, a study was conducted to measure PCBs and PBDEs in whole water samples from major rivers in the Puget Sound Watershed (Gries and Osterberg, 2011). Gries and Osterberg found that PCB congeners were detected 100% of the time (n = 15) and total PBDEs were detected 47% of the time in surface water.

Two of the Spokane River surface water sampling locations, Ninemile Dam and Upriver Dam, will also be sampled using CLAM samplers. This will allow for comparisons of results from direct analysis of surface waters (composite sample collected twice in 24 hours) and the CLAMs, which will be deployed during the same 24-hour period.

Dioxins/furans will not be analyzed in whole water as they are less likely to be detected than PCBs and PBDEs. Dioxins/furans will be analyzed in CLAM and particulate samples. Metals are routinely monitored for and detected in Spokane River surface waters, so they do not need to be analyzed as part of this preliminary monitoring plan. Metals will be analyzed in particulate samples.

#### CLAM

The CLAM is a pre-concentration collection method for water that should allow for much lower (up to 100 times lower) detection limits than direct analysis of surface water samples. This is because the CLAM can filter up to 100 liters of surface water through an SPE (solid phase extraction) disk over a 24 - 28 hour deployment period. More information on CLAM technology can be found at the manufacturer's website:

http://www.ciagent-stormwater.com/products/water-monitoring/.

The objectives for using the CLAM technology are as follows:

- Test the precision and reproducibility of high resolution analyses for PBDEs, PCBs, and dioxins/furans and low-resolution methods for PBDEs and PCBs using CLAM. This will be achieved by analyzing numerous field duplicates and conducting laboratory QA.
- Compare between results from direct surface water collection and CLAM for PBDEs and PCBs, especially if some analytes are not detected with direct surface water collection.
- Receive preliminary indications on the fraction of PCBs that are dissolved versus total. This will be done by using a pre-filter on a few of the SPE disks. Sample disks both with and without a pre-filter will then be analyzed for PCB congeners.

### **Particulates**

Sediment traps will be deployed in the reservoirs behind Upriver Dam and Ninemile Dam in order to collect suspended particulates over an extended period of time. Total suspended solids (TSS) are generally very low in the Spokane River, so it is anticipated that up to 6 months of deployment time may be needed to accumulate enough material for analysis of PCBs, PBDEs, dioxins/furans and metals. The purpose of this sampling is to determine how long it will take to collect sufficient material to conduct the planned analysis.

Two traps (each holding 2 collection cylinders) will be deployed in each reservoir, for a total of 4 cylinders in each reservoir. One trap will be placed closer to the right bank and one will be placed closer to the left bank of the reservoirs. Several factors support this design:

- With low sediment rates, more cylinders means more material can be collected.
- There is a back-up sampler in case something happens to one of the traps.
- Coverage of the left and right banks is more representative as the hydrology likely varies between the two sides of each reservoir.

The sediment trap cylinders will be swapped out after 2-3 months of deployment (by mid-January 2013). New cylinders will then be deployed for another 2-3 months. This will allow for sedimentation rates to be calculated for the 2 separate deployment periods. Traps will be removed from the reservoirs before spring runoff (by early April 2013).

#### Fish

Fish tissue monitoring for toxics in the Spokane River in fall of 2012 will be a comprehensive effort, with funding and support from several different entities both within and outside of Ecology. Ecology's Washington State Toxics Monitoring Program (WSTMP) has adopted the Spokane River as one of their long-term trend monitoring sites. They intend to re-visit the Spokane River every 5 years for toxics monitoring.

Collection of fish for the 2012 effort in the Spokane River will follow procedures outlined in the current WSTMP QA project plan (Seiders, 2002). WSTMP will update the QA project plan which will include a description of the long-term trend monitoring for toxics in the Spokane River.

The major objectives for fish tissue monitoring are to:

- Assess long-term trends for PCBs in fish throughout the Spokane River, comparing to current historical data and also creating a baseline for future monitoring efforts. Largescale suckers, analyzed as whole body, will be the main species used for long-term trends as they are present in almost every section of the river and much historical data has been collected on them. Mountain Whitefish (analyzed as fillet) will be used as a supporting species for trends.
- Provide data to support a review by the Washington State Department of Health (DOH) for them to determine if any updates are needed for the current fish consumption advisories.

Other objectives are to:

- Work with the Spokane Tribe of Indians, the SRRTTF, and other interested entities to best meet everyone's needs for fish tissue data.
- Create a list of archived samples from the current effort and share the list with interested entities, so that samples can have additional analysis if additional funding becomes available.

Fish will be collected from 7 river reaches as listed in Table 6. Historical data exists for all of these locations. In 2005 Ecology conducted a large fish study for PBDEs, PCBs, and metals in the Spokane River (Serdar and Johnson, 2006). The 2005 study overlaps with all but the 2 most downstream monitoring reaches in the current study: Little Falls Pool and Below Little Falls Pool.

	Dimor	Bottom Fish	Sport Fish		
River Reach	River Mile	LSS	MWF	RBT	NPM
		Numbers of Comp		osite <sup>†</sup> Samples	
Stateline	95 – 96	5			
Plante Ferry	81 - 86	7		3	
Mission Park	75 – 77	7	5	3	
Ninemile	60-64	7	5	3	
Upper Lake Spokane	52 - 56	7	5		
Little Falls Pool	32 - 34	5			3
Below Little Falls	20 - 29	5	TBD	TBD	TBD

Table 6. Fish Composite Samples for PCB Aroclor Analysis.

<sup>†</sup> Composite samples consist of 3-5 individual fish per composite.

LSS: Largescale suckers

MWF: Mountain whitefish

NPM: Northern Pike Minnow

TBD: to be determined; collection by the Spokane Tribe of Indians

**RBT:** Rainbow trout

Table 6 shows the tentative analysis plan for PCB Aroclors in fish. Analyzing for PCB Aroclors meets the needs for both determining long-term trends for PCBs in the Spokane River as well as providing PCB toxicity information to DOH. PCB Aroclor analysis is significantly more affordable than PCB congener analysis. This allows for more samples to be analyzed which, in turn, improves statistical comparisons when determining trends, i.e., greater statistical power.

Most of the samples will also be analyzed for PBDEs and metals (cadmium, lead, and zinc). Subsets of the samples will be analyzed for PCB congeners, dioxins/furans, and mercury. As mentioned previously, archive samples will be available for future analysis if funding becomes available. If the budget allows, Ecology researchers will plan to analyze all samples for PCB congeners.

The final sample and analysis plan will be decided after these steps are completed:

- All fish have been collected.
- Fish size data have been reviewed.
- The laboratory contract for PCB congeners and dioxins/furans has been awarded and analysis costs determined.
- Interested parties have had a chance to comment.

### **Sampling Procedures**

All field data will be recorded on field data sheets prepared specifically for the study. Coordinates for each monitoring location will be recorded using a global positioning system (GPS) following Ecology's Standard Operating Procedure (SOP) EAP013 – *Standard Operating Procedure for Determining Coordinates via Hand-Held GPS Receivers*, Version 1.0 (Janisch, 2006).

#### **Surface Water**

Surface water samples will be collected as whole water composite grabs following SOP EAP015 – *Standard Operation Procedure for Manually Obtaining Surface Water Samples, Version 1.0* (Joy, 2006). A 1-liter glass jar, certified organics-free, will be used to collect subsamples for each composite sample. Half of the sample will be collected and stored on ice in a cooler and the second half of the sample will be collected approximately 24 hours later.

Sampling containers, preservation, and holding times are shown in Table 7. Information for analyses being conducted at MEL was adapted from the Manchester Laboratory User's Manual and through conversations with MEL and the contract laboratories (MEL, 2008).

Temperature, pH, and conductivity will be measured at the time of each composite grab sample with a Hydrolab MiniSonde® meter following SOP EAP033 – *Standard Operating Procedure for Hydrolab*® *DataSonde*® *and MiniSonde*® *Multiprobes, Version 1.0* (Swanson, 2007).

Whole water collections at Ninemile and Upriver Dams will coincide with deployment and retrieval of CLAM samplers at those sites.

Parameter	Matrix	Container	Preservation	Holding Time	
DOC		60 mL poly bottle; 0.45 um pore size filters	Filter in field with 0.45um pore size filter; 1:1 HCl to pH<2;Cool to 4°C	28 days	
TOC	Water	60 mL poly bottle	1:1 HCl to pH<2; Cool to 4°C		
TSS		1 L poly bottle		7 days	
PCB congeners		2 - 1 L amber glass bottles	Cool to 4°C	1 year	
PBDEs – HR		(certified)		•	
PCB congeners PCB Aroclors PBDEs – HR PBDEs – LR PCDD/Fs	CLAM	The self-contained C-18 SPE disks are placed in amber plastic bags provided by the manufacturer	Cool to 4°C	14 days	
Percent Solids		From same jar as particulate organics (4-oz jar)	Cool to 4°C	7 days or 6 months frozen	
TOC		Certified 2-oz amber glass w/ Teflon lid liner		14 days or 6 months frozen	
Cd, Pb, & Zn	Particulates			6 months or 2 years frozen	
PCB congeners PBDEs – HR PCDD/Fs		Certified 4-oz amber glass w/ Teflon lid liner	Transport at 4°C; can store frozen at -18°C	1 year extraction; 1 year analysis	
Lipids		From same jar as fish tissue metals (4-oz jar)	Transport at 4°C; can store	1 year extraction; 14 days analysis	
As, Cd, Pb, & Zn		Certified 4-oz amber glass w/ Teflon lid liner	frozen at -18°C	6 months cold or 2 years frozen	
Hg	Fish	Certified 2-oz amber glass w/ Teflon lid liner	Cool to 4°C	28 days	
PCB Aroclors PCB congeners PBDEs – LR PCDD/Fs		Certified 4-oz amber glass w/ Teflon lid liner	Transport at 4°C; can store frozen at -18°C	1 year extraction; 1 year analysis	

Table 7. Sample Containers, Preservations, and Holding Times.

CLAM: Continuous Low-Level Aquatic Monitoring device

SPE: Solid Phase Extraction

HR: high resolution (isotopic dilution) methods (EPA 1614 for PBDEs)

LR: low resolution methods (EPA 8270 for PBDEs)

#### CLAM

CLAM samplers will be deployed twice as back-to back deployments, first at 1 location (Ninemile Dam) then at 2 locations (Ninemile Dam and Upriver Dam) in the Spokane River as shown in Figure 1. Each deployment will last approximately 24 - 28 hours.

Figure 1. CLAM Monitoring Plan for Spokane River, October 2012.

Deploy	yment # 1 (October 23 - 24)		
Monit	oring Site # 1		
0	PCB congeners (PRL)		
0	PCB congeners (PRL)		
0	PCB congeners (PRL)		
0	PCBa/PBDEs (MEL)		
0	PCBa/PBDEs (MEL)		
0	PCBa/PBDEs (MEL)		
Deploy	yment # 2 (October 24 - 25)		
Monit	oring Site # 1	Monit	oring Site # 2
0	PCBs/PBDEs/dioxins (PRL)	0	PCBs/PBDEs/dioxins (PRL)
0	PCBs/PBDEs/dioxins (PRL)	0	PCBs/PBDEs/dioxins (PRL)
0	PCB congeners (PRL)	0	PCB congeners (PRL)
•0	PCB congeners (PRL)*	•0	PCB congeners (PRL)*
_	filter + C-18 SPE disk in 1 CLAM fo ust analyzing the C-18 SPE disk ar		
0	C-18 SPE disk		
	prefilter disk acific Rim Laboratory Manchester Laboratory		
	PCB Aroclors		

Staff from the CLAM manufacturing company (C.I. Agent) will be present to assist in the deployment and retrieval of the samplers. The filter pumps for each CLAM sampler must be calibrated with on-site water before deployment and directly after retrieval to calculate the total filtered volume. Calibration is conducted by measuring the rate at which water is pumped through the CLAM. This is done by attaching a tube to the outflow of the CLAM and timing how long it takes to fill a 60 mL syringe. Measuring the pump rate must be repeated until the exact pump rate is achieved 3 times in a row.

Field studies conducted by C.I. Agent have shown a linear relationship between the starting pump rate and ending pump rate, allowing for a relatively accurate calculation of total water filtered during each deployment (Jamie Aderhold, personal communication). A video explaining the deployment and retrieval process is available on YouTube at <u>http://youtu.be/TKybXgT0DoI</u>.

The CLAM works by pumping surface water continuously through an EPA-approved SPE disk when deployed in the field. Before deployment, the SPE disks are sent to the analytical laboratories for conditioning. C.I. Agent has an SOP for the conditioning process that should be followed by the analytical laboratories. The "conditioning" process includes preparing the disks by running clean solvents through them and then spiking them with analytical method-specific surrogates.

Several different types of SPE disks are available for the CLAM, depending on the analytes of concern. For the non-polar organics such as PCBs, PBDEs, and PCDD/Fs, a high capacity C18 SPE disk is used. More information on SPE disks and CLAM technology can be found at the manufacturer's website: <u>http://www.ciagent-stormwater.com/products/water-monitoring/</u>.

Biofouling is typically not a problem for the SPE disks due to the short deployment period. Surface water with high suspended particulates can clog the disks, which slows down the pumping rate. Thus, deployment time in water with a high suspended particulate content may be shortened to less than 24 hours.

Two of the samples for the current study will have a pre-filter attached in front of the SPE disk. In theory, the pre-filter will filter the particulates out of the water, leaving only the dissolved fraction of toxics to attach to the SPE disk. SPE disks both with and without a pre-filter will be analyzed for PCB congeners, giving an indication of dissolved versus total PCBs in surface water.

After retrieval, samples will be labeled, put back into their special plastic bags, and shipped directly to the MEL and Pacific Rim Laboratories (PRL) for SPE disk elution and sample analysis. The holding time for CLAM (SPE) disks before elution is 14 days (Table 7).

The final technical memo for this study will include a detailed summary of the SPE disk conditioning and elution process used. Furthermore, if the results for the current study show promise and Ecology chooses to use CLAM technology in future field studies, then an SOP must be developed before further use of CLAM.

#### **Particulates**

The Ecology EA Program's standard sediment trap deployment method for reservoirs and deep water is to suspend a trap in the middle of the water column with an anchor, snag line, and hardball float. This method is described in detail in Norton (1996) and a schematic of the sediment trap design and deployment configuration is displayed in Figure 2. The hardball float sits 6 feet below the water surface so that it can stay taut with fluctuating water levels and so it's not disturbed by vessel traffic or floating debris. The trap is then retrieved by dragging a hook to grab the snag line underwater.

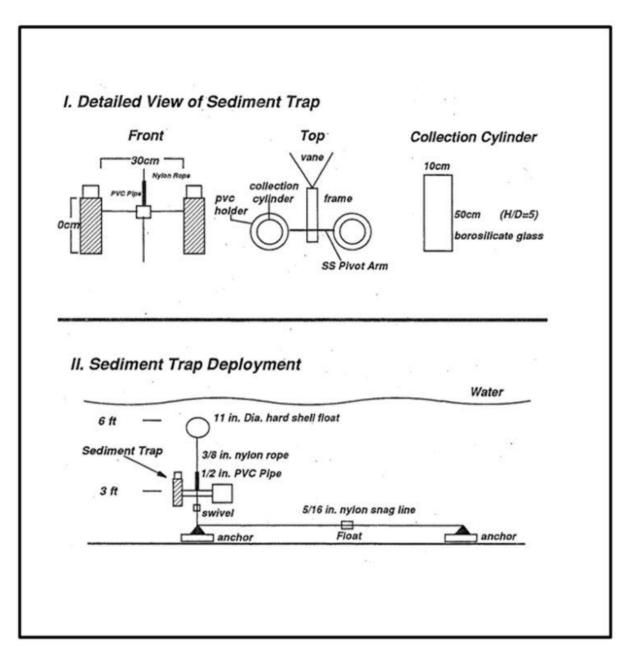


Figure 2. Schematic of Sediment Trap Design and Deployment Configuration (Norton, 1996).

Each sediment trap holds two glass collection cylinders each with a collection area of  $78.5 \text{ cm}^2$  and a height-to-width ratio of 5. This same trap was used at Ninemile Dam in spring of 2009, though the deployment consisted of only an anchor and hardball float just below the water surface.

Researchers will use the same sediment trap deployment system at the two sites chosen for the preliminary monitoring: Upriver Dam and Ninemile. Two independent moorings will be deployed in the reservoirs behind the dams, such that each site will have 4 cylinders for collecting suspended particulates. An effort will be made to deploy one set-up near the right bank and one set-up near the left bank of the river reservoir.

Before deployment, cylinders will be cleaned with Liquinox soap and hot water, followed by 10% nitric acid, and then rinsed with deionized water. Cylinders will then be rinsed with pesticide-grade acetone and finally hexane. During transport to the field, the tops of each cylinder will be covered with clean aluminum foil.

At deployment, the cylinders are filled partway with high salinity water (4% sodium chloride – NaCl), which contains mercuric chloride (HgCl) as a preservative to reduce microbial degradation of the samples.

The sediment trap cylinders will be swapped out after 2-3 months (by mid-January 2013) of deployment. New cylinders will be deployed for another 2-3 months. Traps will be removed from the reservoirs before spring runoff (by early April 2013).

#### Fish

Fish will be caught primarily by electrofishing boat in the river above Ninemile Dam and by gill nets in the river below Little Falls Dam. Aging structures will be taken from each fish and sent to the Washington State Department of Fish and Wildlife (WDFW) for age determination.

Fish will be collected and processed following SOP EAP009 – *Standard Operating Procedure for Field Collection, Processing and Preservation of Finfish Samples at the Time of Collection in the Field* (Sandvik, 2010a) and SOP EAP007 *Standard Operating Procedure for Resecting Finfish Whole Body, Body Parts or Tissue Samples* (Sandvik, 2010b). Sample containers and holding times for the fish tissue samples are shown in Table 7.

### **Measurement Procedures**

Desired reporting limits, expected concentrations, and analytical methods for the 2012 - 2013Spokane River toxics project are shown in Table 8. The expected concentration ranges for most of the organic parameters in surface water, CLAM, and particulates are an estimate because very little data exists for these chemical-matrix combinations in the Spokane River.

Both MEL and PRL will be conducting analyses on the SPE disks from the CLAM samplers. Planning meetings were held between the laboratories, the project manager, and C.I. Agent (the CLAM manufacturer) to agree upon details surrounding preparation, extraction, and analytical methods. The labs will follow C.I. Agent's SOP for conditioning of disks before CLAM deployment and elution of the disks after retrieval. Both labs will also conduct IDCs (initial demonstration of capability) using SPE disks.

Disks will be spiked with labeled compounds during the conditioning process. These compounds will not interfere with other QA analyses and their recovery will indicate potential loss rates of specific compounds during deployment in the field. The labs and project manager will refer to these spiked compounds as "field spikes".

Parameter	Desired Laboratory Reporting Limits	Expected Concentrations <sup>†</sup>	Preparation Method	Analytical Method	Lab
Water					
DOC & TOC (mg/L)	1	1 - 2	DOC field filtered	SM 5310B	MEL
TSS (mg/L)	1	1-4	SM 2540	0D	MEL
PCB congeners (pg/L)	10 per congener	10 – 1,000 total	EPA 166	58C	PRL
PBDEs – HR (pg/L)	35 – 625** per cong.	10 – 1,000 total	EPA 16	14	PRL
CLAM*					
PCB congeners (pg/L)	10 per congener	10 – 1,000 total	EPA 3535	EPA 1668C	PRL
PBDEs – HR (pg/L)	35 – 625** per cong.	10 – 1,000 total	EPA 3535	EPA 1614	PRL
PCDD/Fs (pg/L)	2.5 – 25 per cong.	10 – 500 total	EPA 3535	EPA 1613B	PRL
PCB Aroclors (ng/L)	25 ng per Aroclor per sample	0.01 – 10 total	EPA 3535	EPA 8082	MEL
PBDEs – LR (ng/L)	2 – 10 ng per cong. per sample	0.01 – 10 total	EPA 3535	EPA 8270	MEL
Particulates					
Solids	1%	50%	SM 2540G		PRL
TOC	0.1%	1 - 6%	PSEP – TOC		PRL
Cd, Pb, & Zn (mg/Kg dw)	0.1 (5 for Zn)	Cd 5-30; Pb 100-1,000; Zn 1,000-5,000	EPA 200.7 or 200.8; SM		MEL
PCB congeners (ng/Kg dw)	5 per congener	1,000 – 100,000 total	EPA 1668C		PRL
PBDEs – HR (ng/Kg dw)	5 – 1,500 per cong.	100 – 100,000 total	EPA 1614		PRL
PCDD/Fs (ng/Kg dw)	0.5 - 5 per cong.	50 – 2,000 total	EPA 161	3B	PRL
Fish					
Lipids (%)	0.1	0.1 - 20	MEL SOP 730009		MEL
As, Cd, Pb, Zn (mg/Kg ww)	0.1 (5 for Zn)	0.1 – 100 ug/Kg	EPA 200.7 or 200.8; SM		MEL
Hg (ug/Kg ww)	17	10 - 1,000	EPA 245.6		MEL
PCB Aroclors (ug/Kg ww)	1.1 – 44 per Aroclor	0.5 – 1,000 depending on Aroclor	EPA 8082		MEL
PBDEs – LR (ug/Kg ww)	0.1 – 2.6 (1.9 – 4.3 for PBDE 209)	0.1 – 100 per congener	EPA 8270		MEL
PCB congeners (ug/Kg ww)	0.005 – 0.8 per cong.	2-3,000 total	EPA 16	68	Contract
PCDD/Fs (ng/Kg ww)	0.03 – 0.5 per cong.	0.005 – 1 as 2,3,7,8, TCDD	EPA 1613B		Contract

#### Table 8. Parameters, Reporting Limits, Expected Concentrations and Analytical Methods.

<sup>†</sup> The expected concentration ranges for organics in water, CLAM, and particulates are an estimate as very little data exists for these chemical-matrix combinations.

\* CLAM results will be reported by the laboratories as mass per sample as either picograms per sample (pg/S) or nanograms per sample (ng/S). With the known sampling rate, results can be calculated as a mass per volume (e.g. pg/L and ng/L).

\*\* PBDE-209 reporting limits expected to be higher.

CLAM: Continuous Low-Level Aqueous Monitoring device

MEL: Manchester Laboratory

PRL: Pacific Rim Laboratory

HR: high resolution (isotopic dilution) methods

- LR: low resolution methods
- SM: Standard Methods
- dw: dry weight

ww: wet weight

### **Budget**

The funding for the Spokane River Toxics project comes from multiple sources. Table 9 shows the current allotted budget. The Spokane Tribe of Indians is contributing \$21,000 towards fish tissue and surface water sampling. Ecology is currently working with them on a funding agreement. The rest of the funding comes from different sources within Ecology. In the future, if more funding becomes available from interested parties, especially for additional PCB congener analysis of fish tissue samples, this budget could increase.

Funding Source	Amount	Percentage
EAP Pool	\$ 54,000	41%
WQ ERO	\$ 8,000	6%
WSTMP - Fish	\$ 28,000	21%
WSTMP - CLAM	\$ 20,000	15%
Spokane Tribe	\$ 21,000	16%
Total	\$ 131,000	

Table 9. Funding for the Spokane River Toxics FY13 Project.

EAP Pool: Environmental Assessment Program Pool Funding WQ ERO: Water Quality Program – Eastern Regional Office WSTMP: Washington State Toxics Monitoring Program

The estimated laboratory analysis budget is given in Table 10. This is the current best estimate on the number and cost of analyses. The final analysis budget will likely shift when the fish tissue laboratory analysis contract is awarded and the final fish collection numbers are known. As mentioned previously, Ecology will be developing a final analysis plan for fish tissue by November 2012.

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost per Sample	5	Subtotal
Water						
DOC	10	2	12	40	\$	480
TOC	10	2	12	40	\$	480
TSS	10	2	12	12	\$	144
PCB Congeners	10	2	12	815	\$	9,780
PBDEs - HR	10	2	12	750	\$	9,000
	•			Subtotal	\$	19,884
CLAM						
PCB Congeners	11	1	12	815	\$	9,780
PCB Aroclors	3	1	4	100	\$	400
PBDEs - HR	4	1	5	750	\$	3,750
PBDEs	3	1	4	190	\$	760
PCDD/Fs	4	1	5	625	\$	3,125
SPE Disks	16	0	16	95	\$	1,520
	•			Subtotal	\$	19,335
Particulates						,
% Solids	2	1	3	12	\$	36
TOC	2	1	3	45	\$	135
Cd, Pb, & Zn	2	1	3	90	\$	270
PCB Congeners	2	1	3	815	\$	2,445
PBDEs - HR	2	1	3	750	\$	2,250
PCDD/Fs	2	1	3	625	\$	1,875
	•			Subtotal	\$	7,011
Fish						·
Lipids	73	6	58	NA*	\$	-
Arsenic	28	3	31	18	\$	558
Cd, Pb, & Zn	52	6	58	90	\$	5,220
Mercury	51	5	56	50	\$	2,800
PCB Congeners	29	1	30	856	\$	25,680
PCB Aroclors	73	6	79	205	\$	16,195
PBDEs	52	6	58	209	\$	12,122
PCDD/Fs	26	3	29	750	\$	21,750
				Subtotal	\$	84,325
			Project	Total Costs	\$	130,555

Table 10. Estimated Laboratory Analysis Budget for the Spokane River Toxics FY13 Project<sup>†</sup>.

\* Cost for lipid analysis included with other toxics analyses. <sup>†</sup> Costs include 50% discount for samples analyzed at MEL and a 25% contracting fee for analyses contracted through MEL.

# **Quality Control Procedures**

### Field

Field quality control samples for the project are shown in Table 11.

Parameter	Field Duplicates	Field Blank
Water		
DOC, TOC, and TSS	1/batch and 2/project	NA
PCB congeners	1/batch and 2/project	2/project
PBDEs – HR	1/batch and 2/project	2/project
CLAM		-
PCB congeners	6/project	NA
PCB Aroclors	2/project	NA
PBDEs – HR	2/project	NA
PBDEs – LR	2/project	NA
PCDD/Fs	2/project	NA
Fish		
Lipids	1 – 6 per location	NA
As, Cd, Pb, & Zn	1 – 6 per location	NA
Hg	1 - 4 per location	NA
PCB Aroclors	1 – 6 per location	NA
PCB congeners	<1 per location	NA
PBDEs – LR	1 – 6 per location	NA
PCDD/Fs	1-4 per location	NA

CLAM: Continuous Low-Level Aquatic Monitoring Device

HR: high resolution (isotopic dilution) methods (EPA 1614 for PBDEs)

LR: low resolution methods (EPA 8270 for PBDEs)

One field replicate will be analyzed for whole surface water sample during each of the two monitoring events (October 2012 and May 2013). One field blank will be analyzed during each sampling event for a total of 2 field blanks for the project. Blanks will be transfer blanks with laboratory deionized water and will be conducted in the field.

Numerous field duplicates will be conducted for the CLAM, especially for PCB congeners. No field blanks will be performed for the CLAM samples. A blank run on a pre-conditioned SPE disk in the labs during the time of analysis will be used instead. Field spikes will be spiked into each disk during the conditioning process before deployment to account for loss rates.

Fish sample replicates will be analyzed at most of the monitoring locations. Up to 6 replicate samples will be analyzed at the locations that will be used for evaluating long-term trends.

No field duplicates will be analyzed for particulate samples. Since particulates will be composited from 4 sample containers, the results should be representative of the monitoring location. No field blanks will be analyzed. Laboratory duplicates will be performed for a measurement of precision.

#### Laboratory

Laboratory quality control samples for the project are shown in Table 12.

Parameter	Laboratory Control Sample	Method Blank	Surrogate Spikes	Matrix Spikes	Duplicate Analysis
Whole Water					
DOC & TOC		1/batch		1/batch	1/batch
TSS		1/batch			1/batch
PCB congeners	1/batch	2/batch	All samples		1/batch
PBDEs – HR	1/batch	1/batch	All samples		1/batch
CLAM					
PCB congeners	1/batch	2/batch	All samples		NA*
PCB Aroclors	1/batch	2/batch	All samples	1/batch	NA*
PBDEs – HR	1/batch	1/batch	All samples		NA*
PBDEs – LR	1/batch	1/batch	All samples	1/batch	NA*
PCDD/Fs	1/batch	1/batch	All samples		NA*
Particulates					
TOC		1/batch		1/batch	1/batch
Cd, Pb, and Zn	1/batch	1/batch		1/batch	1/batch
PCB congeners	1/batch	1/batch	All samples		1/batch
PBDEs – HR	1/batch	1/batch	All samples		1/batch
PCDD/Fs	1/batch	1/batch	All samples		1/batch
Fish					
Lipids		1/batch			1/batch
PCB Aroclors	1/batch	1/batch	All samples	1/batch	1/batch
As, Cd, Hg, Pb, & Zn	1/batch	1/batch		1/batch	1/batch
PCB congeners	1/batch	1/batch	All samples		1/batch
PBDEs – LR	1/batch	1/batch	All samples	1/batch	1/batch
PCDD/Fs	1/batch	1/batch	All samples		1/batch

Table 12. Laboratory Quality Control Samples.

HR: high resolution (isotopic dilution) methods (EPA 1614 for PBDEs)

LR: low resolution methods (EPA 8270 for PBDEs)

\* Field duplicates will serve as laboratory duplicate analyses.

### **Data Management Procedures**

Field data will be recorded in a field notebook. Relevant information will be carefully transferred to electronic data sheets and reviewed for potential transfer errors.

The data packages from MEL and the contract laboratories will include case narratives discussing any problems encountered during analysis, corrective actions taken, and an explanation of data qualifiers. The project manager will then review the data packages to determine if analytical MQOs (laboratory control samples, laboratory duplicates, and matrix spikes) were met.

All 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 water column data generated using CLAM. CLAM is still in the developmental phase and until standard operating procedures have been approved for the CLAM, 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.

### **Audits and Reports**

MEL participates in performance and system audits of their routine procedures. The results of these audits are available on request.

The fish tissue component of the Spokane toxics study will be published in the WSTMP report and will be available on Ecology's Internet homepage (<u>www.ecy.wa.gov</u>). The preliminary monitoring results for surface water, CLAM, and particulates will be written up by the project manager in a technical memo to Ecology's Eastern Regional Office. Both documents will be made available for review by the SRRTTF, collaborating entities, external reviewers, and other interested parties. The collaborating entities for the project may also publish reports relating to their part of the project.

The schedule for the technical memo, shown in Table 4, will be available for review by October 2013 and will be finalized by December 2013. The slated publication date for the WSTMP fish tissue report is yet to be determined but should occur in a similar timeframe.

The WSTMP report and the technical memo will both contain the following elements:

- Information about the sampling locations, including geographic coordinates and maps.
- Descriptions of field and laboratory methods.
- Tables presenting all the data.
- Discussion of project data quality.
- Summary of significant findings.

The technical memo will also include an evaluation of collection methods (CLAM, sediment traps, and surface water) and recommendations for inclusion in future monitoring in the Spokane River.

### **Data Verification**

The project manager will review laboratory data packages and data verification reports. Based on these assessments, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

To determine if analytical MQOs (Table 3) have been met, the project manager will compare results of the field and laboratory quality control samples to MQOs.

Formal (third party) validation of the data will not be necessary for this project.

## Data Quality (Usability) Assessment

Once the data have been reviewed and verified, the project manager will determine if the data are useable for the purposes of the project.

### References

Era-Miller, B., 2012. Recommendations for the Design of a Long-term Toxics Monitoring Program in the Mainstem of the Spokane River (Working Draft) – June 19, 2012. Prepared by the Environmental Assessment Program – Toxics Studies Unit for the Water Quality Program Eastern Regional Office and the Spokane Regional Toxics Task Force.

Gries, T. and D. Osterberg, 2011. Control of Toxic Chemicals in Puget Sound: Characterization of Toxic Chemicals in Puget Sound and Major Tributaries, 2009-10. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-008. https://fortress.wa.gov/ecy/publications/summarypages/1103008.html

Janisch, J., 2006. Standard Operating Procedure for Determining Global Position System Coordinates, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP013. <u>www.ecy.wa.gov/programs/eap/quality.html</u>

Joy, J., 2006. Standard Operating Procedure for Manually Obtaining Surface Water Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. <a href="https://www.ecy.wa.gov/programs/eap/quality.html">www.ecy.wa.gov/programs/eap/quality.html</a>

Lombard, S. and C. Kirchmer, 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030. https://fortress.wa.gov/ecv/publications/summarypages/0403030.html MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Norton, D., 1996. Commencement Bay Sediment Trap Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 96-315. https://fortress.wa.gov/ecy/publications/summarypages/96315.html

Sandvik, P., 2010a. Standard Operating Procedures for Field Collection, Processing and Preservation of Finfish Samples at the Time of Collection in the Field. Washington State Department of Ecology, Olympia, WA. SOP Number EAP009. www.ecy.wa.gov/programs/eap/quality.html

Sandvik, P., 2010b. Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples. Washington State Department of Ecology, Olympia, WA. SOP Number EAP007. <u>www.ecy.wa.gov/programs/eap/quality.html</u>

Seiders, K. and W. Yake, 2002. Quality Assurance Project Plan: Washington State Toxics Monitoring Program, Exploratory Monitoring of Toxics Contaminants in Edible Fish Tissue and Freshwater Environments in Washington State. Washington State Department of Ecology, Olympia, WA. Publication No. 02-03-065. https://fortress.wa.gov/ecy/publications/summarypages/0203065.html

Serdar, D. and A. Johnson, 2006. PCBs, PBDEs, and Selected Metals in Spokane River Fish, 2005. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-025. https://fortress.wa.gov/ecy/publications/summarypages/0603025.html

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. <a href="https://www.ecy.wa.gov/programs/eap/quality.html">www.ecy.wa.gov/programs/eap/quality.html</a>

USGS, 2005. National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, Chapters A1-A4. <u>http://pubs.water.usgs.gov/twri9A</u>.

# Appendices

### Appendix A. Figures Showing Monitoring Locations

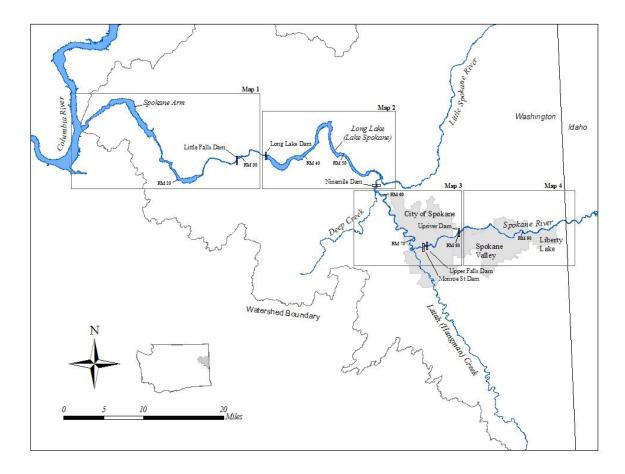


Figure A-1. Spokane River Monitoring Reaches for the FY13.

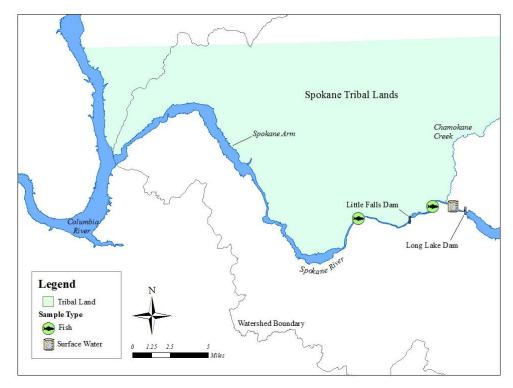


Figure A-2. Sampling Map 1: Lower Spokane River and Spokane Arm.

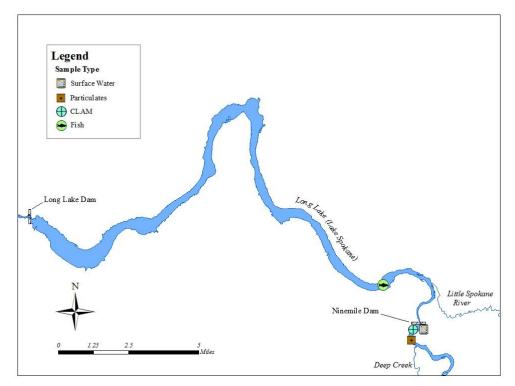


Figure A-3. Sampling Map 2: Long Lake (Lake Spokane) Dam to Ninemile Dam.

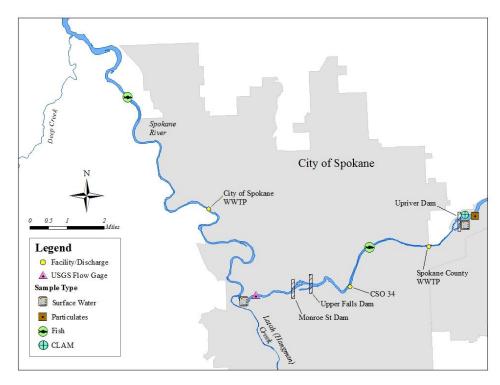


Figure A-4. Sampling Map 3: Deep Creek to Upriver Dam.

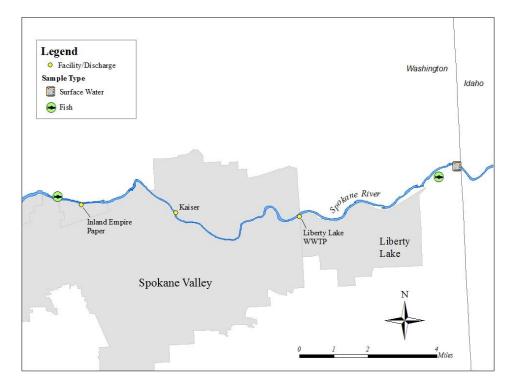


Figure A-5. Sampling Map 4: Upriver to Stateline.

### Appendix B. Glossary, Acronyms, and Abbreviations

#### Glossary

**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.

Mainstem: The main downstream course of a river, as contrasted to its tributaries.

**Parameter:** A physical chemical or biological property whose values determine environmental characteristics or behavior.

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

**Reach:** A specific portion or segment of a stream.

**Solid Phase Extraction (SPE):** A separation process by which compounds that are dissolved or suspended in a liquid mixture are separated from other compounds in the mixture according to their physical and chemical properties. It is commonly used by laboratories to concentrate or purify samples for analysis.

Streamflow: Discharge of water in a surface stream (river or creek).

**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.

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

DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
GPS	Global Positioning System
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective

PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
QA	Quality assurance
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SRM	Standard reference materials
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
	-
dw	dry weight
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
mg	milligram
mg/Kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliters
mm	millimeter
ng/g	nanograms per gram (parts per billion)
ng/Kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
s.u.	standard units
ug/g	micrograms per gram (parts per million)
ug/Kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter
uS/cm	microsiemens per centimeter, a unit of conductivity
WW	wet weight