

Addendum 3 to Quality Assurance Project Plan

Freshwater Fish Contaminant Monitoring Program, 2023: Spokane River

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Addendum 3 to Quality Assurance Project Plan

Freshwater Fish Contaminant Monitoring Program, 2023: Spokane River

by Shannon Nardi and Jakub Bednarek

March 2023

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The numbered headings in this document correspond to the headings in the original QAPP. Only relevant sections are included above; therefore, some numbered headings may be missing.

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2.0 Abstract

The Department of Ecology's Freshwater Fish Contaminant Monitoring Program characterizes persistent, bioaccumulative, and toxic chemicals in freshwater fish throughout Washington state. In 2009, a long-term monitoring component was added to determine if changes in contaminant levels occur over time.

The Spokane River was sampled in 2003, 2005, and 2012. The 2023 study will repeat historical work in the Spokane River to determine whether changes in fish tissue contaminant concentrations can be discerned.

The goals of 2023 sampling are to (1) measure concentrations of PCBs, PBDEs, PFAS, PCDD/Fs, and metals in various fish in the Spokane River and (2) compare results to previous studies to determine temporal changes.

Results from the 2023 study will inform resource managers about potential risks to human health from eating fish that may be contaminated. Data from this study will be entered into Ecology's EIM database and used in future water quality assessments.

This document is an addendum to the most recent Quality Assurance Project Plan (Seiders and Sandvik, 2020) and gives information that is specific to the 2023 sampling in the Spokane River.

3.0 Background

This document is an addendum to the most recent programmatic Quality Assurance Project Plan (QAPP) (Seiders and Sandvik, 2020) for the Washington State Department of Ecology's (Ecology's) Freshwater Fish Contaminant Monitoring Program (FFCMP). This document gives specific details about the 2023 sampling in the Spokane River and addresses only those sections in Ecology's current QAPP format where such detail is needed. For additional information, refer to the 2020 programmatic QAPP referenced above.

3.1 Introduction and problem statement

3.1.1 Spokane River

Under the federal Clean Water Act, the Middle and Lower sections of the Spokane River are listed as impaired for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in fish tissue. The Spokane River Toxics Reduction Strategy (Ecology, 2012) describes PCBs, PBDEs, polychlorinated dibenzo-p-dioxin and -furan (PCDD/Fs), and metals impairments in the Spokane River. This Strategy includes a thorough bibliography of studies in the Spokane River watershed.

Risks to human health from toxic chemicals remain an important concern. Levels of lead and PCBs in mountain whitefish resulted in a FCA (fish consumption advisory) issued in 1999 and revised in 2007 (Health, 2007). Continued high levels of PBDEs and PCBs in fish tissue led to a Washington State Department of Health (Health) consultation report in 2011 on the accumulative health effects of eating Spokane River fish (Health, 2011).

A study conducted by Serdar et.al. (2011) assessed sources of PCBs using various monitoring data and past FFCMP fish sampling results from the Spokane River. Findings from the study suggested that levels of PCBs and PBDEs remained elevated compared to other areas in Washington; Seiders et al. (2014) conducted additional monitoring based on the 2011 study results.

This 2023 study will monitor at locations with the highest levels of PCBs and PBDEs in past studies. As part of Ecology's broader monitoring strategy, Ecology's FFCMP has committed to monitoring Spokane River fish on an ongoing basis.

3.2 Study area and surroundings

3.2.1 Summary of previous studies and existing data

There are many previous studies and existing data for fish contaminant monitoring in the Spokane River.

Table 1 summarizes these studies by showing sampling years, fish species collected, locations, and target analytes. Table 2 provides names and abbreviations for fish caught in this watershed in previous studies. Results from a 1984 study (Hopkins et al., 1985) raised concerns due to high levels of metals and organic pollutants throughout Washington. This prompted follow-up studies (Serdar et al., 1994; Johnson et al. 2004) and further investigation (Ecology 1995). These studies confirmed problematic levels of PCBs and other pollutants in the Spokane river between Lake Spokane and the WA/Idaho state line. Follow-up studies by Johnson (1997, 2000; Jack and

Roose, 2002) and outside contractors (SAIC, 2003) showed mixed trends likely due to small sample sizes and high variability associated with fish tissue studies.

	Sample Year:	1980- 1983	1992	1993- 1994	1996	1999	2001	2002	2003- 2005	2005	2008- 2009	2012	2014	2016
River Mile	Station													
27-28	Spokane Arm (FDR Lake)			KOK LSS SMB WAL								BNT LSS RBT*		
34	Little Falls Pool											LSS NPM		
40	Lower Lake Spokane		LSS YP	LMB LSS MWF YP			LMB LSS SMB YP		LSS MWF SMB	MWF SMB	LSS NPM			
55	Upper Lake Spokane						LMS LSS MWF SMB YP		BNT LSS MWFS MB	BNT LSS MWF SMB	LSS MWF NPM SMB	LSS MWF NPM RBT*	ССР	
62-64	Above Ninemile Dam	BLS LSS MWF NPM		LSS MWF RBT	LSS MWF RBT	LSS MWF			BLS MWF RBT	BLS MWF RBT	LSS MWF	LSS MWF RBT*		LSS
74-78	Above Monroe Dam/ Mission Pk			LSS MWF RBT	LSS MWF RBT				LSS MWF RBT		LSS MWF	LSS MWF RBT*		
80	Above Upriver Dam			LSS MWF RBT	LSS RBT									
85	Plante Ferry Park	LNS CTT							LSS RBT	LSS RBT	LSS RBT	LSS NPM RBT*		
96	Stateline Bridge								LSS	LSS	LSS	LSS		
99+	Idaho			LSS				LSS KOK LMB						
	Analytes				[1	r	r	-	r	1	1	T	
	CPs	Х	Х	Х										
	PCBs	Х	Х	Х	Х	Х	Х	Х	Х	X		X	Х	
	PBDEs								v	Х	X	X		
	PCDD/Fs	v					v		X X					
	Mercury Lipids	X X					X X		А	X		X	X	
	PFAS	Λ					Λ			Λ	X	Λ		Х
	EIM Study ID	BHOP 0002	DSER 0002	WSPMP 93T; AJOH0005	AJOH0 008	AJOH 0022	RJAC 0002	N/A	WSTM P03; DSER0 010	DSER 0016	CFUR0 003; CFUR0 005	WSTM P12	BERA 0011	CAM E002
	References	1	2	3, 4, 5	6	7	8	9	10, 11	12	13, 14	15	16	17

Table 1. Species and analytes from Spokane River studies that included fish tissue.

*RBT collected for FFCMP 2012 (Seiders et al. 2014) were undifferentiated from redband trout and steelhead in data. See Table 2 for fish species abbreviations.

References:

1. Hopkins et al. 1985; 2. Serdar et al. 1994; 3. Johnson et al. 1994; 4. Davis et al. 1995; 5. Ecology 1995; 6. Johnson 1997;

7. Johnson 2000; 8. Jack and Roose 2002; 9. SAIC 2003; 10. Seiders, Deligeannis, and Kinney 2006; 11. Serdar et al. 2011.

12. Serdar and Johnson 2006; 13. Furl and Meredith, 2010a; 14. Furl and Meredith, 2010b; 15. Seiders et al. 2014;

16. Era-Miller 2015; 17. Mathieu and McCall, 2017.

Regardless of trends, PCB concentration remained elevated. These studies resulted in the establishment and inclusion of the Spokane River in the Washington State Toxics Monitoring Program (now the Freshwater Fish Contaminant Monitoring Program) to continually monitor PCBs and other contaminants in fish tissue (Seiders, Deligeannis, and Kinney, 2006; Seiders et al., 2007, 2014). Other studies have explored the extent of contamination in sediment and invertebrates (Johnson, 2000) as well as the sources of contamination in the Spokane River, including industrial/business activities, sewers, stormwater runoff, atmospheric deposition, and fish hatcheries (Ecology, 2007; Serdar et al., 2011; Fernandez, 2012; Wong, 2018; Era-Miller and Wong, 2019).

Common Name	Scientific Name	Abbreviation
Bridgelip sucker	Catostomus columbianus	BLS
Brown trout	Salmo trutta	BNT
Common carp	Cyprinus carpio	ССР
Cutthroat trout	Oncorhynchus clarki	CTT
Kokanee salmon	Oncorhynchus nerka	КОК
Largemouth bass	Micropterus salmoides	LMB
Longnose sucker	Catostomus Catostomus	LNS
Largescale sucker	Catostomus macrocheilus	LSS
Mountain whitefish	Prosopium williamsoni	MWF
Northern pikeminnow	Ptychocheilus oregonensis	NPM
Rainbow trout	Oncorhynchus mykiss	RBT
Smallmouth bass	Micropterus dolomieui	SMB
Walleye	Sander vitreus	WAL
Yellow perch	Perca flavescens	YP

Table 2. Fish species from the Spokane River analyzed for contaminants in past studies.

3.2.3 Parameters of interest and potential sources

Primary target analytes for long-term trend assessments are PCBs, PBDEs, PFAS, PCDD/Fs, mercury, arsenic, and metals, including cadmium (Cd), lead (Pb), and zinc (Zn). PCBs, PBDEs, and Pb are the Fish Consumption Advisory contaminants (Seiders and Sandvik, 2020). See Tables 3 and 4 for potential sources and 303(d) listings. Additionally, PCBs are the subject of an ongoing process to create a TMDL for the Spokane River. Chlorinated pesticides will not be targeted in this study due to low or non-detectable concentrations results from the Spokane River in 2012 (Seiders et al., 2014).

We plan to look for contaminants primarily in largescale suckers because that was the species of focus in 2012. If we can collect a sample size of largescale sucker that is comparable to the sample size collected in 2012, we will increase our likelihood of detecting temporal changes. Also, we will likely target mountain whitefish to match the 2012 study, contingent on project funding and fishing conditions. Other species collected in past studies are listed in Table 2, but most of these studies do not have sufficient sample sizes to detect meaningful trends.

Contaminant	Potential Source			
PBDEs	Flame retardants, plastics, building materials, textiles, electronics			
PCBs	Electrical transformers, hydraulic fluids, caulks, atmosphere			
PCDD/Fs	Combustion processes, paper production			
Arsenic	enic Pesticides, soil erosion			
Mercury	Iercury Gold mining, fossil fuels, atmosphere			
PFAS	Firefighting foams, consumer products, atmosphere			

Table 3. Contaminants in the Spokane River and their potential sources.

3.2.4 Regulatory criteria and standards

Table 4. Ca	tegory 5 and 2	listings for fish	tissue from Spol	kane River.

Contaminant	Category	Location - WRIA
PCBs	5	
2,3,7,8-TCDD (Dioxin)	5	54- Middle Spokane
2,3,7,8-TCDD TEQ	2	River
4,4'-DDT	2	from Washington state line
4,4'-DDE	2	to Hangman Creek [about RM 72]
Methyl mercury	5	
PBDEs	5	
PCBs	2	57- Lower Spokane
4,4'-DDE	2	River from Hangman Croals
Hexachlorobenzene	2	from Hangman Creek [about RM 72] to confluence
Methyl mercury	5	with Lake Roosevelt

Category 5- Polluted water that requires a water improvement project.

Category 2- Some evidence of a water quality problem, but not enough to show persistent impairment.

WRIA: Water Resource Inventory Area

RM: River Mile

Ecology uses total mercury analyses in lieu of methylmercury for comparison to water quality standards because it is easier and less costly to analyze total mercury than methylmercury. Total mercury was the target analyte used in other fish tissue studies in Washington as well as in past water quality assessments in Washington.

The EPA has a health advisory for drinking water for three of the PFAS substances: 0.004 parts per trillion (ppt) for PFOA, 0.02 ppt for PFOS, and 2,000 ppt for PFBS (U.S. EPA 2022b). Also, the Washington State Department of Health (Health) recently released State Action Levels for five PFAS compounds in drinking water. These include PFOA and PFOS, at 10 and 15 ppt, respectively, as well as PFNA (9 ppt), PFHxS (65 ppt), and PFBS (345 ppt) (Health, 2022b). See Table 5 for these and other thresholds used to determine threats to human health in fish tissue.

Table 5. Thresholds used by Ecology and Health for protecting human health from contaminants in fish tissue.

Analyte (ppb ww) ¹	Risk	Ecology's Thresholds used in Narrative Scr Criteria		Thresholds used in Narrative Health's Screening Levels EPA's Screening Values (2000)		EPA Draft Recommended Aquatic Life Water Quality Criteria (2022)			
(իիր ատ)		TECn	10x TECc	FCASL Higher FCR	FCASL Lower FCR	Subsistence Fishers Recreational Fishers		Whole fish ⁶	Fish muscle ⁶
Mercury ²	nc	30		34	101	49	400		
Total PBDEs	nc			34	101				
$T + 1 \text{ DCD}^3$	nc	9.1		8.0	23	9.38	80		
Total PCBs ³	с		2.3	0.20	0.59	2.45	20		
2,3,7,8-TCDD ⁴	nc	0.32		0.280	0.821				
0.2.7. 0 TEO (5)	nc	0.32		0.280	0.821				
2,3,7,8-TEQ ^{4,5}	с					0.0315	0.256		
PFOA	nc			0.17	1.87			6.1	0.125
PFOS ⁸	nc			0.6	1.8			6.75	2.91

Nc: non-carcinogenic effects; c: carcinogenic effects

FCASL: Fish Consumption Advisory Screening Level

FTEC: Fish Tissue Equivalent Concentration (old water quality narrative standard).

TEC: tissue exposure concentration

1 - Values in in parts per billion wet-weight (ug/kg ww) unless otherwise noted

2 - The criterion for methylmercury is a true numeric criterion for fish tissue as opposed to a narrative criterion which

incorporates a TEC. The interpretation of tissue methylmercury results used the TECn pathway described in Policy 1-11. Fish tissue was analyzed for total mercury.

3 – Total PCBs in sum of Aroclors or congeners.

4 - Values in parts per trillion wet-weight (ng/kg ww)

5 – The cumulative toxicity of a mixture of congeners in a sample can be expressed as a TEQ to 2,3,7,8-TCDD. EPA (2010) states that the criterion for dioxin is expressed in terms of 2,3,7,8-TCDD and should be used in conjunction with the international convention of TEFs and TEQs to account for the additive effects of other dioxin-like compounds. When the TEQ is used, the toxicity of the single congener 2,3,7,8-TCDD is incorporated.

6 - Values in parts-per-million wet weight (mg/kg ww); based on U.S. EPA 2022a.

7 - E. Christie, 10/2022 personal communication, state Department of Health (Health)

8 – Values based on Health (2022a).

4.0 Project Description

4.1 Project goals

- Characterize temporal trends for PCBs, PBDEs, dioxins/furans, mercury, and metals in largescale suckers, mountain whitefish, and northern pikeminnow.
- Confirm data on PFAS in fish in the Spokane River and contribute to baseline data for future trends monitoring.
- Compare results to water quality standards and screening levels for the protection of human health.
- Support fish consumption risk assessments conducted by state and local health jurisdictions.
- Inform current and future water quality improvement work.

4.2 Project objectives

- Collect at least 21 (but no more than 35) largescale suckers and/or mountain whitefish of various sizes from six stations in the Spokane River; collect at least 21 (but no more than 35) northern pikeminnow from one station in the Spokane River.
- Process and analyze up to 70 composite samples (42 whole body and 28 filet) for target analytes.
- Compile and review laboratory analytical results; upload results to Ecology's EIM database.
- Characterize contaminant levels found in the sampled area; evaluate temporal trends, water quality standards, and other thresholds for the protection of human health.
- Share results through various media such as reports, Ecology website, and presentations.

4.3 Information needed and sources

Previous studies and associated data described above were obtained from Ecology project files, EIM database, and reports from other entities. All information was reviewed to guide development of project objectives and the sampling plan. This project will use data collected through past monitoring studies conducted by Ecology and others to characterize temporal trends.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 6. Organization of project staff and responsibilities.

Staff All staff are with EAP	Title	Responsibilities
Jessica Archer SCS 360-407-6698	Section Manager	Conducts annual planning to assess client/program needs and scope, reviews deliverables and products, provides upper management support. Approves the final QAPP and addenda.
Jakub Bednarek Toxic Studies Unit SCS 360-584-8318	TSU Project Manager and Principal Investigator	Oversees all aspects of the project. Writes QAPP, addendums, and reports. Reviews historical data and develops sample strategy for different sites, annually. Works with labs to obtain analytical services. Reviews, analyzes, and interprets data. Guides field assistants.
Shannon Nardi Toxic Studies Unit SCS 360-878-4857	TSU Project Assistant, Field Lead and EIM Lead	Co-authors QAPP addendum. Leads sample collection, processing, and transportation of samples to the lab. Ensures that field and processing information is recorded. Enters field and lab data into EIM. Helps write reports and project plans.
Jim Medlen Toxic Studies Unit SCS 360-480-6175	TSU Unit Supervisor Project Manager	Reviews the project scope and budget, tracks progress, reviews and approves the draft and final QAPP, reviews draft and final project reports, helps resolve work issues with client and management.
Dean Momohara Manchester Environmental Lab 360-871-8801	Acting Director	Reviews and approves final QAPP and addenda. Ensures MEL performs all chemical analyses as requested, including work contracted out. Ensures lab results are validated in timely manner.
Christina Frans Manchester Environmental Lab 360-871-8801	MEL QA Coordinator	In addition to QA Coordinator role, leads technical aspects related to contract lab work. Develops Statements of Work, reviews labs' capabilities to meet project needs, reviews data packages from contract labs for compliance with contracts; leads or coordinates data validation work (in- house or through vendor). Works with MEL's Project Coordinator and TSU Project Manager to accomplish tasks described within for contract lab data.
Nancy Rosenbower Manchester Environmental Lab 360-871-8801	MEL Project Coordinator	Coordinates communication between MEL staff and TSU Project Manager. Conducts sample receipt, tracking, storage, shipment to other labs. Disseminates labs result reports. Works with MEL QA Coordinator and TSU Project Manager to accomplish tasks described within for contract lab data.
Arati Kaza 360-407-6964	Ecology QA Officer	Reviews and approves draft QAPP and final QAPP and addendums. Ensures EAP adheres to QC-related SOPs and practices.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QA: Quality Assurance

QAPP: Quality Assurance Project Plan

MEL: Manchester Environmental Laboratory

SCS: Statewide Coordination Section

TSU: Toxics Studies Unit

QC: Quality Control

The 2023 FFCMP study on the Spokane River requires the use of contract labs because Ecology's Manchester Environmental Laboratory is not equipped to conduct all needed analyses. The process for obtaining contract lab services involves varied staff having different expertise and roles. To help facilitate communication among all parties involved in this process, the checklist in Appendix A of the 2021 QAPP Addendum (Seiders and Sandvik, 2021) was developed. The Project Manager will use this checklist to track the process during the 2023 study.

5.3 Organization chart

The FFCMP will establish contact and coordinate with stakeholders including, but not limited to, local tribes, agencies, and organizations. Contact will be made to ensure the community is aware of our activity, to allow for collaboration, and to answer questions about sampling work and goals. Input on project objectives will be accepted if they do not impede project goals and objectives. Table 7 lists the stakeholders who may be interested in our sampling.

Washington Department of Fish and Wildlife	Kalispell Tribe
Manchester Environmental Laboratory (MEL)	Spokane River Association
Spokane Tribe	Spokane Riverkeeper
Avista Utilities	Spokane River Regional Toxics Task Force

Table 7. Organizations that may be involved with the FFCMP 2023 sampling.

5.4 Proposed project schedule

Table 8. Prop	posed project	t schedule and	l deadlines.	FFCMP 2023.
	posed project	seniculie and	i acaamicoy	

Field and laboratory work	Due date	Lead staff			
Field work completed	December 2023	Shannon Nardi			
Sample processing	March 2024	Shannon Nardi			
Lab analyses and data validation (varies, depends	January to	MEL Director, Christina			
on time of sample delivery and lab capacity)	May 2024	Frans, Nancy Rosenbower			
Environmental Information System (EIM) database					
EIM Study ID	FFCMP23				
Product	Due date	Lead staff			
EIM data loaded*	August 2024	Shannon Nardi			
EIM quality assurance**	October 2024	Varies by year			
EIM complete	December 2024	Shannon Nardi			
Final Report for 2023 Study					
Author lead / Support Staff	Jakub Bednarek / Shannon Nardi				
Schedule:					
Draft due to supervisor	September 2025				
Draft due to client/peer reviewer	October 2025				
Draft due to external reviewer(s)	November 2025				
Final (all reviews done) due to publications team	December 2025				
Final report due on web	March to Sept 202	26			

* All data entered into EIM by the lead person for this task. ** Data verified to be entered correctly by a different person; any QA issues identified. Allow one month for this step in your schedule.

*** All QA issues identified in the previous step are fixed (usually by the original entry person); EIM Checklist signed off and submitted to Melissa Petersen (who then enters the "EIM Completed" date in the tracking system). Allow one month for this step. Normally the final EIM completion date is no later than the final report publication date.

Station		Target	Target				Numbe	er of Analys	es		
[River Site Species	Sample #	Hg	Cd, Pb, Zn	As	Lipid	PBDE	PFAS	PCDD/Fs	PCB Cong.		
Stateline Bridge [96]	SL	LSS	7	3	5	5	7	7	3		7
Plante Ferry [85]	PF	LSS	7	3	5	5	7	7	3		7
Mission Park	MP	LSS	7	3	5	5	7	7	3		7
[75-78]	MP	MWF	7	3		5	7	7	3	3	7
Ninemile Dam	NM	LSS	7	3		5	7	7	3		7
[62-64]		MWF	7	3	5	5	7	7	3	3	7
Upper Lake		LSS	7	3	5	5	7	7	3		7
Spokane [55]	UL	MWF	7	3		5	7	7	3	3	7
Little Falls	LF	LSS	7	3	5	5	7	7	3		7
Pool [34]	LF	NPM	7	3		5	7	7	3	3	7
Total # Field	I Sample	es	70	30	30	50	70	70	30	12	70
Total # Lab	QC Ana	lyses	67	7	7	10	12	13	6	4	13
Total # of Analyses 429		37	37	60	82	83	36	16	83		
Cost per an	alysis			\$50	\$100	\$20	\$35	\$240	\$800	\$917	\$1164
		Subtot	al costs	\$1850	\$3700	\$1200	\$2870	\$19,920	\$28,800	\$14,672	\$96,612
	Total	Analytic	al Cost								\$169,624

Table 9. Sampling plan and estimated laboratory costs, FFCMP 2023.

*Full analysis plan contingent on funding and subject to fishing conditions. In the event of reduced funding or difficulty catching target species at any sites, analysis priorities will focus on PCBs in LSS across the Spokane River watershed, and other analyses will be performed as practicable.

6.0 Quality Objectives

6.1 Data quality objectives

The data quality objectives for this project are to obtain data of sufficient quantity and quality for use in comparisons to (1) results from previous and future studies and (2) thresholds for the protection of human health. Objectives will be achieved through attention to sample design, sample collection and processing, laboratory measurement of target analytes, collection and review of historical data, data management, and quality control (QC) procedures described or referenced in this plan.

6.2 Measurement quality objectives

The measurement quality objectives (MQOs) for calibration verification, ongoing precision and recovery, and labeled compound recovery correspond to the QC acceptance limits of the analytical methods. Even though fish tissue is a challenging matrix for organics analyses and subject to interferences due to lipids and other compounds, certain lab practices (e.g., sample preparation and cleanup) allow MQOs to be achieved most of the time.

These MQOs correspond to MEL's QC limits (metals and ancillary parameters), or the acceptance limits specified in the analytical methods (organic compounds). The lowest concentrations of interest shown in Tables 10, 11, and 12 below are currently attainable by MEL and contract labs, in most cases. MEL and contract labs are expected to meet the MQOs in Table 10. Results not meeting these MQOs will be evaluated for possible corrective action or use with qualification.

For most analytes, the designated method's achievable reporting limits (RL) will be adequate for this project. For organics, MEL will continue the current practice of reporting results down to their in-house detection limit (DL) and qualify results between the DL and practical quantitation limit (PQL) or estimated quantitation limit (EQL). For PCDD/Fs, contract labs will be required to report down to their in-house DL for all congeners and to qualify results between the DL and PQL or EQL as estimates. These reporting practices improve the ability to compare results to thresholds for the protection of human health and aquatic life.

6.2.1 Targets for precision, bias, and sensitivity.

The MQOs for lab analyses are expressed in terms of acceptable precision, bias, and sensitivity for each analytical method in Table 10. Tables 11 and 12 expand on the sensitivity for individual analytes within a suite of analytes. These MQOs are then briefly discussed. Laboratory Case Narratives will discuss the outcomes of QC practices and address these MQOs for each batch of sample analyses.

		_			(0)		0
	Amplette	Precisio	n (RPD)	Bia	as (% recovery	Sensitivity	
Parameter	Analytical Method	Lab Duplicate	Matrix Spike Duplicate	Lab Control Sample	Surrogate ^a	Matrix Spike ^a	Reporting Limits (ug/kg) ^b
Mercury	EPA 245.6 (CVAA)	0%-20% (for results > 5x RL)	0%-20%	85%- 115%	NA	75%- 125%	17 ug/kg
Arsenic	EPA 6032A or equiv.	0%-20% (for results > 5x RL)	0%-20%	85%- 115%	NA	75%- 125%	0.05 - 0.10 ug/g (dry wt)
PCB congeners (high resolution)	EPA 1668C (HR GC/MS)	0%-40%	NA	g	NA	NA	0.003-0.01 ug/kg
PBDEs	EPA 8270 (SIM); SOP 730104	0%-40%	NA	50%- 150%	50%-150%	50%- 150%	0.10-2.6 ug/kg; PBDE 209 1.9-4.3 ug/kg
PCDD/Fs (high resolution)	EPA 1613B (HR GC/MS)	0%-40%	NA	g	NA	NA	EQL 0.017 – 0.5 ng/kg
PFAS	EPA 1633 ^d	0%-40%	0%-40%	50%- 150%	50%-150%	50%- 150%	0.5-12.5 ug/kg
Lipids	MEL SOP 730009	0%-20%	0%-40%	NA	NA	NA	0.10%

Table 10. Measurement quality objectives by analyte and method.

a - Different ranges of limits can be specific to the surrogate used or to different target analytes.

b - Value reflects typical range.

c - Typical RL; yet interferences may drive the RL higher.

d – MEL is currently analyzing samples using this method under a waiver; project lead will review MDLs of this method prior to processing; if IDCs and MDL study cannot be completed prior to sampling, analysis will be contracted out to an accredited lab.

NA - Not applicable.

Congener	CAS Number	Quantitation Limit (pg/kg)	Detection Limit (pg/kg)	TEF (WHO 2005)
2,3,7,8-TCDD	1746-01-6	0.03	0.013	1
1,2,3,7,8-PeCDD	40321-76-4	0.03	0.022	1
1,2,3,4,7,8-HxCDD	39227-28-6	0.1	0.018	0.1
1,2,3,6,7,8-HxCDD	57653-85-7	0.1	0.019	0.1
1,2,3,7,8,9-HxCDD	19408-74-3	0.1	0.019	0.1
1,2,3,4,6,7,8-HpCDD	35822-46-9	0.2	0.034	0.01
OCDD	3268-87-9	0.5	0.034	0.0003
2,3,7,8-TCDF	51207-31-9	0.05	0.019	0.1
1,2,3,7,8-PeCDF	57117-41-6	0.1	0.023	0.03
2,3,4,7,8-PeCDF	57117-31-4	0.05	0.019	0.3
1,2,3,4,7,8-HxCDF	70648-26-9	0.1	0.024	0.1
1,2,3,6,7,8-HxCDF	57117-44-9	0.1	0.023	0.1
1,2,3,7,8,9-HxCDF	72918-21-9	0.1	0.031	0.1
2,3,4,6,7,8-HxCDF	60851-34-5	0.1	0.025	0.1
1,2,3,4,6,7,8-HpCDF	67562-39-4	0.2	0.008	0.01
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.2	0.012	0.01
OCDF	39001-02-0	0.5	0.042	0.0003

Table 11. Quantitation and detection limits and TEFs for PCDD/F congeners.

TEF - Toxic Equivalency Factor

PCDD/F - Polychlorinated dibenzo-p-dioxin and -furan

Analyte	LLOQ (ug/kg)	MDL (ug/kg)
PFBA	2.0	0.593
PFPeA	1.0	0.083
PFHxA	0.5	0.096
PFHpA	0.5	0.088
PFOA	0.5	0.086
PFNA	0.5	0160
PFDA	0.5	0.124
PFUnA	0.5	0.152
PFDoA	0.5	0.130
PFTrDA	0.5	0.086
PFTeDA	0.5	0.185
PFBS	0.5	0.070
PFPeS	0.5	0.032
PFHxS	0.5	0.083
PFHpS	0.5	0.043
PFOS	0.5	0.294
PFNS	0.5	0.114
PFDS	0.5	0.101
PFDoS	0.5	0.177

Analyte	LLOQ (ug/kg)	MDL (ug/kg)
4:2 FTS	2.0	0.740
6:2 FTS	2.0	1.149
8:2 FTS	2.0	0.373
3:3 FTCA	2.5	0.247
5:3 FTCA	12.5	1.537
7:3 FTCA	12.5	0.845
N-MeFOSAA	0.5	0.093
N-EtFOSAA	0.5	0.138
HFPO-DA	2.0	1.161
ADONA	2.0	0.082
9CI-PF3ONS	2.0	0.152
11CI-PF3OUdS	2.0	0.312
NFDHA	1.0	0.294
PFMPA	1.0	0.070
PFMBA	1.0	0.069
PFEESA	1.0	0.045
PFOSA	0.5	0.094
N-MeFOSA	0.5	0.161
N-EtFOSA	0.5	0.169
N-MeFOSE	5.0	9.978
N-EtFOSE	5.0	1.501

1100

МП

Table 12. Quantification and detection limits for PFAS.

For PFAS compounds, the reporting convention seems to vary among labs and methods. For the compounds in Table 12, the analytical method to be used (EPA 1633) measures the anionic form of PFAS compounds; this is the form that is present in the environment. However, MEL reports results for the acid form of the compounds because the acid form is the form that the analytical standards come in. While the anionic forms of PFAS have been reported by other labs in other studies, this project will use reporting convention of the acid form for the time being. The Interstate Technology Regulatory Council (2020) addresses naming conventions for individual and groups of PFAS compounds. See table 16 for a complete list of PFAS forms.

7.0 Study Design

7.1 Study boundaries

The study boundaries are within the mainstem of the Spokane River between the Washington/Idaho border and Little Falls Dam.

Figure 1 shows the target locations in the Spokane River for 2023 sampling.

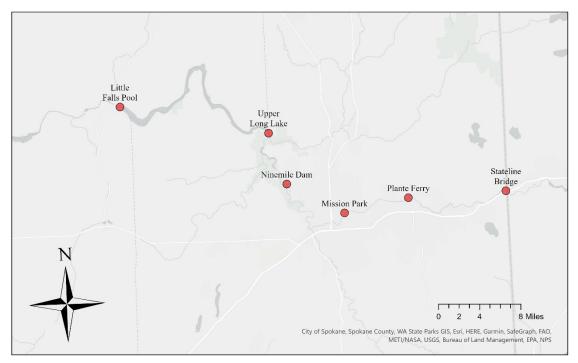


Figure 1. Fish collection sites in the Spokane River for FFCMP 2023.

7.2 Field data collection

7.2.1 Sampling strategy, frequency, and locations

Strategy

The selection of sampling location, species, fish size, and tissue type for the 2023 study was influenced by past sampling studies to capture temporal trends in contaminants. Previous studies (Seiders et al., 2014) recommended the use of largescale suckers (LSS) due to their abundance throughout the sampling area. The 2023 study will also include mountain whitefish (MWF) if possible, and target both species in the same size range as previously sampled (Table 13).

Sample Size

Generally, the sample size needed to detect a given change is dependent upon the sample variance and the statistical parameters of the test (Fabrizio, et al., 1995; Zar, 1984). The number of samples needed to determine the Minimum Detectable Change (MDC) between two data sets using a two-sample test (ex. student's t-test) were estimated using power analyses as described in

Zar (1984). One analyte, PCBs, was the focus of these analyses because PCBs are of greatest interest for temporal trends and had some of the highest variabilities of target analytes.

Sample size estimates were conducted for PCBs in one species (Largescale sucker) from several sites sampled in 2012. For these cases, we set the significance level (alpha) to 0.05 and power (B-1) to 0.8. A series of calculations were made using historical sample variance and different MDCs; the results from these were plotted (Figures 2 and 3) to show the sample sizes needed for given MDCs. These plots were then used to help determine the sampling strategy for the 2023 sampling.

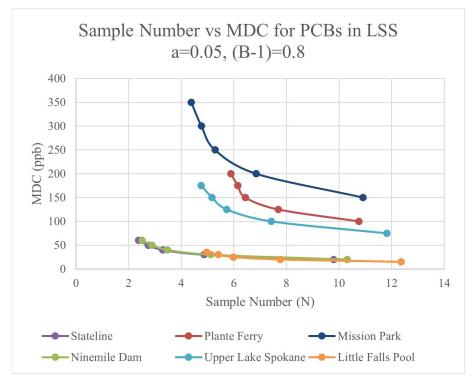


Figure 2. Sample size estimates and MDCs for PCBs in LSS from sites in the Spokane River.

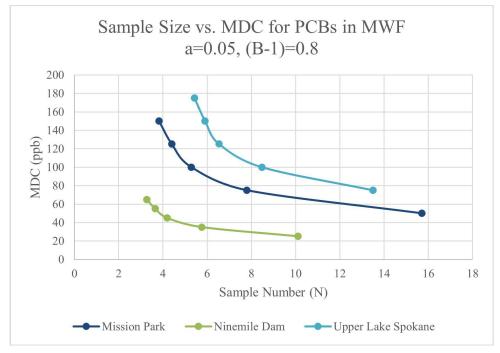


Figure 3. Sample size estimates and MDCs for PCBs in MWF from sites in the Spokane River.

0							
Sample Location [River Mile]	Site Code	Target Species	Target Number of Fish	Target Total Length (mm)	Historical Total Length (mm)		
Stateline Bridge [96]	SL	LSS	21	470-520	473-518		
Plante Ferry [85]	PF	LSS	21	500-530	500-528		
Mission Park		LSS	21	450-540	456-541		
[75-78]	MP	MWF	21	360-390	365-380		
Ninemile Dam	NM	LSS	21	420-490	424-485		
[62-64]	INIVI	MWF	21	290-340	298-333		
Upper		LSS	21	460-520	467-518		
Lake Spokane [55]	UL	MWF	21	260-300	264-296		
Little Falls Pool		LSS	21	410-430	419-430		
[34]	LF	NPM	21	350-360	353-360		

Table 13. Target numbers and size ranges for Spokane River fish, FFCMP 2023.

8.0 Field Procedures

8.4 Equipment decontamination

Decontamination procedures for the 2023 study will be slightly modified to accommodate for the addition of PFAS analytes. The modification substitutes methanol for acetone and hexane for the final solvent rinses of equipment used to process samples. The original decontamination procedure is documented in Standard Operating Procedure (SOP) EAP007, Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2018) and Ecology's Chemical Hygiene Plan (Ecology, 2019). The modified practice is found in SOP EAP090, Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples (Friese, 2014).

9.0 Laboratory Procedures

Multiple labs will be used to analyze samples collected from the Spokane River. Many analyses will be performed by MEL whereas contract labs will conduct analyses for arsenic speciation and PCB congeners using High Resolution Mass Spectrometry (HRMS).

The process for obtaining contract lab services involves varied staff having different expertise and roles. To help communication among all involved with this process, the checklist in Appendix A was developed. The Project Manager will track the progress of the process by using the checklist.

9.1 Lab procedures table

Parameter	Number of Samples, Arrival Date	Expected Range of Results	Reporting Limits ^a	Analytical Method	Sample Preparation Method
Mercury	N=30 Jan. 2024	10-500 ug/kg	17 ug/kg	EPA 245.6 (CVAA)	EPA 245.6
Arsenic: MMA, DMA, InorgAs	N=50 Jan. 2024	Likely non-detect to low (up to 5x RL)	0.05-0.10 ug/kg ww	EPA 1632A or equivalent	Per method
Metals: Cd, Pb, Zn	N=30 Jan. 2024	0.1-100 ug/kg	100-5000 ug/kg ^e	EPA 6020B	EPA 3050B
PCB congeners (high resolution)	N=70 Jan. 2024	0.005-100 ug/kg, depending on congener	0.003-0.01 ug/kg	EPA 1668C (HR GC/MS)	EPA 1668C, lab SOPs
PBDEs	N=70 Jan. 2024	0.1-50 ug/kg	0.10-2.6 ug/kg; BDE 209 1.9- 4.3 ug/kg	EPA 8270E (SIM) SOP 730104	Prep: EPA 3541 Modified Cleanup: EPA 3620C Modified, EPA 3665A Modified
PFAS	N=30 Jan. 2024	<0.2-300 ug/kg per analyte	0.5-12.5 ug/kg	EPA 1633 ^b	EPA 1633 ^b ; lab SOPs
PCDD/Fs	N=12 Jan. 2024	0.005 – 5.0 ng/kg, depending on congener	0.017 – 0.5 ng/kg ^d	EPA 1613B (HR GC/MS)	EPA 1613B, lab SOPs
Lipids	N=70 Jan. 2024	0.1-20%	0.10%	MEL SOP 730009	EPA 3541 Modified

Table 14. Measure methods (laboratory).

a - The reporting limit for low-resolution methods is the Lower Limit of Quantitation while for high resolution methods it is the Estimated Detection Limit.

b - MEL is currently analyzing samples using this method under a waiver. The project lead will review MDLs of this method prior to processing. If the IDCs and MDL study cannot be completed prior to sampling, analysis will be contracted out to an accredited lab.

MMA - monomethylarsonic acid DMA - dimethylarsinic acid

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 15. Laboratory quality control sample types and frequencies.

Parameter	Analytical Method	Lab Duplicates	Lab Control Standards	Surrogates	MS/ MSD	Method Blanks
Mercury	EPA 245.6 (CVAA)	1/ batch ^a	1/batch	NA	1/batch	1/batch
Arsenic: As(III), As(V), MMA, DMA, InorgAs	EPA 6032A or equiv.	1/batch	1/batch	NA	1/batch	1/batch
Metals: Cu, Pb, Zn	EPA 6020D	1/batch	1/batch	NA	1/batch	1/batch
PCB congeners ^b	EPA 1668C (HR GC/MS)	1/batch	each sample & 1/batch ^b	NA	NA	1/batch
PBDEs	EPA 8270 (SIM), MEL SOP 730104	1/batch	1/batch	each sample	1/batch	1/batch
PCDD/Fs	EPA 1613B (HR GC/MS)	1/batch	each sample & 1/batch	NA	NA	1/batch
PFAS °	EPA 8327 modified (LC-MS/MS with isotopic dilution)	1/batch	1/batch	each sample	1/batch	1/batch
Lipids	MEL SOP 730009	1/batch	1/batch	NA	NA	1/batch

a - "Batch" is defined as up to 20 samples analyzed together.

b – Certified Reference Material "CARP-2" from National Research Council Canada to be analyzed once per sample delivery group.

c – Standard Reference Material 1947 from National Institute for Standards and Technology (NIST) to be analyzed once per batch.

MMA - monomethylarsonic acid

DMA - dimethylarsinic acid

11. Data Management Procedures

11.2 Laboratory data package requirements.

Lab results from MEL analyses will be sent to the Project Manager via LIMS transfer to EIM and be accompanied by a Case Narrative. The Case Narrative will address various data verification and validation checks described in Section 13 below. Results from contract labs will be delivered to MEL. These results will contain information specified in one of two documents, depending on how contract labs are selected. For labs that are already on the State Master Contract List, one document called a Statement of Work (SOW) will describe the project needs for analysis and reporting. For other labs, the same SOW can be used. If a bid process is needed, the SOW will be incorporated into a document called a Request for Quotes (RFQ).

For work conducted by contract labs, MEL's Data Validation Chemist will review the Level 4 data package from the contract lab and summarize findings in a Case Narrative like that of MEL-generated data and validated Electronic Data Deliverable (EDD).

11.3 Electronic transfer requirements

MEL staff will enter lab data generated by MEL into their Laboratory Information Management System (LIMS). When notified of the availability of data, project staff can then access LIMS data and receive the data in an Excel file formatted similar to the EIM loading template.

For PFAS compounds, there are different reporting conventions among labs and methods. To help promote more consistent nomenclature, the Interstate Technology Regulatory Council (2020) addresses naming conventions for individual and groups of PFAS compounds.

Abbreviation	Name	CAS#
PFBA	Perfluorobutanoate	45048-62-2
TTDA	Perfluorobutyric acid	375-22-4
PFPeA	Perfluoropentanoate	45167-47-3
1110/1	Perfluoropentanoic acid	2706-90-3
PFHxA	Perfluorohexanoate	92612-52-7
	Perfluorohexanoic acid	<u> </u>
PFHpA	PFHpA Perfluoroheptanoate	
1	Perfluoroheptanoic acid	375-85-9
PFOA	Perfluorooctanoate Perfluorooctanoic acid	<u>45285-51-6</u> <u>335-67-1</u>
	Perfluorononanoate	72007-68-2
PFNA	Perfluorononanoic acid	375-95-1
	Perfluorodecanoate	73829-36-4
PFDA	Perfluorodecanoic acid	335-76-2
	Perfluoroundecanoate	196859-54-8
PFUnA	Perfluoroundecanoic acid	2058-94-8
Abbreviation	Name	CAS#
	Perfluorododecanoate	171978-95-3
PFDoA	Perfluorododecanoic acid	307-55-1
	Perfluorotridecanoate	862374-87-6
PFTrDA	Perfluorotridecanoic acid	72629-94-8
	Perfluorotetradecanoate	365971-87-5
PFTeDA	Perfluorotetradecanoic acid	376-06-7
PFBS	Perfluorobutanesulfonate	45187-15-3
1105	Perfluorobutanesulfonic acid	375-73-5
PFPeS	Perfluoropentanesulfonate	175905-36-9
11105	Perfluoropentanesulfonic acid	2706-91-4
DELL C	Perfluorohexanesulfonate	108427-53-8
PFHxS	Perfluorohexanesulfonic acid	355-46-4
DELL C	Perfluoroheptanesulfonate	146689-46-5
PFHpS	Perfluoroheptanesulfonic acid	375-92-8
PFOS	Perfluorooctanesulfonate	45298-90-6
1105	Perfluorooctanesulfonic acid	1763-23-1
DENIC	Perfluorononanesulfonate	474511-07-4
PFNS	Perfluorononanesulfonic acid	68259-12-1
PFDS	Perfluorodecanesulfonate	126105-34-8
1105	Perfluorodecanesulfonic acid	335-77-3
PFDoS	Perfluorododecanesulfonate	343629-43-6
	Perfluorododecanesulfonic acid	79780-39-5
4:2 FTS	4:2 fluorotelomersulfonate	414911-30-1
	4:2 fluorotelomersulfonic acid	757124-72-4
6:2 FTS	6:2 fluorotelomersulfonate	425670-75-3
9.2 ETC	6:2 fluorotelomersulfonic acid	27619-97-2
8:2 FTS	8:2 fluorotelomersulfonate	481071-78-7

Table 16. PFAS abbreviations with corresponding anionic and acid forms.

	8:2 fluorotelomersulfonic acid	39108-34-4		
3:3 FTCA	3:3 perfluorohexanoate	1169706-83-5		
5.5 FICA	3:3 perfluorohexanoic acid	356-02-5		
5:3 FTCA	5:3 perfluorooctanoate			
5.5 FICA	5:3 perfluorooctanoic acid	914637-49-3		
7:3 FTCA	7:3 perfluorodecanoate	1799325-95-3		
7.5 FICA	7:3 perfluorodecanoic acid	812-70-4		
		-		
N-MeFOSAA	N-Methylperfluorooctanesulfonamidoacetate	n.a.		
N-MEPOSAA	N-Methylperfluorooctanesulfonamidoacetic acid	2355-31-9		
N-EtFOSAA	N-Ethylperfluorooctanesulfonamidoacetate	n.a.		
N-EIFOSAA	N-Ethylperfluorooctanesulfonamidoacetic acid	2991-50-6		
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3- heptafluoropropoxy)propanoate	122499-17-6		
nff0-da	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3- heptafluoropropoxy)propanoic acid	13252-13-6		
ADONA	Dodecafluoro-3H-4,8-dioxanonanoate	2127366-90-7		
ADONA	Dodecafluoro-3H-4,8-dioxanonanoic acid	919005-14-4		
Abbreviation	Name	CAS #		
9C1-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	1621485-21-9		
9CI-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1		
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	2196242-82-5		
TICI-FF500us	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9		
		-		
NFDHA	Perfluoro-3,6-dioxaheptanoate	39187-41-2		
NIDIIA	Perfluoro-3,6-dioxaheptanoic acid	151722-58-6		
PFMPA	Perfluoro-3-methoxypropanoate	n.a.		
TIMIA	Perfluoro-3-methoxypropanoic acid	377-73-1		
PFMBA	Perfluoro-4-methoxybutanoate	1432017-36-1		
TTWIDA	Perfluoro-4-methoxybutanoic acid	863090-89-5		
PFEESA	Perfluoro(2-ethoxyethane)sulfonate	220689-13-4		
FFEE5A	Perfluoro(2-ethoxyethane)sulfonic acid	113507-82-7		
PFOSA	Perfluorooctanesulfonamide	754-91-6		
N-MeFOSA	N-Methylperfluorooctanesulfonamide	31506-32-8		
N-EtFOSA	N-Ethylperfluorooctanesulfonamide	4151-50-2		
N-MeFOSE	N-Methylperfluorooctanesulfonamidoethanol	24448-09-7		
N-EtFOSE	N-Ethylperfluorooctanesulfonamidoethanol	1691-99-2		

13. Data Verifications

13.1 Laboratory data verification, requirements, and responsibilities

Results generated by MEL will follow the same verification processes for managing contract laboratory expectations as described in QAPP Addendum 2 (Seiders and Sandvik, 2021).

13.2 Laboratory data verification

As previously described, MEL will oversee the review and verification of all lab 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.
- Preparation benchsheets.

MEL must provide all necessary QA/QC documentation, including results from matrix spikes, replicates, and blanks.

A Level 4 data validation of all contracted data will be requested for this project and will include the conversion of contract laboratory flags to MEL-amended qualifiers. Data validation will be carried out by the MEL Data Validation Chemist. A Level 4 data package will be required from the contract lab if a Level 4 data validation be necessary in the future.

13.3 Validation requirements, if necessary

Validation is not required for the 2023 study. However, to provide confidence in report data and potential trends, MEL will conduct a "same-party validation" on their analyses. Contract lab data will be validated as stated above.

14. Data Quality (Usability) Assessment

14.2 Treatment of non-detects

Results of lab analysis will be reported down to the method reporting limit (MRL). Results below reporting limits will be qualified as non-detects. In cases where target analytes are detected in the method blank above the MRL, the reporting limit will be raised to three times the concentration detected in the method blank. Censoring levels are typically 3x, 5x, or 10x the concentration of the method blank. The 3x level is the censuring level recommended by the Spokane River Toxics Task Force for studies in the Spokane River. Although this censuring level has a higher chance of producing false positives, we consider it appropriate based on the goals of this study: trend detection.

Method 1633 requires that water samples be rejected if they are over the holding time of 90 days and qualified as a non-detect. We will not reject PFAS results over holding time because studies have shown that most PFAS compounds are relatively stable in fish tissues and relatively stable when stored properly at -20 to 0 degrees Celsius (Woudneh et al. 2019). We expect PFAS samples to be analyzed close to the 90-day holding time and no more than 180 days. Tissue sample holding times recommended by other methods are one year.

15.0 References

 Davis, D., A. Johnson, and D. Serdar, 1995. Washington State Pesticide Monitoring Program: 1993 Fish Tissue Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication 95-356. https://apps.ecology.wa.gov/publications/summarypages/95356.html.

Ecology, 1995. Department of Ecology 1993-94 Investigation of PCBs in the Spokane River. Washington State Department of Ecology. Publication 95-310. <u>https://apps.ecology.wa.gov/publications/SummaryPages/95310.html</u>.

- Ecology, 2007. Spokane River PCB TMDL Stormwater Loading Analysis Final Technical Report. Washington State Department of Ecology, Olympia, WA. Publication 07-03-055. <u>https://apps.ecology.wa.gov/publications/SummaryPages/0703055.html</u>.
- Ecology, 2012. Spokane River Toxics Reduction Strategy. Washington State Department of Ecology, Olympia, WA. Publication 11-10-038. https://apps.ecology.wa.gov/publications/SummaryPages/1110038.html.
- Ecology, 2019. Chemical Hygiene Plan and Hazardous Materials Management Plan. February 2019. Washington Department of Ecology, Olympia, WA.
- Ecology and Health, 2022. Per- and Polyfluoroalkyl Substances Chemical Action Plan. Washington State Department of Ecology and Department of Health, Olympia, WA. Publication 21-04-048. https://apps.ecology.wa.gov/publications/SummaryPages/2104048.html.
- Era-Miller, B., 2004. Verification of 303(d)-listed Sites in Northwest, Central, and Eastern Regions of Washington State. Washington State Department of Ecology, Olympia, WA. Publication 04-03-035. https://apps.ecology.wa.gov/publications/SummaryPages/0403035.html.
- Era-Miller, B., 2015. Lake Spokane: PCBs in Carp. Washington State Department of Ecology, Olympia, WA. Publication 15-03-022. <u>https://apps.ecology.wa.gov/publications/SummaryPages/1503022.html</u>.
- Era-Miller, B. and S. Wong, 2015. Atmospheric Deposition of PCBs in the Spokane River Watershed. Washington State Department of Ecology, Olympia, WA. Publication 19-03-003.

https://apps.ecology.wa.gov/publications/SummaryPages/1903003.html.

- Fabrizio, M.C., A.M. Frank, and J.F. Savino, 1995. Procedures for formation of composite samples from segmented populations. Environmental Science and Technology, Vol. 29(5):1137-1144.
- Fernandez, A., 2012. Spokane River Urban Waters Source Investigation and Data Analysis Progress Report (2009-2011): Source Tracing for PCB, PBDE, Dioxin/Furan, Lead, Cadmium, and Zinc. Urban Waters Initiative, Washington State Department of Ecology, Spokane, WA. Publication 12-04-025. https://apps.ecology.wa.gov/publications/SummaryPages/1204025.html.

- Friese, M., 2014. Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP EAP090.
- Furl, C. and C. Meredith, 2010a. PBT Monitoring: PBDE Flame Retardants in Spokane River Fish, 2009. Washington State Department of Ecology, Olympia, WA. Publication 10-03-015. <u>https://apps.ecology.wa.gov/publications/SummaryPages/1003015.html</u>.
- Furl, C. and C. Meredith, 2010b. Perfluorinated Compounds in Washington Rivers and Lakes. Washington State Department of Ecology, Olympia, WA. Publication 10-03-034. <u>https://apps.ecology.wa.gov/publications/SummaryPages/1003034</u>.
- Health, 2011. Potential Cumulative Health Effects Associated with Eating Spokane River Fish. Washington State Department of Health, Olympia, WA. Publication DOH 334-275.
- Health, 2022a. Fish Advisory Evaluation: PFOS in Fish from Lakes Meridian, Sammamish, and Washington. Washington State Department of Health, Olympia, WA. Publication DOH 334-470.
- Health, 2022b. Focus on: PFAS Cleanup Levels. Washington State Department of Health, Olympia, WA. Publication 22-09-075. <u>https://apps.ecology.wa.gov/publications/SummaryPages/2209075.html</u>.
- 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 85-7. <u>https://apps.ecology.wa.gov/publications/SummaryPages/857.html</u>.
- Interstate Technology Regulatory Council, 2020. Naming conventions and physical and chemical properties of per- and polyfluoroalkyl substances (PFAS). Interstate Technology Regulatory Council, Washington D.C. April 2020.
- Jack, R. and M. Roose, 2002. Analysis of Fish Tissue from Long Lake (Spokane River) for PCBs and Selected Metals. Washington State Department of Ecology, Olympia, WA. Publication 02-03-049. https://apps.ecology.wa.gov/publications/summarypages/0203049.html

https://apps.ecology.wa.gov/publications/summarypages/0203049.html

- Johnson, A., 1994. Planar PCBs in Spokane River Fish. Memorandum to C. Nuechterlein. Washington State Department of Ecology, Olympia, WA. Publication 94-e23. <u>https://apps.ecology.wa.gov/publications/summarypages/94e23.html</u>
- Johnson, A., 1997. 1996 Results on PCBs in Upper Spokane River Fish. Memorandum to C. Nuechterlein and D. Knight. Washington State Department of Ecology, Olympia, WA. Publication 97-e04. https://apps.ecology.wa.gov/publications/documents/97e04.pdf
- Johnson, A., 2000. Results from Analyzing PCBs in 1999 Spokane River Fish and Crayfish Samples. Memorandum to J. Roland. Washington State Department of Ecology, Olympia, WA. Publication 00-03-040. <u>https://apps.ecology.wa.gov/publications/summarypages/0003040.html</u>
- Johnson, A. and D. Norton, 2011. Spokane River PCB Source Assessment, 2003-2007. Washington State Department of Ecology, Olympia, WA. Publication 11-03-013. https://apps.ecology.wa.gov/publications/summarypages/1103013.html

- Limnotech, 2016. Spokane River Regional Toxics Task Force 2015 Technical Activities Report: Continued Identification of Potential Unmonitored Dry Weather Sources of PCBs to the Spokane River.
- Mathieu, C. and M. McCall, 2017. Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016. Washington State Department of Ecology, Olympia, WA. Publication 17-03-021.

https://apps.ecology.wa.gov/publications/SummaryPages/1703021.html.

- SAIC, 2003. Report of Sampling and Analysis for PCBs in Fish Tissue from Lake Coeur d'Alene. *Prepared for* Washington State Department of Ecology, Eastern Regional Office by Science Applications International Corporation, Bothell, WA.
- Sandvik, P., 2018. Standard Operating Procedure EAP007, Version 1.2: Resecting Finfish Whole Body, Body Parts, and Tissue Samples. Washington State Department of Ecology, Olympia, WA. SOP EAP007.
- Seiders, K., C. Deligeannis, P. Sandvik, 2007. Washington State Toxics Monitoring Program: Contaminants in Fish Tissue from Freshwater Environments in 2004 and 2005. Washington State Department of Ecology, Olympia, WA. Publication 07-03-024. <u>https://apps.ecology.wa.gov/publications/summarypages/0703024.html</u>.
- Seiders, K. and P. Sandvik, 2021. Addendum 2 to Quality Assurance Project Plan, Freshwater Fish Contaminant Monitoring Program, 2021: Lake Chelan. Washington State Department of Ecology, Olympia, WA. Publication 21-03-117. <u>https://apps.ecology.wa.gov/publications/SummaryPages/2103117.html</u>.
- Seiders, K., C. Deligeannis, P. Sandvik, and M. McCall, 2014. Freshwater Fish Contaminant Monitoring Program: 2012 Results. Washington State Department of Ecology, Olympia, WA. Publication 14-03-020. https://apps.ecology.wa.gov/publications/SummaryPages/1403020.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 06-03-025. https://apps.ecology.wa.gov/publications/summarypages/0603025.html
- Serdar, D., A. Johnson, and D. Davis, 1994. Survey of Chemical Contaminants in Ten Washington Lakes. Washington State Department of Ecology, Olympia, WA. Publication 94-154. <u>https://apps.ecology.wa.gov/publications/documents/94154.pdf</u>
- 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 11-03-013. https://apps.ecology.wa.gov/publications/summarypages/1103013.html.
- U.S. Environmental Protection Agency, 2020. National Coastal Condition Assessment 2015 Technical Support Document. EPA-841-R-20-002. Office of Water and Office of Research and Development. Washington, D.C. <u>https://www.epa.gov/national-aquatic-resource-surveys/ncca</u>.
- U.S. Environmental Protection Agency, 2022a. Lifetime Drinking Water Health Advisories for Perfluoroalkyl Substances. Notice. Document Number: 2022-13158. 87 FR 36848.

- U.S. Environmental Protection Agency, 2022b. Fact Sheet: Draft 2022 Aquatic Life Ambient Water Quality Criteria for Perfluorooctanoic acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS). EPA-842-D-22-005. Office of Water. <u>https://www.epa.gov/system/files/documents/2022-04/pfoa-pfos-draft-factsheet-2022.pdf</u>
- Wong, S., 2018, Evaluation of Fish Hatcheries as Sources of PCBs to the Spokane River. Washington State Department of Ecology, Olympia, WA. Publication 18-03-014. <u>https://apps.ecology.wa.gov/publications/SummaryPages/1803014.html</u>.
- Wong, S. and C. Mathieu, 2020. Quality Assurance Project Plan: Survey of PFAS in the Greater Lake Washington Watershed. Washington State Department of Ecology, Olympia, WA. Publication 12-04-112. https://apps.ecology.wa.gov/publications/SummaryPages/1204112.html.
- Woudneh, Million B., Chandramouli, B., Hamilton, C., Grace, R., 2019. Effect of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage. Environmental Science and Technology. 53(21), 12576 – 12585.

https://pubs.acs.org/doi/pdf/10.1021/acs.est.9b03859

Zar, J.H., 1984. Biostatistical analysis: Second edition. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 718 pp.

16.0 Appendices

Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Analyte: A substance or constituent being measured in an analytical procedure. (Parameter). A physical, chemical, or biological property whose measured value helps determine the characteristics of something of interest.

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

Congener: In chemistry, congeners are related chemicals. For example, polychlorinated biphenyls (PCBs) are a group of 209 molecules that are related by a similar structure and are called congeners.

Fish Tissue Equivalent Concentration (FTEC): The concentration of a contaminant in fish tissue that equates to Washington's water quality standard for toxic substances for the protection of human health. Washington uses the National Toxics Rule Water Quality Criteria for the protection of human health. The FTEC is calculated by multiplying the contaminant-specific Bioconcentration Factor (BCF) times the contaminant-specific National Toxics Rule Water Quality Criterion for water.

Spatial: Relating to space, location, and distance, such as between two sampling sites.

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.

Temporal: Relating to time, such as between one year and another.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Trend: A meaningful change or difference that can be measured and differentiated from measurement error. Often used in the context of time (temporal trend) or space (spatial trend)

Abbreviations and Acronyms

ANOVA	Analysis of Variance
As	Arsenic
BLT	Bull trout (Salvelinus confluentus)
BNT	Brown trout (Salmo trutta)
CB	Chlorinated biphenyl
Cd	Cadmium
CTT	Cutthroat trout (Oncorhynchus clarki)
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
EBT	Eastern brook trout (Salvelinus fontinalis)
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FCA	Fish Consumption Advisory

FFCMP FTEC	Freshwater Fish Contaminant Monitoring Program
Health	Fish tissue equivalent concentration (see Glossary) Washington State Department of Health
J	estimated value
J KOK	
	Kokanee (Oncorhynchus nerka)
LMB LSS	Largemouth bass (Micropterus salmoides)
	Largescale sucker (Catostomus macrocheilus)
m MDC	mean value from multiple samples
MDC	Minimum Detectable Change
MEL	Manchester Environmental Laboratory
MWF	Mountain whitefish (Prosopium williamsoni)
na	Not analyzed
nd	Not detected
NOP	Northern pike (Esox lucius)
NPM	Northern pikeminnow (Ptychocheilus oregonensis)
Pb	Lead
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxin and -furan
PFAS	Per- and polyfluoroalkyl substances
RBT	Rainbow trout (Oncorhynchus mykiss)
SV	Screening value
t-PCBs	Total PCBs
t-PBDEs	Total PBDEs
TCDD	2,3,7,8-tetra-chlorinated dibenzo-p-dioxin
TEF	Toxic equivalency factor
TEQ	Toxicity equivalent
TMDL	Total Maximum Daily Load (see Glossary)
U	Not detected at the reported value
UJ	Undetected at the estimated reported value
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area
YP	Yellow perch (Perca flavescens)
Zn	Zinc

Units of Measurement

< less than > greater than = equal to ft feet g gram, a unit of mass kg kilograms, a unit of mass equal to 1,000 grams mg milligram mg/kg milligrams per kilogram (parts per million) ng/kg nanograms per kilogram (parts per trillion; ppt) ug/g micrograms per gram (parts per million) ug/kg micrograms per kilogram (parts per billion)

Appendix B. Historical Data

Table B-1. Concentrations of mean total PCBs (ug/kg wet weight) in whole fish of all sucker species from past studies.

	1980-83	1993 ¹	1994 ¹	1996 ¹	1999 ¹	2001 ¹	2003-04 ?	2005 ²	2012
Little Falls Pool									33
Upper Lake Spokane						265		327	191
Above Ninemile Dam	195 599*	1210		345	680		29	69*	37
Above Monroe Dam/ Mission Park			201	116	445			1,823	132
Plante Ferry	181.5^	2005	531	530	283		97	122	126
Stateline Bridge					120		100	56	46

All largescale suckers except: *indicates bridgelip sucker, and ^indicates longnose sucker.

¹Arocolor analysis

²Congener analysis

Table B-2: Concentrations of mean total PBDEs (ug/Kg wet weight) in whole suckers and mountain whitefish from past studies.

		2005	2009	2012
Little Falls Pool	LSS			36
Linner Lake Snakana	LSS		237	200
Upper Lake Spokane	MWF	183	173	313
Above Ninemile Dam	LSS		208	204
Above Ninemine Dam	MWF	977	507	1233
Above Monroe Dam/ Mission Park	LSS		33	57
Above Monroe Dani/ Mission Park	MWF	355	249	266
Plante Ferry	LSS		90	126
Stateline Bridge	LSS		115	136