DEPARTMENT OF ECOLOGY
State of Washington

Addendum to
Quality Assurance Project Plan

Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes

December 2018
Publication No. 18-03-117

Publication Information

Addendum

This addendum is on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1803117.html

This addendum is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at EIM Database. Search Study ID: CAME004

Activity Tracker Code

Ecology's Activity Tracker code for this addendum is 15-069.

Original Publication

Quality Assurance Project Plan: Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes

Ecology Publication No. 16-03-110
https://fortress.wa.gov/ecy/publications/SummaryPages/1603110.html

Author and Contact Information

Callie Mathieu
Environmental Assessment Program
Washington State Department of Ecology
PO Box 47600
Olympia, WA 98504-76000

For more information contact:
Communications Consultant
Phone: 360-407-6834

Addendum to Quality Assurance Project Plan

Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes

December 2018

Approved by:

Signature: _____ Date: _____
Debby Sargeant, Client, EAP

Signature: _____ Date: _____
Jessica Archer, Client, EAP

Signature: _____ Date: _____
Callie Mathieu, Author/Project Manager/Principal Investigator

Signature: _____ Date: _____
Patti Sandvik, Field Lead

Signature: _____ Date: _____
Dale Norton, Section Manager for Project Study Area, EAP

Signature: _____ Date: _____
Alan Rue, Director, Manchester Environmental Laboratory

Signature: _____ Date: _____
Tom Gries, Acting Ecology Quality Assurance Officer

Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

3.0 Background

In 2016, The Washington State Department of Ecology (Ecology) conducted a study to characterize levels of per- and poly-fluoroalkyl substances (PFAS) in Washington freshwater systems (Mathieu and McCall, 2018). The goal of the study was to determine if PFAS concentrations and/or compound makeup had changed since the first round of sampling in 2008 (Furl and Meredith, 2010). The study assessed PFAS concentrations in surface water, wastewater treatment plant (WWTP) effluent, freshwater fish tissue, and osprey eggs. The 2016 results showed a general decrease in detection frequencies and concentrations in surface water samples and WWTP effluent compared to 2008; however, no change was seen in fish tissue or osprey egg PFAS levels. The 2016 study concluded that PFAS – and in particular perfluorooctane sulfonate (PFOS) – continue to be a ubiquitous contaminant in aquatic biota.

PFAS concentrations measured in the 2016 fish fillet samples were highest in urban waterbodies collected in Western Washington. Six out of seven samples collected from three urban lakes (Angle Lake, Lake Meridian, and Lake Washington) had PFOS concentrations above (greater than) the Washington State Department of Health's (DOH's) provisional general population screening level for PFOS in edible fish tissue (23 ng/g). The urban lakes were the only waterbodies to exceed the DOH provisional general population screening level. The provisional screening levels may trigger a fish consumption advisory after DOH toxicologists assess a waterbody for fish consumption risk management and risk communication issues. The number of samples collected in 2016 was not enough for DOH to assess the waterbodies.

Because the 2016 study was limited in number of fish tissue samples, Ecology will collect additional fish samples in fall 2018 to gain a fuller understanding of PFAS levels in urban waterbodies. Ecology will revisit two waterbodies where multiple fish fillet tissue samples had PFOS concentrations greater than the DOH provisional screening level in 2016 (Lake Meridian and Lake Washington) as well as an additional urban lake – Lake Sammamish. Angle Lake will not be re-sampled because the fish community is not large enough to collect the number of samples targeted. Lake Sammamish was selected to evaluate levels of PFAS in fish from the waterbody, as PFOS was reported in drinking water well samples in the lake's watershed between 2013 and 2016 (City of Issaquah, 2015).

This addendum outlines the follow-up sampling of PFAS in freshwater fish tissue from three waterbodies and includes only sections that differ from the original QAPP (Mathieu, 2016). For project plan elements not addressed in this addendum, refer to text in the original QAPP that specifically relates to fish tissue. Other media types that were tested in 2016 (surface water, wastewater treatment plant effluent, and osprey eggs) will not be tested in 2018.

3.1 Study area and surroundings

Ecology will collect resident freshwater fish samples from Lake Meridian, Lake Sammamish, and Lake Washington. Figure 1 shows the study locations for the 2018 sampling.

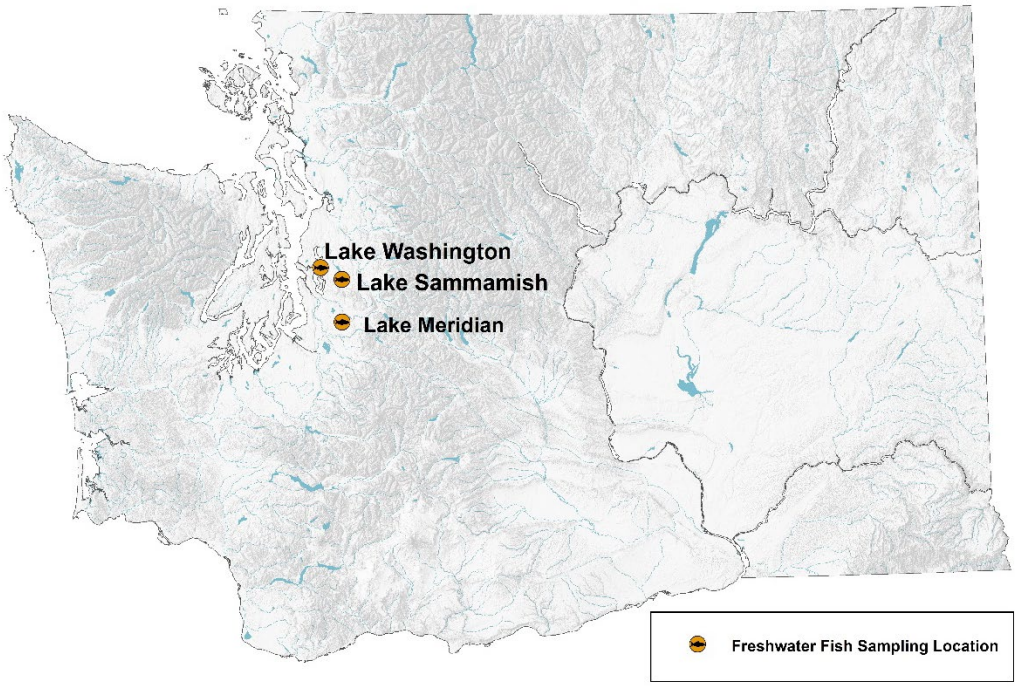

Figure 1. Study locations for 2018 sampling.

3.1.4 Results of previous studies

Three studies have analyzed PFAS in freshwater fish tissue collected from at least one of the 2018 sampling locations (Furl and Meredith, 2010; Johnson and Friese, 2012; Mathieu and McCall, 2017). Table 1 presents the PFAS results from those studies that are relevant to this project.

Table 1. Previous PFAS in freshwater fish fillet tissue data from Lake Washington and Lake Meridian.

Waterbody	Species	Collection Date	No. in Composite	Mean Fish Total Length (mm)	Mean Fish Weight (g)	PFOS (ng/g ww)	PFDA (ng/g ww)	PFDoA (ng/g ww)	PFUnA (ng/g ww)	Reference
Lake Washington	LMB	2008	5	215	131	33.6	5 U	5 U	5 U	Furl and Meredith, 2010
Lake Washington	LSS	2008	4	473	1186	11.1	5 U	5 U	5 U	
Lake Washington	PEA	2008	5	297	241	51.2	5 U	5.5 J	7.15	
Lake Washington	YP	2008	3	198	82	22.5	5 U	5 U	5 U	
Lake Washington	CCP	2011	1	592	3262	15.7	1.17	1.75	1.31	Johnson and Friese, 2012
Lake Washington	LMB	2016	5	341	666	52.7	5.53	6.04	5.51	Mathieu and McCall, 2017
Lake Washington	LSS	2016	3	495	1,408	4.81	0.5 U	0.862	0.553	
Lake Washington	PEA	2016	4	305	273	31.4	2.63	1.88	2.22	
Lake Washington	YP	2016	3	209	115	26.9	2.16	0.633	0.88	
Lake Meridian	LMB	2016	4	228	163	39.6	3.73	1.08	0.952	
Lake Meridian	LMB	2016	3	296	397	23.5	2.01	1.29	0.798	

PFOS = Perfluorooctane sulfonate
PFDA = Perfluorodecanoate
PFDoA = Perfluorododecanoate
PFUnA = Perfluoroundecanoate
LMB = largemouth bass
LSS = largescale sucker
PEA = peamouth
YP = yellow perch
CCP = common carp
U = Analyte was not detected at or above the reported result.
J = Analyte was detected and the result value is an estimate.

4.0 Project Description

4.1 Project goals

This project is being carried out to fulfill two goals from the original QAPP:

- Characterize current levels of PFAS in selected Washington State freshwater systems.
- Provide data to support PFAS chemical action plans and recommendations.

The following goal has been added to this project:

- Provide sufficient data on selected waterbodies so that DOH can assess the waterbodies for human consumption of fish.

4.2 Project objectives

The following objectives will be carried out in 2018 to meet project goals:

- Ecology will collect freshwater fish from Lake Meridian, Lake Sammamish, and Lake Washington in the fall for analysis of PFAS in edible fillet tissue. A target of five composite samples per species of up to three species per waterbody will be analyzed for PFAS. Composite samples will consist of 3 – 5 individual fish.

4.4 Target population

The target population is resident freshwater fish species within each of the three waterbodies. Field crews will attempt to collect 10 – 25 individuals of up to three species from each site. Largemouth bass, yellow perch, and one additional species will be targeted at each site. Additional species will depend on what is encountered during field collections and may include cutthroat trout, brown bullhead, black crappie, common carp, kokanee, largescale sucker, peamouth, or pumpkinseed.

4.5 Study boundaries

The study boundary for Lake Meridian and Lake Sammamish will be the entire lake shoreline. Fish will be collected throughout the lake at those sites. Lake Washington will be separated into three sites: south, central, and north basins (Figure 2). All fish collected in the respective basins will be retained and analyzed separately. The Lake Washington basins will be delineated by the following latitudes:

- South basin: between 47.502 and 47.579.
- Central basin: between 47.579 and 47.664.
- North basin: between 47.664 and 47.756.

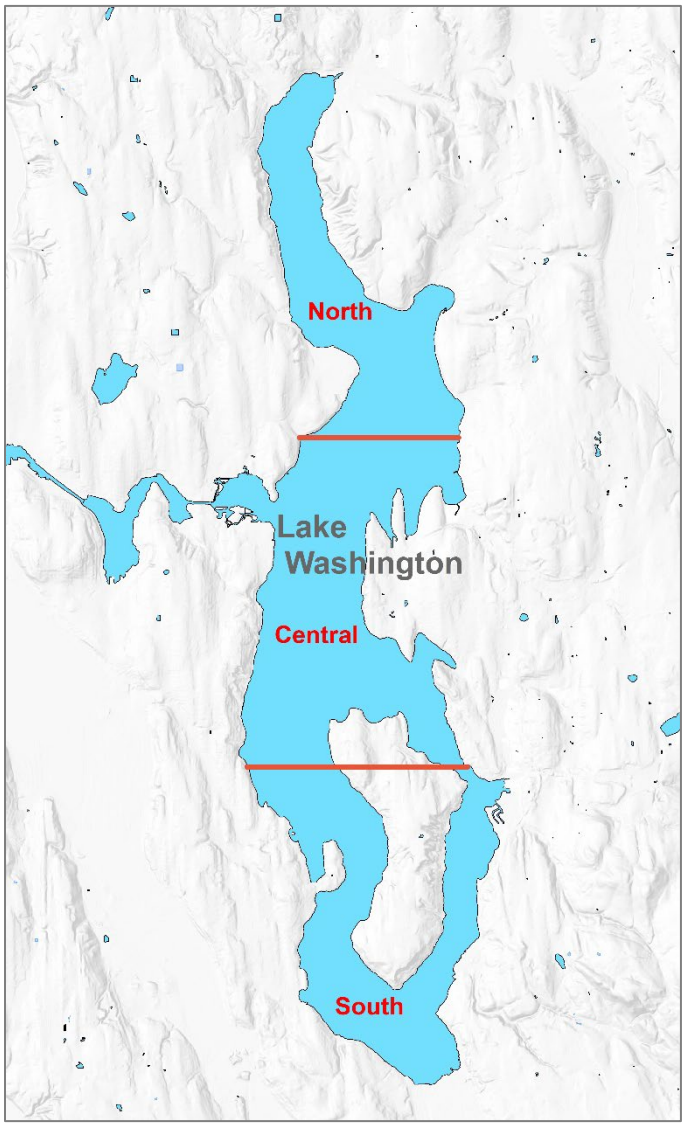

Figure 2. Study boundaries for the three Lake Washington sites.

4.6 Tasks Required

The following tasks will be carried out for this project:

- Determine the appropriate laboratory for analysis following the plan outlined in Section 9.4.
- Collect target fish species in September and October of 2018, homogenize fish samples, and send to laboratory for analysis.
- Review data quality of laboratory results.
- Write draft report summarizing results, route the draft following EAP review procedures, and publish final report.
- Provide the data to DOH in their preferred template.
- Load data into Ecology's EIM database.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 2. Organization of project staff and responsibilities.

Staff (All EAP)	Title	Responsibilities
Debby Sargeant Toxics Studies Unit Statewide Coordination Section Phone: 360-407-6775	Client and Supervisor for the Project Manager	Clarifies scope of the project. Provides internal review of the QAPP addendum and final report. Approves the final QAPP addendum. Manages personnel budget and staffing needs.
Jessica Archer Statewide Coordination Section Phone: 360-407-6698	Client and SCS Manager	Reviews the project scope and budget, tracks progress. Provides internal review of the QAPP addendum and final report. Approves the final QAPP addendum.
Callie Mathieu Toxics Studies Unit Statewide Coordination Section Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the QAPP addendum and final report. Oversees field collections, leads sample processing, and sends samples to laboratory. Coordinates with laboratory and conducts QA review of the data. Analyzes and interprets data. Responsible for final report and project completion.
Patti Sandvik Toxics Studies Unit Statewide Coordination Section Phone: 360-407-7198	Field Lead	Works with Project Manager to schedule and coordinate fieldwork. Leads field collections and records field information.
Dale Norton Western Operations Section Phone: 360-407-6596	Section Manager for the Study Area	Reviews the project scope and budget. Provides internal review of the QAPP addendum and final report. Approves the final QAPP addendum.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Manchester Environmental Laboratory Director	Reviews and approves the final QAPP addendum.
Tom Gries Phone: 360-407-6327	Acting Ecology Quality Assurance Officer	Reviews the draft QAPP addendum and approves the final QAPP addendum.

EIM = Environmental Information Management database
QAPP = Quality Assurance Project Plan

5.4 Project schedule

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and Laboratory Work	**Due Date**	**Lead Staff**
Field work completed	10/31/18	Callie Mathieu and Patti Sandvik
Samples shipped to laboratory	11/19/18	
Laboratory analyses completed	02/28/19	
Environmental Information System (EIM) Database		
EIM Study ID	CAME004	
Product	Due date	Lead staff
EIM data loaded	05/31/19	PBT field lead
EIM QA	06/30/19	Callie Mathieu
EIM complete	07/31/19	PBT field lead
Final Report		
Author lead / support staff	Callie Mathieu	
Schedule		
Draft due to supervisor	04/30/19	
Draft due to client/peer reviewer	05/31/19	
Final (all reviews done) due to publications coordinator	06/30/19	
Final report due on web	07/31/19	

5.6 Budget and funding

The total budget for laboratory services for this project is $53,060. Table 4 presents the estimated costs of PFAS laboratory analysis. The number of quality control (QC) samples in the table includes only those tests that are not included in the cost of the analysis: one matrix spike, one laboratory duplicate, and one SRM per batch. PFAS laboratory analysis and PFAS SRM will be funded by Ecology's PBT Monitoring Program. Fish aging services will be funded by EAP.

Table 4. Project budget.

Analysis	Sample Type	Cost per sample	Total number of field samples	Total number of lab batches	Number of QC samples*	Cost
PFAS	Fish Tissue	$500	75	4	12	$43,500
PFAS SRM						$1,500
Fish Age	Otolith	$34	110	---	---	$3,740
Fish Age	Non-otolith	$12	360	---	---	$4,320
					Total Cost	$53,060

*1 matrix spike, 1 laboratory duplicate, and 1 SRM per batch
QC = quality control

6.0 Quality Objectives

6.2 Measurement Quality Objectives

Table 5 presents measurement quality objectives (MQOs) for PFAS analysis. Additional QC tests (matrix spikes and standard reference materials (SRMs)) are being added to 2018 sampling. MQOs for the SRM must be met for PFOS only. Concentrations of other compounds included in the SRM are below the anticipated reporting limit for this analysis.

Table 5. Measurement quality objectives.

Analyte	Matrix	Lab Duplicates (RPD)	LCS (% recov.)	Method Blanks	Surrogate Standards (% recov.)	Matrix Spikes (% recov.)	SRM (% of known value)[1]	Quantitation Limit
PFAS	Tissue	< 40%	50 – 150%	< 0.5 ng/g ww	20 – 200%	50 – 150%	65 – 135%	0.5 – 2.0* ng/g ww

RPD = relative percent difference
LCS = laboratory control sample
SRM = standard reference material
[1]Applies to PFOS only
*2.0 RL allowed for PFTeA and PFTrA only

7.0 Sampling Process Design (Experimental Design)

7.1 Study design

Ecology will collect up to three freshwater fish species from Lake Meridian, Lake Sammamish, and Lake Washington for PFAS analysis in fall 2018. Individual fish will be filleted (skin-on) and composited into 3 – 5 fish composite samples. A target of five composite samples per species from each site will be analyzed for the compounds listed in Table 6. Section 4.4 lists the target species for each location.

Lake Meridian and Lake Washington were selected for this project based on 2016 PFAS fish tissue results. The majority of fish fillet samples collected from the two waterbodies in 2016 contained PFOS concentrations greater than DOH's provisional screening levels for PFOS. However, the sample sizes were low (two samples from Lake Meridian and four samples from Lake Washington) and DOH was not able to assess the waterbody for fish consumption. Therefore, additional fish samples will be collected from Lake Meridian and Lake Washington in 2018. Fish will also be collected from Lake Sammamish to evaluate levels of PFAS in fish from the waterbody, as PFOS was reported in drinking water well samples in the lake's watershed between 2013 and 2016 (City of Issaquah, 2015). Follow-up testing in the watershed by the City of Issaquah is planned. To the author's knowledge, no PFAS sampling has been conducted within Lake Sammamish itself.

7.1.3 Parameters to be determined

This project will analyze the PFAS compounds listed in Table 6. To be consistent with past PFAS sampling, the analytes will be reported in the anion form.

Table 6. Target analytic parameters.

Analyte	Acronym
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA
Perfluorobutane sulfonate	PFBS
Perfluorodecanoate	PFDA
Perfluorododecanoate	PFDoA
Perfluoroheptanoate	PFHpA
Perfluorohexane sulfonate	PFHxS
Perfluorohexanoate	PFHxA
Perfluorononanoate	PFNA
Perfluorooctane sulfonate	PFOS
Perfluorooctanoate	PFOA
Perfluoropentanoate	PFPeA
Perfluorotetradecanoate	PFTeA
Perfluorotridecanoate	PFTrA
Perfluoroundecanoate	PFUnA

9.0 Measurement Methods

9.2 Lab procedures table

Ecology's Manchester Environmental Laboratory (MEL) is currently developing the capability to analyze PFAS compounds in fish tissue and will perform the analysis for this project if the method is ready in time. The new method development plan is detailed in Section 9.4. If MEL is unable to perform this analysis in time for this project, then Ecology will post a solicitation for bid seeking a laboratory to carry out the analysis and the contract will be managed by MEL. MEL or the contract laboratory will be required to meet the quantitation limits outlined in Table 7 and provide their method for analyzing the target analytes using the outlined instrumentation.

Table 7. Lab procedures.

Parameter	Sample Matrix	Samples [Number, Arrival Date]	Expected Range of Results	Reporting Limit	Method
PFAS	Fish Tissue	75, November, 2018	< 0.5-100 ng/g ww	0.5-2.0 ng/g ww	EPA 537 Mod or EPA 8321B Mod LC-MS/MS; isotopic dilution

PFAS = perfluoroalkyl substances
LC-MS/MS = liquid chromatography – tandem mass spectrometry

9.3 Sample preparation method(s)

Fish fillet samples will be processed and homogenized following the procedure outlined in the original QAPP and Ecology's SOP 007 Version 1.2, Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2017).

Because there are no standard methods for PFAS in tissue, MEL or the contract laboratory may use their laboratory-specific method for preparation and extraction. The laboratory must provide their documented method or standard operating procedure to the project officer and demonstrate the efficiency of the extraction method through SRM recoveries, surrogate recoveries, and past environmental sample results. See Section 9.4 below.

9.4 Special method requirements

MEL completed a method blank contamination investigation and determined no background contamination for the target analytes. Method blank results were less than half of the 0.5 ng/g reporting limit for all compounds. MEL will conduct the following tasks during their method development for PFAS in tissue.

Prior to receiving samples in November, MEL will:

- Establish method-reporting limits (MRLs) and provide these limits to the project officer.
- Complete initial demonstration of capability (IDC) in solid matrix.
- Complete lower limit of quantitation (LLOQ) in solid matrix.
- Analyze SRM NIST 1947 and 10 archived 2016 fillet tissue samples. Results of this analysis will be discussed with the project officer.
- Complete method detection limits (MDLs) in solid matrix. If MEL cannot complete MDLs prior to receiving samples, it will be acceptable to complete the MDLs before generating final analytical results. If MDLs are not completed prior to sample shipment, MDLs must be completed within the analysis turn-around time of 90 calendar days.

Results of the method development (MRLs, IDCs, LLOQs, MDLs, SRM, and archive analysis data) will be shared with the project officer and Ecology's QA Officer prior to sample analysis.

10.0 Quality Control Procedures

10.1 Table of field and lab quality control required

The laboratory will perform the quality control (QC) tests presented in Table 8. Two tests were added to the 2018 project plan for additional confidence in the data: matrix spikes and standard reference materials (SRMs). This project will require the analysis of the National Institute of Standards and Technology (NIST) 1947 SRM with each batch. The NIST 1947 SRM is a Lake Michigan frozen lake trout homogenate with a known PFOS concentration of 5.9 ng/g ww. Other PFAS are present in the SRM – perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnA) – but at concentrations below the expected reporting limit.

Table 8. Lab quality control procedures.

Parameter	Matrix	Lab Duplicate	LCS	Method Blank	Surrogate Standards	Matrix Spike	SRM (NIST 1947)
PFAS	Tissue	1/batch	1/batch	1/batch	Each sample	1/batch	1/batch

PFAS = perfluoroalkyl substance
LCS = laboratory control samples
SRM = standard reference material
NIST = National Institute of Standards and Technology
Batch = 20 samples or fewer

15.0 References

City of Issaquah. 2015. Water Quality Report 2015. City of Issaquah, Washington. http://issaquahwa.gov/ArchiveCenter/ViewFile/Item/347.

Furl, C. and C. Meredith. 2010. Perfluorinated Compounds in Washington Rivers and Lakes. Publication No. 10-03-034. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/1003034.html

Johnson, A. and M. Friese. 2012. PBTs Analyzed in Bottom Fish from Four Washington Rivers and Lakes: Hexabromocyclododecane, Tetrabromobisphenol A, Chlorinated Paraffins, Polybrominated Diphenylethers, Polychlorinated Naphthalenes, Perfluorinated Organic Compounds, Lead, and Cadmium. Publication No. 12-03-042. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/summarypages/1203042.html

Mathieu, C. 2016. Quality Assurance Project Plan: Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes. Publication Number 16-03-110. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1603110.html

Mathieu, C. and M. McCall. 2017. Survey of Per- and Poly-fluoroalkyl substances (PFASs) in Rivers and Lakes, 2016. Publication Number 17-03-021. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1703021.html

Sandvik, P. 2017. Standard Operating Procedure for Resecting Finfish Whole Body, Body Parts or Tissue Samples, Version 1.2. Washington State Department of Ecology, Olympia. SOP EAP009.