



DEPARTMENT OF  
**ECOLOGY**  
State of Washington



## **Quality Assurance Project Plan**

---

### **Non-Targeted Screening of Toxic Organics in Fish Tissue**

September 2019  
Publication No. 19-03-111

## Publication Information

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan (QAPP). 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.

This Quality Assurance Project Plan was approved in March 2019.

It was approved for publication in September 2019 and is available on Ecology's website at <https://fortress.wa.gov/ecy/publications/SummaryPages/1903111.html>.

Data for this project will not be available on Ecology's Environmental Information Management (EIM) website. Data is available upon request.

Ecology's Activity Tracker Code for this study is 19-010.

## Author and Contact Information

James Medlen  
P.O. Box 47600  
Environmental Assessment Program  
Washington State Department of Ecology  
Olympia, WA 98504-7710

Publication coordinator: phone 360-407-6764.

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

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

**Cover photo:** Christopher Clinton and Jim Medlen, Columbia River sturgeon collection processing at marina. Photo: Debby Sargeant.

*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.*

*Accommodation Requests: To request ADA accommodation including materials in a format for the visually impaired, call Ecology at 360-407-6831. People with impaired hearing may call Washington Relay Service at 711. People with speech disability may call TTY at 877-833-6341.*

# Quality Assurance Project Plan

---

## Non-Targeted Screening of Toxic Organics in Fish Tissue

September 2019

**Approved by:**

Author / Project Manager/Principal Investigator, EAP Jim Medlen	Date:
Signature: Section Manager for Project Study Area, EAP Jessica Archer	Date:
Signature: Director, Manchester Environmental Laboratory Alan Rue	Date:
Signature: Arati Kaza , Ecology Quality Assurance Officer	Date:

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

# 1.0 Table of Contents

	Page
Figures.....	4
Tables.....	4
2.0 Abstract.....	5
3.0 Background.....	5
3.1 Introduction and problem statement.....	5
3.2 Study area and surroundings.....	6
4.0 Project Description.....	12
4.1 Project goals.....	12
4.2 Project objectives.....	12
4.3 Information needed and sources.....	13
4.4 Tasks required.....	13
4.5 Systematic planning process.....	13
5.0 Organization and Schedule.....	14
5.1 Key individuals and their responsibilities.....	14
5.2 Special training and certifications.....	14
5.3 Organization chart.....	14
5.4 Proposed project schedule.....	15
5.5 Budget and funding.....	15
6.0 Quality Objectives.....	16
6.1 Data quality objectives.....	16
6.2 Measurement Quality Objectives.....	16
7.0 Study Design.....	18
7.1 Study boundaries.....	19
7.2 Field data collection.....	19
7.3 Assumptions in relation to objectives and study area.....	19
7.4 Possible challenges and contingencies.....	19
8.0 Field Procedures.....	20
8.1 Invasive species evaluation.....	20
8.2 Measurement and sampling procedures.....	20
8.3 Containers, preservation methods, holding times.....	20
8.4 Equipment decontamination.....	21
8.5 Sample ID.....	21
8.6 Chain of custody.....	21
8.7 Field log requirements.....	21
8.8 Other activities.....	21
9.0 Laboratory Procedures.....	22
9.1 Lab procedures table.....	22
9.2 Sample preparation methods.....	22
9.3 Special method requirements.....	22
9.4 Laboratories accredited for methods.....	22
10.0 Quality Control Procedures.....	23

10.1	Table of field and laboratory quality control .....	23
10.2	Corrective action processes.....	23
11.0	Data Management Procedures .....	24
11.1	Data recording and reporting requirements .....	24
11.2	Laboratory data package requirements .....	24
11.3	Electronic transfer requirements .....	24
11.4	EIM/STORET data upload procedures.....	24
11.5	Model information management.....	24
12.0	Audits and Reports.....	25
12.1	Field, laboratory, and other audits .....	25
12.2	Responsible personnel .....	25
12.3	Frequency and distribution of reports .....	25
12.4	Responsibility for reports.....	25
13.0	Data Verification.....	25
13.1	Field data verification, requirements, and responsibilities .....	25
13.2	Laboratory data verification.....	25
13.3	Validation requirements, if necessary.....	25
14.0	Data Quality (Usability) Assessment.....	26
14.1	Process for determining project objectives were met .....	26
14.2	Treatment of nondetects.....	26
14.3	Data analysis and presentation methods .....	26
14.4	Sampling design evaluation .....	26
14.5	Documentation of assessment.....	26
15.0	References.....	27
16.0	Appendices.....	28
	Appendix A. Glossaries, Acronyms, and Abbreviations .....	29

# Figures

	Page
Figure 1. Columbia River sampling area. ....	7
Figure 2. Freshwater Fish Contaminant Monitoring Program 2016 sampling area. ....	8
Figure 3. PBT 2017 sampling area (central Lake Washington).....	9
Figure 4. Simplified workflow for non-targeted screening of freshwater fish tissue samples. ....	18

# Tables

	Page
Table 1. Washington State Department of Health study of total PCB congeners in white sturgeon. ....	10
Table 2. Lower Cowlitz River Castle Rock site results. ....	11
Table 3. Organization of project staff and responsibilities. ....	14
Table 4. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports. ....	15
Table 5. Project budget. ....	15
Table 6. Measurement quality objectives for laboratory analysis of tissue. ....	16
Table 7. Sample containers, preservation, and holding times.....	20
Table 8. Measurement methods (laboratory). ....	22
Table 9. Quality control samples, types, and frequency. ....	23

## 2.0 Abstract

Manchester Environmental Laboratory (MEL) developed the capability for quadrupole time-of-flight (QTOF) analysis through gas chromatography–mass spectrometry (GC-MS) in 2018. Washington State Department of Ecology’s Toxic Studies Unit (TSU) is interested in using this as an opportunity to (1) assess the potential uses and efficacy of QTOF for future fish tissue toxics screening applications, and (2) screen archived fish tissue to better understand the toxics burden of fish above and beyond our current standard practice of analyzing for target analytes.

Three sets of archived tissue will be analyzed using QTOF. They include individual samples of white sturgeon collected in the Lower Columbia River in summer 2017, composited finfish species collected in central Lake Washington in summer 2018, and composited finfish species collected in the Lower Cowlitz River in summer 2016. Laboratory analysis is expected to yield a list of tentatively identified compounds, which will be compared to known sample concentrations of the original sample or to regional values.

## 3.0 Background

### 3.1 Introduction and problem statement

In 2017, MEL purchased an Agilent quadrupole time-of-flight gas chromatography–mass spectrometry (QTOF) system to expand their analysis capacity to include non-targeted environmental screening. This non-targeted approach has the ability to identify compounds through high resolution, accurate-mass data and sensitive detection, and can tentatively identify thousands of analytes (eight to ten thousand) based on their molecular weight and spectra.

In early 2017, the Washington State Department of Health (DOH) solicited the help of Washington State Department of Ecology (Ecology) in partnership with Oregon Department of Fish and Wildlife (ODFW) to collect 20 individual white sturgeon (*Acipenser transmontanus*) tissue samples in the Lower Columbia River. These samples were analyzed for 209 polychlorinated biphenyl (PCB) congeners and total mercury. Tissue analytical results were used to develop and update fish consumption recommendations for white sturgeon.

Sturgeon samples were archived at Ecology Headquarters in Lacey, Washington, after analysis at the Oregon Department of Environmental Quality (ODEQ) laboratory. Due to the limited data collected to date and the range of organic contaminants that have the potential to bioaccumulate in sturgeon, this project provides an excellent opportunity to conduct non-targeted QTOF screening for the archived samples using MEL’s QTOF equipment.

Along with the white sturgeon samples, two additional sets of fish tissue samples will be analyzed via QTOF. Archived samples from Ecology’s TSU Freshwater Fish Contaminant Monitoring Program (FFCMP) that have previously been analyzed at MEL for a range of organic contaminants will be included in the sample set (Seiders 2016). Fish tissue samples from the FFCMP’s Lower Cowlitz River sample site were chosen for analysis due to sample representativeness, modest set of analytes monitored for, and to further assess the reliability of QTOF in detecting positively identified analytes.

In 2018, the persistent and bioaccumulative toxics (PBT) program collected fish tissue in central Lake Washington to determine levels of per-fluorinated compounds (Mathieu 2018a). Archived samples from this study will be analyzed with QTOF to determine how well organic analytes are detected in a water body with known anthropogenic sources of toxics.

## 3.2 Study area and surroundings

### 3.2.1 History of study area

Samples were collected in the Lower Columbia River July through August 2017, the Lower Cowlitz River in August 2016, and Lake Washington in November 2018.

White sturgeon were collected along the Lower Columbia River (river mile 40 to terminus at Pacific Ocean) (Figure 1). The sample collection coincided with the river mile reach of the recreational fishery on the Lower Columbia River Basin. Sturgeon were originally collected to assess consumption health risks by DOH. A QAPP was not developed for the original DOH study.

The Cowlitz River was sampled by the Freshwater Fish Contaminant Monitoring Program (FFCMP) in 2016 (Seiders 2016). The Cowlitz River is a major tributary of the Columbia River. The Cowlitz River's confluence with the Columbia River is downstream of the City of Longview at river mile 68. The FFCMP program collected several fish tissue samples along the Cowlitz River; this project will use archived samples collected in the lowest reach of the Cowlitz River sampled (Figure 2).

Lake Washington is located in King County, on the east side of Seattle and west side of Bellevue. Lake Washington receives anthropogenic sources of pollutants, including toxics from highly urbanized areas and commercial, residential, and industrial land use. The PBT monitoring program sampled the lake in 2018 through an addendum to the program study (Mathieu 2018a) this project will use samples collected in the central, most representative location of the lake (Figure 3).



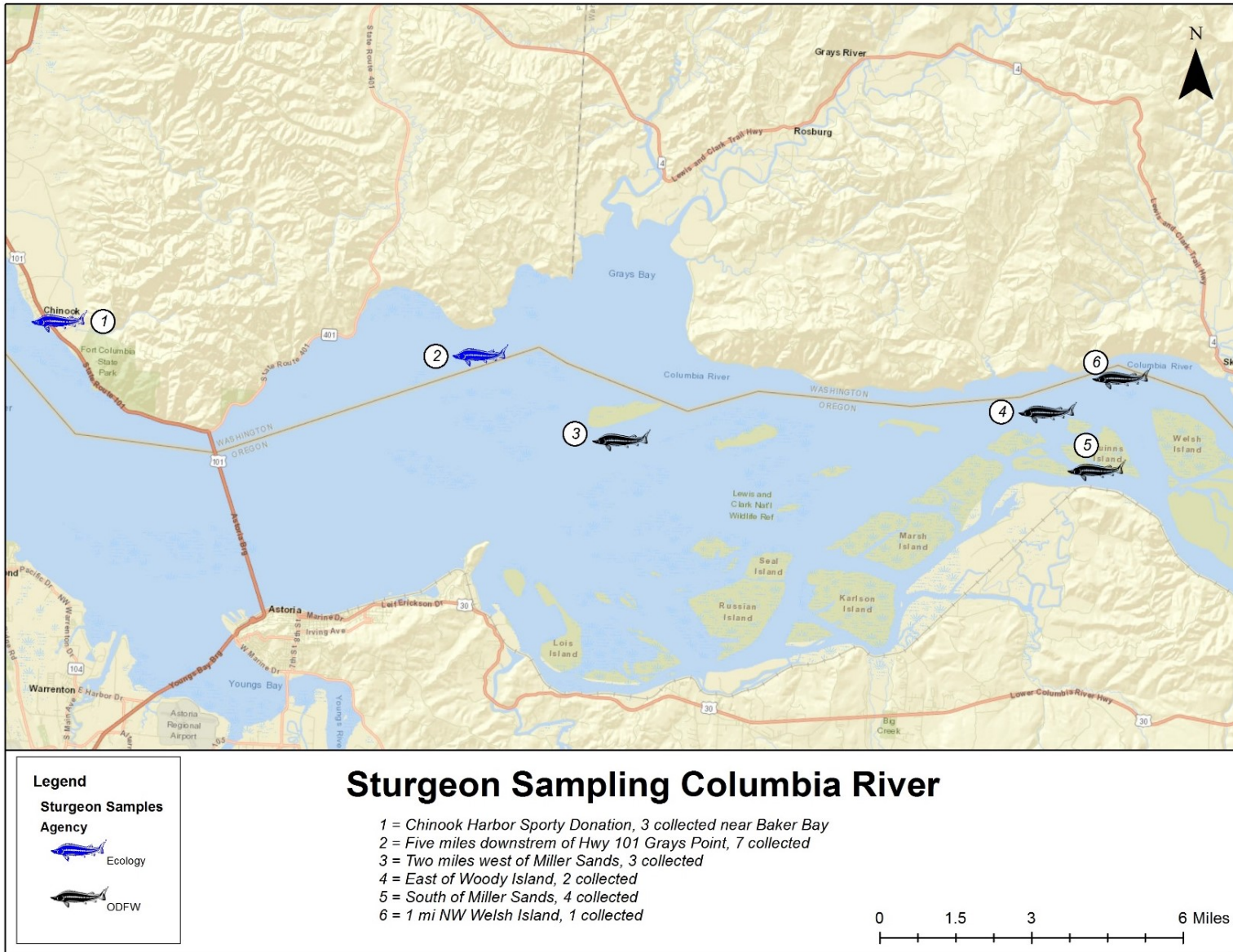
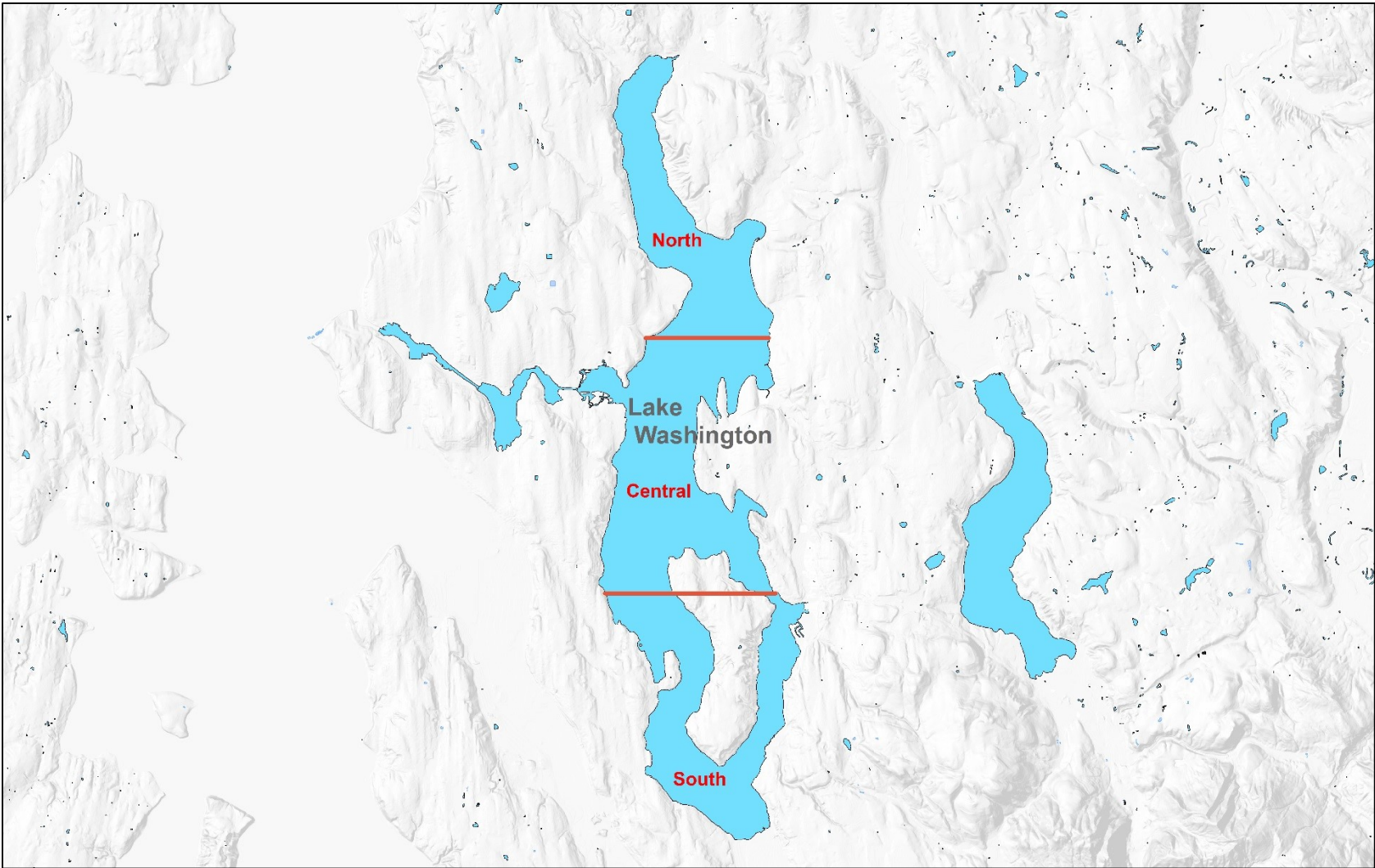


Figure 1. Columbia River sampling area.



**Figure 2. Freshwater Fish Contaminant Monitoring Program 2016 sampling area.**



**Figure 3. PBT 2017 sampling area (central Lake Washington).**

### 3.2.2 Summary of previous studies and existing data

Much of this QAPP is based on standard operating procedures (SOPs) and quality objectives used for QTOF analysis in the Ecology study *Addendum to Quality Assurance Project Plan: Flame Retardants in Ten Washington State Waterbodies* (Mathieu 2018a).

#### *Lower Columbia River Sturgeon (Department of Health Study)*

Through the Washington State Department of Health (DOH) fish advisories program, species of sport fish have been collected in the Lower Columbia River since the early 1990s and analyzed for targeted legacy toxics. Based on concentrations of toxics in fillet tissues, the program provides advice on which species are safe to eat, should be limited to eat, and which ones to avoid.

White sturgeon were collected in June through July 2017 and analyzed at the Oregon Department of Environmental Quality's (ODEQ) lab. Lab analytics run on tissue at ODEQ included both inorganic and organic toxics (mercury and 209 PCB congeners, respectively). Samples from the study were archived and will be used in the analysis for this project. For the purposes of this study using QTOF, only organic toxics will be analyzed. Table 1 summarizes the DOH study's total PCBs concentration results.

**Table 1. Washington State Department of Health study of total PCB congeners in white sturgeon.**

Sample ID	Total PCBs (ng/kg)
5	21,388
6	9,359
7	12,067
8	24,989
9	2,554
10	19,321
11	9,986

There are a number of other studies from the Lower Columbia River, conducted by Ecology, EPA, USGS, Columbia River Inter-Tribal Fish Commission, Lower Columbia River Estuary Partnership, and NOAA. These studies analyzed fish tissue, chiefly salmon, for PCBs, PAHs, perfluorinated compounds, metals, flame retardants, pesticides, and various other organic toxins. To date, white sturgeon toxics data in the Lower Columbia River is sparse. Following is a summary of some of the major toxics studies in the Columbia River Basin:

- EPA and Inter-Tribal Fish Commission — Columbia River Fish Contaminant Survey is a technical report that assessed the amount of toxics found in species collected through tribal fisheries in the Columbia River Basin from 1996 to 1998. The study found high levels of toxics in white sturgeon, largescale sucker, and mountain whitefish.

- United State Geologic Survey — Columbia River Contaminant and Habitat Characterization Study was conducted from 2008 to 2011. This study found contaminants in largescale suckers to be highest in the lower portion of the Columbia River, due to urbanization.
- Lower Columbia River Estuary Partnership, USGS, and NOAA conducted a collaborative investigation from 2004 to 2005 to better understand the presence, distribution, and concentrations of contaminants in water, sediment, and juvenile salmon in six sites. Results from the study found widespread contamination of PCBs, PAHs, pesticides, and PBDEs.

### *Freshwater Fish Contaminant Monitoring Program (Lower Cowlitz River)*

The Freshwater Fish Contaminant Monitoring Program (FFCMP) has been collecting data since 2001 throughout Washington. Over 400 composite fish tissue samples from 150 sites have been analyzed through the FFCMP study. Target analytes included mercury, PCBs, dioxins and furans, chlorinated pesticides, and PBDE flame retardants.

Data from the monitoring program is used for a variety of purposes, such as assessing the quality of water bodies, conducting health risk assessments, assessing water bodies under the Clean Water Act 303(d) listings, and evaluating contaminant trends over time.

In 2005, the FFCMP’s precursor program, the Washington State Toxics Exploratory Monitoring Program, collected fish tissue for analysis. The program analyzed samples for a number of toxics, including mercury, flame retardants, PCB congeners, dioxins/furans, and pesticides in the lower reaches of the Cowlitz River. Table 2 summarizes the 2016 FFCMP’s organic contaminant findings for the Lower Cowlitz River site near Castle Rock.

**Table 2. Lower Cowlitz River Castle Rock site results.**

Parameter	Species	Concentration (µg/kg)	Note
Total PCB congeners	Mountain whitefish	18.3	One composite sample
Total PCB congeners	Mountain whitefish	7.4	One composite sample
Total PCB congeners	Mountain whitefish	8.3	One composite sample
Total PCB congeners	Northern pike minnow	23.5	One composite sample
Total PBDEs	Largescale sucker	26.3	Average of 3 composite samples
Total PBDEs	Mountain whitefish	6.0	Average of 3 composite samples
Total PBDEs	Northern pike minnow	5.1	One composite sample
Dioxins and furans	Mountain whitefish	0.1	Average of 3 composite samples
Dioxins and furans	Northern pike minnow	0.2	One composite sample

This study will use Ecology’s PBT program monitoring data from Lake Washington in 2018 (Mathieu 2018b) to compare detected analytes with detected QTOF results and to determine how well QTOF detects other compounds in an organism known to have a toxic burden.

Other Ecology studies and available data in Lake Washington are as follows:

- In 2005, the PBT monitoring study *Measuring PBDE Levels in Washington Rivers and Lakes* (Johnson and Seiders 2005) was conducted. It provided Ecology’s Industrial

Section with data for future evaluation of the effectiveness of the Interim PBDE Chemical Action Plan and other efforts to reduce PBDE inputs to the environment.

- From 2009 to 2012, Ecology conducted the study *Analyzing Chlorinated Pesticide Residues in Fish from Washington Background Lakes* (Johnson 2011) to assess edible fish tissue in Lake Washington. The study looked at legacy chlorinated pesticides and breakdown products.
- In 2008, Ecology conducted a PBT monitoring study named *PBT Monitoring: Measuring Perfluorinated Compounds in Washington Rivers and Lakes* (Furl and Meredith 2008). The goal of the study was to evaluate the spatial distribution of PFCs in Washington State rivers and lakes and to determine the concentrations at which these contaminants are found. The program conducted monitoring in Lake Washington.
- The study *Statewide Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Washington State Rivers and Lakes* (Mathieu and McCall 2017) was conducted in 2016 as a follow up to the 2008 study. Additional samples were taken at study sample sites in Lake Washington. Parameters included chiefly perfluoroalkyl substances (PFAS).

### 3.2.3 Parameters of interest and potential sources

Parameters of interest include a wide array of organic analytes, particularly those that have been identified by the state of Washington as persistent, bioaccumulative, and toxic. In addition, there is much interest in screening for the unknown, or compounds that aren't normally targeted using standard analytical methods.

The Agilent software being used for analysis is able to tentatively identify 852 compounds. In addition, the National Institute of Standards and Technology (NIST) has a library of over 10,000 compounds that can be referenced by the Agilent software for tentative identification. Results of the analysis will include a qualitative presence or absence of these analytes. The analysis will not provide a quantitative value for identified analytes.

### 3.2.4 Regulatory criteria or standards

Regulatory criteria or standards will not be used to compare findings of QTOF analytics. This is a non-targeted screening level qualitative assessment and will inventory potential toxics for future investigation and quantification.

## 4.0 Project Description

### 4.1 Project goals

The project goals are two-fold: (1) assess the potential uses and efficacy of QTOF for future fish tissue toxics screening applications, and (2) screen archived fish tissue to better understand the toxics burden in fish above and beyond our current practice of analyzing for target analytes.

### 4.2 Project objectives

- Process and prepare archived samples of white sturgeon, largescale sucker, and largemouth bass for laboratory tissue analysis.
- Analyze tissue samples using QTOF at Manchester Environmental Laboratory (MEL).

- Compare tentatively identified compounds found in archived samples to existing data.
- Better understand the capabilities and pros and cons in using QTOF for screening.

### 4.3 Information needed and sources

New data collected under the project will be referenced using a comprehensive library of identified compounds. MEL will use the proprietary Agilent MassHunter software to identify compounds and to report analytics.

### 4.4 Tasks required

Tasks for this project are straightforward and will generally follow the objectives outlined in Section 4.2.

1. Eighteen archived samples of fish tissue will be processed using Standard Operating Procedure EAP007, *Resecting Finfish Whole Body, Body Parts, or Tissue Samples* (Sandvik 2018) fish collection and processing protocols and repackaged in 8 oz. glass jars for laboratory analysis.
2. Samples will be split, with half sent to the laboratory for non-targeted qualitative screening analysis and the other half archived for future quantitative analysis (based on initial results).
3. Project Manager will submit fish tissue samples to MEL laboratory by January 2019.
4. MEL will run non-targeted QTOF qualitative screening of tissue samples.
5. MEL will analyze output results using the proprietary software Agilent MassHunter to identify the presence of compounds.
6. Project Manager will review findings and report based on project objectives.

### 4.5 Systematic planning process

This QAPP is adequate for systematic planning of the project.

## 5.0 Organization and Schedule

### 5.1 Key individuals and their responsibilities

**Table 3. Organization of project staff and responsibilities.**

<b>Staff (all EAP except client)</b>	<b>Title</b>	<b>Responsibilities</b>
Jim Medlen Toxic Studies Unit EAP Section Phone: 360-407-6194	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 report and final report.
Debby Sargeant Toxic Studies Unit EAP Section Phone: 360-407-6775	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer EAP Section Manager 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.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
Joan Protasio Manchester Environmental Laboratory Phone: 360-871-8824	Lab Analyst	Runs QTOF analysis and uses Agilent software to identify compounds.
Arati Kaza Phone: 360-407-6964	Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

QTOF: Quadrupole time-of-flight

### 5.2 Special training and certifications

No special training or certifications are required for key project personnel. Manchester Environmental Laboratory is working on developing QTOF methods for analysis of samples.

### 5.3 Organization chart

Not Applicable. See Table 3.



## 5.4 Proposed project schedule

**Table 4. 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	Completed	Jim Medlen
Laboratory analyses completed	April 2019	Jim Medlen
<b>Environmental Information System (EIM) database</b>		
Data is qualitative in nature and will not be uploaded into EIM.		
<b>Final report</b>		
Author lead / support staff	Jim Medlen	
Schedule		
Draft due to supervisor	September 2019	
Draft due to client/peer reviewer	October 2019	
Draft due to external reviewer(s)	November 2019	
Final (all reviews done) due to publications coordinator	December 2019	
Final report due on web	January 2020	

## 5.5 Budget and funding

The laboratory budget for this project is \$20,000. Money for project analysis will come from EAP's laboratory pool of money (money not spent in the fiscal year). A summary of the project budget can be found in Table 5.

**Table 5. Project budget.**

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab total
QTOF >8,000 compounds	18	2	20	\$1,000.00	\$20,000.00
<b>Total</b>					<b>\$20,000.00</b>

## 6.0 Quality Objectives

### 6.1 Data quality objectives

The data quality objective for this project is the completion of a non-targeted screening of compounds in sturgeon tissue samples via QTOF.

### 6.2 Measurement Quality Objectives

There are no measurement quality objectives (MQOs) for non-targeted screening via QTOF. MEL has developed internal QA/QC procedures and limits for this work. MEL will follow the laboratory's standard operating procedures for non-targeted analysis of trace organic contaminants and ensure that the MQOs listed in Table 6 are met.

**Table 6. Measurement quality objectives for laboratory analysis of tissue.**

MQO	Precision	Bias	Sensitivity
Mass calibration	<2 ppm mass accuracy	NA	Targeted masses: 69 m/z 131 m/z 219 m/z 264 m/z 414 m/z 464 m/z 502 m/z 614 m/z
Pesticide check standard reference mix	Retention time variation <0.2 min; Mass accuracy variation <20 ppm	NA	Area response within ~20% of initial response
Replicates	NA	Features present in $\geq 3$ field replicates	NA
Lab blanks	NA	Sample features present at abundance $\geq 5$ times blank area abundance	NA

For this project, compounds will be identified from the mass spectrometry scan using two libraries: (1) the NIST library of over 10,000 analytes, and (2) Agilent's accurate mass QTOF Personal Compound Database and Library of 850 analytes. The search results will be further evaluated to validate the library identification. If requested, the identified analytes can be further confirmed by running with a reference standard of the analyte.

## 6.2.1 Targets for precision, bias, and sensitivity

### 6.2.1.1 Precision

There are no precision criteria for the non-targeted screening method. Data will be assessed using the manufacturer's instrument tuning criteria and check standards to verify retention times and area counts.

Instrument tuning ensures consistent mass accuracy during a given analytical run and throughout the duration of the project. A mass calibration is performed prior to each analytical run; the mass error should be <2 ppm. The mass calibration may also be repeated every 8 to 12 samples. A pesticide check standard is analyzed every 8 to 12 samples to check chromatography and sensitivity during data acquisition. The mass accuracy limits and retention time limits are included in Table 6.

Each fish tissue sample will be analyzed three times. Only features (peaks of unique exact mass-retention time pairs) present in all three sample results will be included for compound identification.

### 6.2.1.2 Bias

There are no bias criteria for non-targeted screening. Data will be assessed using the manufacturer's instrument tuning criteria and check standards to verify retention times and area counts. Bias will also be assessed by the analysis of laboratory method blanks and instrument blanks. Laboratory blanks are prepared by the laboratory and processed in the same manner as the field samples. Instrument blanks consist of solvents that are analyzed with the sample batch. Both types of blanks can provide information on contamination or bias in the laboratory. For this project, only features that are present at greater than or equal to five times the blank area abundances will be reported as tentatively identified.

For the non-target data, the analytes identified by the library searches will be further evaluated using the match scores, areas, height, ions, spectra patterns, and peak shapes. Only analytes present in all three replicates will be considered.

### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Sensitivity will be assessed using the manufacturer's instrument tuning criteria and check standards.

## 6.2.2 Targets for comparability, representativeness, and completeness

### 6.2.2.1 Comparability

To facilitate comparability of the data generated by this project and potential related future projects, field sampling will follow standardized operating procedures listed in Section 8.2.

### 6.2.2.2 Representativeness

Sturgeon fish samples will be analyzed separately in order to detail the variability among individual fish. Largemouth bass and largescale sucker samples were composited and

homogenized previously and are considered representative of the fish populations in their respective areas.

### 6.2.2.3 Completeness

The project manager will consider the study to have achieved completeness if 80% of the samples are analyzed acceptably.

## 7.0 Study Design

Archived tissue samples from three studies will be analyzed during this project, including:

- 10 individual white sturgeon fillet samples (Columbia River)
- 4 composite samples of largemouth bass fillet tissue (Lake Washington)
- 4 composite samples of largescale sucker fish muscle tissue (Cowlitz River)

The sturgeon will be homogenized individually and sent to Manchester Environmental Laboratory for non-targeted screening of organic compounds by QTOF.

The four largemouth bass and four largescale sucker samples were composited, homogenized, and archived into glass jars and frozen. Sample material will be pulled from these archived sample jars for analysis.

The non-targeted screening will follow the workflow presented in Figure 4, resulting in a list of compounds present in the fish tissue.

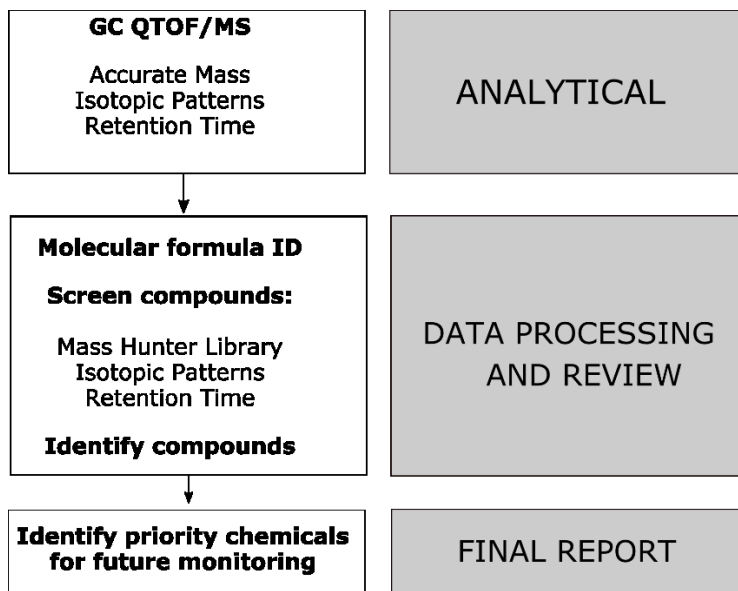


Figure 4. Simplified workflow for non-targeted screening of freshwater fish tissue samples.

## 7.1 Study boundaries

Samples for analysis were collected and archived from three areas:

- Lower Columbia River samples were collected from river mile 40 at the Wauna powerlines downstream to the river's mouth at Buoy 10.
- Cowlitz River samples were collected on the mainstem, north of Castle Rock.
- Lake Washington samples were collected in the central area of the lake.

## 7.2 Field data collection

### 7.2.1 Sampling locations and frequency

Sample locations and frequency can be found in the associated project reports (Seiders 2016; Mathieu 2018b). Sturgeon samples collected on the Lower Columbia were for the Department of Health study and did not have a dedicated QAPP at the time of sampling. Sample locations and a description of the number of sturgeon samples collected in the Lower Columbia River are detailed in Figure 1.

### 7.2.2 Field parameters and laboratory analytes to be measured

Field parameters collected during fishing are limited to time, date, length, species, and weight.

Laboratory analytical parameters are too numerous to list. The software being used to identify compounds, Agilent MassHunter, includes a list of 852 aromatic compounds. In addition, the Agilent software references the NIST/EPA/NIH mass spectral library (NIST 14), which contains an additional 100,000 plus compounds.

## 7.3 Assumptions in relation to objectives and study area

The study design includes qualitative non-targeted screening of organic toxics in archived fish tissue samples. No assumptions are being made.

## 7.4 Possible challenges and contingencies

Challenges will likely be due to cleaning of the equipment between samples, solvent extraction of sample material, and managing the potentially cumbersome amount of data as a result of this analysis. Due to the newness of QTOF equipment and software at MEL, additional challenges are expected, but won't be fleshed out until analysis is conducted.

### 7.4.1 Logistical problems

Logistics are minimal. No logistical challenges and associated contingencies are anticipated for this study.

## 7.4.2 Practical constraints

The QTOF analysis may yield an unwieldy amount of data. It will not be practical to report on all findings, and findings will be prioritized for reporting based on current Washington State toxics priorities developed through policy and research.

## 7.4.3 Schedule limitations

The schedule will depend on whether extraction, cleaning, and analysis of the samples proceeds as expected.

# 8.0 Field Procedures

## 8.1 Invasive species evaluation

Not applicable.

## 8.2 Measurement and sampling procedures

Ecology staff followed EAP SOPs to ensure that samples were collected in a consistent manner and to reduce the chance of contamination of samples. Staff filled out fish collection sheets during collection. The sheets included fields for location, sex, length, weight, and date.

White sturgeon were collected on the Lower Columbia River using rod and reel. Fish were targeted between 44 inches (minimum) and 50 inches (maximum) fork length representative of the targeted recreational fishery. Largemouth bass and largescale sucker on the Lower Cowlitz and Lake Washington were collected using a combination of electrofishing, rod and reel, and seine nets.

## 8.3 Containers, preservation methods, holding times

Table 7 describes the sample matrix, minimum quantity required, container size, preservation, and holding time for samples. At the time of analysis, the one-year holding time will have been exceeded. The purpose of the analysis is to conduct a non-targeted screening. The exceeded holding time could be problematic for detecting the presence of less-persistent organic compounds. For the purpose of this study, the exceedance of the holding time is not seen as problematic.

**Table 7. Sample containers, preservation, and holding times.**

Analysis	Matrix	Minimum quantity required	Container	Preservative	Holding time
Non-targeted screening	Fish tissue	50 g ww	8 oz. glass jar	Freeze at $\leq -10^{\circ}\text{C}$	1 year frozen <sup>1</sup>

<sup>1</sup> Holding time for fish samples exceed the one year limit recommended in the table.

## 8.4 Equipment decontamination

Equipment used to process fish will be decontaminated and cleaned using Ecology's SOP EAP007, *Resecting Finfish Whole Body, Body Parts, or Tissue Samples* (Sandvik 2018).

## 8.5 Sample ID

Samples will be numbered 1 through 18, in order of date first caught (1) to last (18).

## 8.6 Chain of custody

MEL's typical laboratory chain of custody will be used to transfer archived samples to MEL. The original project's fish consumption study chain-of-custody forms have also been obtained for both Ecology and ODFW. In addition, ODEQ completed a chain-of-custody form when archived samples were sent to Ecology.

## 8.7 Field log requirements

Samples were collected in previous sampling efforts. Sample sheets will be viewed for archived information.

## 8.8 Other activities

No other activities are needed.

## 9.0 Laboratory Procedures

### 9.1 Lab procedures table

Many of the laboratory procedures put into place for analysis using more conventional methods will not be applicable to the procedures used in QTOF analysis. Since this is a non-targeted screening, analytes will not be pre-identified. The sample matrix is fish tissue. The number of samples being sent into the lab for analysis is 21. Samples should arrive at the laboratory during February 2019.

There are no expected range of results, because the method will not quantify the concentrations of identified compounds. There will be no detection or reporting limits. The sample prep method will extract organics from the tissue sample using a solvent. The extracted solution will be injected into the sample chamber and volatilized, then run through the spectrometer. Laboratory measurement methods are summarized in Table 8.

**Table 8. Measurement methods (laboratory).**

Analyte	Sample matrix	Samples (number/ arrival date)	Expected range of results	Detection or reporting limit	Sample prep method	Analytical (instrumental) method
Non-targeted screening	Fish tissue	20 samples*	NA	NA	Solvent Extraction	QTOF

\* includes 1 field duplicate and 1 method blank.

### 9.2 Sample preparation methods

Frozen archived fish will be processed at Ecology's headquarters. Individual fish will be assigned numbers 1 through 18 as discussed in the previous section.

Frozen individual samples will be processed using Ecology's SOP EAP007 (Sandvik 2018).

### 9.3 Special method requirements

There are no special method requirements.

### 9.4 Laboratories accredited for methods

Currently, no laboratories are accredited for non-targeted screening. An Ecology waiver for accreditation will be obtained for this project.



## 10.0 Quality Control Procedures

MEL will be expected to perform the quality control procedures listed in Table 9 and described in Section 6. The reference standard mix included in each analytical run as a check on mass accuracy, compound identification, and response will be required to include at least one halogenated organic compound. Sample extracts will be spiked with a known mass of labeled standard as a check on instrument response and matrix interference. Method blanks and instrument blanks will be run as listed in Table 9.

### 10.1 Table of field and laboratory quality control

Table 9 provides the laboratory quality control (QC) procedures required for this project. In addition, three sample duplicates (one per study area) will be submitted to the laboratory as a QC check.

**Table 9. Quality control samples, types, and frequency.**

Parameter	Matrix	Laboratory				Field
		Mass calibration	Method blank	Instrument blank	Lab split (duplicate)	Sample duplicate
non-targeted screening	fish tissue	each analytical run	1 per batch	1 per batch	1 per batch	1 per study area

### 10.2 Corrective action processes

The project manager will meet with MEL staff to discuss the results of non-targeted screening and to address any problems with the analysis.

## **11.0 Data Management Procedures**

### **11.1 Data recording and reporting requirements**

The final deliverable from MEL will be stored on the Environmental Assessment Program's Toxics Technical Coordination Team SharePoint site. This site currently houses data that does not get stored in the EIM database. The project manager will make the data available to the public upon request. Results from the non-targeted screening will be included in the final report for this project.

### **11.2 Laboratory data package requirements**

MEL will provide a written synopsis of the results of the non-targeted screening. The synopsis will include an evaluation of the success of the method and recommendations for future steps in the effort to identify chemicals for further evaluation and monitoring.

MEL will provide the list of chemicals found in the screening in an Electronic Data Deliverable (EDD) Excel format. Compounds will be reported with the following data: compound name, formula, theoretical mass, CAS # (if available), RT (min), relative abundance (or area), and mass error ppm (only for results from Agilent's Personal Compound Database and Library).

The data package from MEL will include documentation of QA/QC tests for each batch, including mass calibration results for each run. Instrument printouts of check tune results will be in PDF format.

### **11.3 Electronic transfer requirements**

MEL will transfer all deliverables via email to the project manager.

### **11.4 EIM/STORET data upload procedures**

Data generated from the QTOF non-targeted screening will not be uploaded into EIM due to the qualitative nature of the data.

### **11.5 Model information management**

NA

## **12.0 Audits and Reports**

### **12.1 Field, laboratory, and other audits**

Not applicable.

### **12.2 Responsible personnel**

The project manager/principal investigator will have lead responsibility for the final report.

### **12.3 Frequency and distribution of reports**

The lab report for analysis findings will be available June 2019. A final report will be available January 2020.

### **12.4 Responsibility for reports**

The project manager will be responsible for all reporting activities and documents generated.

## **13.0 Data Verification**

### **13.1 Field data verification, requirements, and responsibilities**

The project manager will verify that all field data was recorded without error or omission.

### **13.2 Laboratory data verification**

Laboratory data verification involves examining the data for errors, omissions, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project.

MEL staff will provide written reports of their data review, which will include a discussion of whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions.

The project manager/principal investigator will be responsible for the final acceptance of the laboratory data. The laboratory case narratives and EDD, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will be either accepted, accepted with qualifications, or rejected and re-analysis considered.

### **13.3 Validation requirements, if necessary**

Independent data validation will not be required for this project.

## **14.0 Data Quality (Usability) Assessment**

### **14.1 Process for determining project objectives were met**

After the project data have been reviewed and verified, the principal investigator/project manager will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures will provide information to determine if MQOs have been met. Laboratory and QA staff familiar with assessment of data quality will be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of laboratory QC results.

### **14.2 Treatment of nondetects**

Nondetects are not applicable to the non-targeted qualitative screening. Compounds not positively identified are not reported.

### **14.3 Data analysis and presentation methods**

Data analysis and presentation methods will be explored to provide the Toxics Studies Unit ideas for presentation methods that work for this type of analysis. Current ideas under consideration include cluster analysis, multivariate statistical tools, and heat maps.

### **14.4 Sampling design evaluation**

The number and type of samples collected will be sufficient to meet the objectives of this project.

### **14.5 Documentation of assessment**

Documentation of assessment will occur in the final report.

## 15.0 References

- Friese, M. 2017. Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment, Version 1.0. Washington State Department of Ecology, Olympia. SOP EAP090.
- Furl, C., and C. Meredith. 2008. PBT Monitoring: Measuring Perfluorinated Compounds in Washington Rivers and Lakes. Publication 08-03-107. Washington State Department of Ecology, Olympia. Study ID CFUR0003.  
<https://fortress.wa.gov/ecy/publications/documents/0803107.pdf>.
- Johnson, A. 2011. Quality Assurance Project Plan: Analyzing Chlorinated Pesticide Residues in Fish from Washington Background Lakes. Publication 11-03-108. Washington State Department of Ecology, Olympia. Study ID AJOH0065.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/1103108.html>.
- Johnson, A., and K. Seiders. 2005. Quality Assurance Project Plan: PBT Monitoring: Measuring PBDE Levels in Washington Rivers and Lakes. Publication 05-03-113. Washington State Department of Ecology, Olympia. Study ID AJOH0048.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/0503113.html>.
- Lombard, S., and C. Kirchmer. 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia. Publication No. 04-03-030.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html>
- Mathieu, C. 2018a. Addendum to Quality Assurance Project Plan: Flame Retardants in Ten Washington State Waterbodies. Publication 18-03-102. Washington State Department of Ecology, Olympia. Study ID CAME003.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/1803102.html>.
- Mathieu, C. 2018b. Addendum to Quality Assurance Project Plan: Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes. Publication 18-03-117. Washington State Department of Ecology, Olympia. Study ID CAME004.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/1803117.html>.
- Mathieu, C., and M. McCall. 2017. Statewide Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Washington State Rivers and Lakes. Publication 17-03-021. Washington State Department of Ecology, Olympia. Study ID CAME0002.  
<https://fortress.wa.gov/ecy/publications/documents/1703021.pdf>.
- Sandvik, P. 2018. Standard Operating Procedure EAP007, Version 1.2: Resecting Finfish Whole Body, Body Parts, or Tissue Samples. Publication 18-03-235. Washington State Department of Ecology, Olympia.  
<https://fortress.wa.gov/ecy/publications/SummaryPages/1803235.html>.
- Seiders, K. 2016. Addendum 5 to Quality Assurance Project Plan: Freshwater Fish Contaminant Monitoring Program, 2016. Publication 16-03-122. Washington State Department of Ecology, Olympia. <https://fortress.wa.gov/ecy/publications/SummaryPages/1603122.html>.

## **16.0 Appendices**

## Appendix A. Glossaries, Acronyms, and Abbreviations

### Glossary of General Terms

**Anthropogenic:** Human-caused.

**Quadrupole time-of-flight:** Method of mass spectrometry in which an ion's mass-to-charge ratio is determined via a time-of-flight measurement. Ions are accelerated towards a sensor; the time it takes an ion to reach the sensor is recorded for identification of the ion.

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

**Tentatively identified compound:** A compound is positively identified/detected, but the concentration of that compound can not be verified without additional analysis.

**Tissue:** The edible portion of aquatic species, usually made up of muscle and associated lipids.

## Acronyms and Abbreviations

DOH	Department of Health
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FFCMP	Freshwater Fish Contaminant Monitoring Program
GC-MS	Gas chromatography–mass spectrometry
GIS	Geographic Information System software
GPS	Global Positioning System
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MS	Mass spectrometry
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
ODEQ	Oregon Department of Environmental Quality
ODFW	Oregon Department of Fish and Wildlife
PAH	Polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyls
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
QTOF	Quadrupole time-of-flight gas chromatography–mass spectrometry
SOP	Standard Operating Procedure
TSU	Toxic Studies Unit
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife



## Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
dw	dry weight
ft	feet
g	gram, a unit of mass
kcf/s	1000 cubic feet per second
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mm	millimeter
mg	milligram
mgd	million gallons per day
mg/d	milligrams per day
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mg/L/hr	milligrams per liter per hour
mL	milliliter
mmol	millimole or one-thousandth of a mole
mole	an International System of Units (IS) unit of matter
m/z	mass-to-charge ratio
ng/g	nanograms per gram (parts per billion)
ng/kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
oz.	ounce
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
psu	practical salinity units
µg/g	micrograms per gram (parts per million)
µg/kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µm	micrometer
µM	micromolar (a chemistry unit)
ww	wet weight

## Quality Assurance Glossary

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Examples of data types commonly validated would be:

- Gas chromatography (GC).
- Gas chromatography–mass spectrometry (GC-MS).
- Inductively coupled plasma (ICP).

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

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

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

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

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

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

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

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

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

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

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

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

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

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

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

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

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

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

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

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

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

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

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

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

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

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

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

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

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

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

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

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

**Spiked sample:** A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is

available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

**Split sample:** A discrete sample subdivided into portions, usually duplicates (Kammin, 2010)

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

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

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

#### *References for QA Glossary*

- Ecology. 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia. <https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html>
- Kammin, B. 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia.
- USEPA. 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency.
- USEPA. 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. <http://www.epa.gov/quality/qs-docs/g4-final.pdf>.
- USGS. 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. <http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf>.