Quality Assurance Project Plan for Implementation of the Columbia River Mainstem Fish Tissue and Sediment Quality Monitoring Program

A. PROJECT MANAGEMENT

A1. APPROVAL PAGE

Name: Jennifer Morace
Title: Field Sampling Coordinator
Organization: Oregon Water Science Center, USGS
Signature: JENNIFER MORACE Digitally signed by JENNIFER MORACE Date: 2023.04.20 22:53:35 -07'00' Date: 04/20/2023

Name: Patrick Moran
Title: Quality Assurance Coordinator
Organization: Washington Water Science Center, USGS
Signature: PATRICK MORAN Digitally signed by PATRICK MORAN Date: 2023.04.21 17:36:57 -07'00' Date:

Name: Laura Shira
Title: Project Manager
Organization: Yakama Nation
Signature: Laura Shira Digitally signed by Laura Shira Date: 2023.04.20 19:54:09 -07'00' Date:

Name: Lauren McDaid
Title: EPA Project Officer
Organization: US EPA Region 10
Signature: LAUREN MCDAID Digitally signed by LAUREN MCDAID Date: 2023.04.18 13:22:05 -06'00' Date: 4/18/2023

Name: Cindy Fields
Title: EPA Quality Assurance Manager
Organization: US EPA Region 10
Signature: Date: 4/17/2023

A2. TABLES OF CONTENTS

Table of Tables

Table of Figures

A3. DISTRIBUTION LIST

Name:
Title:
Organization:
Signature: _____ Date:_____

Name:
Title:
Organization:
Signature: _____ Date:_____

Name:
Title:
Organization:
Signature: _____ Date:_____

Name:
Title:
Organization:
Signature: _____ Date:_____

Name:
Title:
Organization:
Signature: _____ Date:_____

A4. BACKGROUND

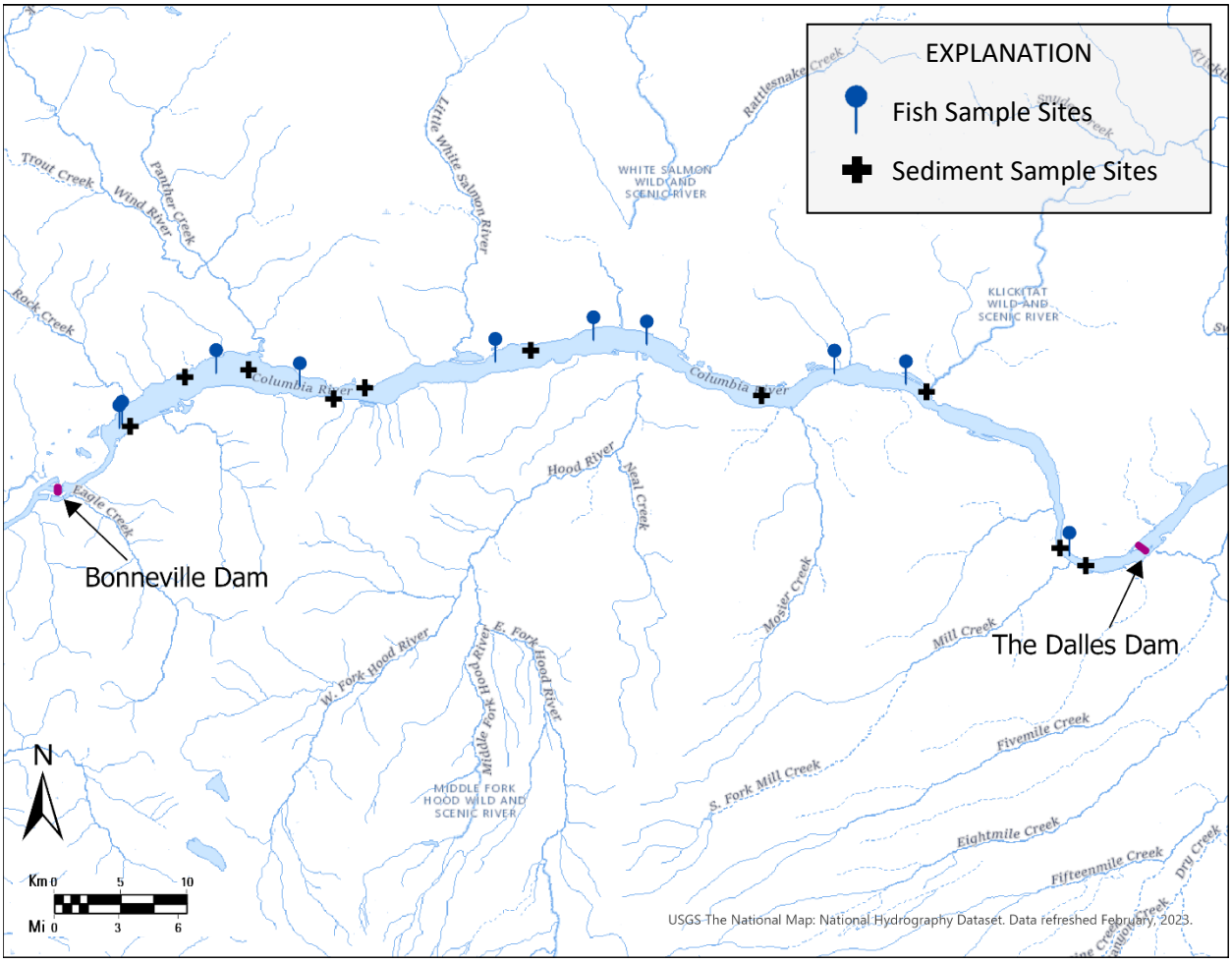
Concern about the health of the aquatic ecosystem of the Columbia River Basin and the potential risk to human health exists due to the exposure of toxic contaminants found in fish, wildlife, and sediment (USEPA, 2009). Several federally listed and tribally important species and their designated critical habitat and essential fish habitat supported by the Columbia River are affected. Past studies have measured key contaminants in Columbia River fish which have included polychlorinated biphenyls (PCBs), dioxins, furans, arsenic, mercury, and organochlorine pesticides (USEPA, 2009). The Columbia River mainstem from the Bonneville Dam to the Canadian border is affected by several site- and species- specific Fish Consumption Advisories issued by the Washington Department of Health (WDOH, 2023). According to fish consumption surveys of tribes (CRITFC, 1994; Polissar and others, 2016), tribal members have relied extensively on fish resources and fishing activities throughout time. These surveys highlight that Tribal fish harvesting and high use and consumption of fish historically, in comparison to the average consumer, is of concern due to toxic accumulation in fish tissue putting tribal members at higher health risk. The advisories result in a reduction of access to healthy food and treaty reserved resources. Despite concerns regarding the effects of contaminants on fish and wildlife and human health; efforts to address the pollution by toxic chemicals in the Columbia River have been limited. The lack of a dedicated contaminant monitoring program in the Columbia River mainstem impedes evaluation and decision making regarding the health of the river. These concerns were recognized in the Columbia River Basin Toxics Reduction Action Plan established in 2010 (USEPA, 2010). The Action Plan identified 61 actions organized into 5 Initiatives that would help achieve the goal of reducing human and ecosystem exposure to toxic contaminants in the Columbia River Basin. Initiatives 3 (Conduct monitoring to identify sources and then reduce toxics) and 4 (Develop a regional, multi-agency research and monitoring program) of the Action Plan address the importance of, and need for, various monitoring actions to help realize the plan's goal.

A5. PROJECT DESCRIPTION

EPA awarded funds to the Confederated Tribes and Bands of the Yakama Nation, who have partnered with the U.S. Geological Survey (USGS), Columbia River Inter-Tribal Fish Commission, Washington State Department of Ecology, and Oregon Department of Environmental Quality to develop a monitoring program aimed at tracking the status and trends of contaminants in fish and sediments in the Columbia River mainstem from Bonneville Dam to near the Dalles Dam (Fig. 1). This long-term monitoring design and rationale was recently published as a "Framework for the Development of the Columbia River Mainstem Fish Tissue and Water Quality Monitoring Program" in 2023 (Counihan et al 2022). The study plan presented here is the pilot implementation of that Framework design specific to the Bonneville Reservoir of the Columbia River specifically. The contaminants of interest include mercury (total and methylmercury (in sediments only)), organochlorine (OC) pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). This quality assurance project plan (QAPP) will focus

on and Phase 2 of a three-phase, multi-year program that will develop a plan to establish a long-term monitoring program. This is an important first step in developing and implementing the materials developed in Phase 1. The USGS will be responsible for the implementation of a Pilot Study for fish tissue and sediment sampling in the Columbia River using the procedures described in this QAPP.

Figure 1. A map of the study reach and sampling sites.



The following provides a brief outline of the three phases:

- In Phase 1 (year 1 and 2), a Monitoring Framework to guide formation of a long-term monitoring program to assess the status and trends of contaminants in fish and sediments in the Middle and Upper Columbia River mainstem was developed and completed in December of 2022. Phase I included reviewing relevant and existing datasets, soliciting feedback on research needs and priorities from key stakeholders, formulating a written conceptual design and distributing it for stakeholder review, and addressing stakeholder comments to produce a Monitoring Framework and an Outreach Messaging Framework.
- Phase 2 (this study, in years 3 and 4) is an implementation of a pilot study of the Columbia River Monitoring Framework. The work in this phase will cover the following EPA's Columbia

River Basin Restoration Program (CRBRP) project categories and priorities (RFA Section 1.B.): **Category 4)** Monitoring to evaluate trends; **Category 7)** Promoting citizen engagement or knowledge**; Priority 1)** Increased monitoring and access to data; and **Priority 3)** Promoting citizen engagement or education. Phase 2 will be an implementation of stakeholder engagement process that supports the larger vision for the monitoring program: A multi-phased approach with dependency on collaboration during all phases including work towards developing a widely available database and document repository.

- Phase 3 (year 5 and further) will implement the monitoring program developed in Phase 1 and 2. The monitoring program will continue annually including data management and community engagement and outreach activities.

A6. PROJECT OBJECTIVES

The primary purpose of this project is to pilot implement the Framework by the collection, process, and analysis of fish and sediment samples from Bonneville Dam to near the Dalles Dam, a 50-mile reach of the Columbia River. This Pilot Study will provide information needed to conduct aquatic monitoring in a large river like the Columbia. The main goal is to further develop a collaborative monitoring program through field sampling, analytical, and reporting effort. This work will directly inform the development of the monitoring program by providing on the ground information to refine media specific QAPPs, field and lab SOPs, Health and Safety Plans (HASPs), Invasive Species Spread and Prevention Plan (ISSPP)**,** laboratory contracting, performance plan and data review, and other plans and permits required to fully implement the Columbia River Mainstem Fish Tissue and Sediment Quality Monitoring Program (i.e., Phase 3).

A7. PROJECT ORGANIZATION

This QAPP covers the study design for sample collection and describes the quality assurance and quality control (QA/QC) methods and procedures that will be used for the collection of fish tissue and sediment samples. This QAPP was prepared according to guidance presented in the 2002 EPA document of Requirements for Quality Assurance Project Plans (USEPA 2002a). Reference to the QAPP elements described in the guidance document are included in this document. Organization of the project team provides the framework for conducting the sample collection tasks to meet study objectives. The organizational structure and function also facilitate project performance and adherence to QA/QC procedures and requirements. Critical roles will be fulfilled by those responsible for ensuring the collection and processing of data and for routinely assessing the data for precision and accuracy, as well as the persons responsible for approving and accepting final deliverables. The project staff include staff from USGS Western Fisheries Research Center (WFRC), the USGS Washington Water Science Center (WAWSC), the USGS Oregon Water Science Center (ORWSC), Washington Department of Fish and Wildlife (WDFW) and the Yakama Nation Tribal staff and their contractors.

USGS Field Sampling Coordinator, or her designee, will supervise the assigned project staff to provide for their efficient operation by directing their efforts either directly or indirectly. The project leads will also have the following responsibilities:

- providing oversight for study design, site selection, and adherence to design objectives,
- reviewing and approving the project work plan, QAPP, and other materials developed
- to support the project.

The USGS Project Leads, Tim Counihan (WFRC), Patrick Moran (WAWSC), and Ian Waite (ORWSC), will be responsible for performing evaluations to ensure that QA/QC protocols are maintained throughout the sample collection and preparation processes for the length of the study. The evaluations will include reviewing all required documentation for completeness and documenting and addressing any problems encountered outside normal operating conditions and verifying all other QA/QC procedures identified in the QAPP are followed.

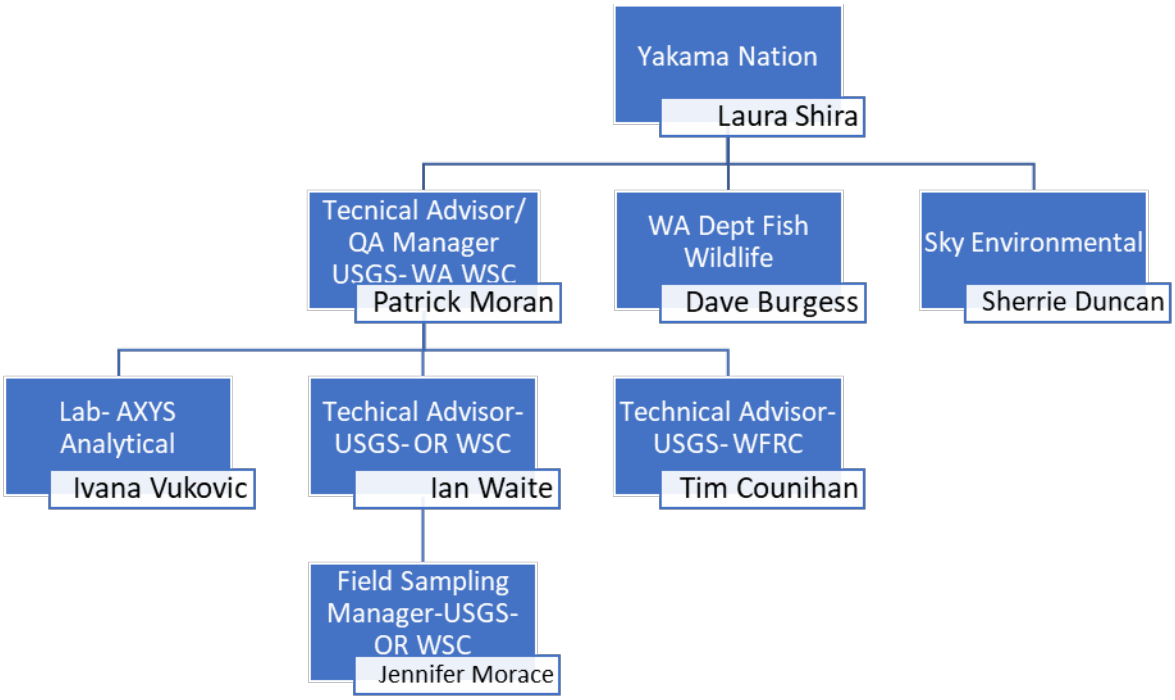
Field Sampling Teams will be composed of:

- Patrick Moran and WAWSC field staff
- Dave Burgess and WDFW field staff
- Tim Counihan and WFRC field staff
- Ian Waite and ORWSC field staff

USGS field staff are responsible for performing the field work, including collection, preparation, and shipment of samples and completion of field sampling records. The Field Sampling Teams will include scientific staff with specialization and technical competence in field sampling activities to perform the required work effectively and efficiently. All work must be performed in adherence with the project work plan and QAPP. Field Sampling Teams will be responsible for:

- receiving and inspecting the sample containers
- completing and signing appropriate field records
- assigning tracking numbers to each sample
- verifying proper handling and storage of the samples
- verifying completeness and accuracy of shipment information
- controlling and monitoring access to samples while in their custody
- initiating shipment of the samples to appropriate destinations.

Figure 2. Project Organizational Chart that follows contractual responsibilities.


Yakama Nation
Laura Shira
Tecnical Advisor/ QA Manager USGS- WA WSC
Patrick Moran
WA Dept Fish Wildlife
Dave Burgess
Sky Environmental
Sherrie Duncan
Lab- AXYS Analytical
Ivana Vukovic
Techical Advisor- USGS- OR WSC
Ian Waite
Technical Advisor- USGS- WFRC
Tim Counihan
Field Sampling Manager-USGS- OR WSC
Jennifer Morace

B. DATA ACQUISITION

B1. SAMPLING PROCESS

Sample Type

To meet the study objectives under this QAPP, sample type will include composite sampling of fish fillets and whole fish composites, as well as composite sediment samples. In addition, biofilm samples from large flat rock surfaces will be collected adjacent to the fish sampling sites as budget and time allow. (More details on sample type is described below.)

Sampling Period

Field sampling will be conducted during the summer of 2023. The primary sampling window will be between July and August 2023 (table 1). If the fish collection methods are not fully successful during this time, boat-based electrofishing may occur in the late October to November time frame when water temperatures have cooled to below 64 degrees F, as per the NOAA Fish Collection permit.

Site Selection

Sites for sample collection from Bonneville Dam to near the Dalles Dam (Bonneville Reservoir) will be selected using the linear Generalized Random Tessellation Stratified (GRTS) method. The GRTS method is designed to produce a probability sample with design-based variance estimators. It provides a spatially balanced, random selection of sites, allowing for unequal probability sampling. If logistical or safety constraints make a site inaccessible, the reason for the site inaccessibility will be recorded and reported, and pre-selected additional randomized sampling sites will be used as a replacement. This GRTS method, as described by Stevens and Olsen (2004) and therein, is analogous to the design approach implemented by the EPA National Streams and Rivers Assessment (NRSA) program, and EPA Office of Research and Development (ORD) scientists were consulted prior to its implementation here.

Sample Frame

Implementation of the field sampling tasks will proceed with several time points, as presented in Table 1. All activities associated with sample collection will be conducted consistent with the requirements and procedures specified in this QAPP.

Table 1. Project timeline associated with fish tissue and sediment sample collection.

Task	Description	Timeline
Project Planning and Monitoring		

Submit QAPP and respond to comments. Plan for field effort.	Plan, task and train staff on appropriate methods. Plan for sample handling (bottles, labels, transport, storage). Schedule. Confirm laboratory contracting.	02/2023-06/2023
Conduct field sampling for fish and sediments.	Document sample collection, locations, collection success, modifications, sample status and proper holding methods and times. Finalize sub-contractor and laboratory payments.	07/2023 - 08/2023
Fish collections/purchase events with Tribal Fishers for salmon collection	Sample collection and locations for adult salmon will be coordinated with Yakama Fisheries staff and documented with the sample collection and location information.	08/2023 - 10/2023
Secondary Fish Collection, if needed	Boat electrofishing maybe utilized during this window if catch rates in July and August were insufficient	10/2023-11/2023
Ship samples to the laboratory.	Samples will be shipped in dry ice in the proper shipping container. Document shipping information	09/2023 - 11/2023
Submit post-sampling reporting for Federal and State permits. Prepare Data Release.	Complete reporting requirements for Federal and State permits. Begin data release for review and public notification.	03/2024 - 05/2024
Review Laboratory Data.	Review all project data, including laboratory QA data. Verify method performance and need for laboratory re-runs or clarifications.	02/2024-03/2024
Laboratory Analysis		
Conduct Quality Assurance checks, data validation and confirmation.	Distribute preliminary dataset and validation package to Team members for additional review.	04/2024 - 05/2024
Archive and distribute data in permanent and publicly available database.	Create data release, submit for peer review, release data via USGS ScienceBase or USGS National Water Information System (NWIS).	05/2024 - 08/2024

Document Pilot sampling efforts, and reference the relevant, aforementioned written products (SOPs, permits, sampling frame, etc)	Produce a Data Summary Report that documents and summarizes overall sampling efforts and observations and supporting materials; including data appendices to the summary report.	01/2024 - 09/2024

B2. SAMPLING METHODS

Field methods described in Hayslip and Herger (2008) will be used for the sampling of fish, as allowed by NOAA permits, and field methods described in Counihan and others (2014) will be used for sediment sampling. Field sampling will be conducted during the Summer of 2023, between July and August. Sampling is planned as a one-time event per site, no scheduled repeat sampling for the base sites. Biofilm samples may also be collected if time and budget allow it. Collection of biofilm samples will follow sampling methods described in Larson and Collyard (2019) and Hobbs (2019). In addition, water temperature and specific conductance readings will be collected at the beginning of each sampling event using a multiparameter meter.

Fish Sampling

The fish collection procedures will follow the methods as outlined by the NOAA and ODFW permit requirements, where this same sampling design request was submitted. Both predatory and prey versions of resident and anadromous salmonids composite samples will be collected.

Adult Salmonids

Returning adult salmon (considered to be >60cm) will be collected from tribal fisherman fishing in Bonneville Reservoir with the assistance of the Yakama Nation and their fisheries management staff during the active Fall adult fishery. Communication and coordination with Tribal Fisherman has already begun through Yakama Nation Fisheries managers, and representative from the project will attend and inform and answer questions from Tribal Fishers during the spring or summer planning meetings. Purchased adult salmon from the Tribal fishers will be cleaned thoroughly with DI water and dissected immediately upon receipt. Two, 10-gram skin-on fillet pieces collected from the largest cross section of the fillet (above the lateral line, posterior to the skull and anterior to the dorsal fin) will be collected. Dissection will use stainless steel dissection tools. Duplicate, 3-5 fish skin-on fillet composites, will be collected, (ie. 2 containers), and placed immediately on dry ice. Lengths and weight and sex of each fish at the time of receipt will be recorded. Adults will be scanned for coded wire tags and PIT tags with a PIT Tag wand and scales of adults will be retained for aging.

Juvenile Salmonids

Juvenile salmonids are considered between 12-17 cm in length and out-migrating juveniles will be collected from the Bonneville Fish Collection facility. Depending upon availability, whole body composite samples of 3-5 juvenile salmon of the same species will be created. Five to ten of these single species, whole body juvenile salmonid samples, composited into a single container per sample, will be collected, depending upon availability. Lengths and weight of each fish at the time of receipt will be recorded.

Resident Fish

Resident prey (forage) fish will consist of fish (< 30cm) and resident predatory (> 30cm) fish species from a targeted resident list will be developed to minimize the effect of sampling different species while still obtaining a representative sample across sites (USEPA 2008). Targeted fish species are listed in table 3. Other species not listed may only be considered if an insufficient number of the targeted resident species is collected.

Ten sample sites were selected (fig. 1) by a statistical random (systematic) process determined by a GRTS sampling design which selects the center channel point. Fish sampling will be within a fixed 1000' section along either the left or right banks from the center channel point. The gear types used to collect fish are determined in the permitting process. Sampling will be performed using passive net gear including hoop nets, fyke nets, large minnow nets and hook-n-line. Using passive net sampling gear allows the release of all non-target fish with minimal effects to the fish, as well as for targeted resident species prior to processing. Deployment of gears and collection of fish samples from shoreline areas in Bonneville Reservoir is planned within a fix location near the shore (approx. within 500'). Boat electrofishing will only be used if various other methods are not effective.

Fish tissue samples will be processed using similar methods to those described in USEPA 2000. Fish will be weighed, measured, sex determined and identified in the field. Composite samples of 5 fish fillets with skin-on of the same species (same species because of the significant species-specific bioaccumulation potential) and of similar size (within 75% total length of the largest fish) will be collected. Whole fish for juvenile fish samples will also be collected (table 2). (Fish for whole body composite analysis may be opened for sex determination.) All samples collected will be analyzed for total mercury, organochlorine (OC) pesticides, PCBs, and PBDEs. Fish samples will be collected in sufficient numbers to provide a 50-g composite homogenate sample of tissue for analysis of recommended target analytes and placed in a borosilicate glass container. All samples will be processed in the field and will be frozen at the sampling site and stored until ready to be shipped on dry ice to the laboratory for analysis.

Table 2. Fish groups and fish size categories

Fish Group	Size Group	Sample Medium	Number of samples per fish group*

Forage fish	<30 cm	Whole fish	10
Predatory fish	>30 cm	Fillets, skin-on	10
Juvenile Salmonids	12-17 cm	Whole fish	5
Adult Salmonids	>60 cm	Fillets, skin-on	5

*Composite of 5 fish fillets or whole fish of the same species equals one sample. QA sample number not included here.

Table 3. Targeted fish species list

Resident Forage Fish	Resident Predatory Fish	Salmonids Juvenile	Salmonids Adults
Speckled Dace	Smallmouth Bass	Coho	Coho
Sculpin	Walleye	Chinook	Chinook
Red Side Shiner	Largemouth Bass		
Largescale Sucker	Northern Pikeminnow		
Chiselmouth			
Peamouth			
Carp			

Sediment Sampling

Sediment samples will be collected in accordance with the permits acquired and this QAPP (table 4). Similar to fish sample sites, up to 7 sample sites were generated to collect sediment samples using a GRTS algorithm that encompasses the Reservoir and contains a grid of sample points at a resolution of 30 m x 30 m (see: https://www.monitoringresources.org/Sites/Master/Detail/2). Sediment samples will be collected along either the left or right banks or the center of the channel within a 30m x 30m grid section. All sediment samples collected will be analyzed for mercury (total and methylmercury), organochlorine (OC) pesticides, PCBs, and PBDEs. In addition, grain size and organic content (loss on ignition) in sediment samples collected will be analyzed.

Sediment samples will be collected from a boat using a standard ponar benthic grab sampler, or a 30 x 30 cm box corer, deployed from a bow-mounted crane and winch (Counihan and others, 2014). Individual ponar grab samples will be collected within a strata and deposited in a stainless steel bin and then composited. Refusal of the ponar or box corer due to hard substrates is possible at some sites and a total of 10 sediment samples may not be collected. Individual samples will be homogenized with a stainless-steel spoon, subsampled, and transferred to a whirlpak for grain size and loss on ignition (LOI) analysis; the remaining sample portion will then be transferred to a bin set up to be composited. Once the sample is composited, the sample will be homogenized again, and a portion will be transferred to a 500 ml glass jar for contaminant analysis. The individual stainless steel collection bins will be rinsed

thoroughly with native water between samples. After the full composite is collected at each site, the bins will be rinsed with native water, cleaned with Liquinox soap and deionized water, rinsed two more times with deionized water, and finally rinsed with methanol from a squirt bottle and rinsed again with deionized water before the next composite sample is collected at the following site. Immediately after collection, samples will be placed in coolers on ice at < 4°C and later freeze until ready to be shipped to analytical laboratory.

Table 4. Criteria and considerations for collecting a representative sample of bottom material

Aspects of Sample Collection	Criteria and Considerations
Equipment	• Sampling equipment penetration must be deep enough to provide a sample mass that meets project objectives • Sampling equipment must be completely closed after proper penetration • Weight of sampler
Techniques and methods	• Quantities of bottom material enclosed each time sampling equipment is deployed should be approximately equal • Speed of sampler through water column • Consistent depth of sediment per grab (ie. top 10 cm)
Sampling environment	• Depth of water column (ensure adequate cable length to control speed of sampler deployment • Physical, chemical, and biological character of water column above sample-collection site • Velocity of water currents (too fast could produce improper deployment of sampler) • If site is inaccessible, avoid site and move to next site on sample list • Sampling platform stability (such waves) • Temperature and conductivity of water at 1m of depth

Biofilm Sampling

Biofilm refers to the mixture of periphyton, microbial biomass, and fine sediments that adheres to solid surfaces in aquatic environments. Periphyton is algae attached to the river bottom, rocks, or debris in freshwater rivers and streams. Standard protocols for sampling attached algae for the collection of biofilm samples will be followed (Larson and Collyard, 2019). Biofilm will be scraped from rocks and collected in the field to confirm that sufficient biomass is retrieved (~10 g wet weight). Samples will be transferred from the collecting bowl to a cleaned glass jar. A sample to assess areal biomass (g dry weight / cm2) will be collected separately. The area scraped from both sample locations for biofilm will be measured by cutting a piece of aluminum foil to trace the sampled area. The area of the aluminum foil is then measured using a 2-D digitizing software (Hobbs, 2019).

Sampling Methods Summary

An overview of the sample types, collection method, parameters, and total number of samples that will be collected for this study are shown in table 5 below. If biofilm samples are collected, dependent on time and budget, these samples will only be analyzed for OC pesticides, PCBs, and PBDEs, with the sample lab method and detection levels as the tissue samples.

Table 5. Sample types and total number of samples planned to be collected, not including QA/QC samples.

Parameter	Sample type	Total number of samples	Collection method
PCBs, PBDE, OC pesticides, total mercury, percent lipids	Fish tissue*	30	Passive net gear
PCBs, PBDE, OC pesticides, total mercury, methylmercury, grain size, loss on ignition	Sediment	10^	Grab sample

*Adult salmonids will be bought from fisherman for analysis. ^Not to exceed number, may be less depending upon sampling success. All juvenile salmonids will be collected from Bonneville Fish Collection Facility for analysis.

B3. QUALITY OBJECTIVES AND CRITERIA FOR DATA COLLECTION

Specific Data Quality Objectives (DQO) generated in this QAPP will help to determine the intended qualitative and quantitative use of the data, define the type of data needed to support the decisions to be made, identify the conditions under which the data should be collected, and specify acceptable limits on the probability of making a decision error due to uncertainty in the data. Laboratory and field methods, contract negotiation and documentation and financial arrangements, and sample preservation and handling documentation will be completed before sample collection begins.

Possible sources of error or uncertainty are listed below:

- Sampling error: The difference between sample values and true values from unknown biases due to collection methods and sampling design
- Measurement error: The difference between sample values and true values associated with the measurement process
- Natural variation: Environmental spatial and temporal variability in population abundance and distribution
- Error sources or biases associated with compositing, sample handling, storage, and preservation

The methods and procedures described in this document are intended to reduce the magnitude of the possible sources of uncertainty listed above, by following the steps listed below:

- use of established and standardized sample collection and handling procedures, and
- use of trained staff to perform the sample collection and sample handling

B4. SAMPLING HANDLING

Sample containers and labels should be prepared before sampling for sample organization and sampling efficiency. Proper labeling of samples is an important quality assurance aspect and all sample containers for each site should be prelabeled prior to sampling. Pre-labeling clean and dry containers helps to ensure that labels adhere properly to the containers. Labels should contain site name, site number, sample date and time, species name (for fish only). Labels should be preprinted on waterproof paper using ink that is resistant to water, and the information should be recorded on the label using a water-resistant pen. Examples of all forms are provided in Appendix B. Sampling crews should be mindful while sampling to prevent contamination of containers, packaging, and sampling equipment used for trace of mercury analysis.

Primary concern with sample handling and processing is to avoid sources of possible tissue contamination including contamination from sampling gear, spilled engine fuel (gasoline or diesel), engine exhaust, dust, ice coolers, and ice used for cooling. All potential sources of contamination in the field should be identified and appropriate steps should be taken to minimize or eliminate them. Wind direction and sources of engine exhaust will be monitored; under some conditions, contact with exhaust may be unavoidable and will be so noted. Ice coolers used should be scrubbed clean with detergent and rinsed with distilled water after each use to prevent contamination. To avoid contamination from melting ice, samples should be placed in waterproof plastic bags. Sampling equipment that has been contaminated by oils, grease, diesel fuel, or gasoline should not be used. All equipment that will be used directly in handling fish (e.g., fish measuring board, scales) should be cleaned in the laboratory prior to each sampling trip, rinsed in acetone and pesticide-grade methanol, and stored in aluminum foil until use. Between sampling sites, each measurement device should be cleaned by rinsing it with ambient water and rewrapping it in aluminum foil to prevent contamination. Similarly, the loss of contaminants is also a concern and can be prevented by ensuring that the sample collected remains intact, i.e., sample collection procedures should be performed with the intention of minimizing the laceration of fish skin. In addition, any sensitive gear such as meters, probes, cameras, rangefinders, and other sensitive gear should be packed to avoid shock, exposure, and other damage during transportation and boat rides.

Individuals of the selected target species will be rinsed in ambient water to remove any foreign material from the external surface. A nine-character composite sample identification number consisting of the two-character state abbreviation, two-number year abbreviation, 3-digit site identification number, and sample type (“BA” for animal tissue sample, “SB” for bed-sediment sample, “BAQ” for animal tissue quality control sample, or “SBQ” for bed-sediment quality

control sample) will be assigned by the field teams for each composite collected. The composite sample specimen number and information regarding the fish specimens will be recorded on the field record forms.

A Laboratory Analytical Services Request (ASR) Form will be completed and submitted together with the samples. ASR should include sample date and time, sample type, site number, site name, and analytical schedules being requested. A copy of the ASR form will be kept as a record. Documentation establishing the collection information, sample shipment information (tracking number, ASR), and sample inventory of the contents of each shipment coinciding with information in the field data forms will act as a record. The information on the field data form is discussed above. No Chain of Custody or signature of the person relinquishing the sample will be required. Any observations regarding the shipment (e.g., torn or damaged packaging, insufficient dry ice) should be documented by the laboratory, however, and should be communicated to USGS project lead.

Sample management, short-term storage, sub-sampling (if needed) and documentation prior to laboratory submittal will primarily be handled by the USGS Oregon Water Science Center (ORWSC) in Portland, OR. Project leads will work with the ORWSC to ensure proper handling of the field samples and generation of key QA samples at various points along the sampling and shipping progression.

Table 6. Sample Preservation Methods and Holding Times

Analyte Class	Media	Holding Times Field (wet or dry Ice)	Holding Times- Lab	Preservation Container*
PCBs	Tissue & Sediments	24 hours	1 year	Certified Baked Glass
PBDEs	Tissue and Sediment	24 hours	1 year	Certified Baked Glass
Organochlorines	Tissue and Sediment	24 hours	1 year	Certified Baked Glass
Mercury	Tissue and Sediment	24 hours	1 year	Certified Baked Glass

*For larger samples (e.g. large fish) wrapping first in aluminum foil prior to ziplock baging may be needed.

B5. ANALYTICAL METHODS

All laboratories will use EPA or other standard methods which have proven performances in tissue and sediment matrices. The laboratories may use other suitable methods, provided that

performance-based measures are achieved. The specific analytical concentration goals (ACGs) were established in a 3-step review process.

1) For the protection of human health, the 2008 Risk Based Concentrations (RBCs) generated by Syracuse Research Corporation for EPA Region 10 in Table B-2 of the "Upper Columbia River Site, Quality Assurance Project Plan for the 2009 Fish Tissue Study" (Parametrix, 2009) were reviewed and considered appropriate ACGs for this study. See Appendix C.
2) For the resident forage fish and for the juvenile salmonids, RBCs for the protection of piscivorous fish and wildlife are rarely defined, but for 5 classes of contaminants (ie. PCBs, PBDEs, DDT, chlordane, dieldrin) were summarized by Batt and others (2017) and deemed suitable ACGs for this study.
3) Factors 1 and 2 were considered, along with laboratory costs, new sample capacity, turnaround time and number of total analytes reported on the method, to arrive at a final decision about which lab and analytical method would be utilized.

The list of laboratory analytes and expected detection limits is shown in Appendix A. With one notable exceptions (eg. PCB-126) the detection limits listed in Appendix A are generally lower than the "Lowest Risk-Based Concentration" reported in Table B-2 of the "Upper Columbia River Site, Quality Assurance Project Plan for the 2009 Fish Tissue Study". Meeting all the lowest risk-based concentration targets in the Table B-2, for such a long list of chemicals is economically unfeasible and was not originally scoped as such.

Tissue

The AXYS Analytical Laboratory will analyze for OC pesticides, PCBs, and PBDEs in fish and sediment samples. Total mercury will be analyzed by Bureau Veritas Laboratory in Mississauga ON. Subsamples of all fish samples processed and homogenized by AXYS Laboratory will be sent to the Bureau Veritas Laboratory for total mercury analysis. Whole fish samples will be retained whole, composited into a single container per sample, frozen in the field and homogenized at the AXYS Analytical Laboratory. Composite fillet tissues will likewise be weighed and composited into single container, and frozen in the field and homogenized at AXYS Analytical Laboratory. The SOPs from both laboratories use appropriate analytical methods to achieve the required measurement quality objectives.

Laboratory method MLA-010 conducted by AXYS Laboratory will be used for the analytical procedures of the quantitative determination of PCBs congeners by high resolution gas chromatography and mass spectroscopy (HRGC/MS). This method is consistent with EPA method 1668A. Organochlorine (OC) pesticides will be measured by low resolution gas chromatography/ mass spectrometry (GC/LRMS) analysis, AXYS method number MLA-007. Prior to processing tissue samples, whole fish and skin on fish fillets (filleted in the field) composite samples will be homogenized. Prior to sample extraction, isotopically labeled surrogate

standards are added to the sample. Tissue samples are dried with sodium sulfate and then Soxhlet extracted with dichloromethane. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use. Fish tissue – A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with anhydrous sodium sulfate, allowed to dry for 30 minutes minimum, and extracted for 18 - 24 hours using methylene chloride in a Soxhlet extractor. During cleanup tissue extracts are always first eluted through a gel permeation column to remove lipids, and the lipid content is determined. Instrument initial calibration is performed using a series of five calibration solutions that encompass the working concentration range of the instrument. The initial calibration solutions contain surrogates, recovery standards and native analytes. The concentration of the native analytes in the solutions varies to encompass the working range of the instrument, while the concentrations of the surrogates and recovery standards remain constant. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution.

Laboratory method MLA-033 conducted by AXYS Laboratory will be used for the analytical determination of the concentrations of PBDEs, according to the protocols described in EPA Method 1614A, in aqueous, solid, and tissue samples. The method uses isotope dilution, and the analysis is performed using a high-resolution gas chromatography to a high-resolution mass spectrometer (HRGC/HRMS). Fish tissue samples - a 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with anhydrous sodium sulfate, dried for a minimum of 30 minutes, and extracted for 18-24 hours using methylene chloride in a Soxhlet extractor. Samples are spiked with isotopically labeled BDE surrogate standards, solvent extracted, spiked with a cleanup surrogate standard and cleaned up on a series of chromatographic columns which may include layered acid/base silica, alumina and Florisil columns. The final extract is spiked with isotopically labeled recovery (internal) standards prior to instrumental analysis. The extract is evaporated to dryness, and the lipid content is determined. A series of calibration solutions covering the working response range of the instrument (CS-1 through CS-5) containing BDEs of Primary Interest and labeled surrogate, cleanup and recovery standards is used to establish initial, multi-level calibration of the GC/MS. An additional, single point calibration solution containing all target BDE analytes is used to determine the relative response factors and retention times of the BDE congeners that are not present in the initial calibration solutions. The single point solution is also used as the calibration verification solution, which is analyzed every 12 hours, to demonstrate stability of calibration.

Sample specific detection limits (SDLs) reported with the analytical results are determined from the analysis data by converting the minimum detectable signal to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as 2.5 times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labeled

surrogate peak. SDLs are prorated depending on sample size, extract dilution/split and final extract volume.

Total mercury analysis in tissues will follow Cold Vapor Atomic Absorption (CVAA) method from Bureau Veritas CAM SOP-0453, with typically a 5 ng/g detection limit in tissues. The entire tissue will be transferred to a digestion vial and weighed, then sample will be freeze-dried and processed on a dry-weight basis with the moisture content determined as part of the process. Composites prepared from multiple samples, sample is homogenized as an entire sample and then digested and analyzed. Samples are typically digested using a mixture of nitric acid, hydrochloric acid, and hydrogen peroxide, which completely dissolves the tissue. The resultant digestate is then analyzed by CVAA (cold vapor atomic absorption) spectrophotometry for total mercury.

Sediment

Sediment samples will be analyzed for same parameters as fish tissue samples, with generally the same methods. AXYS Laboratory will conduct analytical procedures for the determination of PCBs and OC pesticides using method MLA-010, and PBDEs using method MLA-033. Total mercury and methylmercury in sediment samples will be analyzed by USGS Mercury Research Laboratory (MRL) in Wisconsin. In addition, grain size and loss on ignition analyses will be analyzed by USGS Cascades Volcanos Observatory (CVO) Sediment Laboratory in Washington.

Sediment samples for OC pesticides, PCBs, and BDEs analysis will follow the same extraction methods as fish tissue samples. AXYS Laboratory analytical method for PBDEs will use isotope dilution and internal standard high resolution gas chromatography/high resolution mass spectrometry, HRGC/HRMS. And analytical method for PCBs and OC pesticides will be using gas chromatography/low-resolution mass spectrometry (GC/LRMS) analysis. Solid samples are spiked into a sample containing 10g of solids. The sample is mixed with anhydrous sodium sulfate, dried for a minimum of 30 minutes, and extracted for 18-24 hours using methylene chloride in a Soxhlet extractor. Samples are spiked with isotopically labeled BDE surrogate standards, solvent extracted, spiked with a cleanup surrogate standard and cleaned up on a series of chromatographic columns which may include layered acid/base silica, alumina and Florisil columns.

Sample specific detection limits (SDLs) reported with the analytical results are determined from the analysis data by converting the minimum detectable signal to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as 2.5 times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labeled surrogate peak. SDLs are prorated depending on sample size, extract dilution/split and final extract volume.

Analysis for total mercury in sediment samples will be analyzed by atomic adsorption following direct combustion. Samples will be prepared by room-temperature acid digestion and

oxidation with aqua regia. The samples are brought up to volume with a 5% bromine monochloride solution to ensure complete oxidation and heated at 50°C in an oven overnight. Samples are then analyzed with an automated flow injection system incorporating a cold vapor atomic fluorescence spectrometer (CVAFS) (DeWild and others, 2004b). These diluted samples are then analyzed according to USEPA Method 1631, Revision E (USEPA, 2002b). All samples are reported in nanograms per gram (ng/g) dry weight.

Analysis of methylmercury is conducted by distillation, gas chromatography separation, and speciated isotope dilution mass spectrometry. Prior to analysis, distillation is required to disassociate methylmercury from the sample matrix and reduce matrix interference during analysis. Sediments are weighed into Teflon distillation vials, to which 40 ml of reagent water, an isotopically enriched methylmercury spike, and 2 ml of acidified potassium chloride/copper sulfate (KCl/CuSO4) solution are added. The distillation vials are heated to 121°C and purged with nitrogen gas. The resulting water vapor carries the disassociated methylmercury from the sample and is condensed in chilled Teflon receiving vials (distillate). Distillation is stopped when approximately 25% of the water remains in the distillation vessels. Analysis is conducted via the Brooks-Rand “MERX” automated methylmercury analytical system coupled to the Elan inductively coupled plasma-mass spectrometer (ICPMS). Quantification of methylmercury concentrations in the samples are calculated using isotopic dilution (DeWild and others, 2004a). Results are reported on a dry weight basis by dividing the concentration as-processed by the percent dry weight.

Sediment grain size can be used to assess fine-grained particles correlated to concentration of contaminants in sediments. The pipet method is used to determine particle size gradation of fine material. A pipet is used to withdraw fine sediment at known depths over a period of time. These withdrawals are used to determine the concentration of the cylinder at the predetermined depths as a function of settling time. For particle material larger than 0.0625mm, such as sand, the Visual Accumulation (VA) tube method or sieve methods is used. The VA tube method determines the size distribution of a sediment sample in terms of the fundamental hydraulic properties of the particles and the fall velocity or fall diameter (Guy, 1977). A breakdown of sand size through this method includes 9 increments from 0.700mm to 0.0625mm. Fine analysis includes six increments from 0.002mm to 0.0625mm. Sand in the 1mm and 2mm size class are sieved prior to using the settling tube.

Loss on ignition analysis will be used to estimate the organic and carbonate content in the sediment samples collected. At the laboratory, in a first reaction, samples are weighed and heated for two hours at 500-550° C where organic matter is oxidized to carbon dioxide and ash. In a second reaction, carbon dioxide is evolved from carbonate at 900-1000° C, leaving oxide. The weight loss during these reactions is easily measured by weighting the samples before and after heating and is closely correlated to the organic matter and carbonate content of the sediment. The percent of sample mass lost following heating is reported as LOI. This method

estimates organic matter based on weight change associated with high temperature oxidation of organic matter.

B6. QUALITY CONTROL AND QUALITY CRITERIA

Field

Quality control data are generated from the collection and analysis of quality-control samples to quantify the magnitude of the bias and variability in the measurement process of obtaining environmental data. At least ten percent of the total fish and sediment samples will be collected as replicate samples as part of quality control (table 6). The replicate samples will be used to evaluate random variability between samples and analytical results. Fish and sediment replicate samples will consist of a second independently collected sample of the same type (same species for fish) from the same sample site on the same day. The collection process for the replicate sample will follow the same field procedures as the environmental sample. In addition, an equipment blank will be collected for fish and sediment equipment. Equipment blank samples are intended to demonstrate that sample collection and processing equipment and equipment-cleaning procedures are not sources of contamination. A blank solution will be poured through all the equipment used for collecting and processing fish and sediment samples. The blank solution exposed to all the collection and processing equipment will be collected in the sample containers, based on the laboratory analysis, that will be used for fish and sediment samples. Equipment blanks should be collected at least 2 months before beginning of field sampling. Analysis for the replicate samples and equipment blanks will consist of the same as the environmental sample analysis: mercury, OC pesticides, PCBs, and PBDEs.

Laboratory

The laboratory quality control measures include the use of laboratory control standards (LCS), matrix spikes and matrix spike duplicates (MS/MSD), continuing calibration verification (CCV), surrogates, internal standards, laboratory blanks, duplicate analyses, and other method specific quality control activities (table 6). Laboratory control standards in the form of control samples will be used to determine if laboratory equipment and procedures are able to accurately recover a known amount of spiked analyte at an expected range. Laboratory control standards are run alongside of, and in an identical manner as, the sample. Method blanks in the lab will be used to ensure that lab analysis and procedures are not causing contamination to the sample matrix. Matrix spiked samples are used to determine the effect of the matrix on a method's recovery efficiency. For AXYS Laboratory, samples are analyzed in batches consisting of a maximum of twenty samples, one procedural blank and one spiked matrix (OPR) sample. A duplicate is analyzed, provided there is sufficient sample, with batches containing 7-20 samples. Matrix spike/matrix spike duplicate (MS/MSD) pairs may be analyzed on an individual contract basis. The batch is carried through the complete analytical process as a unit. For sample data to be reportable, the batch QC data must meet the established acceptance criteria presented on the analysis reports. Quality assurance and control objectives for the USGS MRL during the

analytical run with each batch of sediment samples include calibration data, method blanks, duplicates analyses, certified reference material (CRM) samples, matrix spikes, reverse ID check standard recoveries to ensure acceptance criteria are being met (table 6). First level Quality Assurance data will be reported with the environmental data to the public. This includes sample-specific reporting levels (as needed), blank performance, and replicate performance. Second level quality performance data, ie. calibration data, matrix spike recovery, blind CRM performance, will be stored and permanently archived via the USGS Oregon Water Science Center's internal Project Folder and Laboratory Evaluation Procedures therein, via electronic server and database.

All laboratory quality controls required to meet project objectives are listed in Appendix B.

Table 7. Field and laboratory Quality Control samples frequency and acceptance criteria

Quality Control Sample	Analysis Type	Analyte	Frequency	Acceptance Criteria
Field				
Replicate	Fish tissue	PBDEs, OC Pesticides, Mercury & PCBs	10% of total samples	±40%
Replicate	Sediment	PBDEs, OC Pesticides, Mercury & PCBs	10% of total samples	±40%
Equipment blank	Fish tissue Sediment	PBDEs, OC Pesticides, Mercury & PCBs	1 sample per analysis type	< MDL
Laboratory				
Blank	Fish tissue Sediment	PCBs, PBDEs & OC Pesticides	Every 20 samples	<10% of analyte value
Duplicate	Fish tissue Sediment	PCBs, PBDEs & OC Pesticides	Every 7-20 samples	≤ 40% of RPD
Matrix spike	Fish tissue Sediment	PCBs, PBDEs & OC Pesticides	Every 20 samples	60-130% recovery
	Fish tissue	**Total Mercury**		
Instrument purge	Sediment	Methylmercury, Total Mercury	Every 10 samples	<0.005 of peak area

Empty boat blanks	Sediment	Methylmercury, Total Mercury	Every 10 samples	<0.01 of peak area
Reagent blanks	Sediment	Methylmercury, Total Mercury	Every 10 samples	<0.05 ng/boat
Certified reference material	Sediment	Methylmercury, Total Mercury	Every 10 samples	80-120% recovery
Check standards	Sediment	Methylmercury, Total Mercury	Every 10 samples	80-120% recovery

Measurement Performance Criteria and Data Quality Indicators

Measurement performance criteria are based on the quantitative statistics and qualitative descriptors that are used to interpret the degree of acceptability or utility of data to the user. These performance criteria are referred to as principal data quality indicators (DQIs). These DQI's are precision, accuracy, representativeness, completeness, and comparability.

Precision

Precision is the degree of mutual agreement among independent measurements from the repeated application of a measurement process under identical conditions. It is the inverse of variability, but unlike variability, precision cannot be directly determined.

Accuracy

Accuracy is commonly defined as the degree of agreement between a measured value and the true or expected value. It is a function of both bias and variability. Bias is the systematic error in a method or measurement process, and variability is random error in independent measurements as the result of repeated application of the process under specific conditions.

Representativeness

Representativeness refers to the degree to which data accurately and precisely represent a characteristic of a population, parameter, variations at a sampling point, a process condition, or an environmental condition (USEPA 2008).

Completeness

Completeness is defined as the amount or percentage of data obtained compared to the amount that is expected to be obtained under normal conditions. To optimize completeness, every effort is made to avoid missing samples. Accidents during sample storage, transport, or laboratory activities, that may cause the loss of the original sample, will result in lost data, could potentially affect the integrate results and final report. Any samples that fail holding time or preservation requirements, will require to be flagged and any related data will be reconsidered. If laboratory activities may be the cause of a sample loss, the project lead will decide if these samples are salvageable and worth analyzing, and how to flag any related data.

Comparability

Comparability is a measure of the confidence with which one data set can be compared with another. It is dependent on the proper design of the sampling program and on adherence to accepted sampling techniques, standard operating procedures, and quality assurance guidelines. Comparability of data will be accomplished by standardizing the field sampling methods and analytical methods, and all samples will be collected and prepared for shipment according to procedures described in this QAPP.

B7. DOCUMENTATION AND RECORDS

The required data to be recorded at each sampling site for each sample medium is identified below. Detailed documentation of all field sample collection and handling methods is necessary for proper sample processing in the laboratory and, eventually, for study results interpretation. Field sample collection and handling will be documented for each sampling site using the following forms:

- Fish Tissue Field Data Sheet (table 7)
- Sediment Field Data Sheet (table 8)
- Analytical Services Request (ASR) Form

All sections in the above forms will be completed for each site, and all entries should be made in permanent ink. The submission of samples to the laboratory will include an ASR Form documenting sampling time and date and information in the ASR forms should be consistent with sample information of the corresponding field data sheet.

Table 8. Explanation of field data sheet sections for fish sampling

Section	Section Description
Sample header	Where and when sample was collected, station description, station name and number, field team member names.
Related sampling activities	Other sampling activities
Physical site conditions	Physical and chemical conditions at the time of the sampling, including specific conductance and water temperature
Sampling information	Sampling methods and effort, and fish specimen data, such as identification, abundance, length, weight, sex and external anomalies

Table 9. Explanation of field data sheet sections for sediment sampling

Section	Section Description
Sample header	Where and when sample was collected, station description, station name and number, field team member names

Related sampling activities	Other sampling activities
Physical site conditions	Physical and chemical conditions at the time of the sampling, including specific conductance and water temperature
Sampling information	Sampling method and device, sample volume
Supporting information	Water depth, velocity, substrate type

Samples will be shipped to the analytical laboratory via priority, overnight express delivery service (table 9).

Table 10. Summary of all sample types for preservation and shipping documentation

Sample Type	Medium	Preservation	Sample destination	Shipping comments
Adult fish	Fish tissue, fillets	Dry Ice	AXYS Laboratory	Frozen, will be shipped in batches
Juvenile fish	Fish tissue, whole	Dry Ice	AXYS Laboratory	Frozen, will be shipped in batches
Sediment	Sediment	Freeze	Mercury Research Laboratory, AXYS Laboratory, CVO Sediment Laboratory	Frozen, will be shipped in batches

If any change(s) in this QAPP is(are) required or needed during the study, a memo will be sent to each person on the distribution list describing the change(s), following approval by the Project Lead. All memos announcing changes must be attached to this QAPP.

All documents and records completed for this project will be maintained by USGS during the project and retained for a period of five years after completion of the project.

B8. EQUIPMENT INSPECTION AND MAINTENANCE

All field equipment will be inspected prior to sampling activities to ensure that proper use requirements are met (e.g., boats are operating correctly, nets are without defects, sondes and other meters are properly calibrated). Inspection of field equipment will occur well in advance of the field operation to allow time for replacement or repair of defective equipment, and the field crew will be equipped with proper backup equipment to prevent lost time on site. Inspection of all equipment on an equipment and supply list prior to each sampling event should be conducted.

B9. INSTRUMENT CALIBRATION

All instruments used in the field will be calibrated according to USGS and manufacturer's operating instructions daily before being used. Multiparameter meter for the collection of water temperature and specific conductance, recently calibrated against known NIST standards, will be used to collect water quality conditions at the time of sampling.

B10. FIELD SUPPLIES INSPECTION

A checklist of field supplies will be created, and it will be the responsibility of each field team to gather and inspect the necessary sampling supplies prior to the sampling event and to inspect the sample

packaging and shipping supplies. Defective packaging and shipping supplies (e.g., torn or damaged polyethylene sample tubing) will be discarded.

B11. DATA MANAGEMENT

All observational data and field measurements at the time of sampling will be recorded using field data sheets. Scanned copies of all paper field data documents will be made immediately (at end of the day) and archived electronically. All data will be managed according to the Data Management Plan of the Washington Water Science Center (Conn and others, 2019). The data sheets will be kept and maintained in an organized file. Field data sheets and other sample documentation will be initially reviewed for transcription errors, precision, completeness, anomalous data, and any other general problems.

Samples will be documented and tracked via Sample Identification Labels, Field Record Forms, and Sample Analytical Services Request Forms. Field team leaders will be responsible for reviewing all completed field forms. Any corrections should be noted, initialed, and dated by the reviewer. Shipment of samples to the laboratory must be conducted by a delivery service that provides constant tracking of shipments (e.g., Federal Express).

C. DATA VALIDATION

C1. DATA REVIEW, VALIDATION, AND VERIFICATION

Data received from the analytical laboratories will be reviewed and validated, and ultimately made publicly available, via a data hosting site such as USGS ScienceBase (www.sciencebase.gov) or in the USGS National Water Information System (NWIS) database (https://waterdata.usgs.gov/nwis/). Yakama Nation will be responsible to uploading finalized dataset into EPA's Water Quality Exchange (WQX) database. These electronic data releases require USGS peer-review and are intended to remain publicly available in perpetuity. All field data sheets, and sample analysis required forms will be reviewed for completeness by the field sampling teams. Any discrepancies in the records will be verified with the associated field staff and will be reported to the Project Lead.

Sample analysis information will be checked by laboratory upon receiving to ensure that holding times have not been exceeded. Violations of holding times will be reported (by the laboratory) to the Project Lead. As soon as laboratory results become available and following completion of the sample collection tasks, precision, accuracy, and completeness, measures will be assessed and compared with EPA national recommended aquatic life criteria (USEPA, 2023) for fish samples, and consensus-based sediment quality guidelines (Ingersoll and others, 2000) in sediment samples. This will help determine quantity and quality of the data collected to support the intended use for this project. Any problems encountered in meeting the performance criteria (or uncertainties and limitations in the use of the data) will be discussed with the Project Lead.

C2. REGULATORY CRITERIA AND STANDARDS

Regulatory criteria and standards for both sediment and aquatic biota will be used to assess when toxics are at a level of concern. Washington's sediment management standard criteria will be used to compare the study's sediment screening results.

D. DATA ASSESSMENT

D1. ASSESSMENT AND REPONSE ACTIONS

Assessment and corrective response actions are identified below to ensure that sample collection activities are conducted as described and the measurement and data quality objectives established by the USGS are met. The essential steps are as follows:

- identify and define the problem
- assign responsibility for investigating the problem
- investigate and determine the cause of the problem
- assign and accept responsibility for implementing appropriate corrective action
- establish effectiveness of and implement the corrective action
- verify that the corrective action has eliminated the problem

Immediate corrective actions form part of normal operating procedures and are noted on project field forms. Problems not solved following these steps will require more formalized, long-term corrective action.

D2. REPORTS TO MANAGEMENT

Annual summary reports will be completed at the end of each fiscal year and will describe activities from the beginning of the year. These summary reports will consist of information on project status, highlights, results of QC audits and internal assessments. The project personnel are responsible for report production and distribution.

REFERENCES

Batt AL, Wathen JB, Lazorchak JM, Olsen AR, Kincaid TM. 2017. Statistical Survey of Persistent Organic Pollutants: Risk Estimations to Humans and Wildlife through Consumption of Fish from U.S. Rivers. Environ Sci Technol. Mar 7, 2017;51(5):3021-3031. doi: 10.1021/acs.est.6b05162.

Columbia River Inter-Tribal Fish Commission. (1994). AFish Consumption Survey of the Umatilla, Nez Perce, Yakama, and Warm Springs Tribes of the Columbia River Basin. Technical Report no. 94-3. Oregon: Columbia River Intertribal Fish Commission (CRITFC).

Conn, K.E., Mastin, M.C., Long, A.J., Dinicola, R.S., and Barton, C., 2019, Data management plan for the U.S. Geological Survey Washington Water Science Center: U.S. Geological Survey Open-File Report 2019-1049, 23 p., https://doi.org/10.3133/ofr20191049.

Counihan, T.D., Waite, I.R., Nilsen, E.B., Hardiman, J.M., Elias, E., Gelfenbaum, G. and Zaugg, S.D., 2014. A Survey of Benthic Sediment Contaminants in Reaches of the Columbia River Estuary Based on Channel Sedimentation Characteristics. Science of the Total Environment, 484, pp.331-343.

Counihan, T.D., Moran, P.W., Waite, I., Duncan, S. and Environmental, S., 2022. Framework for the Development of the Columbia River Mainstem Fish Tissue and Water Quality Monitoring Program–Bonneville Dam to Canadian Border. https://yakamafish-nsn.gov/sites/default/files/projects/2022-12-27_Contaminants%20Monitoring%20Framework_Yakama-USGS_Final.pdf

DeWild, J.F.,Olund, S.D., Olson, M.L., and Tate, M.T. 2004a. Methods for the Preparation and Analysis of Solids and Suspended Solids for Methylmercury. U.S. Geological Survey Techniques and Methods book 5, chapter A7, 13p.

DeWild, J.F.,Olund, S.D., Olson, M.L., and Tate, M.T. 2004b. Methods for the Preparation and Analysis of Solids and Suspended Solids for Total Mercury. U.S. Geological Survey Techniques and Methods book 5, chapter A8, 15p.

Guy, H. P. 1977. Laboratory Theory and Methods for Sediment Analysis. U.S. Geological Survey, Techniques of Water-Resources Investigations. Book 5, Chapter C1.

Hayslip, G. and L. Herger. 2008. Mid-Columbia Field Methods Manual for Probabilistic Sampling in Oregon and Washington. U.S. Environmental Protection Agency, Region 10, Seattle, WA.

Hobbs, W. 2019. Quality Assurance Project Plan: Assessing Sources of Toxic Chemicals Impacting Juvenile Chinook Salmon. Washington State Department of Ecology. Publication No. 19-03-110, 64p.

Ingersoll, C., D. MacDonald, N. Wang, J. Crane, L. Field, P. Haverland, N. Kemble, R. Lindskoog, C. Severn, and D. Smorong. 2000. Prediction of Sediment Toxicity Using Consensus-Based Freshwater Sediment Quality Guidelines. Prepared by U.S. Geological Survey for U.S.

Environmental Protection Agency Great Lakes National Program Office (GLNPO). Chicago. EPA 905/R-00/007. http://www.cerc.usgs.gov/pubs/center/pdfDocs/91126.pdf

Larson, C., and S. Collyard. 2019. Standard Operating Procedure EAP111, Version 1.14: Periphyton Sampling, Processing, and Identification in Streams and Rivers. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1903207.html

Olund, S.D., DeWild, J.F., Olson, M.L., and Tate, M.T., 2004. US Geological Survey, Techniques and Methods 5 A–8. Methods for the Preparation and Analysis of Solids and Suspended Solids for Total Mercury. In- Chapter 8 of Book 5, Laboratory Analysis, Section A, Water Analysis.

Parametrix, Inc. 2009. Upper Columbia River Quality Assurance Project Plan for the 2009 Fish Tissue Study. Prepared for Teck American Incorporated. Prepared by Parametrix, Inc. in association with Integral and Exponent and in consultation with HydroQual.

Polissar, N.L., Salisbury, A., Ridolfi, C., Callahan, K., Neradilek, M., Hippe, D.S., Beckley, W.H. 2016. A Fish Consumption Survey of the Nez Perce Tribe. Prepared under U.S. EPA Contract EP W14 020 Task Order 10 and Contract EP W09 011 Task Order 125 with SRA International.

Stevens Jr, D. L., & Olsen, A. R. (2004). Spatially balanced sampling of natural resources. Journal of the American statistical Association, 99(465), 262-278.

USEPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1: Fish Sampling and Analysis. Third Edition. EPA 823-B-00-007. Environmental Protection Agency, Office of Science and Technology, Office of Water. Washington, D.C.

USEPA. 2002a. Guidance for Quality Assurance Project Plans. Office of Environmental Information, Washington, DC. EPA/240/R-02/009.

USEPA. 2002b. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: EPA-821-R-02-019, Office of Water, Washington D.C., 36 p.

USEPA. 2008. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Section 3.0. EPA-454/B-17-001. Environmental Protection Agency.

USEPA. 2009. Columbia River Basin: State of the River Report of Toxics. EPA 910-R-08-004. Environmental Protection Agency, Region 10.

USEPA. 2010. Columbia River Basin Toxics Reduction Action Plan. Environmental Protection Agency, Region 10 & The Columbia River Toxics Reduction Working Group.

USEPA. 2023. National Recommended Water Quality Criteria – Aquatic Life Criteria Table. Environmental Protection Agency. Accessed on February 2, 2023.

https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table.

WADOH. 2023. Washington Department of Health, Fish Consumption Advisories in Washington State. Online table accessed January 30, 2023. https://doh.wa.gov/data-and-statistical-reports/washington-tracking-network-wtn/fish-advisories/fish-consumption-advisories-washington-state.

Appendix A.

Laboratory analysis sample detection limits (SDL) and method detection limits (MDL) in nanograms per gram (ng/g) for fish tissue and sediment.

[NA – not available]

Parameter	SEDIMENT		TISSUE*	
	SDL (ng/g)	MDL (ng/g)	SDL (ng/g)	MDL (ng/g)
MERCURY				
Methylmercury	NA	0.08	N/A	0.08
Total Mercury	0.6-6.0	0.3	1.38	0.3
ORGANOCHLORINE PESTICIDES				
Hexachlorobenzene	0.1	0.08	0.1	0.01
HCH, alpha	0.2	0.25	0.2	0.03
HCH, beta	0.2	0.27	0.2	0.03
HCH, gamma	0.2	0.18	0.2	0.07
Heptachlor	0.2	0.17	0.2	0.02
Aldrin	0.5	0.21	0.5	0.04
Chlordane, oxy-	0.5	0.22	0.5	0.14
Chlordane, gamma (trans)	0.1	0.06	0.1	0.02
Chlordane, alpha (cis)	0.1	0.17	0.1	0.04
Nonachlor, trans-	0.1	0.29	0.1	0.03
Nonachlor, cis-	0.1	0.25	0.1	0.04
2,4'-DDD	0.1	0.16	0.1	0.01
4,4'-DDD	0.1	0.08	0.1	0.02
2,4'-DDE	0.1	0.07	0.1	0.01
4,4'-DDE	0.1	0.07	0.1	0.01
2,4'-DDT	0.1	0.06	0.1	0.03
4,4'-DDT	0.1	0.08	0.1	0.02
Mirex	0.1	0.11	0.1	0.03
Technical Toxaphene	15	NA	15	NA
HCH, delta	0.1	0.13	0.1	0.08
Heptachlor Epoxide	0.1	0.02	0.1	0.08
alpha-Endosulphan	0.1	0.04	0.1	0.03
Dieldrin	0.1	0.04	0.1	0.03
Endrin	0.1	0.05	0.1	0.02
beta-Endosulphan	0.1	0.08	0.1	0.03
Endosulphan Sulphate	0.1	0.04	0.1	0.03
Endrin Aldehyde	0.1	0.09	0.1	0.03
Endrin Ketone	0.1	0.05	0.1	0.03
Methoxychlor	0.2	0.09	0.2	0.08

PBDEs				
BR2-DPE-7	1	1.3	1	0.61
BR2-DPE-8/11	1	1.5	1	0.42
BR2-DPE-10	1	0.8	1	2.3
BR2-DPE-12/13	1	2.6	1	0.81
BR2-DPE-15	1	0.54	1	0.7
BR3-DPE-17/25	1	1.2	1	1.1
BR3-DPE-28/33	1	1.4	1	1.2
BR3-DPE-30	1	1.8	1	1
BR3-DPE-32	1	0.85	1	0.6
BR3-DPE-35	1	0.59	1	1.4
BR3-DPE-37	1	0.56	1	0.82
BR4-DPE-47	1	2.8	1	3.9
BR4-DPE-49	1	0.78	1	1.4
BR4-DPE-51	1	0.79	1	0.68
BR4-DPE-66	1	1	1	0.98
BR4-DPE-71	1	0.81	1	0.85
BR4-DPE-75	1	1.7	1	0.86
BR4-DPE-77	1	0.8	1	0.56
BR4-DPE-79	1	1.3	1	1.5
BR5-DPE-85	1	0.47	1	0.91
BR5-DPE-99	1	2.6	1	4.2
BR5-DPE-100	1	0.94	1	0.89
BR5-DPE-105	1	1.3	1	1.8
BR5-DPE-116	1	1.4	1	1.9
BR5-DPE-119/120	1	1.3	1	1.3
BR5-DPE-126	1	0.73	1	0.89
BR6-DPE-128	1	1.3	1	4
BR6-DPE-138/166	1	1.6	1	1.7
BR6-DPE-140	1	1	1	0.94
BR6-DPE-153	1	0.63	1	0.93
BR6-DPE-154	1	0.83	1	0.91
BR6-DPE-155	1	0.68	1	0.98
BR7-DPE-181	2	1	2	1.8
BR7-DPE-183	2	0.52	2	1.5
BR7-DPE-190	2	1.4	2	3.4
BR8-DPE-203	2	2	2	1.4
BR9-DPE-206	10	12.3	10	4.5
BR9-DPE-207	10	11	10	7.9
BR9-DPE-208	10	8.8	10	6.3
BR10-DPE-209	20	124	20	23

PCBs (pg/g based on 10g sample)					
PCB	1	0.1	0.42	0.1	0.13
PCB	2	0.1	0.24	0.1	0.14
PCB	3	0.1	0.28	0.1	0.20
PCB	4	0.2	0.53	0.2	0.27
PCB	5	0.2	0.29	0.2	0.24
PCB	6	0.2	0.41	0.2	0.22
PCB	7	0.2	0.40	0.2	0.35
PCB	8	0.2	0.22	0.2	0.29
PCB	9	0.2	0.39	0.2	0.19
PCB	10	0.2	0.34	0.2	0.29
PCB	11	0.2	0.28	0.2	0.24
PCB	12/13	0.2	0.64	0.2	0.36
PCB	14	0.2	0.37	0.2	0.31
PCB	15	0.2	0.33	0.2	0.14
PCB	16	0.1	0.14	0.1	0.45
PCB	17	0.1	0.25	0.1	0.29
PCB	19	0.1	0.24	0.1	0.27
PCB	21/33	0.1	0.55	0.1	0.57
PCB	22	0.1	0.21	0.1	0.30
PCB	23	0.1	0.21	0.1	0.31
PCB	24	0.1	0.24	0.1	0.34
PCB	25	0.1	0.23	0.1	0.27
PCB	26/29	0.1	0.52	0.1	0.52
PCB	27	0.1	0.26	0.1	0.32
PCB	28/20	0.1	0.75	0.1	0.45
PCB	30/18	0.1	0.40	0.1	0.66
PCB	31	0.1	0.20	0.1	0.20
PCB	32	0.1	0.27	0.1	0.30
PCB	34	0.1	0.22	0.1	0.27
PCB	35	0.1	0.23	0.1	0.31
PCB	36	0.1	0.18	0.1	0.40
PCB	37	0.1	0.28	0.1	0.33
PCB	38	0.1	0.20	0.1	0.30
PCB	39	0.1	0.28	0.1	0.32
PCB	41/40/71	0.1	1.02	0.1	1.33
PCB	42	0.1	0.34	0.1	0.44
PCB	43	0.1	0.30	0.1	0.52
PCB	44/47/65	0.1	1.24	0.1	1.23
PCB	45/51	0.1	0.92	0.1	0.87
PCB	46	0.1	0.39	0.1	0.33
PCB	48	0.1	0.38	0.1	0.43

PCB	50/53	0.1	0.64	0.1	0.72
PCB	52	0.1	0.60	0.1	0.50
PCB	54	0.1	0.17	0.1	0.15
PCB	55	0.1	0.63	0.1	0.42
PCB	56	0.1	0.49	0.1	0.54
PCB	57	0.1	0.34	0.1	0.37
PCB	58	0.1	0.42	0.1	0.26
PCB	59/62/75	0.1	1.04	0.1	1.23
PCB	60	0.1	0.65	0.1	0.51
PCB	61/70/74/76	0.1	2.10	0.1	1.81
PCB	63	0.1	0.60	0.1	0.43
PCB	64	0.1	0.42	0.1	0.36
PCB	66	0.1	0.70	0.1	0.43
PCB	67	0.1	0.61	0.1	0.26
PCB	68	0.1	0.54	0.1	0.32
PCB	69/49	0.1	0.73	0.1	0.85
PCB	72	0.1	0.33	0.1	0.36
PCB	73	0.1	0.51	0.1	0.32
PCB	77	0.1	0.15	0.1	0.17
PCB	78	0.1	0.29	0.1	0.39
PCB	79	0.1	0.28	0.1	0.33
PCB	80	0.1	0.54	0.1	0.44
PCB	81	0.1	0.31	0.1	0.20
PCB	82	0.1	0.51	0.1	0.20
PCB	83/99	0.1	0.71	0.1	0.66
PCB	84	0.1	0.41	0.1	0.50
PCB	88/91	0.1	0.54	0.1	0.91
PCB	89	0.1	0.37	0.1	0.50
PCB	92	0.1	0.28	0.1	0.51
PCB	94	0.1	0.22	0.1	0.51
PCB	95/100/93/102/98	0.1	1.65	0.1	2.19
PCB	96	0.1	0.20	0.1	0.32
PCB	103	0.1	0.21	0.1	0.37
PCB	104	0.1	0.28	0.1	0.10
PCB	105	0.1	0.16	0.1	0.17
PCB	106	0.1	0.31	0.1	0.21
PCB	107/124	0.1	0.55	0.1	0.57
PCB	108/119/86/97/125/87	0.1	2.33	0.1	1.41
PCB	109	0.1	0.48	0.1	0.77
PCB	110/115	0.1	1.39	0.1	0.52
PCB	111	0.1	0.33	0.1	0.21
PCB	112	0.1	0.35	0.1	0.32

PCB	113/90/101	0.1	0.48	0.1	0.43
PCB	114	0.1	0.23	0.1	0.21
PCB	117/116/85	0.1	2.11	0.1	0.68
PCB	118	0.1	0.18	0.1	0.28
PCB	120	0.1	0.45	0.1	0.32
PCB	121	0.1	0.38	0.1	0.53
PCB	122	0.1	0.14	0.1	0.42
PCB	123	0.1	0.42	0.1	0.34
PCB	126	0.1	0.25	0.1	0.17
PCB	127	0.1	0.32	0.1	0.28
PCB	128/166	0.1	0.56	0.1	0.50
PCB	130	0.1	0.37	0.1	0.28
PCB	131	0.1	0.36	0.1	0.41
PCB	132	0.1	0.22	0.1	0.29
PCB	133	0.1	0.16	0.1	0.32
PCB	134/143	0.1	0.50	0.1	0.59
PCB	136	0.1	0.40	0.1	0.32
PCB	137	0.1	0.25	0.1	0.26
PCB	138/163/129/160	0.1	0.71	0.1	1.54
PCB	139/140	0.1	0.46	0.1	1.28
PCB	141	0.1	0.29	0.1	0.35
PCB	142	0.1	0.20	0.1	0.26
PCB	144	0.1	0.32	0.1	0.42
PCB	145	0.1	0.25	0.1	0.42
PCB	146	0.1	0.43	0.1	0.35
PCB	147/149	0.1	0.33	0.1	0.75
PCB	148	0.1	0.43	0.1	0.34
PCB	150	0.1	0.35	0.1	0.26
PCB	151/135/154	0.1	1.17	0.1	1.59
PCB	152	0.1	0.13	0.1	0.37
PCB	153/168	0.1	0.30	0.1	0.92
PCB	155	0.1	0.29	0.1	0.12
PCB	156/157	0.1	0.47	0.1	0.32
PCB	158	0.1	0.10	0.1	0.27
PCB	159	0.1	0.37	0.1	0.36
PCB	161	0.1	0.41	0.1	0.25
PCB	162	0.1	0.30	0.1	0.32
PCB	164	0.1	0.31	0.1	0.30
PCB	165	0.1	0.32	0.1	0.26
PCB	167	0.1	0.28	0.1	0.22
PCB	169	0.1	0.34	0.1	0.15
PCB	170	0.1	0.27	0.1	0.73

PCB	171/173	0.1	0.64	0.1	0.32
PCB	172	0.1	0.23	0.1	0.26
PCB	174	0.1	0.80	0.1	0.58
PCB	175	0.1	0.47	0.1	0.11
PCB	176	0.1	0.31	0.1	0.27
PCB	177	0.1	0.44	0.1	0.41
PCB	178	0.1	0.49	0.1	0.25
PCB	179	0.1	0.40	0.1	0.28
PCB	180/193	0.1	0.78	0.1	1.53
PCB	181	0.1	0.35	0.1	0.34
PCB	182	0.1	0.31	0.1	0.26
PCB	183/185	0.1	0.76	0.1	0.43
PCB	184	0.1	0.24	0.1	0.15
PCB	186	0.1	0.42	0.1	0.25
PCB	187	0.1	0.44	0.1	0.43
PCB	188	0.1	0.27	0.1	0.12
PCB	189	0.1	0.38	0.1	0.28
PCB	190	0.1	0.34	0.1	0.18
PCB	191	0.1	0.37	0.1	0.26
PCB	192	0.1	0.41	0.1	0.19
PCB	194	0.1	0.45	0.1	0.38
PCB	195	0.1	0.22	0.1	0.26
PCB	196	0.1	0.37	0.1	0.35
PCB	197/200	0.1	0.37	0.1	1.34
PCB	198/199	0.1	0.63	0.1	0.45
PCB	201	0.1	0.25	0.1	0.39
PCB	202	0.1	0.23	0.1	0.41
PCB	203	0.1	0.38	0.1	0.22
PCB	204	0.1	0.42	0.1	0.17
PCB	205	0.1	0.28	0.1	0.17
PCB	206	0.1	0.18	0.1	0.31
PCB	207	0.1	0.26	0.1	0.21
PCB	208	0.1	0.27	0.1	0.38
PCB	209	0.1	0.47	0.1	0.31

* If budget and time allow, analysis of biofilm samples collected will follow methods for fish tissue.

Appendix B.

Quality Control (QC) acceptance criteria for OC pesticides, PCBs, and PBDEs analysis.

[S:N – Signal-to-Noise; CS – Calibration Standard; RT – Retention Time; CAL-VER – Calibration Verification; RRT – Relative Response Time; RRF – Relative Response Factor; RSD – Relative Standard Deviation; DL – Detection Limit; Ng – Nanograms; Pg – Picograms; µL– microliter]

QC Acceptance Criteria for Analysis of OC Pesticides by GC/MS	
QC Parameter	**Specification**
Analysis Duplicate	The relative difference must be ≤40%, i.e., the duplicates must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)
Procedural Blank	<10% of analyte value
Instrument Sensitivity	S/N 3:1 for 10 pg HCB, for 10 pg p,p'-DDT and for 20 pg oxychlordane. S/N 2:1 for 2.5 ng of Technical Toxaphene with a minimum of 4 peaks detected
Instrument Linearity	For a minimum 5-point calibration, a relative standard deviation of the RRFs 20% for all compounds, except for $^{13}C_{12}$-pp'-DDT where RSD of RRF ≤25%.
RRF: Bracketing Calibration	RRFs from calibration standards must agree to within ±20% over a 12-hour period, i.e., the relative difference must be ≤40%, which is equivalent to 28.3% RSD.
RRF: Continuing Calibration Verification	RRFs for all compounds from opening/closing calibration standards must be within ±20% of the mean RRFs from the initial calibration.
Chromatogram Quality Max Peak Width: Resolution:	1. Peak width at half height for p,p'-DDT is 5 sec. 2.Valley height between p,p'-DDD and o,p-DDT must be less than 10% the height of the peaks 3. PCB 209 peak must be symmetrical with negligible tailing, ≤20 sec. 4. p,p'-DDT breakdown must be ±15%.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. IA Chemists may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Time Window for target compounds	RRT must be within ±3 sec of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (labeled surrogate) Authentic compound must elute after its labeled analogue
QC Acceptance Criteria for Analysis of PCB Congeners by GC/MS	
QC Parameter	**Specification**

Analysis Duplicate	The relative difference must be ≤40%, i.e., the duplicates must agree to within ±20% of the mean (applicable to concentrations >10 times the DL).
Procedural Blank	See above or <10% of analyte value.
Matrix Spike Recovery	See above; PCB 19 must be greater than 55%; PCB 104 must be greater than 60%.
Instrument Sensitivity	S/N ratio 3:1 for 10 pg PCB 118.
Instrument Linearity	Linearity is determined by at least a 5-point calibration with a relative standard deviation of the RRFs ±20%.
RRF: Bracketing Calibration	RRFs from calibration standards must agree to within ±20% over a 12-hour period, i.e., the relative difference must be ≤40%, which is equivalent to 28.3% RSD.
RRF: Continuing Calibration Verification	RRFs from opening/closing calibration standards must be within ±20% of the mean RRFs from the initial calibration for all compounds.
Chromatogram Quality Max. Peak Width: Resolution:	1. PCB 209 peak must be symmetrical with negligible tailing. Peak width should not exceed approximately 20 seconds. 2. Valley height must be 80% of smallest peak height of PCB 28/31 pair.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. IA Chemists may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Time Window for target compounds	RRT must be within ±3 sec of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (labeled surrogate). Authentic compound must elute after its labeled analogue.

QC Acceptance Criteria for Analysis of BDE by GC/MS	
QC Parameter	**Specification**
Closing Calibration Verification	Within ±20% of the opening CAL-VER for all natives compounds except BDE 203, 206, 207 and 208. Within ±35% of the opening CAL-VER for BDE 203, 206, 207 and 208. Within ±35% of the opening CAL-VER for ^{13}C-surrogates except ^{13}C-BDE 209. Within ±70% of the opening CAL-VER for ^{13}C-BDE 209.
Analysis Duplicate	Max. 40% RPD (applicable to concentrations ≥10 times the DL)

Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within ±15% of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for CS1. Minimum absolute response of BDE 209L in the CAL-VER is 5 x 10^6 (Quant. + confirm. ions)
Calibration Verification	Specification for BDE 209L is 25-200% of actual concentration.
Carryover	1st toluene blank: ≥ 90% target compounds ≤ 10 pg/20 µL, BDE 209 ≤ 200 pg/20 µL. 2^{nd} toluene blank: ≤ 5 pg/20 µL, except BDE 209 ≤ 100 pg/20 µL.
Chromatogram Quality	BDE 49 and 71 must be uniquely resolved, valley height ≤ 40% of the shorter peak. Peak tailing ratio of $^{13}C_{12}$-BDE 99 and $^{13}C_{12}$-BDE 77 peaks (baseline peak width back half:front half) ≤ 3:1. RT of BDE 209 must be ≥ 48 min. RT of labeled surrogates in CAL-VER must be within ±15 sec of those of initial calibration.

QC Acceptance Criteria for Analysis of Methylmercury by ICPMS

QC Parameter	Specification
Instrument Calibration	Mass Bias Calibration Curve - five point calibration curve with MeHg working standard to determine the mass bias correction Reverse ID Calibration Curve - created by adding both MeHg working standard and isotopic MeHg spike used during distillation to determine concentration of isotopic MeHg working standard used for the isotopic spike. Reverse ID Check Standard - used to verify instrument calibration in every eighth position and have a measured mass within 80-120% of its true value Fractionation of the Isotopically Enriched MeHg Standard - enriched MeHg isotopes used to create the reverse ID calibration/check standards and to amend environmental samples is contaminated with small amounts of other isotopes.
Certified Reference Material	Recovery within 75-125% of its certified value. CRM SQC-1238
Precision Analysis	Relative standard deviation for triplicate analyses should be less than 25%

Instrument Carryover	5 non-analytical instrument blanks are analyzed previous to calibration to clear sample train of residual MeHg
Sample Triplicate	Two samples from each batch are set up in triplicate to evaluate the precision of the method. DQOs for replicate analyses are a relative standard deviation of less than 25 %
Method Blank	Analyzed every 10 samples. Part of the distillation

QC Acceptance Criteria for Analysis of Total Mercury by CVAFS	
QC Parameter	**Specification**
Instrument Calibration	Created with mercury masses appropriate to the measurement mode Calculated with a polynomial best fit equation with while forcing an intercept of zero, Have an r2 value greater than 0.995. The mass of mercury in analyzed samples should not exceed the standard curve.
Acid Washing	Done in a 10% HNO3 solution. Acid washing, equipment to be soaked in mercury-clean water for 24 hours, dried for 3 days, and heated to 550°C for 2 hours before use.
Standard Reference Material	Recovery of the standard reference material must be within 80-120% of its certified value.
Sample Precision	Relative standard deviation of samples analyzed in triplicate should be less than 15%.
Sample Carryover	A purge mass should not exceed 10% of the mass of mercury measured in any previous sample, up to the previous purge.
Instrument Purge	Acceptable when peak area is < 0.005
Empty boat blanks	Acceptable if peak area is < 0.01
Check Standards	Acceptable if recovery is 90 – 110%
Sample Triplicate	RSD < 15%
Reagent Blank	Reagent blanks analyzed in the initial setup of the instrument should be < 0.05 ng/boat.

Appendix C.

April 23, 2008 Memo from Syracuse Research Corporation to EPA Region 10 “Human Health Risk-Based Concentrations for Surface Water, Fish Tissue and Sediment in Support of Sampling and Analysis Plan Development”