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Quality Assurance Project Plan

Flame Retardants in Ten Waterbodies in Washington State

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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 is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1703116.html

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Author and Contact Information

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

Communications Consultant: phone 360-407-6086.

Washington State Department of Ecology – www.ecy.wa.gov

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

Quality Assurance Project Plan

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November 2017

Approved by:

Signature:	Date:
Debby Sargeant, Client, EAP Signature:	Date:
Jessica Archer, Client, EAP Signature:	Date:
Callie Mathieu, Author / Project Manager / Principal Investigator, EAP Signature:	Date:
Alan Rue, Acting Director, Manchester Environmental Laboratory Signature:	Date:
Bill Kammin, Ecology Quality Assurance Officer	

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

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2.0 Abstract

The Washington State Department of Ecology (Ecology) will carry out a study in fall 2017 and spring 2018 to evaluate current concentrations of flame retardants in ten waterbodies of Washington State. As the flame retardants polybrominated diphenyl ethers (PBDEs) were phased out, new flame retardants were introduced into the market as replacements. Some of these replacement chemicals behave similarly to PBDEs and many have been identified in aquatic systems in the U.S. In Washington State, very little environmental data exists for these alternative flame retardants.

Ecology will carry out a study to address this data gap due to concerns over the persistence and adverse health effects of many alternative flame retardants. Environmental media from ten waterbodies will be sampled for organophosphate flame retardants (OPFRs), halogenated flame retardants, and PBDEs. OPFRs and the halogenated flame retardant analytes represent current-use alternative flame retardants. PBDEs are also being analyzed to compare levels of legacy flame retardants with those of the replacement chemicals.

In fall 2017 and spring 2018, Ecology will collect samples of surface water from ten lakes for analysis of OPFRs and PBDEs. Bottom sediment will be collected from the waterbodies in spring for analysis of OPFRs, halogenated flame retardants, and PBDEs. Ecology will collect freshwater fish from a subset of three waterbodies (Lake Ozette, Lake Spokane, and Lake Washington) in the fall. Two composite fish tissue samples of a bottom feeder species and two composite samples of a predator species will be targeted from each of the three waterbodies. Fish tissue samples will be analyzed for halogenated flame retardants and PBDEs. Due to budget restrictions, the analyte list for each media type is targeted towards those most likely to be detected.

Data generated from this project will support agency prioritization of chemicals to be considered for efforts to reduce toxics in Washington State.

3.0 Background

3.1 Introduction and problem statement

Flame retardants are a broad class of chemicals used in consumer products, such as furniture and electronics, to prevent or slow the spread of fire. A group of these chemicals, polybrominated diphenyl ethers (PBDEs), were widely used in consumer products until regulatory restrictions were enacted in the 2000s after growing concern that the chemicals were accumulating and dramatically increasing in people and the environment (Abbasi et al., 2015). Washington State has identified PBDEs as persistent, bioaccumulative, and toxic (PBT) chemicals and developed a Chemical Action Plan for the group of chemicals in 2006 (Ecology and DOH, 2006).

Chemical manufacturers in the U.S. voluntarily stopped production of two commercial formulations of PBDEs (penta- and octa-) by 2004 and phased out most uses of deca-BDE in 2012. Following this phase out, manufacturers replaced PBDEs with new halogenated flame retardants and organophosphate flame retardants (OPFRs). Many of these alternative flame retardants are not well-studied in the environment, but have similar physical-chemical properties to the PBDEs they replaced (Zhang et al., 2016). Recent studies have detected alternative halogenated flame retardants and OPFRs in dust, air, surface water, and groundwater (reviewed by Iqbal et al., 2017), as well as the arctic (Salamova et al., 2014).

While some OPFRs and halogenated flame retardants have been included as part of a larger investigation of contaminants within the Columbia River (Alvarez et al., 2014; Counihan et al., 2014; Morace, 2012) and four brominated flame retardants were analyzed in fish tissue in Washington State rivers and lakes (Mathieu and Wong, 2016), the number of flame retardants analyzed in Washington State has been limited. No focused investigation has been conducted into which, if any, alternative flame retardants are accumulating in the environment of Washington State.

To help fill this data gap, Ecology will conduct an exploratory study to evaluate the occurrence and concentrations of a large suite of OPFRs, halogenated flame retardants, and PBDEs in ten Washington State waterbodies.

3.2 Study area and surroundings

Figure 1 displays the 2017/2018 study locations. This study will target waterbodies in areas with potential sources and pathways of alternative flame retardants, such as urban waterbodies and those receiving WWTP effluent. One reference site, Lake Ozette, will serve as a reference waterbody where the source of flame retardants is primarily limited to atmospheric deposition. Lake Whatcom and Mayfield Lake represent waterbodies with a mix of contamination potential. Because of their large watersheds made up mostly of undeveloped forest or shrubland, local source inputs would likely be diluted. Lake Spokane also has a mix of land uses in its watershed, but has been identified as a hot spot of legacy flame retardant (PBDE) contamination.

Lake Meridian, Spanaway Lake, Lake Stevens, Vancouver Lake, and Lake Washington have the highest degree of urbanization in their watersheds and are included in this project for having a high potential of contamination. West Medical Lake receives treated wastewater treatment plant effluent (reclaimed water) and has no inflow or outflow. The continued inputs of effluent and long water residence time give this waterbody potential for high contamination.

Study locations for this project include waterbodies covering a range of physical and hydrological characteristics. Table 1 describes physical features of the waterbodies and their watersheds.

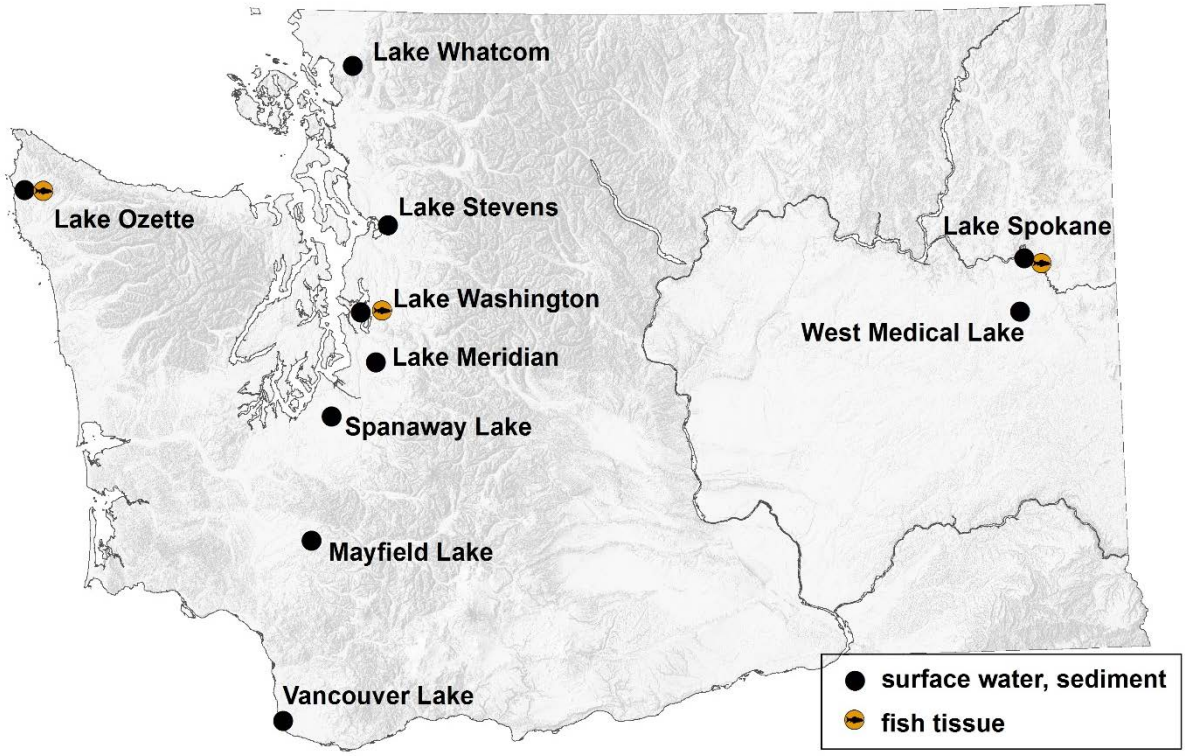

Figure 1. Study Locations for Surface Water, Sediment, and Fish Tissue Sampling.

Table 1. Description of Study Lakes.

Study Location	Elevation (ft)	Watershed Area (acres)	Surface Area (acres)	WA: SA	Max Depth (ft)	Mean Depth (ft)	Watershed Land Use	Potential Sources
Lake Meridian	370	742	150	4.9	90	41	urban	stormwater
Lake Ozette	29	49,600	7,300	6.8	320	130	forested	atmospheric deposition
Lake Spokane	1,530	4,250,000	45,200	94	180	50	forested/ brush/urban	stormwater/ WWTP effluent
Lake Stevens	210	4,370	1,040	4.2	155	63	urban	stormwater
Lake Washington	20	300,000	21,500	14.0	214	108	urban	stormwater
Lake Whatcom	315	35,780	5,000	7.2	330	150	forested/ residential	stormwater/ atmospheric deposition
Mayfield Lake	450	896,000	2,200	407	190	---	forested/ residential	WWTP effluent
Spanaway Lake	320	10,880	280	39	28	16	urban	stormwater
Vancouver Lake	9.0	---	2,300	---	12	3.0	urban	stormwater
West Medical Lake	2,420	1,178	220	5.4	35	22	brush steppe	WWTP effluent

WA:SA = watershed area to lake surface area ratio; WWTP: wastewater treatment plant

3.2.1 History of study area

This study is being carried out as an exploratory investigation into potential flame retardant contamination in Washington State waterbodies. Ten lakes/reservoirs were selected based on the following criteria: (1) contamination potential, (2) range of potential sources, (3) range of size class and physical features, (4) research vessel access for sampling, and (5) historical data on other organic contaminants available.

Legacy flame retardants (PBDEs) have been detected in several waterbodies selected for this study. Total (T-) PBDE concentrations in fish tissue from Mayfield Lake, Lake Meridian, Stevens Lake, Vancouver Lake, Lake Washington, West Medical Lake and Lake Whatcom have generally been in the range of 1-10 ng/g (ppb) wet weight (ww) (Seiders, 2003; Seiders and Kinney, 2004; Johnson et al., 2006; Seiders et al., 2008; Seiders and Deligeannis, 2009; Seiders et al., 2012; Mathieu and Wong, 2016). Fish from Lake Ozette have also analyzed for PBDEs, but results have either been not detected or very low in this remote lake (Johnson et al., 2006; Seiders and Deligeannis, 2009; Seiders et al., 2012). The Spokane River has been the subject of past research into high levels of PBDEs in the fish there (Serdar and Johnson, 2006; Furl and Meredith, 2010). PBDEs have not been previously analyzed in Lake Meridian and Spanaway Lake.

3.2.2 Summary of previous studies and existing data

Very few studies have been conducted on OPFRs and halogenated flame retardants in Washington State. The USGS included OPFRs and halogenated flame retardants in studies of surface water and sediments along the Columbia River. OPFRs were detected and/or quantified infrequently in water from POCIS (polar organic chemical integrative sampler) passive samplers deployed in the lower Columbia River in 2008-2010 (Alvarez et al., 2014). TBP, TCEP, TCPP, and TDCPP[1] were detected at estimated concentrations of 1.6 to 3.6 ng/L (ppt). Several other OPFRs were analyzed but not detected. In sediments collected along the lower Columbia River, triphenyl phosphate was detected in several stations, ranging from 3.2 to 15.1 ng/g (Counihan et al., 2014). Dechlorane plus was detected in one sediment sample, at a much lower level (0.1 ng/g), and TBP, TBEP, TCEP, and TCPP were analyzed but not detected in sediments.

In 2014, Ecology conducted a study to assess levels of emerging contaminants in fish tissue collected from 11 waterbodies throughout the state (Mathieu and Wong, 2016). Table 2 summarizes concentrations of the alternative brominated flame retardants analyzed in this study. A total of 89% of the fish tissue samples contained one or more of the alternative flame retardants analyzed. Decabromodiphenyl ethane (DBDPE) was present in the highest concentrations (range = 14 – 304 ng/kg ww), followed by 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) (0.68 – 44.5 ng/kg ww), and then hexabromobenzene (HBBz) and pentabromoethylbenzene(PBEB) (0.1 – 2.2 ng/kg ww).

Table 2. Summary of Alternative Brominated Flame Retardants Analyzed in Freshwater Fish Tissue from 11 Washington Freshwater Waterbodies by Mathieu and Wong, 2016.

Analyte	No. of Detections	Detection Frequency	Min* (ng/Kg)	Max* (ng/Kg)	Mean* (ng/Kg)	Median* (ng/Kg)
BTBPE	14	32%	0.68	44.5	6.96	2.47
DBDPE	7	16%	14.1	304	91.4	35.0
HBBz	34	77%	0.163	2.20	0.792	0.666
PBEB	3	7%	0.100	0.198	0.133	0.102

*Statistic includes detected values only. BTBPE = 1,2-bis(2,4,6-tribromophenoxy) ethane; DBDPE = decabromodiphenyl ethane; HBBz = hexabromobenzene; PBEB = pentabromoethylbenzene.

[1] TBP = tributyl phosphate; TCEP = tris(2-chloroethyl) phosphate; TCPP = tris(2-chloroisopropyl) phosphate; TDCPP = tris(1,3-dichloro-2-propyl) phosphate.

3.2.3 Parameters of interest and potential sources

PBDEs are persistent, bioaccumulative, and toxic chemicals, and many alternative flame retardants are expected to have similar physical-chemical properties. Zhang et al. (2016) estimated that about half of the halogenated and organophosphate flame retardants they modeled are similar to PBDEs and have a persistence and/or long range transport potential of medium to high level of concern. Research has shown that several current-use halogenated flame retardants have the potential to be highly bioaccumulative (Wu et al., 2011). OPFRs are thought to be much less bioaccumulative, but have been detected in fish tissue (Guo et al., 2017). The toxicity of alternative flame retardants is still largely unknown. Several OPFRs are suspected to be carcinogenic and have neurotoxic, reproductive, and hormonal effects (Wei et al., 2014).

Alternative flame retardants are used in a wide range of consumer products and may leach out of the product over time. Releases can occur through volatilization, abrasion, and leaching during the use, disposal, or recycling of products (Wei et al., 2014). Many OPFRs and halogenated flame retardants have been detected in indoor dust (Dodson et al., 2012; Stapleton et al., 2009; Stapleton et al., 2008), which then enters the wastewater-stream through laundry water (Schreder and La Guardia, 2014).

Halogenated flame retardants and OPFRs are not completely removed through conventional WWTP processes, and thus are released to the aquatic environment through effluent (Kim et al., 2017). Wastewater discharges are thought to be the predominant pathways of OPFRs to surface water and groundwater, while wash-out from the atmosphere via precipitation is important in remote areas (Wei et al., 2014). In Washington State, where no known flame retardant manufacturing facilities exist, these chemicals are likely entering the environment through use and disposal of products containing them, as well as atmospheric deposition.

3.2.4 Regulatory criteria or standards

No environmental criteria or standards exist for the parameters being analyzed in this study.

4.0 Project Description

Very little data exists for alternative flame retardants in Washington State's freshwater environment. Due to concerns over persistence and adverse health effects of many alternative flame retardants, Ecology will conduct a study in 2017/2018 to address this data gap. Environmental media from ten waterbodies will be sampled for OPFRs, halogenated flame retardants, and PBDEs. Flame retardants analyzed will include those that are currently on the market, as well as those that have been largely phased out (PBDEs). Waterbodies were selected over a range of physical characteristics, but targeted towards those with higher contamination potential from urban and WWTP inputs.

Ecology will collect samples of surface water, bottom sediment, and freshwater fish tissue for analysis of alternative flame retardants. Surface water samples collected in fall 2017 and spring 2018 from the ten lakes will be analyzed for OPFRs and PBDEs. Ecology will collect sediments from the ten waterbodies in spring 2018 for analysis of OPFRs, halogenated flame retardants, and PBDEs. Fish tissue samples will be collected from a subset of three of the waterbodies (Lake Ozette, Lake Spokane, and Lake Washington) and analyzed for halogenated flame retardants and PBDEs.

Data generated from this project will support agency prioritization of chemicals to be considered for efforts to reduce toxics in Washington State.

4.1 Project goals

This project will be conducted with the following goals:

- To characterize the occurrence and concentrations of alternative flame retardants in ten waterbodies of Washington State.
- To compare concentrations of alternative flame retardants to the phased out chemicals they have replaced (PBDEs).

4.2 Project objectives

Ecology will carry out the following objectives to meet the project goals:

- Collect surface water samples from 10 waterbodies in fall 2017 and spring 2018 for analysis of OPFRs and PBDEs.
- Collect bottom sediments from 10 waterbodies in spring 2018 for analysis of OPFRs, halogenated flame retardants, and PBDEs.
- Collect freshwater fish from three waterbodies (Lake Ozette, Lake Spokane, and Lake Washington) in fall 2017 for analysis of halogenated flame retardants and PBDEs. Two composite samples of a bottom feeder species and two composite samples of a predator species will be targeted in each of the three waterbodies.

4.3 Information needed and sources

This project is being conducted to generate new environmental data. Previously reported values will be used to provide general context for flame retardant concentrations measured in this project. Previous studies are described in Section 3.2.2.

4.4 Tasks required

The following tasks will be carried out for this project:

- Conduct desktop reconnaissance of study locations.
- Determine which laboratory will carry out analyses. If a contract laboratory will be required, work with Manchester Environmental Laboratory (MEL) to secure a contract laboratory.
- Collect surface water and sediment samples and send to laboratory for analysis.
- Collect target fish species, process fish samples, and send to laboratory for analysis.
- Review data quality of laboratory results and work with MEL's Quality Assurance (QA) Officer to resolve any issues.
- Write draft report summarizing results, route the draft report following Ecology's Environmental Assessment Program (EAP) publication review procedures, and publish final report.
- Load data into Ecology's EIM database, review EIM data following EAP EIM review procedures, and finalize EIM data.

4.5 Systematic planning process used

This Quality Assurance Project Plan addresses the elements of a systematic planning process for this study.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3. Organization of Project Staff and Responsibilities.

Staff (All EAP)	Title	Responsibilities
Debby Sargeant Toxics Studies Unit SCS Phone: 360-407-6775	Client and Supervisor for the Project Manager	Clarifies scope of the project. Provides internal review of the QAPP and final report. Approves the final QAPP. Manages personnel budget and staffing needs.
Jessica Archer SCS Phone: 360-407-6698	Client and SCS Manager	Reviews the project scope and budget, tracks progress. Provides internal review of the QAPP and final report. Approves the final QAPP.
Callie Mathieu Toxics Studies Unit SCS Phone: 360-4047-6965	Field Lead, Project Manager and Principal Investigator	Leads field collections, records field information, and sends samples to laboratory. Enters data into EIM. Writes the QAPP and final report. Coordinates with laboratories and conducts QA review of the data. Analyzes and interprets data. Responsible for final report and project completion.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8844	Acting Director	Reviews and approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section

5.2 Special training and certifications

All staff collecting field samples will be experienced and trained in the sample collection protocols outlined in the respective standard operating procedures. Fish collection efforts require all staff to have specialized training in electro-shocking techniques. Electro-shock boat operators will need to complete the training and proficiency requirements for boat operator status, as well as attend the annual refresher training.

5.3 Organization chart

Not applicable – see Tables 3 and 4.

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 begins	10/2017	Callie Mathieu
Field work completed	06/2018	Callie Mathieu
Laboratory analyses completed	09/2018	
Environmental Information System (EIM) database		
EIM Study ID	CAME003	
Product	Due date	Lead staff
EIM data loaded	02/2019	Callie Mathieu
EIM data entry review	03/2019	Melissa McCall
EIM complete	04/2019	Callie Mathieu
Final report		
Author lead	Callie Mathieu	
Schedule		
Draft due to supervisor	01/2019	
Draft due to client/peer reviewer	02/2019	
Final (all reviews done) due to publications coordinator	03/2019	
Final report due on web	04/2019	

5.5 Budget and funding

The laboratory costs for this project is $65,278. Table 5 presents the estimated costs of laboratory analyses. The number of quality control (QC) tests included in Table 5 includes only those tests that are not included in the cost of analysis (field replicates, field blanks, and laboratory duplicates). All OPFR and halogenated flame retardant analyses will be funded by Ecology's PBT Monitoring Program. PBDE analyses will be funded through a one-time lab budget allocation through the Environmental Assessment Program.

Table 5. Estimated Project Laboratory Budget.

Analyte	Matrix	Number of Samples	Number of QA Samples*	Total Number of Samples	Cost Per Sample	MEL Subtotal
OPFRs	surface water	20	5	25	$800	$20,000
PBDEs	surface water	20	5	25	$177	$4,425
OPFRs	sediment	10	4	14	$800	$11,200
Halogenated FRs	sediment	10	4	14	$800	$11,200
PBDEs	sediment	10	4	14	$198	$2,772
TOC	sediment	10	2	12	$45.52	$546
Halogenated FRs	fish tissue	12	3	15	$800	$12,000
PBDEs	fish tissue	12	3	15	$209	$3,135
Lipids	fish tissue	12	1	13	$0	$0
					Lab Analysis Total	$65,278

OPFRs = organophosphate flame retardants; FRs = flame retardants;
TOC = total organic carbon; PBDEs = polybrominated diphenyl ethers.
*Includes only QA samples that are not free of charge.

6.0 Quality Objectives

6.1 Data quality objectives

The data quality objective for this project is to collect sediment, water, and fish tissue samples and have them analyzed to obtain concentration data on a suite of OPFRs (surface water and sediment) and halogenated flame retardants (sediment and fish tissue) that meet the method QA/QC and instrument performance limits, as well as measurement quality objectives (MQOs) described below.

6.2 Measurement quality objectives

Table 6. Measurement Quality Objectives for Laboratory Analyses.

Analyte	Matrix	Lab Duplicates (RPD)*	LCS (% recov.)	Surrogate Standards (% recov.)	Matrix Spike/MS Duplicate (% recov.)	Matrix Spike Duplicate (RPD)	Quantitation Limit
OPFRs	surface water	≤ 40% if concentrations > 5x QL	50 - 150[1] 70 - 130[2]	40 - 140[4]	50 - 150[1] 70 - 130[2]	≤ 40% if concentrations > 5x QL	0.1 - 5 ng/L
PBDEs	surface water	≤ 50%	50-150	50-150	50-150	≤ 40%	2.0 - 10 ng/L
OPFRs	sediment	≤ 40% if concentrations > 5x QL	50 - 150[1] 70 - 130[2]	40 - 140[4]	50 - 150[1] 70 - 130[2]	≤ 40% if concentrations > 5x QL	0.005 - 0.25 ng/g dw
Halogenated FRs	sediment	≤ 40% if concentrations > 5x QL	50 - 150[5]	30 - 160	50 - 150[5]	≤ 40% if concentrations > 5x QL	0.05 - 12 ng/g dw
PBDEs	sediment	≤ 40%	50-150	50-150	50-150	≤ 40%	0.4 - 2.0 ng/g dw
TOC	sediment	≤ 20%	80 - 120%	---	---	---	0.1%
Halogenated FRs	fish tissue	≤ 40% if concentrations > 5x QL	50 - 150[6]	40 - 160[7]	50 - 150[6]	≤ 40% if concentrations > 5x QL	0.05 - 12 ng/g ww
PBDEs	fish tissue	≤ 40%	50-150	30-166	50-150	≤ 40%	0.4 - 2.0 ng/g ww

[1] V6, TDCPP, TDBPP, TCrP, EHDPP, TEHP, TBEP
[2] TEP, TCEP, TPrP, TCPP, TPP, TBP
[3] ≤ 5 ng/sample for TCEP and TBP; ≤ 100 ng/sample for TBEP
[4] d12-TCEP, d21-TPrP, d18-TCPP, d15-TDCPP, d27-TBP; 15 - 130% for d15-TEP; 50 - 130% for 13C18-TPP
[5] 50 - 200% for Dec 604, EHTBB, PBBB; 70 - 130% for Dechlorane, DP Anti and Syn, Dec 602, HBB; 30 - 180% for DPTE; 20 - 150% for BEHTBP; 15 - 160 for 1,2- and 1,3- DiBB; 5 - 150% for 1,2,4-TriBB
[6] 60 - 140% for Dechlorane, DP Anti and Syn, EHTBB, T-TBECH, HBB, PBBZ; 70 - 130% for BTBPE; 40 - 160% for Dec 604, ATE, BATE, BPTE; 40 - 150% for HCDBCO; 30 - 170% 1,2,4,5-TBB, 1,2,3,5-TBB, 1,2,4-TriBB, 1,4-DiBB; 20 - 180% for PBBB; 10 - 170% for 1,2-DiBB.
[7] 30 - 170% for 13C12-BTBPE
LCS = laboratory control sample; OPFRs = organophosphate flame retardants; FRs = flame retardants; TOC = total organic carbon; PBDEs = polybrominated diphenyl ethers.

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability between the results of replicate measurements due to random error. Laboratory analysis precision will be assessed through laboratory duplicate samples for all matrices and analyses. Table 6 summarizes MQOs for laboratory duplicate samples.

One field replicate per batch of surface water and sediment samples will be collected and analyzed alongside the field samples. A field replicate sample will be collected immediately after the field sample using the same sampling technique. Field replicate relative percent difference (RPD) should be < 40% for concentrations greater than 5 times the quantitation limit.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Laboratory analysis bias will be assessed through laboratory control samples. MQOs for laboratory control sample recoveries are included in Table 6.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Laboratory analysis sensitivity is defined here as the quantitation limit. See Table 6 for estimated quantitation limits.

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. This includes standardized procedures for collecting surface water, sediment, and fish tissue samples. In addition, all sampling will occur during timeframes that have been targeted in the past for similar projects: spring and fall surface water sampling and fall fish tissue sampling. Freshwater fish are generally collected in the fall for toxic contaminant analysis, when lipid content of many species is generally highest. This follows EPA's guidance for fish sampling and analysis for chemical contaminants (EPA, 2000) and allows for consistency between projects.

6.2.2.2 Representativeness

Surface water sampling is being conducted during May and October to capture concentrations occurring during two different seasons – spring and fall. Surface water samples will be collected from the deepest area of the lake, usually the centroid, and far away from point sources near the shoreline. Sediment sampling will consist of three separate grabs within the deepest basin of the lake and composited into a representative sample. Fish samples will be analyzed as 3-5 fish composites in order to integrate variability within a waterbody and among individual fish, providing a representative sample of that species/size and waterbody.

Study locations for this project were targeted to identify occurrence of alternative flame retardants in waterbodies likely to be impacted by urban or WWTP effluent inputs. One waterbody was selected as a reference site, to represent concentrations occurring from

atmospheric deposition. Lakes and reservoirs were selected as target waterbodies to obtain samples integrating many sources within a waterbody. The study locations cover a range of watershed areas, lake surface areas, and elevations.

6.2.2.3 Completeness

The project manager will consider the study to have achieved completeness if 95% of the samples are analyzed acceptably.

6.3 Acceptance criteria for quality of existing data

The use of existing data from previous studies on alternative flame retardants in Washington State will be limited to qualitative comparisons in this project. Alternative brominated flame retardants analyses in freshwater fish tissue by Mathieu and Wong (2016) were reviewed following EPA's *National Functional Guidelines for Superfund Organics Methods Data Review* (EPA, 2014) and deemed usable as qualified for all purposes. Alternative brominated flame retardant data for Mathieu and Wong (2016) were qualified as estimates ("J") because the method used a single point calibration. Methods have improved since this project and the current project will require a multi-point calibration.

Very little to no data exists for many of the parameters being analyzed in this study. This study is being conducted to fill this data gap.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

7.1 Study boundaries

Study boundaries for this project are the shoreline perimeters of each lake/reservoir identified as a study location. Water resource inventory area (WRIA) numbers and hydrologic unit codes (HUCs) for each study location are presented in Table 7. Figure 1 displays where the study locations are located throughout the state. Geographic coordinates of individual sampling sites are given in Section 7.2. For surface water and sediments, discrete samples will be collected at the deepest part of the lake/reservoir or basin. Fish will be collected throughout the entire lake/reservoir.

Table 7. Study Locations WRIA and HUC Numbers.

Study Location	WRIA	HUC
Lake Meridian	9	17110013
Lake Ozette	20	17100101
Lake Spokane	54	17010307
Lake Stevens	7	17110011
Lake Washington	8	17110012
Lake Whatcom	1	17110004
Mayfield Lake	26	17080005
Spanaway Lake	12	17110019
Vancouver Lake	28	17080003
West Medical Lake	43	17020013

WRIA = Water Resource Inventory Area
HUC = Hydrologic Unit Code

7.2 Field data collection

7.2.1 Sampling locations and frequency

Table 8 lists the geographic coordinates and timing of sample collections. Surface water and sediment samples will be collected at the deepest part of the lake/reservoir or the deepest part of the basin identified for sampling (south basin of Lake Washington and northwest basin of Lake Whatcom). The deepest part of the lake/reservoir is targeted to capture an integrated sample far from shoreline inputs and because the finest sediments typically are deposited in this area due to the process of sediment focusing. Fine sediments are desired as contaminant concentrations generally have an inverse relationship with sediment particle size (the finer the sediment, the higher the concentration).

One sampling event will occur once per season for surface water (fall 2017 and spring 2018), sediments (spring 2018), and fish tissue (fall 2017).

Table 8. Sampling Locations and Timing for Surface Water, Sediment, and Fish Collections.

Waterbody	County	Latitude*	Longitude*	Sample Timing			
				Surface Water	Surface Water	Sediment	Fish
Lake Meridian	King	47.363	-122.154	mid-Oct	late-May	late-May	---
Lake Ozette	Clallam	48.082	-124.646	mid-Oct	late-May	late-May	Oct
Lake Spokane	Spokane	47.812	-117.796	mid-Oct	late-May	late-May	Oct
Lake Stevens	Snohomish	48.008	-122.092	mid-Oct	late-May	late-May	---
Lake Washington (south basin)	King	47.520	-122.252	mid-Oct	late-May	late-May	Oct
Lake Whatcom (northwest basin)	Whatcom	48.761	-122.407	mid-Oct	late-May	late-May	---
Mayfield Lake	Cowlitz	46.506	-122.578	mid-Oct	late-May	late-May	---
Spanaway Lake	Pierce	47.113	-122.448	mid-Oct	late-May	late-May	---
Vancouver Lake	Clark	45.674	-122.730	mid-Oct	late-May	late-May	---
West Medical Lake	Spokane	47.575	-117.711	mid-Oct	late-May	late-May	---

*Datum = NAVD88 decimal degree

7.2.2 Field parameters and laboratory analytes to be measured

Field crews will measure temperature, pH, and conductivity at the site of surface water sampling. MEL will analyze total organic carbon (TOC) in all sediment samples.

Table 9 lists the laboratory analytes to be measured by matrix. As many analytes as possible from the list outlined in Table 9 will be analyzed for this study.

Table 9. Laboratory Analytes and Sample Matrices for Each Analyte.

Analyte Group	Chemical Name	Acronym	Surface Water	Sedi-ment	Fish Tissue
OPFRs	2-Ethylhexyl-diphenyl phosphate	EHDPP	X	X	
	Tetrakis(2-chlorethyl)dichloroisopentyldiphosphate	V6	X	X	
	Tributyl phosphate	TBP	X	X	
	Tricresyl phosphate	TCrP	X	X	
	Triethyl phosphate	TEP	X	X	
	Triphenyl phosphate	TPP	X	X	
	Tripropyl phosphate	TPrP	X	X	
	Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	X	X	
	Tris(2,3-dibromopropyl) phosphate	TDBPP	X	X	
	Tris(2-butoxyethyl) phosphate	TBEP	X	X	
	Tris(2-chloroethyl) phosphate	TCEP	X	X	
	Tris(2-chloroisopropyl) phosphate	TCPP	X	X	
	Tris(2-ethylhexyl) phosphate	TEHP	X	X	
Halogenated FRs	Dechlorane (Mirex)	Dechlorane		X	X
	Dechlorane plus® (DP) Anti	DP Anti		X	X
	Dechlorane plus® (DP) Syn	DP Syn		X	X
	Dechlorane 602	Dec 602		X	X
	Dechlorane 603	Dec 603		X	X
	Dechlorane 604 component A	Dec604		X	X
	Rac-(1R,2R,5R,6R,9S,10S)-5,6,dibromo-1,10,11,12,13,13-hexachlorotricyclo[8.2.1.0]tridec-11-ene	HCDBCO		X	X
	2,4,6-Tribromophenylallyl ether	ATE		X	X
	2-Bromoallyl 2,4,6-tribromophenyl ether	BATE		X	X
	2,3-Dibromopropyl 2,4,6-tribromophenyl ether	DPTE		X	X
	1,2-Bis(2,4,6-tribromophenoxy)ethane	BTBPE		X	X
	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	EHTBB		X	X
	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	total TBECH		X	X
	Hexabromobenzene	HBBz		X	X
	Pentabromobenzene	PBBZ		X	X
	1,2,4,5-Tetrabromobenzene	1,2,4,5-TBB		X	X
	1,2,3,5-Tetrabromobenzene	1,2,3,5-TBB		X	X
	1,2,4-Tribromobenzene	1,2,4-TriBB		X	X
	1,2-Dibromobenzene	1,2-DiBB		X	X
	1,4-Dibromobenzene	1,4-DiBB		X	X
	Pentabromotoluene	PBT		X	X
	Pentabromoethylbenzene	PBEB		X	X
	Pentabromobenzyl bromide	PBBB		X	X
	Tetrabromo-p-xylene	pTBX		X	X
	Tetrabromo-o-chlorotoluene	TBCT		X	X
PBDEs	PBDE-47, -66, -71, -100, -138, -153, -154, -183, -190, and -209	PBDEs	X	X	X

OPFRs = organophosphate flame retardants
FRs = flame retardants
PBDEs = polybrominated diphenyl ethers.

7.3 Modeling and analysis design

Not applicable.

7.4 Assumptions in relation to objectives and study area

This study has the underlying assumption that quantitation limits will be low enough to characterize alternative flame retardant concentrations in the study locations. Because these analyses are still very new, no analytical holding times have been established. For this study, we make the assumption that the analytes will not break down in the time between sampling and receipt by the laboratory. This is particularly important for surface water samples. All surface water samples will be shipped within 10 days of sampling and the laboratory will extract samples within 28 days.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Field crews will conduct all sampling by boat. Good public boat access is available at all sites. No logistical problems are expected regarding access or timing of field work.

7.5.2 Practical constraints

Practical constraints may include difficulty in obtaining target fish species at each study location. This will be minimized through reconnaissance of the waterbodies prior to sampling. If target species are not available at a study location, the project officer will make a decision on whether the field collections at that site still meet the project goals. The same number of samples will be analyzed, even if the target number of composites per species is not met. Additional composites of a different species may be substituted.

7.5.3 Schedule limitations

Practical constraints regarding fish collections are not anticipated to impact the schedule of this project.

8.0 Field Procedures

8.1 Invasive species evaluation

Field staff will follow the procedures described within SOP EAP070 – Minimizing the Spread of Invasive Species (Parsons et al., 2012). Vancouver Lake is considered an area of extreme concern due to the documented presence of New Zealand mudsnails (NZMS). Ecology staff will schedule this waterbody for sampling at the end of a field run and will use the following decontamination procedure: inspection, cleaning, draining, and drying.

Inspection consists of visual inspection and physical removal of invasive species and aquatic plants. This will be performed after sampling, once at the site and again at the operations center. Motors and generators will be flushed with clean water. Gill nets, the boat hull, and the boat bilge will be cleaned with hot water (60°C). Nets will be left out to dry and the bilge will be completely drained. The exposed gear will be completely dry for 2 days before the next use. In addition, field staff will make an effort to reduce contact with sediments at the areas of extreme concern, further reducing the possibility of spreading NZMS or other invasive species.

8.2 Measurement and sampling procedures

Field crews will follow the protocols described within the following Ecology SOPs:

- EAP007 – Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2014b)
- EAP009 – Collection, Processing, and Preservation of Finfish Samples (Sandvik, 2014a)
- EAP011 – Instantaneous Measurements of Temperature in Water (Nipp, 2006)
- EAP015 – Manually Obtaining Surface Water Samples (Joy, 2006)
- EAP031 – Collection and Analysis of pH Samples (Ward, 2014a)
- EAP032 – Collection and Analysis of Conductivity Samples (Ward, 2014b)
- EAP040 – Obtaining Freshwater Sediment Samples (Blakley, 2008)
- EAP070 – Minimizing the Spread of Invasive Species (Parsons et al., 2012)
- EAP090 – Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014)

Surface water samples will be collected in laboratory-provided pre-cleaned 1 L amber glass bottles, following the SOP listed above (Joy, 2006). Samples will be collected as near-surface grabs (5-20 cm below water surface) from the coordinates listed in Table 8. A polyethylene and stainless steel telescopic pole sampler will be used for collecting surface water samples from at least 3 feet out from the bow of the research vessel. All field crew will wear clean, new nitrile gloves for every sampling event. Sampling will employ a ‘clean hands, dirty hands’ protocol, with one field staff in charge of removing the sample bottle cap prior to collection and replacing the sample bottle cap when filled. The other field staff will be in charge of collecting the sample grab with the telescopic pole and will not handle the actual sample bottle.

Surface water samples will be placed inside the laboratory-provided plastic bag and stored in a cooler on ice until return to Ecology headquarters. At headquarters, surface water samples will be placed in a temperature-controlled walk-in cooler and then shipped to the laboratory when sampling is complete for that season.

Immediately following surface water sample collections for laboratory analysis, field measurements of pH (Ward, 2014a), conductivity (Ward, 2014b), and temperature (Nipp, 2006) will be recorded, following the SOPs listed above.

Bottom sediments from each study location will be collected using either a standard ponar, petite ponar, or Ekman dredge, depending on the characteristics of the waterbody and sediments. Sediment sampling will follow the SOP listed above (Blakley, 2008). Sediment samples will consist of a composite of three grabs from each site, within a 10 meter radius. Each grab will be inspected to ensure the sampler did not overfill, that the sediment/water interface is intact and clear (not overly turbid), and that the grab achieved at least 5 cm sediment depth. Overlying water will be siphoned off prior to collection of sediment. The top 0-2 cm of sediment not touching the side of the sampler will then be collected with a stainless steel spoon and transferred to a large stainless steel mixing bowl.

Once three successful sediment grabs are collected at a site, the material in the stainless steel mixing bowl will be homogenized into a uniform consistency and color. Homogenized sediment will then be subsampled into the appropriate containers for OPFRs, halogenated flame retardants, and TOC. Sample jars will be placed on ice in coolers in the field, then stored inside a temperature-controlled walk-in freezer at Ecology headquarters before being shipped frozen to the laboratory.

Methods for fish collections will follow the SOP listed above (Sandvik, 2014a), using electrofishing, netting, and/or angling. Fish captured by these methods will be identified to species and target species will be retained if they are in acceptable condition and target size range. Adequate numbers of fish will be collected to form one 3-5 fish composite sample for each species within a size range. The length of the smallest individual fish included in a composite sample will be within 75% of the length of the largest fish in a composite.

Fish will be collected under Ecology's scientific collection permits from the Washington Department of Fish and Wildlife (WDFW), USFWS, and National Oceanographic Atmospheric Administration (NOAA).

8.3 Containers, preservation methods, holding times

Listed in Table 10 are study analytes, sample matrices, sample minimum quantities, container sizes, preservation, and available holding times.

Table 10. Sample Containers, Preservation Methods, and Holding Times.

Analytes	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
OPFRs	surface water	0.2 L	20 mL amber glass vial	cool to ≤ 6° C	14 days
PBDEs	surface water	1 L	1 L amber glass bottle	cool to ≤ 6° C	1 year
OPFRs	sediment	50 g ww	8 oz glass jar	freeze at ≤ -10° C	1 year
Halogenated FRs	sediment	50 g ww	8 oz glass jar	freeze at ≤ -10° C	1 year
PBDEs	sediment	50 g ww	8 oz glass jar	freeze at ≤ -10° C	1 year
TOC	sediment	25 g ww	2 oz glass jar	freeze at ≤ -10° C	6 months frozen
Halogenated FRs	fish tissue	50 g ww	8 oz glass jar	freeze at ≤ -10° C	1 year
PBDEs	fish tissue	50 g ww	8 oz glass jar	freeze at ≤ -10° C	1 year

ww = wet weight
OPFRs = organophosphate flame retardants
FRs = flame retardants
TOC = total organic carbon
PBDEs = polybrominated diphenyl ethers

8.4 Equipment decontamination

All sampling and processing equipment will be decontaminated prior to use with the following procedure: hand washed with Liquinox soap and hot tap water, deionized water rinse, acetone rinse, and a final hexane rinse. After equipment is completely dry, it will be wrapped with aluminum foil (dull side in) for transport to the field. All other aspects of decontamination will follow Ecology's SOP for Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples (Friese, 2014).

8.5 Sample ID

Individual fish will be assigned unique Field IDs at the time of sample collection. After processing individual fish into composite samples in the lab, a sample ID will be given using the MEL work order number followed by a consecutive number.

8.6 Chain-of-custody

Chain of custody will be maintained for all samples throughout the project. Samples will be stored in a cooler or freezer in Ecology's locked HQ chain of custody room. Ecology staff will use MEL's chain of custody form for shipment to the laboratory.

8.7 Field log requirements

Field data will be recorded in a bound, waterproof notebook on Rite-in-the-Rain paper. Corrections will be made with single line strikethroughs, initials, and date. An electrofishing log will be filled out at each sampling location with the following information:

- Name of project
- Date(s)
- Site name
- Field personnel
- Water quality data: temperature, conductivity, pH, and visibility
- Date, time, location, ID, and description of each sample
- Weather
- Field instrument calibrations
- Main engine hours (for electro-shock boat)
- Generator hours (for electro-shock boat)
- Electrofishing shock settings
- Fish species sighted and retained per permit requirements
- Fish lengths and weights of fish retained for analysis
- Any changes or deviations from the QAPP
- Environmental conditions
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

Not applicable. Necessary activities are detailed in other sections of this QAPP.

9.0 Laboratory Procedures

9.1 Lab procedures table

MEL is anticipated to conduct all analyses. MEL will attempt to report to the quantitation limits outlined in Table 11. Because these are new methods, it may not be possible to report down to these levels for all analytes. MEL will discuss with the project manager if quantitation limits are not achievable and the project manager will decide whether to continue with analysis by MEL or subcontract to an outside laboratory.

If necessary, Ecology will post a solicitation for bid seeking a laboratory to carry out the analyses described in Table 11. The contract will be managed through MEL. The contract laboratory will be expected to meet or exceed the quantitation limits outlined below and have established methods for the target analytes using the outlined instrumentation. The laboratory will be required to report percent lipids for fish tissue analysis.

Table 11. Laboratory Procedures.

Analyte	Matrix	Number of Samples	Number of Field QC samples	Expected Arrival Date	Expected Range of Results	Quanti-tation Limit	Analytical Method
OPFRs	surface water	10	2	10/18/2017	< 0.1 - 100 ng/L	0.1 - 5 ng/L	LC-MS/MS; isotopic dilution
		10	2	5/31/2018	< 0.1 - 100 ng/L	0.1 - 5 ng/L	LC-MS/MS; isotopic dilution
PBDEs	surface water	10	2	10/18/2017	< 0.1 - 100 ng/L	2.0 - 10 ng/L	EPA 8270; GC-MS
		10	2	5/31/2018	< 0.1 - 100 ng/L	2.0 - 10 ng/L	EPA 8270; GC-MS
OPFRs	sediment	10	1	5/31/2018	< 0.005 - 100 ng/g dw	0.005 - 0.25 ng/g dw	LC-MS/MS; isotopic dilution
Halogenated FRs	sediment	10	1	5/31/2018	< 0.05 - 100 ng/g dw	0.05 - 12 ng/g dw	ECNI GC-MS/MS
PBDEs	sediment	10	1	5/31/2018	< 0.5 - 1,000 ng/g dw	0.5 - 1.0 ng/g dw	EPA 8270; GC-MS
TOC	sediment	10	1	5/31/2018	< 1 - 30%	0.1%	PSEP 1986
Halogenated FRs	fish tissue	12	---	12/10/2017	< 0.05 - 100 ng/g ww	0.05 - 12 ng/g ww	ECNI GC-MS/MS
PBDEs	fish tissue	12	---	12/10/2017	< 0.05 - 100 ng/g ww	0.5 - 1.0 ng/g ww	EPA 8270; GC-MS

ww = wet weight; OPFRs = organophosphate flame retardants; FRs = flame retardants; TOC = total organic carbon; PBDEs = polybrominated diphenyl ethers; LC-MS/MS = liquid chromatography – tandem mass spectrometry; PSEP = Puget Sound Estuary Program

9.2 Sample preparation methods

As described in Section 8.2, sediment grabs will be homogenized in the field prior to subsampling into analyte bottles. Fish samples will be processed and homogenized according to Ecology's SOP for Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2014b). Composite fish samples will be composed of 3-5 individual fish fillets. Fish fillets will be ground three times or more, until a consistent color and texture is reached. Homogenized samples will be placed in laboratory-provided pre-cleaned amber glass bottles, frozen, and sent to the laboratory with blue ice. After fillets are removed, the sex of the fish will be determined (when possible) and recorded. Otoliths, scales, or other aging structures will be removed from fish and sent to WDFW for age determination.

Analytical preparation for flame retardant analyses will include an extraction and clean up step detailed in the laboratory's method. The laboratory will be required to spike samples with isotopically labelled surrogate standards prior to extraction.

9.3 Special method requirements

The OPFR and halogenated flame retardant analyses are non-standard methods, newly developed, and require measurement of very low analyte concentrations. The laboratory carrying out the analyses must demonstrate the ability to achieve quantitation limits outlined in this QAPP (Section 9.1) and method performance and QA/QC detailed in Section 6.2. If subcontracting any of the analyses, requirements of the contracted analyses will be detailed in an analytical services bid solicitation.

9.4 Laboratories accredited for methods

The OPFR and halogenated flame retardant analyses are non-standard methods. Therefore, a laboratory accreditation waiver will need to be obtained for this project. MEL will work with Ecology's QA Officer to obtain the waiver by providing SOPs and initial demonstration of capability for the analyses.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 12 provides the laboratory QC procedures required for this study. Field QC procedures for measurements of temperature, pH, and conductivity will follow SOPs listed in Section 8.2.

Table 12. Quality Control Samples, Types, and Frequency.

Analyte	Matrix	Field		Laboratory					
		Blanks	Replicates	LCS	Method Blanks	Lab Duplicates	Matrix Spike	Matrix Spike Duplicate	Surro-gates
OPFRs	surface water	1/batch	1/batch	1/batch	1/batch	---	1/batch	1/batch	each sample
PBDEs	surface water	1/batch	1/batch	1/batch	1/batch	---	1/batch	1/batch	each sample
OPFRs	sediment	---	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
Halogenated FRs	sediment	---	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
PBDEs	sediment	---	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
TOC	sediment	---	1/batch	1/batch	1/batch	1/batch	---	---	---
Halogenated FRs	fish tissue	---	---	1/batch	1/batch	1/batch	1/batch	1/batch	each sample
PBDEs	fish tissue	---	---	1/batch	1/batch	1/batch	1/batch	1/batch	each sample

Batch = 20 or fewer samples
LCS = laboratory control samples; OPFRs = organophosphate flame retardants; FRs = flame retardants; TOC = total organic carbon; PBDEs = polybrominated diphenyl ethers

10.2 Corrective action processes

The project manager will work closely with the laboratory and the MEL QA Officer conducting the data quality review to examine data that fall outside of QC criteria. The project manager will determine whether data should be re-analyzed, rejected, or used with appropriate qualification.

11.0 Management Procedures

11.1 Data recording and reporting requirements

All field data and observations will be recorded on waterproof paper kept in field notebooks. Staff will transfer information contained in field notebooks to Excel spreadsheets after they return from the field. Data entries will be independently verified for accuracy by another member of the project team. Laboratory data will be uploaded into EIM using the EIM XML results template.

All fish collected under scientific collection permits will be reported to appropriate state and federal agencies following instructions in the permit.

11.2 Laboratory data package requirements

If a contract laboratory is required, the contract laboratory will deliver a Tier 4 Level data package to MEL with the complete raw laboratory dataset. After reviewing the data package from the contract laboratory, MEL will provide case narratives to the project manager with the final qualified results and a description of the quality of the contract laboratory data. Case narratives should include any problems encountered with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Narratives will also address the condition of samples on receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests.

11.3 Electronic transfer requirements

The contract laboratory will be required to report the analytical results via an electronic data deliverable (EDD) in Excel following the EIM format. MEL will deliver case narratives in PDF format, and final EDDs with MEL-amended result and MEL-amended qualifier columns in an Excel spreadsheet format, to the project manager via email.

For MEL-generated data, MEL will transfer results via their Laboratory Information Management System (LIMS). Case narratives will be provided via email to the project manager.

11.4 EIM/STORET data upload procedures

All result transmittals from laboratories must be provided in an EDD format that meets Ecology requirements for loading to Ecology's Information Management (EIM) database. Analytical data for the project will be entered into Ecology's EIM database following internal Environmental Assessment Program (EAP) protocols and business rules. An independent reviewer will review the QC of this data upload, following internal EAP protocols.

11.5 Model information management

Not applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

MEL and contracted laboratories must participate in performance and system audits of their routine procedures. No audits are planned specifically for this project.

12.2 Responsible personnel

Not applicable. No audits are planned for this study.

12.3 Frequency and distribution of reports

A draft report of the study findings will be completed in January 2019 and a final report published on the Ecology's website in April 2019. The report will include, at a minimum, the following:

- Map showing all sampling locations and any other pertinent features of the study area.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Summary tables of the chemical and physical data.
- Analyte concentrations relative to other studies in the U.S.
- Recommendations for follow-up actions, based on study results.

Upon study completion, all project data will be entered into Ecology's EIM system. Public access to electronic data and the final report for the study will be available through Ecology's Internet homepage (www.ecy.wa.gov).

12.4 Responsibility for reports

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

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. Contract laboratory data packages will be assessed by MEL's QA Officer following MEL's SOPs and the EPA National Functional Guidelines for Organic Data Review (EPA, 2014).

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 contract 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.

Accuracy of data entered into EIM will be verified by someone other than the data engineer per the Environmental Assessment Program's EIM data entry business rules.

13.3 Validation requirements, if necessary

Independent data validation will not be required for this project.

13.4 Model quality assessment

Not applicable.

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 may 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. This will include assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and the success of laboratory QC samples meeting MQOs.

14.2 Treatment of non-detects

Analytical data will be reported down to the method detection limit. Results not detected at or above the method detection limit will be qualified "U" or "UJ". Results above the method detection limit, but below the sample-specific quantitation limit will be qualified "J" as an estimate. Summed values will include only detected concentrations. Results qualified "NJ" (the analyte is tentatively identified and the result is an estimate) will not be included in summed values. Statistical analysis requiring treatment of non-detects will not be included in the final report.

14.3 Data analysis and presentation methods

Data will be summarized in tables and graphs for the final report. See Section 12.3 for more information on how the data will be presented.

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.

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16.0 Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Acronyms and Abbreviations

BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
DBDPE	decabromodiphenylethane
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
HBBz	Hexabromobenzene
HUC	hydrologic unit code
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NOAA	National Oceanic and Atmospheric Administration
OPFR	organophosphate flame retardant
PBEB	Pentabromoethylbenzene
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyls
POCIS	polar organic chemical integrative sampler
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedures
TOC	Total organic carbon
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area

WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
ft	feet
L	liter
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)
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 population 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 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:

$$[Abs(a-b)/((a + b)/2)] * 100$$

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

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