



DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Brominated Flame Retardants, Chlorinated Paraffins, and Hexabromocyclododecane in Freshwater Fish of Washington State Rivers and Lakes

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Quality Assurance Project Plan

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EAP: Environmental Assessment Program

W2R: Waste 2 Resources

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2.0 Abstract

The Washington State Department of Ecology (Ecology) will conduct a study in 2014 to evaluate current levels of emerging contaminants and persistent, bioaccumulative, toxic (PBT) chemicals in freshwater fish tissue in Washington. Fish samples will be collected from eleven waterbodies located throughout the state, across a range of land use types. Ecology will collect two composite fish tissue samples of a bottom feeder species and two composite samples of a predator species for analysis of brominated flame retardants, chlorinated paraffins, and hexabromocyclododecane.

The chemicals being tested for are either on the state's current PBT List or are emerging contaminants that require more information. Data for these contaminants is generally lacking in Washington freshwater systems. Results from this study will support prioritization of chemicals to be addressed by Ecology through chemical action plans (CAPs) and other efforts to reduce toxics in the state.

3.0 Background

Ecology, in collaboration with other state agencies, develops chemical action plans (CAPs) to identify, characterize, and evaluate uses and releases of persistent, bioaccumulative, and toxic (PBT) chemicals in the state. The agencies use CAPs to compile information and recommend actions to protect human health and the environment. CAPs are developed for one chemical or chemical group at a time.

The PBT Rule laid out a process to select which PBTs are given priority for CAP development (WAC 173-333-410). In 2007, Ecology published a “Multiyear PBT Chemical Action Plan Schedule” that outlined priority PBTs and set forth a schedule in which Ecology will address the chemicals (Gallagher, 2007). Ecology periodically reviews and, as appropriate, updates the multiyear schedule. The PBT list which the multiyear schedule draws from will be re-prioritized in the future. It may be expanded to include chemicals that exhibit one or more of the PBT characteristics (i.e., very persistent or very bioaccumulative) or are released into the environment on a regular basis, rendering them “pseudo-persistent.”

To support reprioritization of PBT chemicals and to know whether new chemicals should be added, data is needed on the occurrence and levels present in Washington’s environment. This study will provide data on select emerging contaminants and PBT chemicals in freshwater fish of Washington. Ecology will collect and analyze freshwater fish tissue samples throughout the state for brominated flame retardants (BFRs), chlorinated paraffins (CPs), and hexabromocyclododecane (HBCD).

3.1 Study area and surroundings

Ecology will collect fish from lakes and rivers distributed throughout the state. Eleven waterbodies – three rivers and eight lakes – will be targeted for fish collections. Table 1 describes each location, along with degree of contamination potential, based on the level of development in the watershed and potential inputs from stormwater and wastewater treatment plant effluent.

Table 1. Study Location Descriptions.

Study Location	County	Elevation (ft)	Max Depth (ft)	Mean Depth (ft)	Lake Area (acres)	Watershed Area (sq mi)	Predominant Land Type	Contamination Potential
Lakes								
Banks Lake	Grant	1,570	85	47	27,000	---	agricultural	Low
Clear Lake	Spokane	2,344	110	26	316	10	brush steppe	Moderate
Kitsap Lake	Kitsap	156	29	18	250	3	urban	High
Lake Whatcom	Whatcom	312	330	150	5,000	56	residential/forested	Moderate
Mayfield Lake	Lewis	450	180	61	2,200	1,400	forested	Low
Pierre Lake	Stevens	2,000	75	28	110	27	forested	Low
Sawyer Lake	King	512	58	26	300	13	residential/forested	Moderate
Lake Stevens	Snohomish	210	160	63	1,000	7	urban	High
Rivers								
Mid-Columbia R.	Benton	343	---	---	---	2,214,000	agricultural	Moderate
Snake River	Whitman	760	---	---	---	107,500	agricultural	Moderate
Snohomish River	Snohomish	40	---	---	---	1,720	urban	High

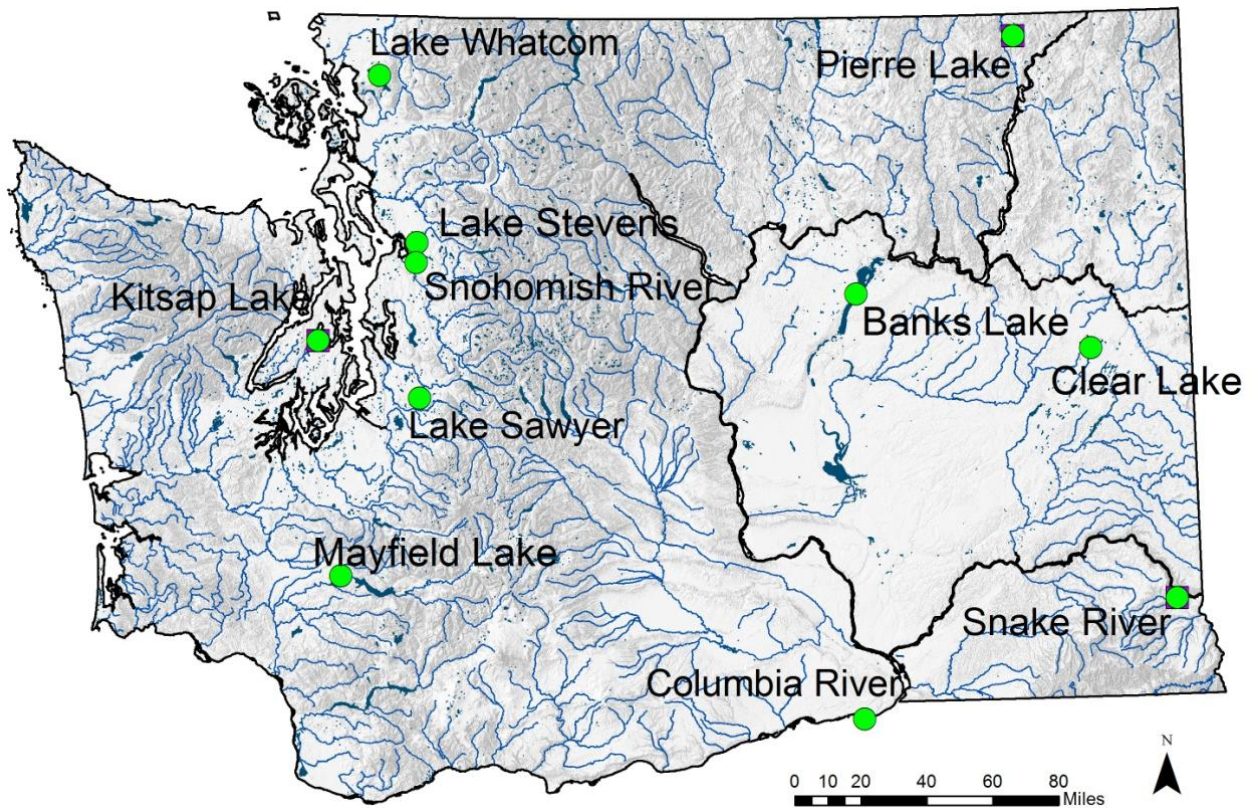


Figure 1. Study Locations.

3.1.1 Logistical problems

Boat access is available at all sites. No logistical problems are expected regarding access or timing of field work.

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.

3.1.2 History of study area

Not applicable. See Section 3.1.4 for information on previous investigative efforts.

3.1.3 Parameters of interest

The parameters listed in Table 2 are either known PBTs or are emerging contaminants with potential for PBT characteristics. Data for these contaminants are generally lacking in freshwater areas of Washington.

Table 2. Parameters of Interest and the Reason for Concern.

Parameter or Parameter Suite	Reason for Concern
Brominated flame retardants (BFRs)	Potential to be persistent, bioaccumulative, and/or toxic
Chlorinated paraffins (CPs)	Known to be persistent, bioaccumulative, and toxic
Hexabromocyclododecane (HBCD)	Known to be persistent, bioaccumulative, and toxic

Brominated Flame Retardants

Brominated 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. Additive flame retardants are not chemically bound to the material in the product and leach out of product over time, accumulating in indoor dust. Ecology developed a CAP for polybrominated diphenyl ether (PBDE) flame retardants in 2006, after growing concern that the chemicals were dramatically increasing in people and in the environment (Ecology et al., 2006). Chemical manufacturers voluntarily stopped production of two commercial formulations of PBDEs (penta- and octa-) in the mid-2000s, and phased out most uses of deca-BDE in 2012.

As commercial uses of PBDEs were phased out, manufacturers started using alternative flame retardants as replacements to meet flammability standards. Many of the replacement chemicals for PBDEs are also brominated, and little is known about their toxicity and fate in the environment. Modeling studies suggest that some of the alternative brominated flame retardants

have similar hazard profiles to PBDEs and may persist in the environment (EPA, 2014a; Kuramochi et al., 2014). This study will analyze the following alternative brominated flame retardants: pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenylethane (DBDPE).

Chlorinated Paraffins

Chlorinated paraffins are a group of chemicals used as industrial flame retardants, lubricants, and plasticizers, as well as additives in adhesives, paints, rubber, and sealants (Muir et al., 2000). The term *chlorinated paraffins* refers to complex mixtures of polychlorinated alkanes with varying carbon chain lengths and chlorine contents. Short-chain chlorinated paraffins (SCCPs) are persistent, bioaccumulative, and toxic to aquatic organisms at low concentrations, and have also been classified as “reasonably anticipated to be human carcinogens” based on animal studies (NTP, 2011). Medium-chain (MCCPs) and long-chain (LCCPs) chlorinated paraffins are also persistent and bioaccumulative but appear to have lower toxicity because of their lower solubility. However, the toxicity of MCCPs and LCCPs is not as well researched as SCCPs (EPA, 2009).

SCCPs have been found in water, sediment, air, aquatic organisms, terrestrial wildlife, and humans (reviewed by Tomy et al., 1998 and Bayen et al., 2006), as well as in remote sediments where long-range atmospheric transport was the attributed source (Tomy et al., 1999). The greatest mode of release to the environment is thought to be from manufacturing and lubricant applications, primarily via metal-working activities (EPA, 2009).

Chlorinated paraffins are one of the chemical groups on the PBT List not yet scheduled for CAP development. The U.S. Environmental Protection Agency (EPA) is currently reviewing SCCPs and intends to initiate action under the Toxic Substances Control Act (TSCA) section 6(a) to ban or restrict the manufacture, import, processing, or distribution in commerce, export, and use of SCCPs based on their PBT properties and their presence in the environment. The EPA also intends to evaluate whether MCCPs and LCCPs should be addressed under TSCA section 6(a). All three chain length mixtures will be analyzed as part of the chlorinated paraffins suite for this study.

Hexabromocyclododecane

HBCD refers to a technical mixture comprised primarily of alpha, beta, and gamma diastereoisomers. It is used as a flame retardant in extruded (XPS) and expanded (EPS) polystyrene for building insulation, as well as in furniture textiles, automotive upholstery, and other consumer products such as electronics. HBCD exhibits high aquatic toxicity and is a human health concern for reproductive, developmental, and neurological effects, based on animal studies (EPA, 2010).

HBCD can be transported long distances and has been found in many different environmental media throughout the world (Covaci et al., 2006). Sources to the environment generally include diffuse particulate releases to soil during construction and demolition of XPS- or EPS-insulated buildings and through the use or disposal of products containing HBCD (EPA, 2010).

Particulates containing HBCD are transferred to air or stormwater runoff and through wastewater treatment plant effluent and landfill emissions (EPA, 2010).

Ecology included HBCD on the agency PBT List, but has not scheduled it for development of a CAP. The Environmental Protection Agency released an action plan summary for HBCD in 2010 (EPA, 2010) and has recently issued an alternatives assessment for its use in XPS and EPS insulation (EPA, 2014b).

3.1.4 Results of previous studies

Very few studies have been conducted on these parameters in Washington's environment. In 2005-2006, Johnson et al. (2006) conducted a statewide survey of polybrominated diphenyl ether (PBDE) flame retardants in freshwater fish for Ecology. This study was carried out to evaluate the effectiveness of the PBDE Chemical Action Plan and other efforts to reduce PBDEs in the environment. Results from the study showed that total PBDE concentrations appeared to be less than 10 ng/g in most Washington rivers and lakes. Several large waterbodies – Palouse River, Columbia River, Lake Washington, Snohomish River, Cowlitz River, and Snake River – had total PBDE levels in the 10-200 ng/g range. Highly elevated PBDE concentrations were found throughout the Spokane River.

In 2011, an Ecology study analyzed CPs and HBCD, as well as other PBT chemicals, in freshwater bottom feeder fish collected from four Washington waterbodies (Johnson and Friese, 2012). This was the first time CPs and HBCD were reported in freshwater fish from the Northwest. CPs and HBCD were detected in all samples tested. Total CPs (sum of short, medium, and long-chain CPs) ranged from 320 – 1,670 ng/g, and levels were highest in the Yakima River and Lake Washington. HBCD concentrations ranged from 0.103 – 0.234 ng/g, with the exception of one much higher concentration in a largescale sucker composite from Lake Washington (1,120 ng/g). The authors recommended including CPs and HBCD in future monitoring studies.

Mathieu and McCall (2014) analyzed HBCD in sediment cores of three lakes in Washington and found increasing levels of the contaminant at all three sites. Upper sediment concentrations (0-2 cm) were particularly high in the two lakes with the highest level of development in the watershed – Sawyer and Kitsap Lakes, at 17.7 and 27.8 ng/g (sum of diastereomers) respectively – compared to the more remote, forested lake watershed of Lake Cavanaugh (8.6 ng/g). Recommendations of this study included increasing spatial coverage of HBCD data in freshwater environments of Washington to help prioritize Ecology efforts in addressing PBT chemicals.

3.1.5 Regulatory criteria or standards

This study will not be used to determine compliance with regulatory standards or criteria, since no such standards exist for fish tissue or sediments for the target parameters.

4.0 Project Description

4.1 Project goals

This project is being carried out for the following purposes:

- To establish current contamination levels of BFRs, CPs, and HBCD in Washington freshwater fish tissue. This data will help characterize fish tissue concentrations from watersheds of varying land uses and types throughout the state.
- To support Ecology's efforts to prioritize chemicals scheduled for chemical action plans (CAPs) and other efforts to reduce toxics in Washington.

4.2 Project objectives

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

- Ecology will collect four composite fish tissue samples of two different trophic levels from eleven waterbodies in Washington.
- Fish tissue samples will be analyzed for brominated flame retardants, hexabromocyclododecane, and chlorinated paraffins.

4.3 Information needed and sources

Not applicable. This study is being conducted to generate new environmental data.

4.4 Target population

Fish collections will target bottom feeder and predator fish species. The following species have been identified through a desk exercise to be available at the study locations: brown bullhead (BBH), brown trout (BT), channel catfish (CC), common carp (CCP), cutthroat trout (CTT), largemouth bass (LMB), largescale sucker (LSS), northern pikeminnow (NPM), smallmouth bass (SMB), walleye (WAL), and yellow bullhead (YBH). Table 3 displays which species will be targeted at the individual waterbodies.

Table 3. Target Fish Species

Study Location	Bottom Feeder	Predator
Banks Lake	CC, CCP	SMB
Clear Lake	YBH	SMB, LMB, BT
Kitsap Lake	BBH	LMB
Lake Whatcom	BBH	SMB
Mayfield Lake	LSS	LMB, NPM
Pierre Lake	BBH	SMB
Sawyer Lake	BBH	LMB, SMB
Lake Stevens	BBH	LMB, SMB
Mid-Columbia River	CCP, LSS	SMB, WAL, NPM
Snake River	CCP, LSS	LMB
Snohomish River	LSS	NPM, CTT

*See above text in Section 4.4 for acronyms.

4.5 Study boundaries

This study is being carried out to characterize fish contamination levels throughout the state (Table 4). At individual study locations, fish will be collected from the entire lake, or within a two river mile stretch of river. Field collections will target areas with habitat that is most likely to contain the species of interest.

Table 4. Water Resource Inventory Area and Hydrologic Unit Code Numbers for the Study Area.

Study Location	WRIA	HUC
Banks Lake	42	17020014
Clear Lake	43	17020013
Kitsap Lake	15	17110019
Lake Whatcom	1	17110004
Mayfield Lake	26	17080005
Pierre Lake	60	17020002
Sawyer Lake	9	17110013
Lake Stevens	7	17110011
Mid-Columbia River	31	17070101
Snake River	35	17060107
Snohomish River	7	17110011

4.6 Tasks required

The following tasks will be carried out for this project:

- Conduct desktop reconnaissance of study locations.
- Compile existing data on target parameters for the study locations and Washington, as well as conduct a larger literature review of data on BFRs, CPs, and HBCD from outside Washington.
- Collect target fish species at the study locations.
- Process fish samples collected for laboratory analysis.
- Send samples to the contract laboratory for analysis of BFRs, CPs, and HBCD.
- Review data quality of laboratory results and work with MEL's QA officer to resolve any issues.
- Write draft report summarizing results, route the draft through EAP review procedures, and publish final report.
- Load data into EIM database.

4.7 Practical constraints

See Section 3.1.1.

4.8 Systematic planning process

This Quality Assurance Project Plan addresses the elements of the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 5. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies W2R Program Phone: 360-407-7398	Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Callie Mathieu Toxics Studies Unit SCS Section Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Michael Friese Toxics Studies Unit SCS Section Phone: 360-407-6060	Field Lead	Leads field collections and records field information.
Christopher Clinton Toxics Studies Unit SCS Section Phone: 360-407-6737	Field Assistant	Helps collect samples and enters data into EIM.
Dale Norton Toxics Studies Unit SCS Section Phone: 360-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS Section Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	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.

EAP: Environmental Assessment Program
 EIM: Environmental Information Management database
 QAPP: Quality Assurance Project Plan
 W2R: Waste 2 Resources

5.2 Special training and certifications

All field crew carrying out sampling have specialized training in electro-shocking techniques for fish collections.

5.3 Organization chart

See Tables 3 and 4.

5.4 Project schedule

Table 6 provides the schedule for field collections, laboratory analyses, data entry, and final report publication.

Table 6. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	12/2014	Michael Friese
Laboratory analyses completed	03/2015	
Environmental Information System (EIM) database		
EIM Study ID	CAME001	
Product	Due date	Lead staff
EIM data loaded	08/2015	Christopher Clinton
EIM data entry review	09/2015	Melissa McCall
EIM complete	10/2015	Christopher Clinton
Final report		
Author lead / Support staff	Callie Mathieu / Christopher Clinton, and Michael Friese	
Schedule		
Draft due to supervisor	07/2015	
Draft due to client/peer reviewer	08/2015	
Final (all reviews done) due to publications coordinator	09/2015	
Final report due on web	10/2015	

5.5 Limitations on schedule

No limitations to the schedule are expected for this project.

5.6 Budget and funding

Table 7 presents the estimated laboratory costs for this project. The numbers of QC samples in the table below reflect only those that are not included in the analysis cost. Quotes received during project planning indicated that all QC tests would be run free of charge, with the exception of matrix spikes and matrix spike duplicates. Matrix spike and matrix spike duplicate analyses will only be requested on CP analysis batches, as the CP method does not employ isotopic dilution.

Table 7. Project Budget and Funding.

Analyte	Matrix	Field Samples (# of samples)	QC Samples* (# of samples)	Total Number of Samples	Cost per Sample	MEL Subtotal	Contract Lab Subtotal	MEL Contract Fee
BFRs	Tissue	44	0	44	\$875	---	\$38,500	\$9,625
CPs	Tissue	44	6	50	\$700	---	\$35,000	\$8,750
HBCD	Tissue	44	0	44	\$525	---	\$23,100	\$5,775
Lipids	Tissue	44	0	44	\$0	---	\$0	\$0
Subtotal						\$0	\$96,600	\$24,150
Lab Grand Total						\$120,750		

*includes only QC samples that are not free of charge.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

This study will not require decision quality objectives.

6.2 Measurement Quality Objectives (MQOs)

The measurement quality objectives (MQOs) outlined in Table 8 are estimates only. The laboratory methods for analysis of chemicals of emerging concern are relatively new and MQOs are not available for every method. The following MQOs are guidelines.

Because the method for CP analysis was recently developed, fixed acceptance limits for recovery of target compounds have not been established for ongoing precision and recovery QC tests. The project manager and MEL's QA Officer will review the data from the contract laboratory carefully to determine whether data is of sufficient quality.

Table 8. Measurement Quality Objectives.

Analyte	Bias	Precision	Instrument performance		Sensitivity
	LCS (% recov.)	Lab Duplicates (RPD)	Method Blanks	Surrogate Standards (% recov.)	Lowest Concentration of Interest
BFRs	70 - 130%	<40%	< LOQ	50 - 150%	0.2 ng/g
CPs	n/a	n/a	Sample level must be $\geq 2x$ blank level	n/a	5 ng/g
HBCD	70 - 130%	<40%	< LOQ	40 - 150%	1 ng/g
Lipids	80 - 120%	<20%	n/a	n/a	0.1%

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Laboratory analysis precision will be assessed through laboratory duplicate samples. See Table 8 for MQOs.

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. See Table 8 for MQOs.

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 method detection limit. This will be the lowest concentration of interest. See Table 8 for sensitivity values.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Fish samples will be collected and processed following Ecology SOPs in order to obtain data that will be comparable to other studies (Sandvik, 2014a; Sandvik, 2014b). Fish will be collected in the fall to be comparable to previous studies of organic contaminants in fish tissue. Lipids content of each fish composite sample will be analyzed in order to determine whether lipid-normalization is appropriate for comparison of fish samples.

6.2.2.2 Representativeness

The study locations were chosen to represent various levels of contamination potential. Fish samples will be analyzed as 3-5 fish composites in order to integrate variability within a lake and provide a representative sample.

6.2.2.3 Completeness

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

7.0 Sampling Process Design (Experimental Design)

7.1 Study design

Ecology will collect a total of 44 freshwater fish composite samples from eleven Washington waterbodies in the fall of 2014. At each waterbody, Ecology will aim to collect sufficient numbers of fish for two composite samples of a bottom feeder and two composite samples of a predator species to cover multiple trophic levels. Bottom feeder fish samples will be analyzed as whole body composites to obtain data on ecological exposure and for comparability to previous studies (e.g., Johnson and Friese, 2012). Skin-on fillet tissue (muscle) from the predator fish species will be analyzed to provide data applicable to human health concerns. Composite samples will consist of 3-5 similar-sized individual fish. Ecology will send the fish tissue samples to a contract laboratory for analysis of BFRs, CPs, and HBCD.

In order to characterize contamination levels of BFRs, CPs, and HBCD that may be typical of freshwater fish in the state, waterbodies were selected to be distributed evenly throughout the state and to represent a variety of land use types with varying degrees of contamination potential (Table 1). Lakes located within developed and undeveloped watersheds were chosen, covering urban, residential, forested, and agricultural land uses. Study locations also represent a range of surface area and watershed area sizes. A waterbody was selected from each side of the state, to reflect reference conditions – Mayfield Lake in western Washington and Pierre Lake in eastern Washington. The land surrounding these two lakes is relatively undisturbed forestland, with inputs of the target analytes predominantly coming from atmospheric deposition.

Three urban waterbodies – two lakes and one river – were chosen to represent waterbodies with more significant sources such as stormwater and wastewater treatment plant effluent. Lake Stevens, Kitsap Lake, and the Snohomish River were chosen as the urban/impacted waterbodies. The Snake River and Columbia River sites have moderate contamination potential due to wastewater treatment plant effluent; however, these sites drain large areas and may have a more diluted signal than Snohomish River. Other sites chosen to represent moderate contamination potential include Clear Lake, Lake Whatcom, and Lake Sawyer. Land use surrounding these types covers a mix of undeveloped brush steppe or forested land, and some residential development in the basin.

7.1.1 Field measurements

Conductivity and temperature will be measured at each waterbody before electrofishing. Fish total length (mm) and weight (g) will be measured and recorded in the field after collection.

7.1.2 Sampling location and frequency

Fish samples will be collected once during the fall of 2014. See Table 1 for a list of sampling locations.

7.1.3 Parameters to be determined

Table 9 lists the parameters to be analyzed for this project.

Table 9. Target Parameter Suites and Individual Chemicals.

Parameter Suite	Chemicals Analyzed	Acronym
Brominated Flame Retardants (BFRs)	Polybrominated diphenyl ethers ¹	PBDEs
	Pentabromoethylbenzene	PBEB
	Hexabromobenzene	HBB
	1,2-Bis(2,4,6-tribromophenoxy)ethane	BTBPE
	Decabromodiphenylethane	DBDPE
Chlorinated Paraffins (CPs)	Short-chain chlorinated paraffins (C10-13)	SCCP
	Medium-chain chlorinated paraffins (C14-C17)	MCCP
	Long-chain chlorinated paraffins (C18-20)	LCCP
Hexabromocyclododecane (HBCD)	alpha-HBCD	a-HBCD
	beta-HBCD	b-HBCD
	gamma-HBCD	g-HBCD

¹Congeners to be analyzed: '-7, -8/11, -10, -12/13, -15, -17/25, -28/33, -30, -32, -35, -37, -47, -49, -51, -66, -71, -75, -77, -79, -85, -99, -100, -105, -116, -119/120, -126, -128, -138/166, -140, -153, -154, -155, -181, -183, -190, -203, -206, -207, -208, -209.

7.2 Maps or diagram

See Figure 1 for a map of the study locations.

7.3 Assumptions underlying design

Fish tissue samples were chosen as the medium for analysis with the understanding that the contaminants of interest build up in fish over time. PBDEs, CPs, and HBCD are known to bioaccumulate; thus, fish tissue is a good indicator of environmental levels within a watershed. Data on the bioaccumulation potential of the alternative BFRs (PBEB, HBB, BTBPE, and DBDPE) is lacking, but many of the compounds have similar physicochemical properties to PBDEs and are expected to accumulate in fish tissue.

7.4 Relation to objectives and site characteristics

The study design supports the objectives of this project. Site characteristics, such as access, are not expected to inhibit the fulfillment of objectives for this study.

7.5 Characteristics of existing data

Data on levels of PBDE flame retardants in freshwater fish tissue exists for the state (e.g., Johnson et al., 2006); however, no Ecology study has examined the alternative brominated flame retardants PBEB, HBB, BTBPE, or DBDPE¹ in freshwater fish tissue. Little data exists on levels of these replacement flame retardants in the environment. Studies in other areas of the U.S. have suggested increasing environmental levels of alternative BFRs as a result of the phase out of PBDEs (Salamova et al., 2014; Robson et al., 2013; Gauthier et al., 2009; Chen et al., 2011). This study will help fill in the data gap on environmental levels of these alternative brominated flame retardants in Washington.

The previous Ecology study on CPs and HBCD in freshwater fish tissue was limited to four waterbodies in areas with historical toxic contamination issues (Johnson and Friese, 2012). This study expands on that survey to include waterbodies with a larger variation of contamination potential and also to include alternative brominated flame retardants that were not analyzed previously.

¹ PBEB = pentabromoethylbenzene; HBB = hexabromobenzene; BTBPE = 1,2-bis(2,4,6-tribromophenoxy)ethane; DBDPE = decabromodiphenylethane.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

The field lead and field assistants will be familiar with and adhere to the practices described within the following Ecology Standard Operating Procedures (SOPs).

- EAP070 - Minimizing the Spread of Invasive Species (Parsons et al., 2012).
- EAP009 - Collection, Processing, and Preservation of Finfish Samples (Sandvik, 2014a).
- EAP007 - Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2014b).

Field collections will follow the SOP for collection of fish samples listed above. Methods for fish collections may include electrofishing, netting, and angling. Fish captured by these methods will be identified to species and target species retained if they are in acceptable condition and are in the target size range. Adequate numbers of fish will be collected to form two composite samples of 3-5 fish per composite for each species (one bottom feeder species and one predator species per waterbody).

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

8.2 Containers, preservation methods, holding times

Table 10. Sample Containers, Preservatives, and Holding Times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
BFRs	Fish Tissue	25 g	glass jar	freeze, -10° C	1 year
CPs	Fish Tissue	25 g	glass jar	freeze, -10° C	1 year
HBCD	Fish Tissue	25 g	glass jar	freeze, -10° C	1 year
lipids	Fish Tissue	25 g	glass jar	freeze, -10° C	n/a

8.3 Invasive species evaluation

Field staff will follow the procedures described within SOP EAP070 - Minimizing the Spread of Invasive Species (Parsons et al., 2012).

The Snake River and the Columbia River are considered areas of extreme concern due to the documented presence of New Zealand mudsnails (NZMS). Ecology staff will schedule these waterbodies 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.

8.4 Equipment decontamination

Equipment used to process fish tissue samples will be decontaminated following Ecology's SOP for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014). Briefly, Ecology staff will clean equipment with the following procedure:

1. Brush with hot tap water and Liquinox, and then rinse with tap water.
2. Visually inspect for cleanliness. Step 1 will be repeated, if necessary.
3. Rinse three times with deionized water.
4. Rinse with Acetone.
5. Rinse with Hexane. Let equipment dry.

8.5 Sample ID

Individual fish will be assigned unique Field IDs at the time of sample collection. Sample IDs using MEL's work order number will be assigned at the time of fish tissue processing.

8.6 Chain-of-custody, if required

Chain of custody will be maintained for all samples throughout the project. Samples will be stored in a locked freezer in Ecology's HQ chain of custody room. Ecology staff will use Manchester Environmental Laboratory's (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, and visibility

- Main engine hours
- Generator hours
- Electrofishing shock settings
- Fish species sighted and retained
- Fish lengths and weights
- **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 Measurement Methods

9.1 Field procedures table/field analysis table

Not applicable.

9.2 Lab procedures table

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 reporting limits outlined below and have established methods for the target analytes using the outlined instrumentation.

Table 11. Lab Procedures.

Parameter	Sample Matrix	Samples [Number, Arrival Date]	Expected Range of Results	Reporting Limit	Method
BFRs	Fish Tissue	44, December, 2014	<0.2-1,000 ng/g	0.2 ng/g ww	HRMS; isotopic dilution
CPs	Fish Tissue	44, December, 2014	<5-2,000 ng/g	5 ng/g ww	GC/MS
HBCD	Fish Tissue	44, December, 2014	<1-2,000 ng/g	1 ng/g ww	LC-MS/MS; isotopic dilution
lipids	Fish Tissue	44, December, 2014	0.1 - 20%	0.10%	Gravimetric

HRMS = high resolution gas chromatography – mass spectrometry

LC-MS/MS = liquid chromatography – tandem mass spectrometry

GC/MS = gas chromatography – mass spectrometry

9.3 Sample preparation method(s)

Fish samples will be processed 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. Fillet tissue will be homogenized three times through a KitchenAid® blender attachment before placing in the appropriate sample container.

After fillets are removed, the sex of the fish will be determined (when possible) and recorded. Otoliths and scales will be removed from fish and sent to WDFW biologists to determine age.

9.4 Special method requirements

Many of the methods for emerging contaminants have been recently developed. The project manager will need to work closely with the contract laboratory and MEL's QA officer to ensure that the methods used meet the needs of this study.

9.5 Lab(s) accredited for method(s)

The laboratory awarded the contract for analysis of brominated flame retardants will need to be accredited for EPA Method 1614. No accreditation exists for analysis of CPs or HBCD. A laboratory accreditation waiver will be obtained for the analyses.

10.0 Quality Control (QC) Procedures

10.1 Table of field and laboratory QC required

Table 12. Field and Laboratory QC Procedures.

Parameter	Matrix	Field		Laboratory				
		Blanks	Replicates	LCS	Matrix Spikes/Matrix Spike Dup.	Method Blanks	Analytical Duplicates	Surrogates
BFRs	Fish Tissue	n/a	n/a	1/batch	n/a	1/batch	1/batch	each sample
CPS	Fish Tissue	n/a	n/a	1/batch	1/batch	1/batch	1/batch	n/a
HBCD	Fish Tissue	n/a	n/a	1/batch	n/a	1/batch	1/batch	each sample
lipids	Fish Tissue	n/a	n/a	1/batch	n/a	1/batch	1/batch	n/a

Batch = 20 samples or fewer.

10.2 Corrective action processes

The project manager will work closely with the contract laboratory and the MEL QA Officer conducting the data 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 Data Management Procedures

11.1 Data recording/reporting requirements

All field data and observations will be recorded in notebooks on waterproof paper. 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.

Field and laboratory data for the project will be entered into Ecology's EIM system. 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

The contract laboratory will deliver a Tier 4 Level data package to MEL with all raw laboratory data. 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

MEL will deliver case narratives in PDF format, and electronic data deliverables in an Excel spreadsheet format, to the project manager via email.

11.4 Acceptance criteria for existing data

Not applicable. This project will not be using existing data.

11.5 EIM/STORET data upload procedures

All result transmittals from laboratories must be provided in an electronic data deliverable (EDD) format that meets Ecology requirements for loading to Ecology's Information Management (EIM) database. Data will be uploaded to Ecology EIM database following internal procedures.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of 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 report

A draft report of the study findings will be completed by the principal investigator in July 2015 and a final report in October 2015. The report will include, at a minimum, the following:

- Map showing all sampling locations and any other pertinent features of the study area.
- Coordinates of each sampling site.
- 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.
- Results of the toxic contaminants relative to other studies.
- Recommendations for follow-up actions, based on study results.
- Complete set of chemical and physical data in the Appendix.

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

See section 5.1.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field data verification is not necessary for this project.

13.2 Lab data verification

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. Data packages will be assessed by MEL's QA Officer using the EPA Functional Guidelines for Organic Data Review.

MEL staff will provide a written report 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 principal investigator is responsible for the final acceptance of the project data. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be 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.

13.3 Validation requirements, if necessary

Independent data validation will not be required.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

After the project data have been reviewed and verified, the principal investigator 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 Data analysis and presentation methods

A summary of the data will be presented in the final report. No statistical analysis is planned for this data. See Section 12.3 for how the data will be presented.

14.3 Treatment of non-detects

Laboratory data will be reported down to the reporting limit, with an associated "U" or "UJ" qualifier for non-detects. Statistical tests requiring substitution for non-detects will not be included in the published report.

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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Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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

Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
GIS	Geographic Information System software
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedures

Units of Measurement

ng/g nanograms per gram (parts per billion)

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 is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

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

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

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

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

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

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

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

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

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

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

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

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of

an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split Sample: The term split sample denotes when a discrete sample is further 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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