

# **Quality Assurance Project Plan**

# Freshwater Fish Contaminant Monitoring Program



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### **Publication Information**

Each study conducted by the Washington State Department of 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.

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## **Author and Contact Information**

Keith Seiders and Patti Sandvik P.O. Box 47600 Environmental Assessment Program Washington State Department of Ecology Olympia, WA 98504-7710

Publications Coordinator: Phone: 360-407-6764

Washington State Department of Ecology - ecology.wa.gov

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

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## Freshwater Fish Contaminant Monitoring Program

April 2020

#### Approved by:

Signature:	Date:
Jessica Archer, Client and Author's Section Manager, Statewide Coordination	
Section, EAP	
Signature:	Date:
Annette Hoffmann, EAP Program Manager, Client's Supervisor	
Signature:	Date:
Keith Seiders, Author / Project Manager, EAP	
Signature:	Date:
Patti Sandvik, Co-author / Field Lead, EAP	
Signature:	Date:
Jim Medlen, Author's Unit Supervisor, EAP	
Signature:	Date:
Alan Rue, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date:
Arati Kaza, Quality Assurance Officer, EAP	

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

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## 2.0 Abstract

The Washington Department of Ecology (Ecology) has many efforts underway to address concerns about toxic chemicals in the environment. Many of these chemicals are persistent, bioaccumulative, and toxic substances (PBTs). While environmental monitoring for these chemicals is conducted by different groups to meet varied needs, most of the monitoring of freshwater fish tissue in Washington has been conducted by Ecology's Environmental Assessment Program.

Data from fish contaminant monitoring are used for a variety of purposes, such as: assessing the quality of waterbodies, conducting health risk assessments for fish consumption advisories, developing Total Maximum Daily Loads, and evaluating contaminant trends over time.

Since 2001, the Freshwater Fish Contaminant Monitoring Program has characterized PBTs in freshwater fish throughout Washington. Over 930 fish tissue samples from 180 sites have been analyzed. Target analytes included mercury, polychlorinated biphenyls (PCBs), dioxins and furans, chlorinated pesticides, and polybrominated diphenyl ether (PBDE) flame-retardants.

The goals of this program are to:

- Conduct exploratory monitoring to characterize the extent of toxics contamination in freshwater fish tissue from areas that have not been sampled or where relevant data are greater than ten years old.
- Conduct long-term trend monitoring of toxic contaminants in freshwater fish tissue in selected areas in order to track changes over time.

These goals will be met by sampling fish from selected areas and characterizing their contaminant concentrations in the contexts of statewide findings, water quality standards and related thresholds, and temporal and spatial trends for the sampled area.

This document is a revision of the 2013 Programmatic Quality Assurance Project Plan and describes the framework for monitoring freshwater fish in the coming years. Addenda to this plan will be produced annually to address site-specific objectives for the coming sampling season. This programmatic QAPP will undergo mandatory revision every 5 years.

# 3.0 Background

### 3.1 Introduction and problem statement

Monitoring efforts since the 1980s have found a variety of chemicals in Washington's air, soil, water, sediment, and fish. Many of these chemicals are persistent, bioaccumulative, and toxic substances (PBTs). Monitoring water, sediment, and fish are key activities that help address threats from toxic chemicals. Contaminants in fish tissue in Washington have been the subject of numerous studies by Ecology and other groups. These efforts have advanced the knowledge of contaminants in fish tissue statewide and led to numerous fish consumption advisories and actions to address sources of pollution.

Exposure to contaminants can have a variety of health effects on humans and wildlife, such as reproductive abnormalities, neurological problems, and behavioral changes. A primary route of exposure for people is through the consumption of contaminated fish. The Washington State Department of Health (Health) currently has a statewide fish consumption advisory (FCA) for mercury in bass and northern pikeminnow. There are also numerous site-specific advisories due to contamination of various species of fish due to other chemicals, mainly mercury, PCBs, pesticides, and dioxins/furans.

More information about the benefits and risks of eating fish from these sites is at <u>www.doh.wa.gov/CommunityandEnvironment/Food/Fish.aspx</u>. Because of the great interest in the public health risks, Ecology' long-term monitoring provides critical information for resource managers and the public regarding the status of contamination in fish at targeted waterbodies.

Since 2001, Ecology's Freshwater Fish Contaminant Monitoring Program (FFCMP) has characterized PBTs in freshwater fish statewide with analyses of over 930 fish tissue samples from more than 180 sites. The FFCMP has two broad goals:

- Exploratory monitoring to characterize the extent of contamination in areas where data are limited or non-existent.
- Long-term trend monitoring to track changes over time and which may be used to determine the effectiveness of watershed cleanup efforts.

Results from fish contaminant monitoring are used for a variety of purposes, such as water quality assessments, health risk assessments, determining total maximum daily load (TMDL) effectiveness, and evaluating spatial and temporal trends. For example, FFCMP data has led to FCAs or FCA revisions in watersheds such as the Spokane River, middle Columbia River, Wenatchee River, Snake River, Lake Washington, and Green Lake.

Target analytes for the FFCMP are most often mercury, polychlorinated biphenyls (PCBs), chlorinated pesticides (CPs), such as dichloro-diphenyl-trichloroethane (DDT) and its breakdown products (DDD and DDE), polybrominated diphenyl ethers (PBDEs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Other chemicals identified through the Washington State's "PBT Rule" (Chapter 173-333 WAC, effective 2006) may be added to the list of target analytes in some cases. Such cases would be where sites and species are appropriate for a given chemical. For example, work from the PBT Monitoring Program () recommended sampling for per- and poly-fluoroalkyl substances (PFAS) in fish tissue from urban waterbodies where the potential for contamination is higher than in other waterbodies (Mathieu and McCall, 2016).

This document is a revision of the five-year programmatic Quality Assurance Project Plan for the FFCMP (Seiders, 2013) and follows Ecology's guidance for developing such plans (Lombard and Kirchmer, 2004). Significant revisions include more details as required by a new template for this document and the addition of new sites for the Long Term monitoring component. This plan describes the project in general terms while addendums will be developed each year to describe that year's specific goals and sampling strategy.

### 3.2 Study area and surroundings

The study area encompasses all freshwater environments that support fish in the state of Washington. Figure 1 shows Washington and its natural features as seen from space. Prominent features include the Cascade Mountain range running north to south in the center of the state; the Olympic Mountains and Coast Ranges in the west, the Blue Mountains in the southeast, and the Okanogan Highlands in the northeast. Puget Sound gives the Puget Lowlands a mild maritime climate. The east side of the Cascade Mountains is generally an arid climate. The Central Columbia Plateau to the east of the Cascade Mountains has extensive irrigation systems which supports an important agricultural industry. The Puget Lowlands are heavily urbanized and support various industries.

Land use is predominantly forestry and agricultural/rural. Federal and tribal lands accounts for about 28% of land area. Major land uses and percentages of land area, derived from the 2015 Natural Resources Inventory (USDA, 2015) are shown in Table 1.

Land Use	Area (mi²)	% of Total
Forest	34,872	49%
Agricultural and Rural	26,688	37%
Developed	5,488	8%
Water	2,465	3%
Other	1,875	3%
TOTAL	71,388	100%

Table 1. Major land uses in Washington State.

Washington's lakes, reservoirs, rivers, and streams support over 90 species of freshwater fish. About 55% of these species are native to the state, while the other 45% have been introduced since the arrival of Europeans (Wydoski and Whitney, 2003). Marine and freshwater fish have been a key food source of indigenous peoples for thousands of years. More recently, fish have also become important to commercial and recreational sectors of Washington's economy.

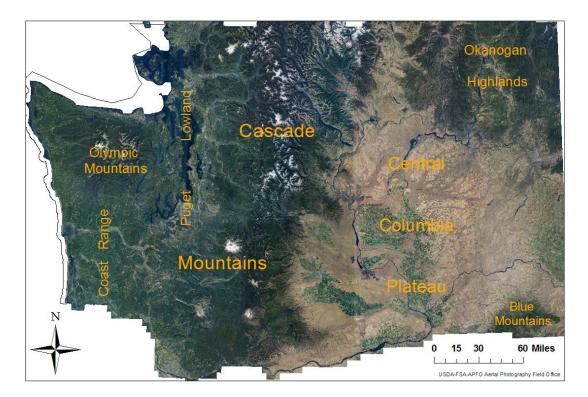


Figure 1. Map of larger study area.

#### 3.2.1 History of study area

Fish are important to the cultural identity of many who reside in Washington. Fish are seen as symbols and an indicator of the health of Washington's environment. The increasing population of Washington and its expanding urban, rural, agriculture, irrigation, industrial, and transportation systems over the past two centuries have impacted the integrity and health of aquatic systems. Many of the chemicals our current society uses ultimately end up in waterbodies where fish can accumulate them.

Past monitoring efforts have found multiple contaminants in Washington's fish. Elevated levels of some chemicals in fish have led to many waterbodies being placed on the Clean Water Act Section 303(d) list as "impaired," or not meeting their designated use for fishing. Table 2 shows the number of waterbody impairments from Ecology's most recent Water Quality Assessment due to specific contaminants that have water quality standards (Ecology, 2012). The 374 impairments in the Category 5 group occur in 179 waterbodies while the 74 impairments in the Category 4A group occur in 38 waterbodies.

The Washington State Department of Health (Health) also reviews fish contaminant data and issues Fish Consumption Advisories in waters where contaminant concentrations in fish exceed certain thresholds. Because Ecology and Health use different methods for assessing risks to human health (Appendix A), there are more impaired waterbodies than those described in Table 2. Health has 112 species- and chemical-specific advisories in place for freshwater sites in Washington (McBride, 2018). Most of these are for mercury, PCBs, DDTs, and dioxins/furans. There is also a statewide fish consumption advisory for mercury in bass and northern pikeminnow.

Parameter	# WQA Category 5	# WQA Category 4A	Total # Impaired Waterbodies	% of total
PCBs	142	12	154	34.3%
4,4'-DDE	56	15	71	15.8%
Dieldrin	36	9	45	10.0%
Toxaphene	17	2	19	4.2%
Chlordane	14	3	17	3.8%
4,4'-DDD	11	5	16	3.6%
4,4'-DDT	10	5	15	3.3%
НСВ	7	2	9	2.0%
DDT (and metabolites)	2	3	5	1.1%
Alpha-BHC	4		4	0.9%
Aldrin	3		3	0.7%
Heptachlor epoxide		2	2	0.4%
2,3,7,8-TCDD (dioxin)	56	17	73	16.3%
Mercury	15		15	3.3%
Arsenic, inorganic	1		1	0.2%
Total Impairments	374	75	449	100%

Table 2. Number of waterbody impairments because of toxic contaminants in fish.

Category 5: the waterbody is impaired and has no approved cleanup plan. Category 4A: the waterbody is impaired and has an approved cleanup plan to locate and reduce the sources of contaminants, such as a TMDL.

#### 3.2.2 Summary of previous studies and existing data

Since the 1980's, Ecology has conducted over 100 studies related to toxic contaminants in freshwater fish tissue from Washington State. Other studies of this nature have been conducted by EPA, USGS, U.S. Department of Energy, Health, tribes, and local governments. Additional studies have also focused on toxics in different matrices, such as water, sediment, osprey tissue, aquatic macroinvertebrates and periphyton. The results from these studies have helped to address specific questions, to characterize the magnitude and extent of contamination, and have informed decisions to pursue cleanup actions like TMDLs and Chemical Action Plans (CAPs).

Figure 2 presents the majority of locations where fish tissue has been sampled in Washington. These locations were taken from Ecology's EIM database, which contains results from a large majority of freshwater fish tissue studies conducted in Washington since the 1980s.

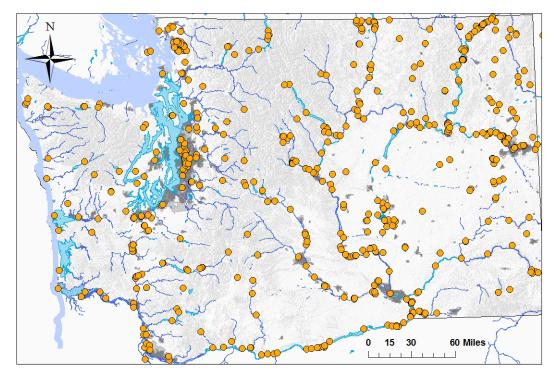


Figure 2. Location of freshwater fish monitoring efforts in Washington, 1984-2018.

Cumulatively, these studies show that the most common contaminants analyzed in fish tissue that have the greatest potential for harm to humans and wildlife are mercury, PCBs, DDTs, PCDD/Fs, and PBDEs. Results from the FFCMP for commonly detected contaminants are summarized with dot plots in Figures 3-7.

These dot plots for mercury, PCBs, DDE, PBDEs, and TCDD-TEQ (Figures 3-7) show concentrations found in fillet tissue between 2001 and 2016 (2017 and 2018 results not yet available). Each dot is the result value from a single composite sample or the mean of field replicate composite samples. Multiple species are represented at some sites such that multiple dots are shown at the same location. In general, the smaller green dots represent lower concentrations and lower health risk. The medium-sized pink dots show elevated concentrations that are of concern. The largest red dots indicate higher concentrations and a higher risk of adverse health effects from consuming contaminated fish.

The values bracketing the different sizes and colors of dots selected in these figures are a mix of thresholds used for protecting human health as described later in Section 3.2.4. A mix of thresholds was used because no single set of thresholds address all contaminants. These thresholds are from:

- Health's FCA Screening Levels for two different consumption rates (McBride, 2018).
- Ecology's thresholds used in narrative criteria of the water quality standards (Ecology, 2018).
- EPA's Screening Values for carcinogenic and non-carcinogenic effects at two different consumption rates (EPA, 2000).

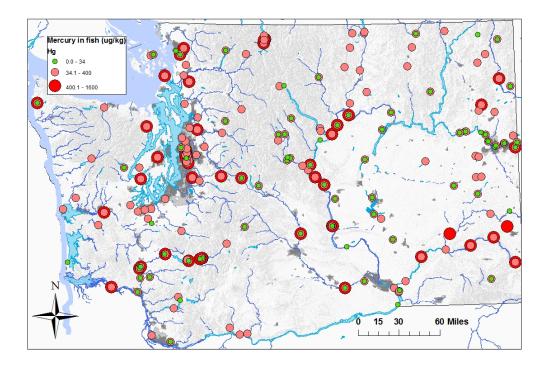


Figure 3. Dot plot for mercury in fillet tissue, FFCMP 2001-2016.

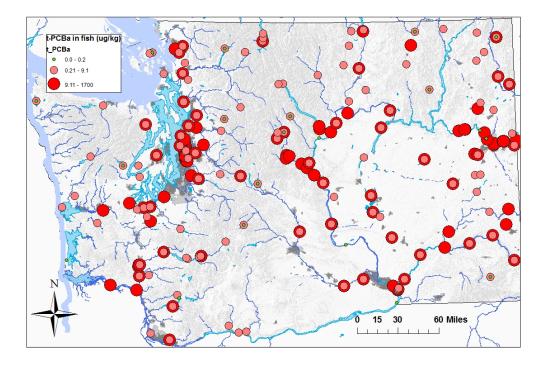


Figure 4. Dot plot for total PCBs in fillet tissue, FFCMP 2001-2016.

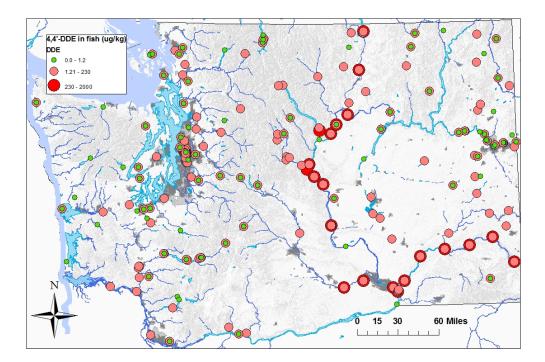


Figure 5. Dot plot for 4,4'-DDE in fillet tissue, FFCMP 2001-2016.

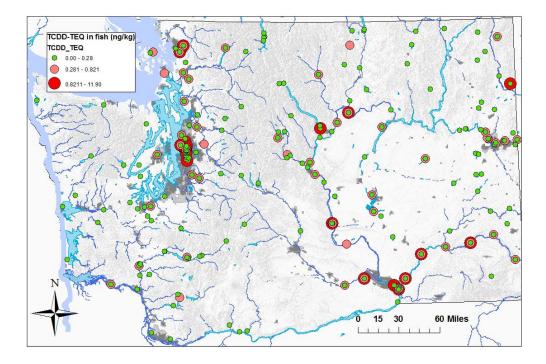


Figure 6. Dot plot for dioxins/furans as TCDD-TEQ in fillet tissue, FFCMP 2001-2016.

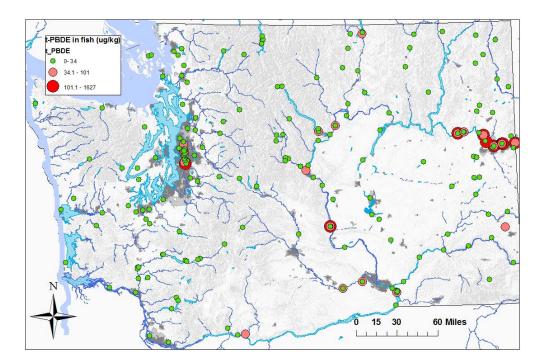


Figure 7. Dot plot for total PBDEs in fillet tissue, FFCMP 2001-2016.

#### **3.2.3** Parameters of interest and potential sources

The environmental pollutants of interest are persistent, bioaccumulative, and toxic substances (PBTs) found in fish throughout Washington. Many of these pollutants are also on the state's "PBT list" (WAC 173-333-310) and described in Washington's PBT rule (WAC 173-333). The main target pollutants for the FFCMP are:

- Mercury.
- Polychlorinated biphenyls (PCBs).
- Chlorinated pesticides (CPs), such as dichloro-diphenyl-trichloroethane (DDT) and its breakdown products (DDD and DDE).
- Polybrominated diphenyl ethers (PBDEs).
- Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs).

These pollutants are summarized below. More information about these and other chemicals is available from the Agency for Toxic Substances and Disease Registry (ATSDR) and other sources.

Secondary pollutants may be incorporated into this program as priorities and capacity dictate. These pollutants would include emerging chemicals of concern such as:

- Per- and poly-fluoroalkyl substances (PFAS): used in water and stain resistant products as well as fire-fighting foams.
- Nonylphenol ethoxylates (NPEs): in widely used surfactants.
- Hexabromocyclododecane (HBCD): a class of flame retardants.
- Pharmaceuticals and personal care products (PPCPs): many consumer products.

#### Mercury

Mercury is widespread in the environment, being released to the atmosphere from varied sources and transported globally. Mercury readily volatilizes, such that 95% of atmospheric mercury is in the elemental form. Natural sources of mercury include weathering of mercury-bearing rocks and soil, volcanic activity, forest fires, and degassing from water surfaces. Anthropogenic sources include combustion of fossil fuels, metal production, and industrial processes. Lake sediment records show that atmospheric mercury has tripled over the last 150 years, suggesting that two thirds of atmospheric mercury is of anthropogenic origin (Morel et al., 1998). Mercury returns to earth mainly via precipitation, settling in waters and land surfaces, and cycling through these environments.

Mercury cycling in freshwater systems is complex. In water, mercury may bind to chloride, sulfide, and organic acids. Methylmercury is the organic form that is bioaccumulated, accounting for 95 - 100% of the mercury found in fish (Bloom, 1995). Methylation of mercury is believed to occur mainly in anoxic environments with sulfate-reducing bacteria playing an important role, particularly at the sediment-water interface in lakes (Morel et al., 1998; Driscoll et al., 1994).

Riparian wetland processes may also be important contributors of methylmercury to some lakes (Watras et al., 1995).

Microbial uptake of mercury is a key step in its methylation and bioaccumulation. The accumulation of mercury in larger organisms is due mainly from consumption of mercury-containing prey. Methylmercury in fish is found mainly in muscle tissue rather than being associated with lipids as many other contaminants are. Bioaccumulation increases with the number of trophic levels in the food web, generally resulting in higher levels of methylmercury in top predators (Morel et al., 1998).

In humans, mercury primarily affects the nervous system, particularly in developing fetuses and children (EPA, 2000). Concern with these health risks resulted in the 2002 state Legislature directing Ecology and Health to develop a plan targeting mercury as the first priority pollutant in the state's Strategy to Continually Reduce Persistent, Bioaccumulative Toxins (PBTs) in Washington State (Gallagher, 2000). The Washington State Mercury Chemical Action Plan (Peele, 2003) identifies sources of mercury in Washington, current institutional structures related to mercury, and strategies for reducing mercury in the environment.

The Chemical Action Plan (Peele, 2003) also called for monitoring mercury concentrations in fish. In 2005, the *Measuring Mercury Trends in Freshwater Fish in Washington State* program began. This companion monitoring program aims to measure temporal trends in mercury and learn about its behavior in Washington's waters. The most recent report from this program summarizes findings from sampling six sites in 2005, 2010, and 2015 (Mathieu, 2017).

#### PCBs

PCBs are a group of 209 synthetic chemicals whose production in the United States was virtually banned in 1979 due to their toxicity and persistence in the environment. PCBs were manufactured in complex mixtures to attain desirable properties for varied applications — such as fire-retarding properties for lubricating and electrical transformer oils. These mixtures were manufactured under many names, the most common being the "Aroclor" series.

The major source of PCBs in the environment is from historical manufacturing, storage, use, and disposal practices. Throughout the world, PCBs are found in air, soil, waters, and biota. PCBs have low solubility in water yet have a high affinity for sediments and animal fats; they readily bioaccumulate in the aquatic food chain (EPA, 1999).

A broad range of adverse health effects have been associated with exposure to PCBs. These include toxic effects on the nervous, endocrine, digestive, immune, and reproductive systems. PCBs are classified as a probable human carcinogen by the EPA.

Concern with these health risks led Ecology and Health to develop a Chemical Action Plan for PCBs. Washington's PCB Chemical Action Plan (Davies, 2015) identifies sources of PCBs in

Washington, current institutional structures related to PCBs, and strategies for reducing PCBs in the environment.

#### **Chlorinated Pesticides**

Chlorinated pesticides have been used for decades as insecticides in agricultural and home environments. These compounds have low solubility in water and are not readily metabolized or excreted. They are readily stored in fat tissue and biomagnify to high concentrations in the food web.

Many are neurotoxins and are suspected or known carcinogens (EPA, 2000). Many of these compounds (e.g., DDT, chlordanes, and dieldrin) were banned from use in the United States during the 1970s and 1980s as their hazards became evident. Due to their high persistence, chlorinated pesticides continue to be found in fish and wildlife throughout the world.

Many watersheds with historical and current agricultural land use have elevated levels of chlorinated pesticides in their soils and waterbodies. Ecology has developed TMDLs to address these problems in the Yakima River, Mission Creek, Lake Chelan, Okanogan River, Palouse River, and the Walla Walla River.

#### **PBDEs**

Polybrominated diphenyl ethers (PBDEs) are a group of chemicals used as flame retardants in electronics, plastics, building materials, and textiles. There are 209 theoretically possible congeners of PBDEs. Like PCBs, PBDEs are resistant to physical, chemical, and biologic degradation. The little data available suggests that PBDEs are transported and distributed in the global environment similarly to PCBs. The PBDEs are lipophilic (have an affinity to fat) and some appear to bioaccumulate in aquatic environments.

Information on the possible health impacts of PBDEs comes from animal toxicity studies. These studies indicate that PBDEs are associated with developmental neurotoxicity, thyroid hormone disruption, reproductive effects, and liver changes (Darnerud et al., 2001; Birnbaum et al., 2004). Recent studies estimate diet as the main route of exposure to PBDEs for the general public (Harrad et al., 2004).

Due to limited research on the possible consumer health risk from PBDEs, concern remains about the effects of these compounds on humans and biota. PBDEs were the focus of Washington's second Chemical Action Plan (Ecology et al., 2006) to be developed under the state's PBT Initiative (Gallagher, 2000). Currently, Washington has no water quality standards for PBDEs for the protection of human health or wildlife.

#### PCDD/Fs

Dioxins and furans, commonly used terms for PCDD/Fs, are unintended byproducts of combustion processes, chlorine bleaching in paper production, and contaminants in some chlorinated pesticides. Like PCBs, they are highly persistent and widely distributed in the environment. Adverse health effects have been associated with the digestive, endocrine, immune, nervous, and reproductive systems. The dioxin compound, or congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is the most potent animal carcinogen EPA has evaluated and is a probable human carcinogen (ATSDR, 1998). There are 17 PCDD/F toxic congeners and they have different levels of toxicity compared to 2,3,7,8-TCDD, the most toxic form.

To assess the cumulative risks to human and environmental health, PCDD/F concentrations are expressed as "Toxic Equivalents" (TEQs). The TEQ is calculated by multiplying each congener result by its congener-specific Toxicity Equivalent Factor (TEF) and then summing to obtain the overall TEQ. Various TEFs have been developed over time as a result of research into the toxicity of individual congeners. The 2005 World Health Organization TEFs are used in summarizing results for the FFCMP and Ecology's Water Quality Assessment process, because they are based on more recent research and are internationally accepted. These TEFs are described by Van den Berg et al. (2006).

#### **Mixtures of Chemicals**

The common occurrence of these and other chemicals in fish raises concerns about the health effects from mixtures of chemicals. Many chemicals have similar mechanisms for toxicity, so there are possible additive or synergistic effects. The ATSDR evaluated possible associations between health effects and mixtures of five chemicals commonly found in fish (2,3,7,8-TCDD, HCB, 4,4'-DDE, MeHg, and PCBs). They developed profiles with the purpose to:

- Evaluate data on health hazards, and their dose-response relationships, from oral exposure to this five-component mixture.
- Evaluate data on the joint toxic actions of components of this mixture.
- Make recommendations for exposure-based assessments of the potential impact of joint toxic action of the mixture on public health.

Table 3 from the ATSDR (2004) shows common health effects across different chemicals, the same chemicals that are often found in fish together.

Chemicals of concern <sup>a</sup>	2,3,7,8 -TCDD	HCB °	4,4' -DDE	Methyl mercury	PCBs
Wasting syndrome	x	x			x
Kidney damage				x	
Liver damage	x	Xp	x <sup>b</sup>		
Immunosuppression	xb	х	х	x	xb
Thyroid hormone disruption	x	x			х
Female reproductive organ disruption	x	Xp		x	х
Male reproductive organ disruption	x		x	x	x
Neurological impairment	x	х	х	x	x
Altered neurological development (pre- and/or post-natal)	xb	Xp	Xc	Xp	Xp
Altered female reproductive organ development	x				х
Altered male reproductive organ development	x		xb		х
Other developmental effects (malformations or fetotoxicity)	x	x	х	x	х
Cancer <sup>d</sup>	x	x	х	x	x

#### Table 3. Health effects observed in humans or animals after oral exposure to five chemicals.

a - Upper case and **bolded X** indicates that effects have been observed in humans. Lower case and nonbolded x indicates that effects have been observed only in animals.

b - Indicates that these are the most sensitive noncancer health effects from oral exposure (i.e., they occur at lower dose levels than other noncancer effects).

c - No data are available for p,p'-DDE effects on this endpoint, but altered neurobehavior was observed in adult rats following exposure to single oral doses of 0.5 mg p,p'-DDT/kg on postnatal day 10 (Eriksson et al., 1990, 1992 as cited in ATSDR, 2004).

d - Carcinogenic responses have been demonstrated in animals exposed to each of the chemicals. EPA has derived oral slope factors for humans exposed to 2,3,7,8-TCDD, hexachlorobenzene, p,p'-DDE, and PCBs based on tumor responses in animals (see Appendices A, B, C, and E in ATSDR, 2004). EPA did not derive a slope factor for humans exposed to methylmercury based on evidence that effects on the nervous system and its development would occur at exposure levels much lower than those necessary to produce cancer (see Appendix D in ATSDR, 2004).

e - HCB - Hexachlorobenzene (a chlorinated pesticide).

#### 3.2.4 Regulatory criteria or standards

Various fish tissue contaminant concentration thresholds for the protection of human health exist because of evolving knowledge about the toxic effects of chemicals and society's responses to estimate risks and protect consumers of fish. These thresholds are often based on various assumptions used in determining risk, such as daily consumption rates, toxicological data used in calculations, and risk levels. Thresholds that are relevant in the state of Washington are described below. These are:

- Washington's water quality standards.
- Washington Department of Health screening levels.
- EPA's fish tissue screening values.

#### Washington's Water Quality Standards

Washington's water quality standards protect the health of people, fish, shellfish, and wildlife and were revised in October 2017 (Ecology, 2017). These standards are codified in Washington Administration Code Chapter 173-201A.

The water quality standards "consist of water quality criteria, designated uses, and antidegradation components. The water quality standards represent the chemical, physical, and biological conditions necessary to support the state designated uses of a waterbody." (Ecology, 2018). Ecology's Water Quality Program Policy 1-11 describes the methodologies for using environmental data to assess the health of surface waters by determining whether water quality standards are met (Ecology, 2018). For toxic substances, Washington's water quality standards employ both numeric and narrative criteria for both marine and fresh water.

Numeric criteria are based on data and scientific assessment of adverse effects from specific chemicals or conditions. A typical numeric criterion for protecting aquatic life usually contains a concentration and averaging period. For example, the aquatic life chronic criterion for cyanide is 5.2 ug/L as a 4-day average concentration. The numeric criteria found in WAC 173-201A-240 (Ecology, 2017) were developed to protect both aquatic life and human health from toxic chemicals at given concentrations in the water column (ug/L). An exception is for methylmercury (MeHg), which is expressed as a fish tissue concentration (30 ug/kg, or 0.03 mg/kg).

Narrative criteria are statements that describe the desired water quality goal, such as waters being "free from" pollutants like oil and other substances or conditions that can harm people or aquatic life. These criteria protect water bodies from pollutants for which numeric criteria are difficult to specify. Narrative criteria for toxic substances are rooted in WAC 173-201A-260(2)(a), which protects existing and designated uses for fresh and marine water (Ecology, 2017):

(2) Toxics and aesthetics criteria. The following narrative criteria apply to all existing and designated uses for fresh and marine water:

(a) Toxic, radioactive, or deleterious material concentrations must be below those which have the potential, either singularly or cumulatively, to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent upon those waters, or adversely affect public health (see WAC 173-201A-240, toxic substances, and 173-201A-250, radioactive substances).

The narrative criteria for toxic pollutants are also described in Ecology's WQP Policy 1-11, Section 1E, which states that "Ecology will consider the assessment of narrative criteria that demonstrates the impairment of a designated use:

Assessment of Studies to Determine Impairment based on Narrative Standards

Parts 2 and 3 of this policy describe the methodology for assessing specific water and sediment quality parameters. Most of the parameter sections focus on evaluations based on numeric criteria. However, Ecology also evaluates the attainment of designated uses based on narrative criteria. For example, narrative criteria are applied for the bioassessment parameter (to protect aquatic life uses), and for human health toxics parameters (to protect fish and shellfish harvesting and domestic water supply uses). Ecology may use narrative criteria in conjunction with numeric criteria as described in the parameter sections."

The narrative criteria incorporate factors, such as a chemical-specific tissue exposure concentration (TEC) and environmental data requirements (e.g., sample size, species and tissue types analyzed, and sample results), to help determine whether the designated use of fish and shellfish harvest is supported in a waterbody.

#### **Tissue Exposure Concentration (TEC)**

The TEC is a tissue concentration that Ecology developed to represent exposure to a potentially harmful level of a pollutant through the consumption of fish or shellfish. The TEC was developed using parts of the EPA's human health criteria equations. When the concentration of a pollutant in composite samples of fish or shellfish is greater than a threshold related to the TEC, the designated use of harvest is considered impaired, indicating that the waterbody may not be meeting water quality standards for the State of Washington, and may be placed on the Clean Water Act 303(d) list.

Ecology's WQP Policy 1-11, Section 2I(2) describes this approach:

Assessment of harvest use support will rely upon tissue exposure concentrations (TEC) for pollutants. The TECs are rooted in the human health criteria equations, but expressed as a tissue consumption exposure threshold. They do not represent a water quality criteria because they have not been adopted into Chapter 173-201A WAC, except for methylmercury. TEC thresholds for carcinogenic and non-carcinogenic effects differ because the underlying assumptions associated with the two types of health effects are different.

- For chemicals that have non-carcinogenic effects (TECn): (Reference dose) x (Body weight) ÷ Fish consumption rate = TECn
- For chemicals that have a carcinogenic effect level (TECc): (Risk level) x (Body weight) ÷ (Cancer slope factor) x (Fish consumption rate) = TECc

The thresholds used to determine if the narrative water quality criteria are not met are unique to each chemical. For carcinogens, the threshold is ten times the TECc while for non-carcinogens, the threshold is the TECn. Ecology will determine that a waterbody is impaired (does not meet water quality standards) when the data meet either of the following conditions:

- "The median composite sample value(s) from one or more resident species exceeds the TECc by a factor of 10 or more. A minimum of 3 composite samples is required".
- "The median composite sample value(s) from one or more resident species exceeds the TECn. A minimum of 3 composite samples is required".

#### **Comparison to water quality standards**

This project will conduct preliminary assessments of sampling results to determine the likelihood of compliance with water quality standards. The results will be reviewed and reduced using methods in Policy 1-11 and its supporting documentation to determine whether water quality standards are met. The data reduction process essentially compares the median value of multiple composite samples from a sampling location, also termed an Assessment Unit (AU), to thresholds related to the TECs. Table 4 is an example using 2016 FFCMP results to show how data are reduced for preliminary water quality assessments. Sample results and related information are processed in a sequential manner to determine:

- 1. The site-specific median value for each species.
- 2. The number of samples used in calculating the median for each site/species pairing.
- 3. The number of samples used in medians which exceed the numeric or narrative criteria for the parameter for each site.
- 4. The likelihood that the site will/will not meet water quality standards for the parameter.

Ecology's Water Quality Program will make the final determination about compliance with standards during the formal Water Quality Assessment process which is conducted periodically.

More information about Ecology's Policy 1-11 is available at <u>https://ecology.wa.gov/Water-Shorelines/Water-quality/Water-improvement/Assessment-of-state-waters-303d/Assessment-policy-updates</u>

#### Fish Tissue Equivalent Concentration (FTEC)

The Fish Tissue Equivalent Concentrations (FTECs) were narrative criteria used by Ecology to determine whether water quality standards were being met during assessments prior to the 2018 revisions to Ecology's Water Quality Program Policy 1-11. Fish tissue contaminant concentrations that were lower than the contaminant-specific FTEC implied water quality standards were being met in the waterbody where fish samples were collected. Where concentrations were greater than the FTEC, the water body was considered to not meet standards and was placed on the 303(d) list.

The FTEC was calculated by multiplying the contaminant-specific bio-concentration factor (BCF) times the contaminant-specific water quality criterion found in the National Toxics Rule (NTR). For example, the water quality criterion in the NTR for PCBs was 0.00017 ug/L. The BCF for PCBs is 32,000. The resulting FTEC was 0.00017 ug/L x 32,500 = 5.3 ug/kg.

Washington's previous water quality standards for toxic contaminants were issued to the state by EPA through the 1992 National Toxics Rule (NTR) in 40 CFR 131.36 as described in the Federal Register Vol. 57 No. 246 pp. 60848, 1992, and Vol. 64 No. 216 pp. 61182 1999. The FTECs were narrative criteria derived from the NTR criteria. The BCFs for toxic pollutants were taken from EPA's Ambient Water Quality Criteria development documents from the early 1980's archived at <u>https://nepis.epa.gov</u>.

Nearly all fish tissue and toxics-related 303(d) listings and TMDLs were based on use of the FTEC approach. Results from FFCMP should be compared to the FTEC to help with the transition from use of the old standards and policy to the new standards and policy. The transition will take time, in order to update decisions based on older data with decisions based on newer data. Ecology's Rule Implementation Plan (Ecology, 2016) describes transition approaches for various situations regarding:

- Currently approved TMDLs: retain targets based on old standards (FTECs) but compare to new standards.
- The 303(d) list: retain listings based on old standards.
- TMDL effectiveness monitoring: base on monitoring strategy in the TMDL but also compare to new standards.

Site	Reach Code (AU)	Species	MEL Sample ID	# Fish in Sample	PCB Aroclor Result (μg/kg)	PCB Congener Result (μg/kg)	Median for Species (µg/kg)	Median Exceed 10x TECc (2.3 μg/kg)?	Median Exceed TECn (9.1 µg/kg)?	# Samples Used in Median for Species	# Samples Used in Medians from AU Which Are > 10xTECc	# Samples Used in Medians from AU Which Are > TECn	AU Likely to Meet Water Quality Standards?																
Caulta F		MWF	1701015-43	3	2.23 J	1.46	1.46	No	No	1			na Insufficient data																
Cowltz-F- Rndl-1	17080004005729	NPM	1701015-45	5	9.19 J	3.51	3.51	Yes	No	1	2	na																	
		RBT	1701015-48	5	7.82 J		7.82	Yes	No	1																			
Mar Cald	46122F5E4, 17080005000913		1701015-27	5	2.97 U	1.50			No																				la sufficient
Mayfield- F5E2		NPM	1701015-28	5	2.99 U	1.79	1.66	No		3	na	na	Insufficient data																
			1701015-26	5	3 U	1.66																							
	17080005000220	СТТ	1701015-08	5	10	8.24	8.24	Yes	No	1																			
Cowlitz-F		MWF	1701015-17	3	9.6 J	5.00	7.48	Yes	No	2	4	1	No																
COWIICZ-F	17080003000220	IVIVVF	1701015-14	5	18.51 J	9.96	7.40	785	NO	2	4																		
		NPM	1701015-20	3	49.3 J	24.71	24.71	Yes	Yes	1																			
			1701015-06	5	11.18 J	8.28																							
Cowltz-F-	17080005000069	MWF	1701015-04	5	27 J	18.27	8.28	Yes	No	3	4	1	No																
CasRk	1708000300009		1701015-05	5	7.13 J	7.38					4																		
		NPM	1701015-07	5	39.7 J	23.53	23.53	Yes	Yes	1																			

Species Codes:

CTT: Cutthroat trout

LMB: Largemouth bass

MWF: Mountain whitefish

NPM: Northern pikeminnow

RBT: Rainbow trout.

Italicized result values are the ones used in calculating medians: PCB Aroclor data are used only if PCB congener data are not available.

#### Washington State Department of Health Screening Levels

The Washington Department of Health (Health) also developed Screening Levels (SLs) for the carcinogenic or non-carcinogenic effects of toxic substances to help determine whether contaminant concentrations are elevated and pose a potential health risk to the public. Sampling results that show fish tissue contaminant levels higher than these SLs may lead to Fish Consumption Advisories for a specific site and species (McBride, 2018).

Health calculates two SLs in order to address risks to the general public and risks to populations who eat larger amounts of fish. Two different fish consumption rates are used, and these consumption rates are expressed in both grams per day (g/d) and meals per month. The daily consumption rate is used in risk assessment equations, whereas the meals-per-month expression is determining meal limits for communicating risks to the public. The lower consumption rate of 59.7 g/d corresponds to eight meals per month and is used for assessing risks to the general public. The higher consumption rate of 175 g/day corresponds to 23 meals per month and is more characteristic of high consuming populations.

Ecology and Health evaluate fish tissue data a bit differently in order to address different needs. Appendix A describes these approaches in more detail.

More information about the health benefits of eating fish and fish consumption advisories in Washington are at: <a href="http://www.doh.wa.gov/CommunityandEnvironment/Food/Fish">www.doh.wa.gov/CommunityandEnvironment/Food/Fish</a>.

#### **EPA Screening Values**

In 1988, the EPA and the American Fisheries Society identified the need for standard approaches to evaluating risks and developing fish consumption advisories for the public. EPA then developed guidance to help state, local, regional, and tribal jurisdictions address the problems of contaminated fish, using more comparable ways than were being practiced. The resulting documents were volumes 1 - 4 of "Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories" (EPA, 2000).

While the guidance provides standardized approaches, flexibility is provided so that risk assessors can incorporate circumstances that are unique to their jurisdictions. The guidance is neither prescriptive nor regulatory in nature. Both Ecology and Health reference EPA's guidance in their development of thresholds to protect human health.

For jurisdictions that choose not to conduct their own risk assessments, the guidance developed Screening Values for carcinogenic and non-carcinogenic effects of substances that could be used to help prioritize areas that may present risks to humans from fish consumption. A Screening Value (SV) is the concentration of a chemical in fish tissue that constitutes a potential public health concern; this concentration can be used as a threshold value for comparing results from fish that were collected from the environment. The SVs were developed for two broad groups having different fish consumption rates: Recreational Fishers and Subsistence Fishers.

The SVs were developed using EPA-recommended risk-based methods, the approach also used by EPA in developing water quality criteria (EPA 2000). The risk assessment process for any chemical uses information about the hazard, dose-response, exposure, and risk characterization. Risk-based SVs were derived from general models which incorporate the factors relevant to assessing risks.

#### Fish Tissue Thresholds and Risk Assessment Inputs

Table 5 shows Washington's Policy 1-11 tissue exposure concentrations, or TECs, along with Health's and EPA's threshold values for contaminants frequently detected in fish across Washington.

Approaches for addressing several contaminants differ among Ecology, Health, and EPA. As seen in Table 5, Health has Screening Levels for PBDEs, whereas Ecology and EPA have not yet adopted protections for this group of chemicals. For PCDD/Fs, Ecology uses the single congener TCDD (tetrachlorodibenzo-p-dioxin) for evaluating risks, while Health and EPA use the dioxin/furan Toxic Equivalent (TCDD-TEQ) value. Another difference is for the pesticide DDT and its breakdown products: Ecology and Health use three individual isomers (DDD, DDE, and DDT), while EPA uses the sum of all DDT analogs and breakdown products. Health will also use the sum of analogs when they are available.

Table 6 shows the key inputs into risk assessment equations used by evaluators for protecting consumers of contaminated fish. Differences in several inputs are reasons why threshold values developed by Ecology, Health, and EPA are different. For example, Ecology and Health use a Risk Level of 10<sup>-6</sup> while the EPA SVs use a less protective Risk Level of 10<sup>-5</sup>. The Risk Level is an acceptance threshold which, for 10<sup>-6</sup>, means that an increased risk of harm in one in a million cases of exposure is acceptable. Ecology's TECs use a Body Weight of 80 kg, while Health and EPA use 70 kg. The Consumption Rates used also differ among the agencies. Of particular note is Ecology now uses a much higher Consumption Rate (175 g/d) than was used in the past (6.5 g/d).

## 3.3 Water quality impairment studies

While the FFCMP is not a formal water quality impairment study, data generated by the FFCMP will be used to determine whether sampled waterbodies are impaired. This determination will be made during Ecology's periodic Water Quality Assessment which uses all available data for the waterbody. Annual reports for the FFCMP will also determine whether water quality standards were met and summarize the likelihood of impairment based on the data collected during the FFCMP study.

Table 5. Thresholds used by Ecology, Health, and EPA for protecting human health from the most commonly detected contaminants in freshwater fish tissue.

Analyte	Risk		ogy's Thre used in rrative Cr	iteria	Screeni (2	alth's ng Levels 018)	EPA's Screening Values (2000)		
(ppb ww) <sup>1</sup>	Effect	TECn (2018)	10x TECc (2018)	Old FTEC (1996- 2016)	FCASL: Higher FCR	FCASL: Lower FCR	Subsistence Fishers	Recreational Fishers	
2,3,7,8-TCDD <sup>3</sup>	nc c	0.32		0.065	0.280	0.821			
2,3,7,8-TCDD TEQ <sup>3, 4</sup>	nc c	0.32			0.280	0.821	0.0315	0.256	
4,4'-DDD	nc c	230	19	44	1.7	4.9			
4,4'-DDE	nc c	230	27	32	1.2	3.4			
4,4'-DDT	nc c	230	13	32	200 1.2	586 3.4			
Total DDT <sup>5</sup>	nc c				200 1.2	586 3.4	245 14.4	2000 117	
Beta-BHC	nc c		2.5	1.8					
Chlordane <sup>6</sup>	nc c	230	13	8	200 1.1	586 3.4	245 14	2000 114	
Dieldrin	nc c	23	0.29	0.65	20 0.025	58.6 0.073	24 0.307	200 2.5	
gamma-BHC (Lindane)	nc c	2100		2.5	120	352	147 3.78	1200 30.7	
Hexachlorobenzene (HCB)	nc c	370	4.5	6.5	320 0.25	938 0.73	393 3.07	3200 25	
Mercury <sup>7</sup>	nc	30		770	34	101	49	400	
Total PBDEs	nc				34	101			
Total PCBs <sup>2</sup>	nc c	9.1	2.3	5.3	8.0 0.20	23 0.59	9.83 2.45	80 20	
Toxaphene	nc c	160	4.2	9.6	0.36	1.1	122 4.46	1000 36.3	

Key for this table is on the following page.

#### Key to Table 5:

FCASL: Fish Consumption Advisory Screening Level.

FCR: Fish Consumption Rate.

FTEC: Fish Tissue Equivalent Concentration (old water quality narrative standard).

c: carcinogenic effects

nc: non-carcinogenic effects

TEC: Tissue Exposure Concentration; c=for carcinogenic effect; n=for non-carcinogenic effects.

1 - Values in parts per billion wet-weight ( $\mu\text{g}/\text{kg}$  ww) unless otherwise noted.

2 - Total PCBs is sum of Aroclors or congeners.

3 - Values in parts per trillion wet-weight (ng/kg ww).

4 - The cumulative toxicity of a mixture of congeners in a sample can be expressed as a TEQ to 2,3,7,8-TCDD. EPA (2010) states that the criterion for dioxin is expressed in terms of 2,3,7,8-TCDD and should be used in conjunction with the international convention of TEFs and TEQs to account for the additive effects of other dioxin-like compounds. When the TEQ is used, the toxicity of the single congener 2,3,7,8-TCDD is incorporated.

5 - Total DDT is typically the sum of the 2,4'- and 4,4'isomers of DDD, DDE, and DDT. DDD: 4,4'dichlorodiphenyldichloroethane. DDE: 4,4'dichlorodiphenyldichloroethylene. DDT: 4,4'dichlorodiphenyltrichloroethane. Where data for the 2,4' isomers are lacking, the sum of the 4,4'- isomers is used.

6 - The criterion for chlordane is interpreted as the sum of five chlordane components; these can be individually quantified through laboratory analyses while chlordane cannot. The EPA screening values are for "Total Chlordanes" which is the sum of five compounds: cis- and trans- chlordane, cis- and trans-nonachlor, and oxychlordane.

7 - The criterion for methylmercury is a true numeric criterion for fish tissue as opposed to a narrative criterion, which incorporates a TEC. The interpretation of tissue methylmercury results uses the TECn pathway described in Policy 1-11. Fish tissue was analyzed for total mercury, which has been deemed to adequately represent the concentration of methylmercury. Table 6. Summary of key inputs into risk assessment equations used for protecting people from consumption of contaminated fish.

Term	Ecology TECc 2018	Ecology TECn 2018	Ecology FTEC/NTR 1996-2016	Health (FCASL) 2018	EPA SV Subsistence 2000	EPA SV Recreational 2000
Risk Level	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>
Exposure Time	70 yr	7-70 yr	70 yr	30/70 yr*	70 yr	70 yr
Body Weight	80 kg	80 kg	70 kg	70 kg**	70 kg	70 kg
Consumption Rate	175 g/d	175 g/d	6.5 g/d	175 g/d	142.4 g/d	17.5 g/d
Cancer Slope Factor	а	а	а	а	А	а
Reference Dose	а	а	а	а	A	а

\* 30 years used for non-carcinogenic effects, 70 years used for carcinogenic effects.

\*\* 60 kg used for methylmercury and PBDEs: also used when evaluating combined effects of methylmercury, PBDEs, and PCBs.

a = Specific to each chemical evaluated; and may also vary among evaluators.

FCASL = Fish Consumption Advisory Screening Level.

FTEC/NTR = Fish Tissue Equivalent Concentration based on National Toxics Rule water column criteria. SV = Screening Value.

### 3.4 Effectiveness monitoring studies

TMDL effectiveness monitoring is a fundamental component of any TMDL implementation activity. It measures to what extent the water body has improved and whether it has been brought into compliance with the state water quality standards. Effectiveness monitoring takes a holistic look at TMDL implementation, watershed management plan implementation, and other watershed-based cleanup efforts. Success may be measured against TMDL load allocations or targets, correlated with baseline conditions or desired future conditions.

The FFCMP long term monitoring component will support TMDL and Water Clean-up Plan effectiveness monitoring by providing information about:

- The extent of improvement (i.e. significant reductions of toxics in fish tissue).
- Compliance with water quality standards after long periods of non-compliance.

# 4.0 Project Description

### 4.1 Project goals

The primary goals of the Washington Freshwater Fish Contaminant Monitoring Program are to:

- Conduct exploratory monitoring to characterize the extent and location of toxics contamination in freshwater fish tissue from aquatic areas that have not yet been monitored or where relevant data are greater than 10 years old.
- Conduct long-term trend monitoring of toxic contaminants in freshwater fish tissue in selected areas in order to track changes over time.

Results from such monitoring support natural resource management across Washington by providing data and information which complement specific efforts, such as:

- Ecology's periodic Water Quality Assessment.
- Water cleanup planning (Ecology, other groups).
- TMDL effectiveness monitoring (Ecology, other groups).
- Chemical Action Plans for mercury, PCBs, PBDEs (mainly Ecology and Health)
- Risk assessments of consuming contaminated fish (Health, other government groups).

The two monitoring components are characterized below.

### **Exploratory Monitoring**

The exploratory component remains flexible to serve various needs:

- Continue screening-level monitoring at sites lacking historical data.
- Target 3-5 sites per year for exploratory monitoring. Sites would be selected in the spring of each year and consider interests from others, the location of long-term monitoring sites for that year, and available resources.
- Provide information to Health and others for evaluating the risks of eating contaminated fish.
- Cooperate with other projects and agencies where involvement benefits all parties.
- Address other concerns related to contaminants in fish, such as:
- Waterbodies on Washington's 303(d) list where new data would conform to revised data quality requirements and improve the quality of the listing decision.
- Columbia River: sample returning adult salmon (particularly Chinook) and steelhead to help characterize potential risks to humans from eating contaminated salmon.
- Puget Sound's major rivers: sample resident (non-anadromous) fish from rivers where the health of Chinook salmon and steelhead smolts appear to be impacted by toxic contaminants, as determined by Washington Department of Fish and Wildlife (WDFW) and National Marine Fisheries Service (NMFS) research.
- Lakes and waterways in the central Columbia Basin that are part of the extensive irrigation network.

- Other topics to consider in the future that may address impacts to fish health, such as: biomarkers that are produced in resident fish upon exposure to toxic chemicals and contaminant burdens in juvenile lamprey from the Columbia River system.
- Include emerging chemicals of concern as target analytes when warranted, such as:
- Per- and poly-fluoroalkyl substances (PFAS): used in water and stain resistant products, as well as fire-fighting foams.
- Nonylphenol ethoxylates (NPEs): in widely used surfactants.
- Hexabromocyclododecane (HBCD): a class of flame retardants.
- Pharmaceuticals and personal care products (PPCPs): many consumer products.

#### Long-Term Trend Monitoring

The long-term component targets specific sites, species, and chemicals with the goal to determine changes over time (temporal trends) in concentrations of PBTs in fish tissue. The long-term component will:

- Focus on sites with known high levels of contaminants, such as where TMDLs, Water Cleanup Plans, source assessments (SA), or fish consumption advisories for PBTs exist (see Table 7). Such sites are likely to garner attention from Ecology, Health, tribes, local governments, and the public for many decades.
- Repeat sampling at selected sites on an approximate 10 15 year cycle (once initial monitoring is done), maintaining the same sampling season and target species as historical efforts in order to reduce seasonal and inter-species variability.
- Analyze for chemicals that are most often found at higher levels of concern, such as: mercury, PCBs, DDT and its metabolites, PCDD/Fs, and PBDEs.
- Allow flexibility in site selection over time and help maximize opportunities for complementary efforts, particularly with other groups concerned with the quality of these waters and in determining progress in reducing contaminant levels.
- Characterize temporal trends where possible. The larger sample sizes used for temporal trends may also be used to determine spatial trends in waterbodies having multiple sampling sites.

While the exploratory and long-term monitoring components of this project have different goals, the two efforts often overlap, in order to use resources more efficiently. The overlap is typically related to sample planning, sample collection, and laboratory analyses. Information gathered to meet objectives for one component can often be used to help meet objectives for the other component. For example, when sampling to determine changes in levels of PCBs or DDTs between a TMDL study and subsequent sampling, samples from the subsequent sampling might also be analyzed for mercury, PBDEs, or other analytes that were not measured in a previous study.

Table 7. Waterbodies for long-term trend monitoring component, FFCMP 2019–2031.

Fish Sampling Area	Latest Sampling Year	Proposed Sample Year	FCA Chemical	TMDL, WCP, or SA Chemical
Snake R (Ice Harbor Dam to Clarkston)	2009	2019	Hg	PCDDFs
Lake Chelan	2010	2020	DDT	DDT, PCBs
Wenatchee R (mouth to Lake Wenatchee and Nason Cr)	2010	2020	PCBs	PCBs
Columbia R-1 (estuary to Bonneville Dam)	2005	2021	Hg, PCBs	PCDDFs
Spokane R (Lake Spokane to state line)	2012	2022	PCBs, PBDEs, Pb	PCBs
Columbia R-2, lower (Bonneville Dam to McNary Dam)	2009	2023	Hg, PCBs	PCDDFs
Walla Walla R (lower and upper mainstem)	2002	2024	Hg, PCBs	CPs, DDTs, PCBs
Columbia R-4, middle (Priest Rapids Dam to Grand Coulee Dam)	2013	2025	Hg, PCBs, PCDDFs	PCDDFs
Yakima R (canyon to Horn Rapids)	2014	2026	Hg, PCBs	DDT, PCBs
Columbia R-5, upper (Grand Coulee Dam to Northport)	2005 and 2009	2027	Hg, PCBs	PCDDFs
Lake Washington	2015	2028	PCBs	
Green Lake (Seattle)	2015	2028	PCBs	
Columbia R-3, middle (McNary Dam to Priest Rapids Dam)	2009	2029	Hg, PCBs, PCDDFs	PCDDFs
Okanogan R (Pateros L to Osoyoos)	2017	2030	DDT, Hg, PCB	DDT, PCBs
Cowlitz R (Castle Rock to I5)	2016	2030		
Palouse R (Hooper to Pullman on SF)	2018	2031		Dieldrin, PCBs

## 4.2 Project objectives

Project goals will be realized by objectives that are refined each year to meet site-specific needs for the exploratory and long-term trend monitoring components. In general, objectives are:

- Review status of information about toxic contaminants in fish from locations across Washington for the purpose of selecting sites for exploratory monitoring.
- Compile historical data to inform sampling designs to meet site-specific goals, such as determining temporal trends in target chemicals.
- Work with other groups concerned about toxic contaminants in fish. Help with monitoring where cooperation is beneficial to all, particularly with local, state, tribal, and federal groups.
- Review target analytes in order to address current and emerging chemicals of concern.
- Determine appropriate analytical methods, and arrange for chemical analyses of tissue samples by accredited laboratories.
- Document each year's monitoring plan in a formal addendum to this project plan.
- Assemble crews, equipment, and permits to conduct annual sampling at selected sites and for target numbers and species of fish.
- Revise sample analysis plan based on fish actually collected; process fish to form composite samples; send prepared tissue samples to laboratories for analyses.
- Compile and review laboratory analytical results; upload results to EIM database.
- Characterize contaminant levels found in the sampled area: compare to statewide values, water quality standards, and other thresholds; evaluate temporal and spatial trends.
- Share results through various media such as reports, Ecology website, and presentations.

### 4.3 Information needed and sources

The information needed to meet project objectives includes defining the needs of groups using fish tissue contaminant data, characteristics of the sites and available species, and historical data. Groups needing fish tissue data will be contacted before each sampling season to define how the data will be used, such as for health risk assessments or supporting TMDL and water cleanup plan evaluations. For sites, permission and access for sampling activities need to be determined and appropriately documented. For fish, species presence and abundance need to be estimated to help determine methods for successful sample collection.

The target fish population will vary each year and will depend on the site and sampling objectives. In general, the target population will be resident freshwater fish throughout Washington. The target size of fish will usually meet any legal requirements of harvestable size or weight, as defined by WDFW in their sport fishing rules, or at least be of consumable size if no legal harvest requirements are in effect. Anadromous fish species may also be sampled, on occasion, to help address concerns by cooperating groups, such as tribes, federal agencies, and Health.

Historical information such as fish species and sizes, sample sizes, contaminant concentrations, sample collection dates, and locations of sampling will help determine site-specific sampling strategies. Most historical information to be used will come from EIM and publications that describe the past sampling efforts and results.

## 4.4 Tasks required

The tasks required to collect data and generate information involve various efforts that are repeated each year. Broadly, these tasks are generally the same as the project objectives, as described in Section 4.2 above. This project also uses various tools to accomplish the needed tasks, such as:

- SOPs for field and lab work.
- Checklists for guiding various operations.
- Sample collection gear such as electrofishing systems, nets, boats, trucks, and freezers.
- Sample processing gear such as lab space, decontamination chemicals, tools, and tissue grinders, sample jars and labels.
- Computer programs for compiling, storing, organizing, and reporting of information such as field and laboratory sample data.

## 4.5 Systematic planning process used

This document represents the systematic planning process for this project and is a revision of the five-year programmatic Quality Assurance Project Plan for the FFCMP (Seiders, 2013). This plan describes the project in general terms following Ecology's guidance for developing such plans (Lombard and Kirchmer, 2004). Annual addenda to this plan will provide more detail for each year's activities.

# **5.0 Organization and Schedule**

### 5.1 Key individuals and their responsibilities

Table 8. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Jessica Archer EAP-SCS 360-407-6698	Client. Manager, Statewide Coordination Section (SCS)	Reviews the project scope and budget, tracks progress, reviews the draft QAPP/addendums, and approves the final QAPP/addendums. Works with management team to help resolve issues affecting the project.
Keith Seiders Toxics Studies Unit EAP-SCS 360-407-6689	Project Manager and Principal Investigator	Writes the QAPP, addendums, and reports. Reviews historical data and develops sample strategy for different sites on annual basis. Works with laboratories to obtain analytical services. Reviews, analyzes, and interprets data. Guides field assistants in various roles and tasks.
Patti Sandvik Toxics Studies Unit EAP-SCS 360-407-7198	Project Assistant, Field and EIM Lead	Leads efforts for sample collection, processing, and transportation of samples to the laboratory. Ensures that field and processing information is recorded. Enters field and laboratory data into EIM. Compiles and summarizes historical and current-year data. Assists report effort.
<b>Jim Medlen</b> Toxics Studies Unit EAP SCS 360-407-6194	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, addendums, and reports. Approves the final QAPP and addendums. Manages budget and staffing needs. Works with management team to help resolve issues affecting the project.
Alan Rue EAP Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP and addendums. Ensures MEL performs all chemical analyses as requested, including work contracted out. Ensures laboratory results are validated in timely manner.
<b>Arati Kaza</b> EAP Manager's Unit Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP and addendums. Ensures EAP adheres to QC-related SOPs and practices.

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

SCS: Statewide Coordination Section

### 5.2 Special training and certifications

Ecology staff conducting fieldwork under this program obtain needed training through education and field experience. Staff working in the field are led by a senior staff member who is responsible for making sure procedures are followed. Training in activity-specific SOPs are provided through on-the-job training. As required by federal and state scientific collection permits, field leads are required to attend an approved class on electrofishing basics.

Field staff are required to obtain training and then adhere to various task- and operation-specific procedures that are described in EAP's Safety Program. Field staff certify that they review these procedures every two years. Boat operators must also be certified to operate boats used in this project: this certification involves boat-specific training. Documentation of these certifications is retained by staff supervisors.

All personnel who conduct laboratory activities are expected to have a college degree in chemistry and experience with sample analysis, sample handling, QA/QC, and chemical safety. These personnel are also expected to meet laboratory accreditation requirements and follow laboratory-specific SOPs for sample processing, preparation, analysis, and data review.

## 5.3 Organization chart

Organization	Role	Persons
Ecology WQP HQ	Water Quality Program: watersheds and NPDES permits	Melissa Gildersleeve, Chad Brown, Susan Braley
Ecology WQP Regions	Regional WQ Program staff: watershed and TMDL leads,	Mark Peterschmidt (CRO), Adriane Borgias (ERO), Rachael McCrea (NWRO), Andrew Kolosseus (SWRO)
Ecology EAP Region	Regional EAP staff: liaison with regional staff, field support	George Onwumere
Ecology	Agency Liaison to Tribes: awareness of monitoring activities	to be determined
WDFW	Fish Age Lab: fish age determination	Andrew Clairborne
WDFW	Scientific Collection Permits	Bruce Baker, others at ScientificCollection.Permits @dfw.wa.gov
WDFW	Regional and District biologists: local knowledge, sampling permissions, possible collaboration	multiple
NOAA	Scientific Collection Permits	Claire McGrath, Mitch Dennis
USFWS	Scientific Collection Permits, local biologist liaison, possible collaboration	Jeffery Chan, Erin Britton-Kuttel
NPS	Scientific Collection Permits, local biologist liaison, possible collaboration	Matthew Dubeau
WDOH	Uses FFCMP data to conducts risk assessments for Fish Consumption Advisories	Dave McBride
WCC and CDs	WCC and CD staff: possible collaboration	multiple
Tribes	Tribe Leadership Councils: permission to sample as needed, possible collaboration	multiple
Local Government	Local governments: counties, cities, PUDs, special districts: permissions to sample as needed	multiple
Private Citizens	Private citizens and businesses: permissions to sample as needed	multiple
USACOE, BOR, PUDs, Private Corporations	Operators of dams: need notify them of our field activities near dams and related structures	multiple
Law Enforcement	Law Enforcement: notifications of field work	multiple

### 5.4 Proposed project schedule

Table 10. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff	
Field work (varies annually, depends on site characteristics)	Typically Aug-Nov	Patti Sandvik	
Sample processing	Typically Dec-Feb	Patti Sandvik	
Laboratory analyses and data validation completed (varies, depends on time of sample delivery and lab capacity)	Typically Feb-Dec Alan Rue		
Environmental Information System (EIM)	database		
EIM Study ID	FFCMPyy ("yy" = las	st two digits of sample year)	
Product	Due date	Lead staff	
EIM data loaded <sup>1</sup>	Varies by year	Patti Sandvik	
EIM data entry review <sup>2</sup>	Varies by year	Varies by year	
EIM complete <sup>3</sup>	Varies by year	Patti Sandvik	
Final report			
Author lead / Support staff	Keith Seiders / Patti Sandvik		
Schedule (highly variable, more details give	en in annual addendu	ms)	
Draft due to supervisor	Variable, about 2 years from sample collection.		
Draft due to client/peer reviewer	Variable, about one month after draft to supervisor		
Draft due to external reviewer(s)	Variable, about six v	weeks after draft to client/peer review	
Final (all reviews done) due to publications coordinator	Variable, about six v	weeks after draft to external reviewers	
Final report due on web	Varies by year, about Publications Coordin	ut three to nine months after draft to nator	
QAPP Addenda			
Author lead / Support staff	Keith Seiders / Patti	Sandvik	
Schedule (highly variable, more details given in annual addendums)			
Draft due to supervisor	Variable, usually April – June for sample year		
Draft due to client/peer reviewer	Variable, about one month after draft to supervisor		
Draft due to external reviewer(s)	Variable, about six weeks after draft to client/peer review		
Final (all reviews done) due to publications coordinator	Variable, about six weeks after draft to external reviewers		
Final report due on web	Variable, about thre Publications Coordin	e to nine months after draft to nator	

<sup>1</sup> All data entered into EIM by the lead person for this task.

<sup>2</sup> Data verified to be entered correctly by a different person; any data entry issues identified. Allow one month.

<sup>3</sup> All data entry issues identified in the previous step are fixed (usually by the original entry person); EIM Data Entry Review Form signed off and submitted to EIM coordinator (Melissa Petersen, who then enters the "EIM Completed" date into Activity Tracker; allow one month for this step). The final EIM completion date is usually targeted to be no later than the final report publication date.

## 5.5 Budget and funding

The client for FFCMP is the Environmental Assessment Program. While two staff are dedicated to FFCMP, additional staff are typically recruited to assist with field collections and sample processing. Table 11 shows estimated annual costs for the FFCMP.

Category	Project Manager: NRS3 (75%)	Field Lead: ES3 (75%)	Field Assistance: ES1 (20%)	Total
Salary, benefits, and indirect	\$134,099	\$106,038	\$84,590	\$324,727
Equipment	\$1,265	\$1,265	\$1,265	\$3,795
Travel and other	\$7,029	\$7,029	\$7,029	\$21,087
Contracts (fish age)				\$3,500
Laboratory (MEL and contract lab)				\$88,000
Totals	\$142,393	\$114,332	\$92,884	\$441,109

Table 11. Estimated annual costs for the program.

The lab budget for the FFCMP is \$176,000 per biennium. While we aim to spend \$88,000 on lab services each year, the ability to adjust annual spending allows some flexibility to meet sampling goals. For example, if lab costs are higher in the first year of the biennium, we may spend less during the second year of the biennium. The lab budget can also be supplemented by funds contributed by Ecology regional offices or other partners, in order to address specific concerns they may have.

Some laboratory analyses are conducted by contract labs, because they have equipment and expertise that MEL does not. Such analyses typically use isotopic dilution method with high-resolution gas chromatography mass spectrometry (HR CG/MS) and include: PCB congeners, PCDD/Fs, and chlorinated pesticides. Contract laboratories are hired using a request-for-proposal and bidding process, with selection based on various factors such as: demonstrated capability, past experience, performance factors, and bid amount. Additional analytes and costs that may be added in the future will be described in addenda to this project plan. Table 12 shows the most commonly used analyses, methods, and cost per analysis.

Table 12. Commonly used analysis suites for the FFCMP.

Analysis suite	Method	Cost per analysis
4,4-DDD, -DDE, -DDT; and PCB Aroclors 1248, 1254, 1260	EPA 8081/8082	\$230
Chlorinated Pesticides (34)	EPA 8081	\$420
Chlorinated Pesticides (34) and PCB Aroclors (9)	EPA 8081/8082	\$453
Chlorinated Pesticides * (~24-30)	EPA 1699 or equiv	\$1,235
Lipids (with other organics analysis)	gravimetric, MEL SOP	\$35
Mercury	EPA 245.6	\$50
Metals, priority pollutant (12)	EPA 6020B (6010D for Al)	\$220
PBDEs (13)	EPA 8270	\$240
PCB congeners * (209, about 50 as coeluters)	EPA 1668C	\$780
PCB Aroclors (9)	EPA 8082	\$200
PCDD/Fs * (17)	EPA 1613B	\$702

\* Includes 30% surcharge by MEL for contracting and data review services.

The majority of the annual laboratory budget of \$88,000 will go towards the long-term trend monitoring component. Over a 10-year period, initial lab cost estimates show that the long-term trend component will need about 90% of the laboratory budget; the remainder will go to the exploratory component. The share between the two components may vary according to the specific goals for any one year. Each year's analytical plan will be developed using information about site-specific goals, priorities, and the nature of collaborative efforts.

The age of fish that are used in samples is determined by the Fish Aging Team at the Washington Department of Fish and Wildlife. Annual costs for these services depends on the number, species, and sizes of fish needing to be aged. The \$3,500 estimated cost in Table 11 was derived from past years' work.

# 6.0 Quality Objectives

## 6.1 Data quality objectives

The data quality objective for this project is to obtain data of sufficient quantity and quality for use in comparisons to results from previous and future studies and thresholds for the protection of human health. This objective will be achieved through attention to sample design, sample collection and processing, laboratory measurement of target analytes, collection and review of historical data, data management, and quality control procedures described or referenced in this plan.

## 6.2 Measurement quality objectives

Measurement quality objectives (MQOs) are shown in Table 13. The MQOs for calibration verification, ongoing precision and recovery, and labeled compound recovery correspond to the quality control acceptance limits of the analytical methods. Even though fish tissue is a challenging matrix for organics analyses and subject to interferences due to lipids and other compounds, certain lab practices (e.g., sample preparation and cleanup) allow MQOs to be achieved most of the time.

These MQOs correspond to MEL's quality control limits (metals and ancillary parameters) or the acceptance limits specified in the analytical methods (organic compounds). The lowest concentrations of interest shown in the tables are currently attainable by MEL and contract laboratories, in most cases. MEL and contract labs are expected to meet the MQOs in Table 13. Results not meeting these MQOs will be evaluated for possible corrective action or use with qualification.

For most analytes, the designated method's achievable reporting limits (RL) will be adequate for this project. For organics, MEL will continue the current practice of reporting results down to their in-house DL (detection limit) and qualify results between the DL and PQL (practical quantitation limit) or EQL (estimated quantitation limit) as estimates. For PCDD/Fs, contract labs will be required to report down to their in-house DL for all congeners and qualify results between the DL and PQL or EQL as estimates. These reporting practices improve the ability to compare results to thresholds for the protection of human health and aquatic life.

#### 6.2.1 Targets for precision, bias, and sensitivity

The MQOs for laboratory analyses are expressed in terms of acceptable precision, bias, and sensitivity. These MQOs are summarized in Table 13 for each analytical method. Tables 14-16 expand on the sensitivity for individual analytes within a suite of analytes. These MQOs are then briefly discussed. Laboratory Case Narratives will discuss the outcomes of quality control practices and address these MQOs for each batch of sample analyses.

 Table 13. Measurement quality objectives by analyte and method.

	Analytical	Precision (RPD)		Bias (% recovery)			Sensitivity	
Parameter	Method *	Lab Duplicate	Matrix Spike Duplicate	Lab Control Sample	Surrogate	Matrix Spike	Reporting Limits (ug/kg) <sup>a</sup>	
Mercury	EPA 245.6 (CVAA)	0%-20% (for results > 5x RL)	0%-20%	85%-115%	NA	75%-125%	17 ug/kg	
Metals (one or more of: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ti, V, Zn)	EPA 6020B (6010D for Al)	0%-20% (for results > 5x RL)	0%-20%	85%-115%	NA	75%-125%	100-5000 ug/kg <sup>f</sup>	
Chlorinated pesticides (low resolution)	EPA 8081 (GC/ECD); MEL SOP	0%-40%	0%-40%	50%-150%	20%-120%, 30%-130 <sup>b</sup>	50%-150%	most 0.5-3.0 ug/kg °	
Chlorinated pesticides (high resolution)	EPA 1669 (HR GC/MS) or equivalent	0%-40%	NA	g	NA	NA	0.01-0.10 ug/kg °	
PCB Aroclors (low resolution)	EPA 8082 (GC/ECD); MEL SOP	0%-40%	0%-40%	50%-150%	50%-150%	50%-150%	1.1 - 10 ug/kg <sup>d</sup>	
PCB congeners (high resolution)	EPA 1668C (HR GC/MS)	0%-40%	NA	g	NA	NA	0.003-0.01 ug/kg	
PCDD/Fs (high resolution)	EPA 1613B (HR GC/MS)	0%-40%	NA	g	NA	NA	EQL 0.017 - 0.5 ng/kg <sup>e</sup>	
PBDEs	EPA 8270 (SIM); SOP 730104	0%-40%	NA	50%-150%	50%-150%	50%-150%	0.10-2.6 ug/kg; PBDE 209 1.9-4.3 ug/kg	
Lipids	MEL SOP 730009	0%-20%	0%-40%	NA	NA	NA	0.10%	

\* - Sample preparation methods are given later in Section 9.1, Lab procedures table.

a - Value reflects typical range. Required RLs for some samples may vary by site and species.

b - These limits are specific to the surrogate used.

c - See Table 15 for analyte-specific RLs for chlorinated pesticides by different methods.

d - Typical RL; yet interferences may drive the RL higher.

e - See table 17 for analyte-specific RLs for dioxins/furans.

f - See table 16 for analyte-specific RLs for metals.

g - Per method for OPR, Internal Standards, and Labelled Compounds.

NA - Not applicable.

Table 14. Reporting limits for chlorinated pesticide analyses by different methods and expected
range of results for fish tissue (ug/kg).

Analyte	CAS #	RL for low-res (EPA 8081) <sup>a</sup>	EDL for Hi-res (EPA 1699 or similar)	EQL for Hi-res (EPA 1699 or similar)	Expected range of results
2,4'-DDD	53-19-0	0.5 - 1.0	0.02	0.2	ND - 20
2,4'-DDE	3424-82-6	0.5 - 1.0	0.02	0.2	ND - 20
2,4'-DDT	789-02-6	0.5 - 1.0	0.02	0.2	ND - 4.0
4,4'-DDD	72-54-8	0.5 - 1.0	0.02	0.2	ND - 400
4,4'-DDE	72-55-9	0.5 - 1.0	0.02	0.2	ND - 4000
4,4'-DDT	50-29-3	0.5 - 1.0	0.02	0.2	ND - 40
Aldrin	309-00-2	0.5 - 2.0	0.02	0.4	ND - 1.0
alpha-BHC (alpha-HCH)	319-84-6	0.5 - 2.0	0.02	0.4	ND - 0.5
beta-BHC (beta-HCH)	319-85-7	0.5 - 1.0	0.02	0.4	ND - 1.0
<i>Chlordane, total</i> (sum of 5 addends)	-	0.4 <sup>c</sup> - 1.0 c	0.02 °	0.4 °	ND - 70
Chlorpyriphos	2921-88-2	0.25 - 0.5	0.02	0.4	ND - 5.0
Chlorthal-dimethyl (Dacthal)	1861-32-1	0.25 - 0.5	0.02	0.2	ND - 1.0
cis-Chlordane (alpha-Chlordane) <sup>b</sup>	5103-71-9	0.5 - 1.0	0.02	0.4	ND - 10
cis-Nonachlor <sup>b</sup>	5103-73-1	0.5 - 1.0	0.02	0.4	ND - 10
DDMU	1022-22-6	0.25 - 0.5	nt	nt	ND - 7.0
delta-BHC (delta-HCH)	319-86-8	0.5 - 1.0	0.05	0.20	ND - 1.0
Dieldrin	60-57-1	0.5 - 2.0	0.05	0.16	ND - 7.0
Endosulfan I	959-98-8	1.0 - 2.0	0.05	0.16	ND - 1.0
Endosulfan II	33213-65-9	1.0 - 2.0	0.05	0.16	ND - 1.0

QAPP: Freshwater Fish Contaminant Monitoring Program

Analyte	CAS #	RL for low-res (EPA 8081) <sup>a</sup>	EDL for Hi-res (EPA 1699 or similar)	EQL for Hi-res (EPA 1699 or similar)	Expected range of results
Endosulfan Sulfate	1031-07-8	1.0 - 2.0	0.05	0.16	ND - 1.0
Endrin	72-20-8	1.0 - 2.0	0.05	0.16	ND - 1.0
Endrin Aldehyde	7421-93-4	1.0 - 2.0	0.05	0.16	ND - 1.0
Endrin Ketone	53494-70-5	0.5 - 1.0	0.05	0.16	ND - 1.0
Heptachlor	76-44-8	0.5 - 2.0	0.02	0.2	ND - 1.0
Heptachlor Epoxide	1024-57-3	0.5 - 2.0	0.05	0.16	ND - 1.0
Hexachlorobenzene	118-74-1	0.5 - 1.0	0.01	0.2	ND - 60.0
Lindane (gamma-BHC, -HCH)	58-89-9	0.5 - 1.0	0.02	0.4	ND - 2.0
Methoxychlor	72-43-5	0.5 - 1.0	0.10	0.16	ND - 2.0
Mirex	2385-85-5	0.5 - 2.0	0.02	0.2	ND - 2.0
Oxychlordane <sup>b</sup>	27304-13-8	0.5 - 1.0	0.02	0.4	ND - 10
Pentachloroanisole	1825-21-4	0.25 - 0.5	nt	nt	ND - 2.0
Toxaphene <sup>d</sup>	8001-35-2	2.0 - 10	0.10	0.4	ND - 300
trans-Chlordane (gamma- Chlordane) <sup>b</sup>	5103-74-2	0.5 - 1.0	0.02	0.4	ND - 10
trans-Nonachlor <sup>b</sup>	39765-80-5	0.5 - 1.0	0.02	0.4	ND - 90

Analytes in **bold** are the more commonly detected pesticides of concern.

a = Typical RL for past FFCMP, extract split).

b = One of five addends used for determining "Chlordane, total".

c = As the sum of five addends.

d = While not a target analyte of EPA 1699, HR GCMS can be used to quantify major components of this analyte.

nt = Not listed as a target analyte.

Metal	Symbol	Reporting Limit (ug/kg)	EPA Method Number
Aluminum	AI	2500	6010D
Antimony	Sb	200	6020B
Arsenic	As	100	6020B
Beryllium	Be	100	6020B
Cadmium	Cd	100	6020B
Chromium	Cr	500	6020B
Copper	Cu	100	6020B
Lead	Pb	100	6020B
Mercury	Hg	17	245.6
Nickel	Ni	100	6020B
Selenium	Se	500	6020B
Silver	Ag	100	6020B
Titanium	Ti	100	6020B
Vanadium	V	500	6020B
Zinc	Zn	5000	6020B

Table 15. Reporting limits for individual metals in fish tissue.

Congener	CAS Number	Quantitation Limit (pg/kg)	Detection Limit (pg/kg)	TEF (WHO 2005)
2,3,7,8-TCDD	1746-01-6	0.03	0.013	1
1,2,3,7,8-PeCDD	40321-76-4	0.03	0.022	1
1,2,3,4,7,8-HxCDD	39227-28-6	0.1	0.018	0.1
1,2,3,6,7,8-HxCDD	57653-85-7	0.1	0.019	0.1
1,2,3,7,8,9-HxCDD	19408-74-3	0.1	0.019	0.1
1,2,3,4,6,7,8-HpCDD	35822-46-9	0.2	0.034	0.01
OCDD	3268-87-9	0.5	0.034	0.0003
2,3,7,8-TCDF	51207-31-9	0.05	0.019	0.1
1,2,3,7,8-PeCDF	57117-41-6	0.1	0.023	0.03
2,3,4,7,8-PeCDF	57117-31-4	0.05	0.019	0.3
1,2,3,4,7,8-HxCDF	70648-26-9	0.1	0.024	0.1
1,2,3,6,7,8-HxCDF	57117-44-9	0.1	0.023	0.1
1,2,3,7,8,9-HxCDF	72918-21-9	0.1	0.031	0.1
2,3,4,6,7,8-HxCDF	60851-34-5	0.1	0.025	0.1
1,2,3,4,6,7,8-HpCDF	67562-39-4	0.2	0.008	0.01
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.2	0.012	0.01
OCDF	39001-02-0	0.5	0.042	0.0003

Table 16. Quantitation and detection limits, and TEFs, for PCDD/F congeners.

#### 6.2.1.1 Precision

Precision is a measure of variability between results of replicate measurements that is due to random error. Sampling precision will be estimated using results from true field replicates and expressed as the Relative Standard Deviation (RSD). Field replicate samples consist of another set of fish of the same species and size range as the sample. Field replicates are usually formed by random assignment of individual fish to a composite group. For example, 15 fish of the same species collected from the same site and all within a given size range could be assigned to three different composite samples of five fish each. This project has no acceptance limits for estimates of sampling precision: the information helps to characterize the variability of the sampled population and inform evaluation and analyses of results.

Laboratory precision will be estimated by the labs most often using results from duplicate analyses and expressed as Relative Percent Difference (RPD). Table 13 includes acceptance limits which are typically set by the lab.

#### 6.2.1.2 Bias

Bias is the difference between the sample result and the true value. Bias will be evaluated and compared to method-specific limits by using various control standards and surrogate compounds that are analyzed along with study samples. Laboratory control samples contain known amounts of analyte and indicate bias due to sample preparation and/or calibration. Matrix spikes may indicate bias due to matrix effects, and matrix spike duplicates provide an estimate of the precision of this bias. Where isotopic dilution methods are used (e.g., PCB and PCDD/F congeners), each sample is spiked with labeled congeners. The concentration of target compounds is corrected for recovery of labeled congeners or other techniques allowed by the analytical method. Table 13 shows targets for acceptable bias.

#### 6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as a detection limit. Targets for acceptable sensitivity for lab measurements are given in Table 13. Sensitivity may be reduced in some samples because of matrix interferences such as lipids.

#### 6.2.2 Targets for comparability, representativeness, and completeness

#### 6.2.2.1 Comparability

The comparability of study results to findings from historical work and thresholds for the protection of human or aquatic life will be maximized, as well as possible, through sample design, sample collection, laboratory analyses, and data evaluation. Sample design will be tailored annually for each target site and described in annual addenda to this project plan. Design factors such as sampling season, species, target fish size, sample size, and sample compositing

schemes will be based on site-specific objectives, historical data, and best professional judgment. Ancillary data on fish, such as size, age, lipid content, and sample tissue type, will be evaluated for their effects on comparability.

Fish will most often be collected in the fall of each year, which coincides with the timing of most other fish collections by Ecology and other agencies. However, there will be cases where fish need to be collected in a different season in order to be comparable to historic data (e.g., Lake Chelan trout collected in late spring). The collection and processing of fish samples will follow these SOPs:

- SOP EAP009, V1.2: Field Collection, Processing, and Preservations of Finfish Samples at the Time of Collection in the Field (Sandvik, 2018c).
- SOP EAP007, V1.2: Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2018a)
- SOP EAP008, V1.2: Standard Operating Procedures for Resecting DNA Samples and Aging for Finfish (Sandvik, 2018b).

Laboratory analyses will follow the methods described in Table 13 for each suite of analytes. Sample preparation will follow the methods described later in Table 22 (lab procedures table) for each suite of analytes. Laboratory-specific SOPs for the preparation and analysis of samples, data reduction, and data review for each analysis are expected to be followed. These are not listed here but should be available at each laboratory conducting the analyses.

Where analytical methods or laboratories conducting the analyses differ among data sets from different times, the comparability of the methods and results will be evaluated. Examples include:

- *Mercury:* EPA method 245.5 was used for most Ecology fish tissue samples before 2004, while EPA 245.6 has been used by Ecology since 2004. Furl (2007) examined paired results from use of both methods and found a relative bias of nearly 30% between the two methods. Linear regression was used to establish a relationship that could be used to compare results coming from the two analytical methods.
- *PCBs:* PCBs in fish tissue have been measured using two different analytical methods. The low-resolution EPA Method 8082 produces Aroclor data while the hi-resolution EPA Methods 1668A and 1668C yield data for individual or co-eluting congeners. The comparability of Aroclor to congener results was examined in previous tissue sampling efforts and found good correlation over three orders of magnitude (Seiders et al., 2009; Johnson et al., 2010). The differences between the two methods were generally greater where total PCB concentrations were less than 10 ppb. This project will most often use EPA 8082 because of its lower cost. When mixtures of data from both methods are used in comparisons, the comparability from the different methodology will be addressed during sample design and data evaluations.

- *Dioxins/furans:* Data from at least two methods may be involved, specifically EPA Methods 8290 (historical data) and 1613B. As with PCB methodology above, when mixtures of data from both methods are used in comparisons, the comparability will be addressed during data analysis and reporting.
- *HR-GC/MS methods:* Analyses for PCB congeners and dioxins/furans by these methods are done by contract labs and reviewed by MEL. A consequence of contract labs is that different labs may be used over time: this inconsistency can potentially affect the comparability of data sets from different labs. We expect that if the analyses by these methods meet the method-required QC procedures and limits, then the data will adequately comparable for the FFCMP.

Differences in data reduction practices over time may also affect the comparability of results. One example includes methods of summing analytes having similar properties to yield "total" values, such as in total PCBs, total DDT, and toxic equivalents (TEQ) for dioxin/furan congeners expressed as TCDD TEQ. Where data reduction practices for historical results are not documented or comparability is otherwise uncertain, sums or TEQs may be recalculated using original laboratory data, following guidance developed by Ecology's Toxics Studies Unit (TTCT, 2008).

#### 6.2.2.2 Representativeness

The fish collected for this project are considered to be representative of the existing exposures to humans or wildlife that may consume these fish from the collection area at the time they were collected. Target species were selected based on EPA recommendations (2000) and previous experience with fish collection in Washington. The following criteria were used to select target species:

- Commonly captured and likely to be consumed by humans.
- Likely bioaccumulate chemicals of concern. Abundant, easy to identify, and easy to capture.
- Large enough to provide adequate tissue for analysis.
- Resident fish likely to stay relatively close to the sampling site.

Target species for this study are listed in Appendix B. Efforts will focus on collecting the desired species and number of fish, yet the outcome of field sampling will depend on the availability and abundance of fish at the study sites. In many cases, multiple species may be sought at any one site because of differences among species' abilities to bioaccumulate certain types of chemicals. While edible game fish are preferred over bottom-dwelling species, bottom- dwelling species may also be collected.

A challenge in sampling fish and interpreting results is their mobility and its effects on representativeness. The degree of migratory behavior of fish is driven by a variety of factors, alone or in combination, and unique to each species, such as:

• Age and life stage: young may seek out and remain in habitats different from adults.

- Food: movements to feed on different food sources throughout a waterbody.
- Reproduction: movement to and from spawning habitat.
- Water temperature: seasonal migration to avoid non-optimal temperatures (cold or heat).

While the potential effects of migratory behavior are difficult to control for, the factors above will be considered in sampling and subsequent interpretation of data. Where the objective is to compare results to historical data for determining temporal trends, samples will be collected at the same site and during the same season as was done for historical samples. This approach should yield a similar degree of representativeness for each group of samples. Where the objective is general characterization of contaminants in fish, interpretation of results will consider factors affecting site fidelity and representativeness.

Many of Washington's lakes and streams also contain fish that originate from hatchery programs. Hatchery-origin fish can be released in the wild as fry, fingerlings, or adult fish. Hatchery and naturally-produced fish may bioaccumulate different types and amounts of contaminants because of the different places, time periods, and food they are exposed to.

Sample planning includes evaluating the likelihood of collecting hatchery fish and identifying potential hatchery fish upon collection. Hatchery fish are typically marked by clipping an adipose fin (for trout) or other visual mark. Information about the species, numbers, sizes, dates, and locations of release for hatchery-origin fish can also be obtained from hatcheries, WDFW biologists, and others with local knowledge. Such information can help with the interpretation of results that include hatchery fish which are collected under this program.

The area where fish are collected is usually defined as the reach of stream or river that is actually sampled. For lake sampling, the collection area is usually defined as the entire lake. However, when data are used in Ecology's periodic Water Quality Assessment, the collection area is usually defined as a stream segment or grid cell that is much smaller than the actual area sampled. This approach is used in order to simplify the data reduction process used in the Assessment: yet this approach can introduce spatial bias into the interpretations made during the Assessment. To help reduce this spatial bias, the location of sample collection follows EIM guidance with additional directions to improve clarity and consistency. Determining the location to associate a composite sample of fish tissue is a multi-step process and is described below in Section 8.5 Sample ID.

#### 6.2.2.3 Completeness

The goal of completeness for laboratory analytical data and for field measurements is 99%. The loss of any analytical or field data may decrease the ability of this project to achieve its objectives for either exploratory monitoring or trend monitoring. When needed, additional efforts will be taken to achieve 99% completeness of field and laboratory data. For example, aliquots of

ground tissue will be archived in case re-analysis is needed and iterative reviews or corrections of laboratory data may be requested until a data set is complete and accurate.

Achieving the sampling goals for each site and species is challenging and can be complicated to quantify. The completion rates for past years sampling goals have been in the range of about 50-80%. Sampling goals for each site are typically framed as a given number of fish of a particular species that are within a given size range. Specific goals for sites usually include several species and may include different size ranges within a species. Ideally, collection at a site continues until the numbers of target species and size ranges are collected. However, when the goal is unlikely to be met, secondary strategies are accepted if the result will meet the study objectives. These strategies include:

- Collecting fewer numbers of fish (e.g., accepting 15 fish to allow creation of 5 composites of 3 fish each rather than 5 composites of 5 fish each).
- Accepting fish of different size range than the target range.
- Collecting alternate species in adequate numbers and size ranges.

## 6.3 Acceptance criteria for quality of existing data

This project will use data collected through monitoring efforts conducted by others, such as Ecology, EPA, tribes, and other organizations. The primary sources of historical data will be Ecology's EIM database and project files for Ecology-sponsored studies. EIM is the source for data related to analytical results whereas project files contain valuable field-related information such as more detailed sample location and collection method descriptions, and the size and age of individual fish used in composite samples. These data and associated documentation (e.g., project plans, project reports, and laboratory data reports) will be reviewed to assess their usability in this project.

## 6.4 Model quality objectives

Not applicable – no modeling done for this project.

# 7.0 Study Design

## 7.1 Study boundaries

This study includes all accessible freshwater areas of Washington State where fish of adequate size and numbers can be collected. Any of these areas may be sampled as part of the exploratory monitoring component. Sites suspected of having no contamination, or "reference" sites, may be chosen to gain perspective on the results from sites closer to sources of contamination. Such reference sites will be streams and lakes far from potential sources or contaminant transport mechanisms. Areas of focus for the long-term trend-monitoring component will be waters that currently have in place TMDLs, FCAs, and Source Assessment efforts for toxic contaminants. Site-specific study boundaries will be determined each year and based on that year's objectives, site characteristics, and historical data. Figure 8 shows the nearly 150 sites sampled between 2001 and 2018 for the FFCMP.

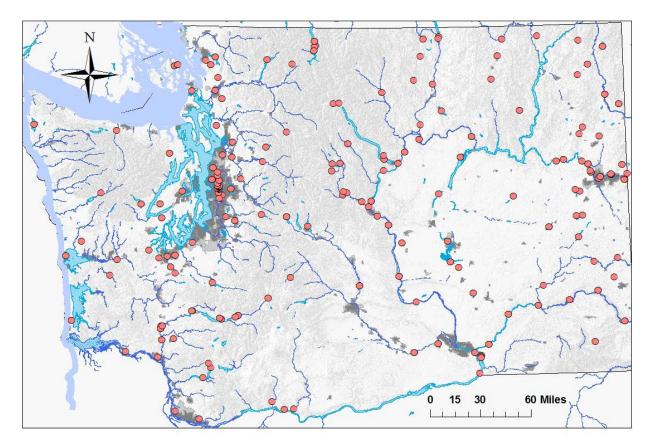


Figure 8. Map showing boundary of project study area and sites sampled during the FFCMP 2001-2018.

## 7.2 Field data collection

The exploratory monitoring component targets sites lacking historical data or where those data are more than ten years old. Sites would be selected in the spring of each year and consider interests from others, the location of long-term monitoring sites for that year, and available resources. Because only about 10% of the FFCMP's lab budget is available for the exploratory component, the number of sites sampled will be small. General locations of recent interest include:

- Puget Sound's major rivers.
- Central Columbia River basin waterbodies that are part of the irrigation network.
- Waterbodies on Washington's 303(d) list where new data would help address concerns about the quality of previous listing decisions.

The long-term monitoring component targets specific sites, species, and chemicals with the goal to determine changes over time (temporal trends) in concentrations of PBTs in fish tissue. The long-term component focuses on sites with known high levels of contaminants such as where TMDLs, WCPs, source assessments, or fish consumption advisories for PBTs exist (see Table 7). Sampling at long term trend sites will be done on an approximate 10-15 year cycle. Figure 9 and Table 17 show proposed locations for the long-term trend-monitoring component.

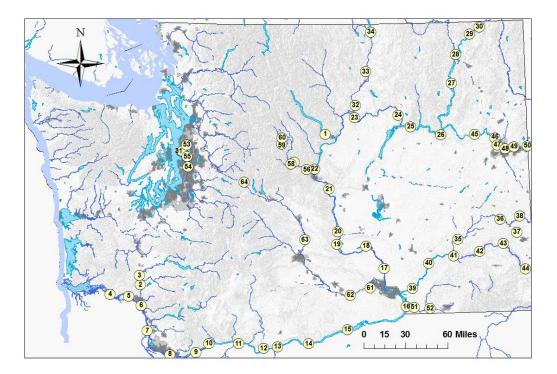


Figure 9. Proposed sample sites for long term trend monitoring, FFCMP 2019-2031.

Map ID	Sample Site	Latitude	Longitude	Sampling Area
1	Chelan L	47.8681	-120.1422	Chelan
2	Cowlitz-CasRk	46.2862	-122.9138	Cowlitz
3	Cowlitz-Vader	46.3836	-122.9323	Cowlitz
4	Columbia R, tidal, RM 38-42	46.1784	-123.3531	Columbia, tidewater
5	Columbia R, tidal, RM 58-60	46.1648	-123.0771	Columbia, tidewater
6	Columbia R, tidal, RM 68-72	46.0742	-122.8910	Columbia, tidewater
7	Columbia R, tidal, RM 88-92	45.8143	-122.7911	Columbia, tidewater
8	Columbia R, tidal, RM 116-120	45.5730	-122.4455	Columbia, tidewater
9	Columbia R, tidal, RM 136-142	45.6026	-122.0631	Columbia, tidewater
10	Columbia R, lwr, RM 148-154	45.6965	-121.8695	Columbia, lower
11	Columbia R, lwr, RM 170-176	45.7002	-121.4374	Columbia, lower
12	Columbia R, lwr, RM 194-198	45.6549	-121.0669	Columbia, lower
13	Columbia R, lwr, RM 204-210	45.6708	-120.8584	Columbia, lower
14	Columbia R, lwr, RM 228-236	45.7034	-120.3989	Columbia, lower
15	Columbia R, lwr, RM 258-268	45.8478	-119.8220	Columbia, lower
16	Columbia R, mid, RM 292-339	46.0750	-118.9424	Columbia, middle
17	Columbia R, mid, RM 340-365	46.4772	-119.2636	Columbia, middle
18	Columbia R, mid, RM 366-387	46.7083	-119.5352	Columbia, middle
19	Columbia R, mid, RM 388-420	46.7288	-119.9734	Columbia, middle
20	Columbia R, upr, RM 414-416	46.8595	-119.9600	Columbia, upper
21	Columbia R, upr, RM 448-452	47.2989	-120.0869	Columbia, upper
22	Columbia R, upr, RM 471-474	47.5085	-120.3064	Columbia, upper
23	Columbia R, upr, RM 538-545	48.0360	-119.6915	Columbia, upper
24	Columbia R, upr, RM 586-590	48.0573	-119.0169	Columbia, upper
25	Columbia R, L Roosevelt, RM 601-610	47.9341	-118.8262	Columbia, FDR
26	Columbia R, L Roosevelt, RM 634-637	47.8432	-118.3655	Columbia, FDR
27	Columbia R, L Roosevelt, RM 673-689	48.3704	-118.1797	Columbia, FDR
28	Columbia R, L Roosevelt, RM 703-709	48.6681	-118.0976	Columbia, FDR
29	Columbia R, L Roosevelt, RM 720-734	48.8724	-117.8712	Columbia, FDR
30	Columbia R, L Roosevelt, RM 735-741	48.9442	-117.7160	Columbia, FDR
31	Green L	47.6783	-122.3383	Green
32	Okanogan R, Lwr	48.1625	-119.6705	Okanogan
33	Okanogan R, Mid	48.5093	-119.5074	Okanogan
34	Okanogan R, Upr	48.9178	-119.4235	Okanogan
35	Palouse R, Lower	46.7590	-118.1479	Palouse
36	Palouse R, Middle	46.9528	-117.5042	Palouse
37	Palouse R, South Fork	46.8108	-117.2583	Palouse

 Table 17. Proposed sample sites for long term trend monitoring, FFCMP 2019-2031.

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Map ID	Sample Site	Latitude	Longitude	Sampling Area
38	Palouse R, North Fork	46.9750	-117.2108	Palouse
39	Snake R, Ice Harbor Dam	46.2627	-118.8490	Snake
40	Snake R, Lwr Monumental Dam	46.5196	-118.5983	Snake
41	Snake R, Lyon's Ferry	46.5902	-118.2187	Snake
42	Snake R, Central Ferry	46.6256	-117.8305	Snake
43	Snake R, Lwr Granite Dam	46.7000	-117.4700	Snake
44	Snake R, Clarkston	46.4293	-117.1531	Snake
45	Spokane R, Little Falls Pool	47.8371	-117.8427	Spokane
46	Spokane R, Upper Spokane L	47.7927	-117.5344	Spokane
47	Spokane R, Ninemile reach	47.7204	-117.5006	Spokane
48	Spokane R, Mission Park reach	47.6766	-117.3823	Spokane
49	Spokane R, Plante Ferry reach	47.6945	-117.2483	Spokane
50	Spokane R, Stateline reach	47.6983	-117.0445	Spokane
51	Walla Walla R, lower	46.0673	-118.8255	Walla Walla
52	Walla Walla R, upper	46.0510	-118.5936	Walla Walla
53	Washington L, north	47.7452	-122.2654	Washington
54	Washington L, south	47.5185	-122.2343	Washington
55	Washington L, central	47.6222	-122.2538	Washington
56	Wenatchee R, Monitor Br	47.5018	-120.4268	Wenatchee
57	Wenatchee R, Peshastin	47.5822	-120.6152	Wenatchee
58	Wenatchee R, Icicle Cr	47.5606	-120.6691	Wenatchee
59	Wenatchee R, Nason Cr	47.7688	-120.8076	Wenatchee
60	Wenatchee L	47.8314	-120.8022	Wenatchee
61	Yakima R, Kiona-Horn Rapids	46.2737	-119.4781	Yakima
62	Yakima R, Prosser	46.2015	-119.7796	Yakima
63	Yakima R, Canyon	46.7784	-120.4565	Yakima
64	Yakima R, Keechelus L	47.3687	-121.3809	Yakima

#### 7.2.1 Sampling locations and frequency

#### **Strategy and Sampling Frequency**

The sampling strategy used for this project is a subjective best-professional-judgement approach to select the locations, season, species, tissue type (i.e. fillet or whole), fish size, sample size, and frequency of sampling. The sampling design for each year's effort will relate to the objectives specific to the site, species, and use of the data for each of the exploratory and long-term trend monitoring components.

The type of tissue to be analyzed is determined by the objectives for each site to be sampled. Where study objectives include comparison to water quality standards, TMDL goals, or trends, the tissue type used is fillet tissue. Most historical data are from fillet tissue so this project will use the same tissue type to allow appropriate comparisons. Species from the sucker family, most often largescale suckers, are targeted for processing as whole fish. These suckers are widespread, abundant, and be more easily collected within a common size range across the state. This project began using whole fish in 2012 in order to improve the robustness of data from sites for use in trends analyses.

Exploratory monitoring sites will typically be sampled only once: additional sampling could be done depending on the results and interest in the site from others.

For long-term trend monitoring, most selected sites will be where contaminant levels are relatively high such that temporal trends can be detected. Sampling objectives will be to obtain multiple replicates of composite samples for each species at each site in order to provide an adequately robust data set that will meet objectives. The sampling frequency will be around 10-15 years. This time frame allows sampling to occur at the many sites of interest and also allow time for new generations of most fish to be sampled. Figure 10 presents ages for the 15 species that are typically collected for long term trend monitoring. See Appendix B for species codes and names.

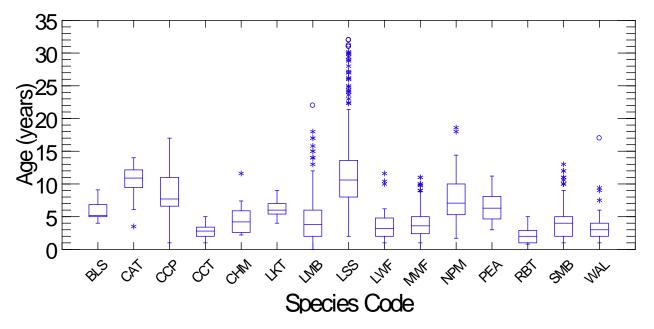


Figure 10. Boxplots of age for species to be collected for the long term monitoring component.

#### Locations

Specific sample locations are determined each year prior to the sampling season and will be described in the QAPP Addendum for that year. Factors considered in determining the suitability of a site for fish collection are:

- Specific goals and objectives for the specific year of sampling.
- Nature of historical monitoring efforts.
- Location and proximity to potential contaminant sources.
- Nature of the fish resource and use by humans and wildlife.
- Need for, and type of, contaminant data from that site and species.
- Need for scientific collection permits from other entities.
- Ability to access the site and collect adequate numbers of target species.
- Interest from other organizations (e.g., Ecology regions, Health, tribes, EPA).

For exploratory monitoring, sites will be selected that lack historical data or have data that is more than 10-15 years old. This may include sites that were recently sampled for some analytes and species, yet not for other analytes and species. The sampling objective will be to obtain at least one sample from three different species in order to provide a general screening-level assessment of contaminants in fish. Results will be compared to water quality standards or findings from studies in Washington or beyond.

Streams and lakes far from potential sources or contaminant transport mechanisms and suspected of having no contamination may be selected as "reference sites" and sampled to gain perspective on the results from sites closer to sources of contamination.

Table 18 lists sites and associated information for the long-term component. Additional sites may be added as desired, or sites dropped. The proposed schedule in Table 18 should be flexible to accommodate Ecology and Health who are primary users of the data. For example, Ecology's Eastern Regional Office in 2012 requested work on the Spokane River as part of watershed source assessment. The data from the Spokane monitoring also supported Health's effort in re-evaluating the fish consumption advisory based on data collected in 2005 (Diaz, 2007). Sampling of the Walla Walla River was deferred to a future date (~2024) in order to determine whether turbidity and suspended sediments have decreased before expending resources on fish tissue monitoring. Similar requests for schedule adjustments are expected in the coming years.

Fish Sampling Area	Latest Sampling Year	Proposed Sample Year	FCA Chemical	TMDL, WCP, or SA Chemical
Snake R (Ice Harbor Dam to Clarkston)	2009	2019	Hg	PCDDFs
Lake Chelan	2010	2020	DDT	DDT, PCBs
Wenatchee R (mouth to Lake Wenatchee and Nason Cr)	2010	2020	PCBs	PCBs
Columbia R-1 (estuary to Bonneville Dam)	2005	2021	Hg, PCBs	PCDDFs
Spokane R (Lake Spokane to state line)	2012	2022	PCBs, PBDEs, Pb	PCBs
Columbia R-2, lower (Bonneville Dam to McNary Dam)	2009	2023	Hg, PCBs	PCDDFs
Walla Walla R (lower and upper mainstem)	2002	2024	Hg, PCBs	CPs, DDTs, PCBs
Columbia R-4, middle (Priest Rapids Dam to Grand Coulee Dam)	2013	2025	Hg, PCBs, PCDDFs	PCDDFs
Yakima R (canyon to Horn Rapids)	2014	2026	Hg, PCBs	DDT, PCBs
Columbia R-5, upper (Grand Coulee Dam to Northport)	2005 and 2009	2027	Hg, PCBs	PCDDFs
Lake Washington	2015	2028	PCBs	
Green Lake (Seattle)	2015	2028	PCBs	
Columbia R-3, middle (McNary Dam to Priest Rapids Dam)	2009	2029	Hg, PCBs, PCDDFs	PCDDFs
Okanogan R (Pateros L to Osoyoos)	2017	2030	DDT, Hg, PCB	DDT, PCBs
Cowlitz R (Castle Rock to I5)	2016	2030		
Palouse R (Hooper to Pullman on SF)	2018	2031		dieldrin, PCBs

#### Table 18. Candidate sites and primary analytes for long-term monitoring component.

#### **Sample Sizes**

Review of field replicate data from historical efforts shows that variance is inconsistent and can be high for organic contaminants, ranging up to 100% RPD for PCBs, DDTs, and PCDD/Fs.

The number of samples that are needed to see the Minimum Detectable Change (MDC) between two data sets using a two-sample test (e.g., student's t-test) can be estimated using power analyses. These estimates should be specific for each combination of site, species, fish size, and target analyte.

For example, results from the 2013 FFCMP were used for estimating sample sizes needed for differing MDCs using techniques described in Zar (1984). These estimates were conducted for three analytes (DDE, mercury, and PCBs) in three species (whole largescale sucker, mountain whitefish fillet, and northern pikeminnow fillet) from a reach of the Columbia River between Priest Rapids Dam and Rocky Reach Dam (upstream of Wenatchee). Replicate samples from different locations within this reach were pooled. Table 19 summarizes the results used for sample size calculations.

Species	n 1	DDE		Mercury		PCBs	
opecies		Mean	pooled SD	mean	pooled SD	mean	pooled SD
NPM	4 of 3 ea	203.2	93.5	400.3	114.4	50.2	24.0
MWF	2 of 3 ea	150.2	59.3	28.4	5.2	51.4	43.8
LSS	3 of 5 ea	315.9	53.8	70.6	7.2	73.8	16.7

<sup>1</sup> – The number of replicate groups with the number of composite samples in each replicate group.

#### Species Codes

LSS: Largescale sucker (whole fish) MWF: Mountain whitefish NPM: Northern pikeminnow

Generally, the sample size needed to detect a given change is dependent upon the sample variance and the statistical parameters of the test (Fabrizio et al., 1995; Zar, 1984). For the cases examined here, we set the significance level (alpha) to 0.05 and power (B-1) to 0.8. A series of calculations were made using historical sample variance and different MDCs: the results from these were plotted to show the sample sizes needed for given MDCs. Figures 11 - 13 show these curves for each species and analyte of interest.

The curve for MWF in Figure 11 shows that a sample size of 8 should be adequate to detect a difference of about 90 ppb of DDE. With the 2013 average concentration of 150 ppb (Table 19), 8 samples may allow us to detect a 60% decrease in DDE, from a mean of 150 ppb to 60 ppb. Similarly, a larger sample size of 22 would increase sensitivity so that a difference of just 50 ppb, or a 33% decrease, would be detectable.

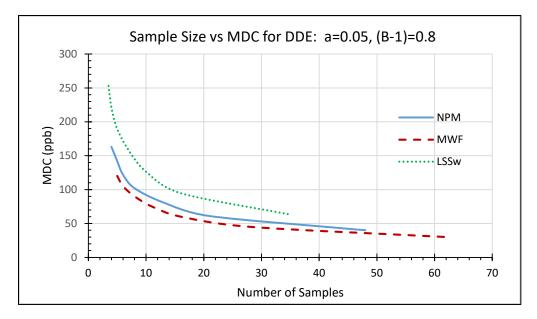


Figure 11. Sample size versus MDC for DDE based on results in three species from the Columbia River between Priest Rapids Dam and Rocky Reach Dam.

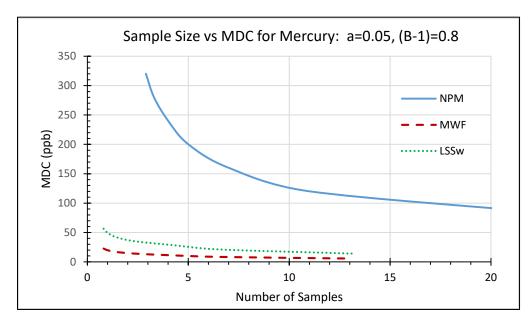


Figure 12. Sample size versus MDC for mercury based on results in three species from the Columbia River between Priest Rapids Dam and Rocky Reach Dam.

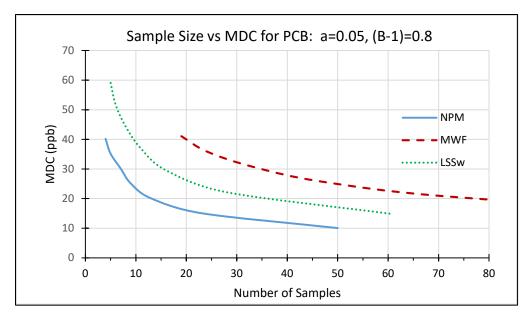


Figure 13. Sample size versus MDC for PCB Aroclors based on results in three species from the Columbia River between Priest Rapids Dam and Rocky Reach Dam.

Planning for each sampling season should use historical data to estimate the sample sizes needed for the site-specific situations for that year. For initial planning, a sample size of five to ten composite samples should be adequate to reduce sampling variability and improve the ability to determine change among sample results over time. While a larger number of samples would improve the ability to determine change in many cases, the project needs to balance the cost of additional samples with the need to achieve other objectives.

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

Four attributes of fish are recorded for each fish that is retained for analysis:

- Fish total length (mm).
- Fish fork length (mm) in cases where historical data used this fish length measurement.
- Fish weight (gram).
- Fish sex (M or F). Determined when resecting.
- Fish age (year). Performed by WDFW Fish Age Laboratory.

The fish length, weight, and age measurement typically go into EIM as average values for each multi-fish composite sample. These attributes, along with lipid content, can affect contaminant levels in fish tissue (Exponent, 2003). Relationships between contaminant concentrations and these attributes vary among species and sites and over time, and can confound comparisons to other data sets.

The following water quality characteristics are measured at the fish collection site. This information is required by Scientific Collection Permits and is not entered into EIM:

- Water temperature (C). For permits only, data are not entered into EIM.
- Water conductivity (uS). For permits only, data are not entered into EIM.
- Water visibility (feet). For permits only, data are not entered into EIM.

Table 20 lists chemical contaminants in fish tissue that may be measured in an environmental laboratory.

Chlorinated Pesticides	PCB Aroclors	PBDEs
2,4'-DDD	PCB-aroclor 1016	PBDE-047
2,4'-DDE	PCB-aroclor 1221	PBDE-049
2,4'-DDT	PCB-aroclor 1232	PBDE-066
4,4'-DDD	PCB-aroclor 1242	PBDE-071
4,4'-DDE	PCB-aroclor 1248	PBDE-099
4,4'-DDT	PCB-aroclor 1254	PBDE-100
Aldrin	PCB-aroclor 1260	PBDE-138
alpha-BHC	PCB-aroclor 1262	PBDE-153
beta-BHC	PCB-aroclor 1268	PBDE-154
Chlorpyriphos		PBDE-183
Chlorthal-dimethyl (Dacthal)	PCB Congeners	PBDE-184
cis-Chlordane (alpha-Chlordane)	209 congeners	PBDE-191
cis-Nonachlor		PBDE-209
DDMU	Lipids	
delta-BHC		Metals
Dieldrin	Dioxins and Furans	Hg, Mercury
Endosulfan I	2,3,7,8-TCDD	Al, Aluminum*
Endosulfan II	1,2,3,7,8-PeCDD	Sb, Antimony*
Endosulfan Sulfate	2,3,4,7,8-PeCDF	As, Arsenic*
Endrin	1,2,3,4,7,8-HxCDD	Be, Beryllium*
Endrin Aldehyde	1,2,3,4,7,8-HxCDF	Cd, Cadmium*
Endrin Ketone	1,2,3,6,7,8-HxCDD	Cr, Chromium*
Heptachlor	1,2,3,6,7,8-HxCDF	Cu, Copper*
Heptachlor Epoxide	1,2,3,7,8,9-HxCDD	Pb Lead*
Hexachlorobenzene	1,2,3,7,8,9-HxCDF	Ni, Nickel*
Lindane (gamma-BHC)	2,3,4,6,7,8-HxCDF	Se, Selenium*
Methoxychlor	2,3,7,8-TCDF	Ag, Silver*
Mirex	1,2,3,7,8-PeCDF	Ti, Titanium*
Oxychlordane	1,2,3,4,6,7,8-HpCDD	V, Vanadium*
Pentachloroanisole	1,2,3,4,6,7,8-HpCDF	Z, Zinc*
Toxaphene	1,2,3,4,7,8,9-HpCDF	
trans-Chlordane (gamma-Chlordane)	1,2,3,4,6,7,8,9-OCDD	
trans-Nonachlor	1,2,3,4,6,7,8,9-OCDF	
* Infrequent		

Table 20. Chemical contaminants in fish tissue that may be measured in and environmentallaboratory.

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## 7.3 Modeling and analysis design

Not applicable – no modeling done for this project.

#### 7.4 Assumptions in relation to objectives and study area

Major assumptions that underlie the study designs for this program include:

- Funding and resources will continue for the long-term trend monitoring component over the coming decades; such a timeframe is needed to detect changes.
- Scientific collection permits required by federal, tribal, state, and other entities will be obtained in timely manner, which will allow sample collection at selected sites.
- Water quality management actions such as water cleanup plans will eventually reduce contaminant loading to waterbodies and result in decreasing contaminant concentrations in fish over time.
- The species and size ranges of fish will be available at selected sites over time.
- Fish are adequately representative of the area where they are collected. Fish are integrators of pollutants in their environment. This integration occurs during the lifespan of the fish and mostly through bioaccumulation processes.
- Fish of the same species and size range collected from same location and season during historical studies are comparable to fish from more recent studies having the same species and size range from same location and season.
- Variability from laboratory analyses, sampling procedures, and natural sources are not easily controlled and will affect the ability to detect differences in contaminant concentrations over time and space. Larger differences (e.g., by a factor of 10) will be easier to detect than smaller ones (e.g., by a factor of 4).
- Total PCB concentrations derived from PCB Aroclors and PCB congener analyses are comparable, in most cases, for the objectives of this program.

### 7.5 Possible challenges and contingencies

The design for any one year's effort considers likely challenges and logistical problems, and plans ways to minimize the impacts those challenges may present.

#### 7.5.1 Logistical problems

Each year's effort considers likely challenges and plans ways to minimize the impacts those challenges may present. For example, some common challenges and possible contingencies are:

- Scientific collection permit restrictions: Use alternate sampling timeframe or method (e.g., angling instead of electrofishing or gillnetting).
- Target species not present in sufficient numbers or size range: Resample another time; move location; select alternate species; use alternate collection method (e.g., set gill nets if electrofishing is not productive.

- Access to waterbody via boat launches or trails: Access at different point and travel on-water to sampling location; seek cooperation from private/public landowners. Use alternate site.
- Troublesome wind and water conditions (e.g., waves, high or low flow): Postpone, return when calmer; use alternate access point.
- High water temperatures: Sample when water is cooler, such as early morning or earlier in the season. Postpone sampling to later date. Use different collection method such as angling or gill net.
- Problematic conditions at field processing site (e.g., heat, cold, wind, precipitation): Set up shade/rain canopies for protection; move to better site (e.g., covered area, motel room); conduct sensitive work inside truck cab or canopy.
- Equipment failure: Attempt to troubleshoot in the field and fix; seek on-site mechanical help; use different collection method; rent or purchase equipment from vendors; postpone or abandon work.

#### 7.5.2 Practical constraints

Each year's effort has to address likely challenges and plans ways to minimize the impacts of those challenges. Some common constraints and possible responses are:

- Staff reductions and vacancies: Postpone or abandon work; change schedules to accommodate available resources.
- Obtaining and compiling data from older formats (e.g., hardcopy reports): Attempts will be made to compile such data to the extent that it can be loaded into EIM; when not possible, only portions of the data might be used.
- Shifting Priorities and re-assignment to higher priority work: Delay or abandon work.

#### 7.5.3 Schedule limitations

Schedules are expected to be impacted by various factors described above. The schedules outlined in this QAPP and in the addendums are best case scenarios. Typically, schedules are adjusted to accommodate circumstances such as staffing limitations and changing priorities.

# 8.0 Field Procedures

## 8.1 Invasive species evaluation

Invasive or unwanted aquatic species may be encountered during fish collections for this project. Environmental ethics and Washington law prohibit the transportation of all aquatic plants, animals, and many noxious weeds. Sample collection efforts for this project will follow the Ecology Environmental Assessment Program's SOP to Minimize the Spread of Invasive Species (Parsons et al., 2018). The Ecology SOP supersedes the Washington Invasive Species Council SOP "Reducing Accidental Introductions of Invasive Species". It covers all points considered in that protocol and is more stringent in some areas.

## 8.2 Measurement and sampling procedures

#### **Field Collection**

Tissue samples will be collected, preserved, and transported following procedures designed to maintain the integrity, quality, and identification of the sample. Methods for the collection, handling, and processing of fish tissue samples for analysis will follow the EA Program's Standard Operating Procedure (SOP) for Field Collection, Processing, and Preservation of Finfish Samples at the Time of Collection in the Field (Sandvik, 2018c). These methods are summarized below.

Fish will be collected using a combination of methods such as electrofishing, netting, and angling. Fish may also be collected during cooperative efforts by other organizations, such as tribes, EPA, and WDFW. Upon capture in the field, fish will be identified to species and target species retained; non-target species will be released. Fish that are retained will be inspected to ensure that they are acceptable for further processing (e.g., proper size, no obvious damage to tissues, skin intact).

Fish to be kept will be euthanized by a blow to the head with a dull object, rinsed in ambient water to remove foreign material from their exterior, weighed to the nearest gram, and their total lengths measured to the nearest millimeter. Individual fish will then be double-wrapped in foil and placed in a plastic Ziploc bag along with a sample identification tag. The sample tag will include the date, the site, and the field ID assigned to the individual fish. The bagged specimens will be placed on ice in the field. Fish may remain on ice for 24-72 hours and then frozen to -10° C. The fish will remain frozen until samples are prepared and transported to MEL.

Field crews will have a sampling guide for each site which details specific plans for sample locations, species, fish sizes, numbers of fish, collection methods, and alternative actions in case of unforeseen circumstances. Field crews will consult the Project Manager when circumstances are beyond those described in the year-specific sampling plan. Field notes will be kept during each sampling event as described in Section 8.7 below.

#### Sample Preparation and Homogenization

Further preparation of fish samples will occur after the sample compositing scheme and lab analysis plans are finalized. The use of composite samples helps decrease analytical costs and improve estimates of chemical concentrations in fish tissue (Rohlf et al., 1996). Tissue samples will be prepared following the EA Program's SOP (Sandvik, 2018a). During processing, a hardcopy form (the "bench sheet") will be used to record various data, such as: processing date, processing crew, lab sample ID names, lab sample numbers, fillet weights, sex of individual fish, age structure container references, and relevant comments as described in section 8.8 below. The cleaning and decontamination of equipment used in processing fish is described below in Section 8.4.

Fish will be selected for processing in batches. Fish processed as fillets will be removed from the freezer, partially thawed, slime and scales removed, rinsed in tap water followed by a rinse in deionized water. Fish will then be filleted with the skin left on (except some species like catfish). Fillets will be cut into small cubes and passed three times through a commercially available food grinder (e.g., Kitchen-Aid). The ground tissue will be homogenized by stirring to a consistent texture and color. Subsamples from the homogenate will be taken and placed into appropriate containers and refrozen (to -20° C) until shipped to MEL. The samples will be stored frozen at MEL until analyses by MEL or shipped to a contract laboratory for other analyses. Excess tissue will be retained for all samples and stored frozen at Ecology Headquarters.

Additional data are collected from individual fish during processing. Before fish are filleted, a section of the caudal or other fin may be removed and preserved in ethanol and sent to WDFW (upon their request) for DNA archiving following the EA Program's SOP (Sandvik, 2018b). Species-appropriate structures (e.g., otoliths, scales, opercula) will be removed and sent to WDFW Fish Age Lab who will determine the age of individual fish. After fillets are removed, the sex of the fish will be determined and recorded.

Fish processed as "whole" fish will follow similar procedures described above except that a larger, commercial-grade grinder will be used. For whole fish samples, the only parts removed before grinding are structures for determining age (e.g., scales, opercula).

## 8.3 Containers, preservation methods, holding times

Sampling containers, sample preservation, and holding times for fish tissue are shown in Table 21. Pre-cleaned sample containers will be obtained prior to sample processing. Containers should be suitable for the specific analyses to be performed on the sample. Containers should also be free of contaminants according to EPA (1992) and meet quality assurance certification from the supplier.

Parameter	Minimum Amount Required *	Container	Preservation	Holding Time
Mercury	5g	2 oz. precleaned glass jar w/teflon lid	freeze, -10 C	6 months to extraction, then 28 days to analysis
Metals (one or more of: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ti, V, Zn)	10g	2 oz. precleaned glass jar w/teflon lid	freeze, -10 C	6 months to extraction, then 28 days to analysis
Chlorinated pesticides	30g, 60g preferred	4 oz. precleaned glass jar w/teflon lid	freeze, -10 C	1 year to extraction, then 40 days to analysis
PCB Aroclors	30g, 60g preferred	4 oz. precleaned glass jar w/teflon lid	freeze, -10 C	1 year to extraction, then 40 days to analysis
PCB congeners	30g, 60g preferred	4 oz. precleaned glass jar w/teflon lid	freeze, -10 C	1 year to extraction, then 40 days to analysis
PCDD/Fs	30g, 60g preferred	4 oz. precleaned glass jar w/teflon lid	freeze, -10 C	1 year to extraction, then 40 days to analysis
PBDEs	30g, 60g preferred	4 oz. precleaned glass jar w/teflon lid	freeze, -10 C	1 year to extraction, then 40 days to analysis
Lipids 30 g 4 oz. precleaned glass jar w/teflon lid		freeze, -10 C	1 year to extraction, then 40 days to analysis	

\* The minimum amount may be reduced if multiple parameters can be analyzed at the same lab from a single container. For example, 30 g tissue may be enough for analyses for chlorinated pesticides, PCB Aroclors, and lipids. Project staff will ask laboratory staff (MEL and contract lab) about minimum amounts needed when multiple analyses are performed on the same sample.

## 8.4 Equipment decontamination

Fish samples will be processed using methods that minimize the potential for sample contamination. Most fish will be processed on aluminum foil that covers a nylon cutting board laid on the workbench. The foil will be placed so that fish contact only the dull side of the foil. People preparing the samples will wear non-talc nitrile gloves. They will change gloves and foil between samples and cover the cutting board with new foil between samples.

All utensils used for processing tissue samples will be cleaned and decontaminated in order to prevent contamination of the sample. Utensils include bowls and knives of stainless steel and tissue grinding appliances having plastic, wood, stainless steel, bronze, steel, and tin parts. The typical cleaning steps are: soap (e.g., Liquinox) and water wash, tap water rinse, 10% nitric acid rinse, deionized water rinse, and acetone and hexane rinses. Utensils will be air-dried and then

packaged in aluminum foil until used. Decontamination procedures specific to this project are described in SOP EAP007, *Resecting Finfish Whole Body, Body Parts, or Tissue Samples* (Sandvik, 2018a) and in Ecology's Chemical Hygiene Plan (Ecology, 2019).

# 8.5 Sample ID

### Sample ID

The identification, labelling, and documentation of sample IDs are addressed in the three SOPs that deal with fish sampling as described above. There are two types of samples, which require different sample ID protocols: individual fish at field collection and composite samples formed during the processing steps.

The first type of sample ID occurs in the field when individual fish are retained for potential inclusion in composite samples that would be analyzed for contaminants. Individual fish are assigned a unique fish field ID. After recording the weight and total length in field notebook, the fish field ID is written on a sample tag which is wrapped in foil with the individual fish. This tag gives the sample site name or abbreviation, the collection date, and the unique ID consisting of an abbreviation for species and a sequential number (e.g., "RBT 01").

The second type of sample ID occurs in the office at the time individual fish are assigned to composite samples and before the fish are actually processed to create samples destined for lab analyses. The tabulated field data are used to group fish by site and species, and then multiple fish of similar size range within these groups are randomly assigned to composite samples. A composite sample is a group of fish, typically containing 3-5 individual fish, whose tissues are combined and homogenized to produce a tissue sample for analysis.

Each composite sample is assigned a unique Lab Sample Number and a Field Station Identification. The Lab Sample Number consists of a 9-digit number beginning with the 7-digit, MEL-assigned Work Order Number, followed by a dash ("-"), and ending with a 2-digit number assigned by the Project Manager (e.g.1701015-19). The Field Station Identification is assigned by the Project Manager and typically incorporates abbreviations for the site, species, field replicate number, and size (e.g., OL-MWF-L3).

### Location ID

A related aspect of sample ID is determining the location which is representative of the area where the individual fish used in the composite sample were collected. Determining this location follows EIM guidance with additional directions below to improve clarity and consistency. These additional directions also help to minimize the spatial bias that is introduced in the Water Quality Assessment process. Determining composite sample location is a multi-step process:

- 1. The locations where the individual fish used in the composite sample were captured are determined from field notes and maps. Upon collection in the field, individual fish may be segregated into different holding bins on the boat, which correspond to the geographical unit the fish were collected in. These geographical units are typically identified as one or more of the: NHD Reach Code, Ecology Grid Cell, and Ecology Assessment Unit Code.
- 2. The location for each composite sample is determined following EIM guidance which is to "use the centroid of the sampling area". Often, fish from multiple geographical units are used to form a composite sample, especially when the geographical units are relatively small. The centroid of the sampling area for each composite sample is determined by finding the centroid of the polygon formed by the point locations where individual fish were collected. This centroid is determined graphically using triangulation techniques and then becomes the location for that particular composite sample. This is repeated for each composite sample so that each composite samples has its own unique centroid.
- 3. The centroids for each sample are plotted on a map to see how these centroids are distributed across the entire sampling area. Then determinations are made about how the samples can best represent the geographic units that were sampled.
- 4. Where multiple centroids are within a unique geographic unit, the centroid of these centroids is determined and this final centroid becomes the location associated with the related composite samples.
- 5. Where only a single centroid (indicating a single composite sample) is within a geographic unit and: 1) multiple samples are needed to meet a sampling objective, and 2) additional samples are in adjacent geographic units; best professional judgment will be used, with specific attention to spatial representativeness, to assign sample centroids to geographic units in order to meet sampling goals.

## 8.6 Chain of custody

Chain-of-custody procedures for project samples will follow guidance in MEL's Lab User's Manual (MEL, 2016). During field collection and tissue resection work, samples will be secured in locked vehicles or rooms when personnel are not present. When samples are ready for transport to MEL, the standard Lab Analysis Required format will be used to serve as the Chain of Custody record. This form lists all sample IDs and the analyses required for each. Persons releasing or receiving the samples record the date, time, location, sample condition, and their identity in designated spaces on this form.

### 8.7 Field log requirements

Field log requirements for sample collection are addressed in SOP EAP009, V1.2: Field Collection, Processing, and Preservations of Finfish Samples at the Time of Collection in the Field (Sandvik, 2018c). The field logs consist of 5" x 7", loose-leaf pages that fit into a six-ring binder. Many pages are pre-printed templates for recording information (e.g., date, location, crew, electrofishing settings). In summary, the field logs and maps are used to record information about:

- Field personnel.
- Information about location, method, and timing of fish sampling (e.g., boat electrofishing, gill netting, angling).
- Field measurement result (temperature and conductivity).
- Electrofishing parameters for boat or backpack electrofishing operations.
- Estimates of species and sizes encountered while fishing.
- Location that retained fish were collected.
- Field ID, total length, and weight of each retained fish.
- Unusual circumstances that might affect interpretation of results.

Field logs for the processing of fish to remove tissue, formation of composite samples, and filling of sample jars are addressed in two SOPs:

- SOP EAP007, V1.2: Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2018a).
- SOP EAP008, V1.2: Standard Operating Procedures for Resecting DNA Samples and Aging for Finfish (Sandvik, 2018b).

The two forms used during processing are printouts of tables generated in Excel:

- The "Benchsheet" which contains information for each fish and used to record processing information such as: date of resection, fillet weight removed, sex, and age structure ID.
- The "Lab Analysis Tracking Plan" which contains information about each composite sample, such as: laboratory sample IDs, tissue aliquot used in composite sample, and amount of tissue placed in each sample jar.

## 8.8 Other activities

Other activities related to field work involve coordinating many activities.

Field crew preparation includes annual refresher training for field operations, such as general field safety and more focused boat and backpack electrofishing work. Prior to actual field work, field crews discuss the sampling plan and area of operation, and address the needed target species, sizes, and numbers of fish.

The Field Lead is responsible for coordinating the maintenance of the electrofishing boat, towing vehicle, backpack electrofishing unit, angling supplies, nets, related fish collection gear, and consumable supplies such as foil, bags, gloves, and decontamination chemicals. Other Ecology staff are designated for coordinating the maintenance of processing lab deionized water maker and the fume hood.

We communicate with MEL about timeframes for delivery of samples to the lab and needed analyses. The lab will be updated via email regarding post-field estimates of the numbers of analyses and timeframes. After sample processing, the lab is updated again with more accurate information about sample numbers and delivery time. At appropriate times, we describe the needs for analyses that are contracted out: these are then articulated in a Statement of Work which is then used in a bidding process. We also notify WDFW about our fish age determination needs when we have initial estimates of the numbers and delivery date for age structures to them.

The Field Lead is also designated to maintain required Scientific Collection Permits and coordinate activities as the permits dictate. For fish collection work throughout most of Washington, these permits are required by WDFW, NMFS, and the USFWS. Additional permits may be required by those having jurisdiction in some areas, such as NPS, tribes, cities, counties.

# 9.0 Laboratory Procedures

### 9.1 Lab procedures table

Table 22. Measurement methods (laboratory).

Parameter	Analysis Frequency, Number of Samples, Arrival Date <sup>a</sup>	Expected Range of Results	Reporting Limits <sup>c</sup>	Analytical Method	Sample Preparation Method
Mercury	common, 50-100, January	10 - 1000 ug/kg	17 ug/kg	EPA 245.6 (CVAA)	EPA 245.6
Metals (one or more of: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ti, V, Zn)	uncommon, 10-20, January	0.1 - 100 ug/kg	100-5000 ug/kg <sup>e</sup>	EPA 6020B (6010D for Al)	EPA 3050B
Chlorinated pesticides <sup>b</sup> (low resolution)	common, 50-100, January	0.1 - 4000 ug/kg	most 0.5- 3.0 ug/kg	EPA 8081 (GC/ECD) MEL SOP	Prep: EPA 3541 Modified, Cleanup: EPA 3620C/3665A, EPA 60014-81-045
Chlorinated pesticides <sup>b</sup> (high resolution)	less common, 10-50, January	0.01 - 20 ug/kg for most; DDTs 0.01- 4000 ug/kg,	0.01-0.10 ug/kg	EPA 1669 (HR GC/MS) or equivalent	EPA 1669, lab SOPs
PCB Aroclors (low resolution)	common, 50-100, January	0.5 - 800 ug/kg, depending on Aroclor	1.1 - 10 ug/kg	EPA 8082 (GC/ECD) MEL SOP	Prep: EPA 3541 Modified, Cleanup: EPA 3620C/3665A, EPA 60014-81-045
PCB congeners (high resolution)	less common, 10-50, January	0.005 - 100 ug/kg, depending on congener	0.003-0.01 ug/kg	EPA 1668C (HR GC/MS)	EPA 1668C, lab SOPs
PCDD/Fs (high resolution)	less common, 10-50, January	0.005 - 5.0 ng/kg, depending on congener	0.017 - 0.5 ng/kg <sup>d</sup>	EPA 1613B (HR GC/MS)	EPA 1613B, lab SOPs
PBDEs	common, 50-100, January	0.1 - 100 ug/kg	0.10-2.6 ug/kg; PBDE 209 1.9-4.3 ug/kg	EPA 8270 (SIM) SOP 730104	Prep: EPA 3541 Modified, Cleanup: EPA 3620C Modified, EPA 3665A Modified
Lipids	common, 50-100, January	0.1 - 20 %	0.10%	MEL SOP 730009	EPA 3541 Modified

a - Range of values shown. Sample numbers vary each year and will be given in annual addendums.

b - See Table 14 for analyte-specific RLs and expected range of results for chlorinated pesticides.

c - The reporting limit for low-resolution methods is the Lower Limit of Quantitation while for high-

resolution methods it is the Estimated Detection Limit.

d - See Table 16 for analyte-specific RLs for dioxins/furans.

e - See Table 15 for analyte-specific RLs for metals.

### 9.2 Sample preparation method(s)

Sample preparation methods are shown along with analytical methods in Table 22.

### 9.3 Special method requirements

For chlorinated pesticide and PCB Aroclor analyses where the tissue matrix and high levels of some target analytes presents many interferences, MEL may perform extra steps during the extraction and clean up phases. These extra steps may help reduce interferences and improve analyte identification and quantitation.

## 9.4 Laboratories accredited for methods

This project aims to use accredited labs for all analyses. Exceptions may occur in cases where sample preparation and analyses involve techniques that are in a research and development phase. In these cases, the project will seek a waiver from the requirement to use accredited labs.

# **10.0 Quality Control Procedures**

### Field

Quality control procedures for the field work of fish collection and fish processing will follow Ecology's EA Program SOP related to fish collection (Sandvik, 2018a, b, and c). Field crews encountering unusual situations will typically resolve them using guidance at hand or consultation with others, including the Project Manager.

There are few field measurements made when collecting and processing the fish: weight and total length. For weights, the accuracy of the bench scale for measuring the weights of whole or partial fish will be checked before and after each field season using primary weight standards maintained by Ecology's Marine Monitoring Unit. Secondary weight standards are used on a daily basis. For determining total length, a ruler graduated to millimeters is used.

Annual fish collection will include gathering enough fish for true field replicates for selected sites and species as described in the Quality Objectives section above. The number of field replicates will vary each year and depend on site-specific sampling objectives. For trend analyses objectives, multiple field replicates (e.g., 5-9 replicates of same species at same site) may be collected to improve the sensitivity of statistical testing.

### Laboratory

Laboratory quality control procedures will include various analyses such as calibration standards, lab control samples, matrix spikes, standard reference materials, blanks, and replicates to evaluate the quality of data that are generated. Precision will be estimated using laboratory duplicate analyses for tissue by calculating the Relative Percent Difference (RPD) of the results. Matrix spikes may be used to indicate the presence of bias due to the sample matrix. The Project Manager may indicate which samples should be used for laboratory duplicates and matrix spikes.

### **10.1** Table of field and laboratory quality control

Parameter	Analytical Method	Lab Duplicates	Lab Control Standards	Surrogates		Method Blanks
Mercury	EPA 245.6 (CVAA)	1/ batch <sup>a</sup>	1/batch	NA	1/batch	1/batch
Metals (one or more of: Al, Sb, As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ti, V, Zn)	EPA 6020B (6010D for Al)	1/batch	1/batch	NA	NA 1/batch	1/batch
Chlorinated pesticides	EPA 8081 (GC/ECD), MEL SOP	1/batch	1/batch	each sample	1/batch	1/batch
Chlorinated pesticides <sup>c</sup>	EPA 1699 or equivalent (HR GC/MS)	1/batch	each sample & 1/batch <sup>b</sup>	NA	NA	1/batch
PCB Aroclors	EPA 8082 (GC/ECD), MEL SOP	1/batch	1/batch	each sample	1/batch	1/batch
PCB congeners °	EPA 1668C (HR GC/MS)	1/batch	each sample & 1/batch <sup>b</sup>	NA	NA	1/batch
PCDD/Fs °	EPA 1613B (HR GC/MS)	1/batch	each sample & 1/batch <sup>b</sup>	NA	NA	1/batch
PBDEs	EPA 8270 (SIM), MEL SOP 730104	1/batch	1/batch	each sample	1/batch	1/batch
Lipids	MEL SOP 730009	1/batch	1/batch	NA	NA	1/batch

 Table 23. Laboratory quality control sample types and frequencies.

a - "Batch" is defined as up to 20 samples analyzed together.

b - Labeled compounds in each sample and Ongoing Precision and Recovery standards in each batch.

c – CRM likely to be analyzed once per 1 or 2 batches.

### **10.2 Corrective action processes**

Corrective actions will be taken if activities are found to be inconsistent with the QAPP, field procedures, laboratory analyses, data review processes, MQOs or performance expectations, or if some other unforeseen problem arises. Such actions may include:

- Collecting new samples using the method described in the approved QAPP.
- Accepting and qualifying lab results that do not meet all QC criteria.
- Reanalyzing lab samples that do not meet QC criteria.
- Convening project personnel and technical experts to decide on the next steps that need to be taken to improve performance of project components.

# **11.0 Data Management Procedures**

As field and lab data are completed, data will be organized using various tabular and graphical formats for additional review, calculations, characterization and reporting.

Data from historical efforts will be obtained from various sources. The primary source will be Ecology's EIM databases and other Ecology repositories. Data from other agencies may also be used (e.g., EPA, USGS, tribes, WDFW). The quality of such data will be reviewed for its usability on a case-by-case basis and factors leading to its use documented in quality assurance reviews for each year's effort.

## 11.1 Data recording and reporting requirements

### Field

Data management for this project will include written and electronic media generated from field activities. The EA Program SOPs for the collection and processing of fish samples describes formats to be used for all phases of recordkeeping (Sandvik 2018a, b, and c).

Field notes and observations will be recorded by hand into prepared field forms, notebooks, and/or maps/sketches. Pertinent data collected in field books will be transferred to electronic media using Microsoft Office products (Word, Excel, and Access) and ArcView GIS.

After entry into electronic media, about 10% of the electronic data will be reviewed and compared to handwritten data to check and correct data entry errors. Some field data will be reduced before further use. For example, field measurements of length and weight from the individual fish used in a composite sample are reduced to an average value for the associated composite sample. These calculations are done in a separate Excel file before transferring values to the EIM upload template.

After these reviews, pertinent field data will be reduced and entered into Ecology's electronic Environmental Information Management (EIM) system. Hardcopy and electronic data not entered into EIM will be retained in a file system maintained by the Project Manager.

### Lab

Laboratory analyses of samples generate data recorded in handwritten and electronic formats. These data will be verified and validated as described in Section 13 below. Laboratory data generated by MEL will be entered into the Laboratory Information System (LIMS) by MEL staff. When notified of the availability of data, project staff can then access LIMS data and load appropriate data into EIM via the EIM template. Laboratory data generated by contract labs will be verified and validated as described in Section 13 below. After errors and concerns are addressed, these data will be loaded into EIM via the EIM template.

Results from some groups of target analytes are summed in order to account for their additive effects and comparability to various criteria or benchmarks. Procedures for summing and handling qualified values such as non-detects will follow Ecology's TSU guidance or be explained in reports. Parameters that are commonly summed include: PCBs, PBDEs, PCDD/Fs, DDTs, and Chlordanes. Summed values are used in reports and not usually uploaded to databases.

For dioxins and furans (PCDD/Fs), the cumulative toxicity of the 17 most toxic congeners will be calculated using the international convention (Van den Berg et al., 2006) as recommended by EPA (2010) of expressing the cumulative toxicity of mixtures of congeners as a toxic equivalent (TEQ) to 2,3,7,8-TCDD. This TEQ is calculated by multiplying the result for each congener by its congener-specific Toxicity Equivalent Factor (TEF) and then summing the products (which are congener-specific TEQs) to obtain the 2,3,7,8-TCDD TEQ.

# 11.2 Laboratory data package requirements

Laboratory results from MEL analyses will be sent to the Project Manager in hardcopy format (from LIMs) and be accompanied by a Case Narrative. The Case Narrative will address various data verification and validation checks described in Section 13 below

Results from contract laboratories will be delivered to MEL and contain information specified in two documents: one called a Request for Qualifications and Quotes (RFQQ) and the other known as the Request for Analysis (RFA). The RFQQ and RFA are developed by designated MEL staff and the Project Manager. The RFQQ contains a Scope of Work which specifies the requirements of the analytical work: this RFQQ is used as a solicitation for bids from analytical laboratories for the work to be done. A MEL-designated expert will review the Level 4 data package from the contract lab and summarize findings in a Case Narrative similar to that for MEL-generated data. The Level 4 data package, in addition to the EDD described below, provides everything needed for a Stage 1 through Stage 4 data validation. Section 13 describes th the data verification and validation process.

## **11.3 Electronic transfer requirements**

Laboratory data generated by MEL will be entered into the Laboratory Information System (LIMS) by MEL staff. When notified of the availability of data, project staff can then access LIMS data and receive the data in an Excel file formatted similarly like the EIM loading template.

Results from contract labs will be provided in Excel-compatible (e.g., .csv) format for ease of review, editing, and transfer into EIM. The typical electronic data deliverable (EDD) format is shown in Table 24. Other items may be included as needed to help understand the data package.

Results from contract labs are reviewed by MEL staff who will then prepare a case narrative for the Project Manager (see Section 13 for more detail).

Ref #	Field Name	Example Value
1	Study ID (Project Name provided to contract lab)	FFCMP 2018
2	Field Station Identification (Ecology Field ID provided to contract lab)	STA5-CCC
3	Contract Lab Sample ID	L180327-5
4	MEL Work Order Sample ID (Ecology Sample ID provided to contract lab)	1803015-01
5	Field Collection Date (listed in COC)	10/25/2018
6	Date of Receipt at Contract Lab	3/15/2019
7	Sample Matrix (provided to contract lab)	Tissue
8	Sample Preparation Method	1668C
9	Analysis Method	1668C
10	Parameter Name (the 7-character format for PCBs is required)	PCB-001
11	CAS Number	2051-60-7
12	Sample Extraction Date	3/30/2018
13	Analysis Date	4/10/2018
14	Analysis Time	12:22
15	Lab Batch ID (to associate results with QC samples)	L80882
16	Contract Lab Name	MegaMSLab
17	Result Value	0.743
18	Result Value Units	ng/g
19	Result Reporting Limit	4.33
20	Result Reporting Limit Type (e.g., LOQ/MRL)	LOQ
21	Result Detection Limit	0.743
22	Result Detection Limit Type (e.g., EDL/CRDL/MDL)	EDL
23	Result Value Qualifier	UJ
24	Result Basis (Wet/Dry)	Wet
25	Lab Duplicate (Y/N)	N
26	Lab Reanalysis (Y/N)	N
27	Amended Result Value (entered by data reviewer)	0.743
28	Amended Result Value Qualifier (entered by data reviewer)	U
29	Reason for Amendment(s) (entered by data reviewer)	Blank contamination

Table 24. Required fields for electronic data deliverables from contract labs.

Where the verification/validation process for contract lab data results in changes to qualifiers and reported values, the person conducting the verification/validation will create three new fields in the EDD and enter the amended values along with the reason for the change (as in items #27-29 in Table 24 above).

## 11.4 EIM/STORET data upload procedures

Data will be loaded into Ecology's Environmental Information Management (EIM) database following EIM guidance. Data from the field, MEL, and contract labs will be entered into an EIM upload template.

After laboratory data are entered into EIM, the EIM Data Review Procedure requires checks about 10% of the data to ensure that it was entered correctly.

### **11.5 Model information management**

Not applicable – no modeling done for this project.

# 12.0 Audits and Reports

### 12.1 Field, laboratory, and other audits

Audits of field procedures, sample processing, or other components outside of the analytical laboratory environment are not planned.

The laboratories conducting sample analyses are accredited through Ecology's Laboratory Accreditation Program. This program audits laboratories and establishes whether they have the capability to provide accurate, defensible data. Accreditation involves an evaluation of the laboratory's quality system, staff, facilities and equipment, test methods, records, and reports.

## 12.2 Responsible personnel

Audits of field procedures, sample processing, or other components outside of the laboratory environment may occur at the discretion of Ecology's Quality Assurance Manager, supervisors, or the Project Manager. Ecology's Laboratory Accreditation Program conducts audits on laboratories according to their program guidance.

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

Annual reports will be generated to describe results for the year of sampling. Other formats may be used to report findings, such as Ecology's "Focus Sheet", blogs, website, or other summaries as needed.

Annual reports will address elements outlined in Ecology report templates:

- Table of Contents, List of Tables and Figures
- Abstract or Executive Summary
- Acknowledgements
- Introduction
- Methods
- Results
- Discussion
- Conclusions
- Recommendations
- References
- Glossary, Acronyms, and Abbreviations
- Appendices

The reports will address the sampling objectives, background, methods, data quality, results, statistical procedures, data analyses for trends, comparisons to various thresholds for protection of human health, significant findings, and recommendations. Due to the large amount of data

collected and many potential analyses that could be done, annual reports will only summarize key results in order to keep the report manageable. Other results from annual effort will be made available to audiences upon request.

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

## 12.4 Responsibility for reports

The Project Manager is responsible for annual reports. The Field Lead and other staff that contribute significantly to the reporting or field effort may be co-authors.

# 13.0 Data Verification

This section describes data verification and validation which are typically sequential steps. EPA (2002) defines Data verification as "The process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements." Data validation is defined as "The analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual requirements (i.e. data verification) to determine the analytical quality of a specific data set".

For this project, data verification and validation may be performed by various parties. For results generated by MEL, the data are verified and validated using MEL SOPs for data review. The validation steps in this case are considered "same-party" validation. For results generated by laboratories other than MEL (contract labs), data verification and validation is performed by MEL staff and is considered "third-party" validation. For data generated by field staff, data are verified by the field leader or Project Manager, usually before leaving the fish collection site or sample processing site where the measurements and notes were made.

# 13.1 Field data verification, requirements, and responsibilities

Field data are collected in two locations: the sample collection site and the sample processing spaces. Field-collected data will be verified by examining logs such as field notes, maps, sample processing bench sheets, lab analysis and tracking sheets, age structure labelling, and other notes for legibility, completeness, and errors.

Where omissions or errors in the data are found, the source of the data (e.g., field crew, sample processing crew) will be consulted to determine the correct value or form of the data in question. Corrections or qualifications will be made where possible. Where corrections cannot be made, additional information will be noted to explain the error. The data in question may also be qualified or rejected for further use.

Both sets of data will be verified by the field lead prior to leaving either of the locations where field data are collected. To indicate that the data have been verified, the field lead will mark each page thus: "VER, date, initials". This marking will be circled so that it can be easily distinguished from other notes.

After field data are entered into EIM, the EIM Data Review Procedure checks about 10% of the data to ensure it that was entered correctly.

# **13.2 Laboratory data verification, requirements, and responsibilities**

All laboratory data will be, at a minimum, verified and validated to the Stage 2B standard described in EPA's Guidance for Labeling Externally Validated Lab Data for Superfund Use (EPA, 2009). Additional verification/validation will be performed as recommended by the data reviewer and/or the Project Manager.

For results generated by MEL, a "same-party validation" will be performed by MEL staff according to MEL's internal procedures. For example, MEL SOP 730022 describes the peer and final review of organics data. This SOP performs the same tasks through Stage 2B above, and includes some tasks in Stage 3.

For results generated by a Contract Lab, the verification will include checks to see whether specific requirements described in the contracts' Statement of Work (SOW) were followed, such as using the proper EDD format and analyzing QC samples as specified in the SOW. There are several options for verification and validation:

- "Third-party validation" by MEL staff using MEL's most recent SOP.
- "Third-party validation" by an outside contractor.

For validation of Contract Lab data, the Project Manager will define the level of validation required for each data package. Annual addendums will state whether a Stage 2B, 3, or 4 validation is needed. The amount of recalculation done during Stage 3 will also be defined and will typically be in line with industry standards, which is recalculation of about 10% of sample results in a batch, all initial calibrations, and many other QC samples. This amount of sample recalculation depends in part on the number of detections because it is not useful to recalculate non-detected results. Data validators may preferentially choose to recalculate results that have dilutions and detections, and then if there are no detections, they may recalculate QC samples with positive results.

The outcome of the verification and validation process will be documented in Case Narratives and related documents provided by the analytical laboratories and data verifiers/validators. These documents identify the person(s) who conducted the review on each particular data set. The Project Manager reviews the Case Narratives and works with the data reviewers to resolve any concerns. The Case Narratives typically summarize:

- The nature of the verification and validation effort.
- The location where results and related details are stored, such as: the analytical method used, sample ID scheme, QC results, and batch IDs.
- Compliance with analytical method, lab QA/QC limits, and the MQOs described in this QAPP or subsequent QAPP addendums.
- Explanations and discussion about challenges or circumstances that affect the quality of the data.
- The assignment, and definitions, of data qualifiers.

Data qualifiers are typically assigned to results as part of the analysis and data review process. Qualifiers may also be assigned or changed during the data validation process or by the Project Manager during the broader data quality assessment effort. Table 25 shows the most common data qualifiers used with results for the FFCMP.

Table 25	. Data	qualifiers	and	definitions.
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Qualifier	Definition
U	The analyte was analyzed for but was not detected at the reported quantitation limit.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample.
UJ	The analyte was not detected at or above the reported quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
NJ*	The analysis indicates the presence of the analyte, has been tentatively identified, and the associated numerical value represents an approximate concentration. (For isotopic dilution methods, the mass-ion abundance ratio was not met and identification needs further confirmation).
NUJ**	The analyte was tentatively identified in both sample and associated method blank and the sample concentrations is $\leq 5x$ the blank value. (Most often used with isotopic dilution methods, the mass-ion abundance ratio was not met and identification needs further confirmation).
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet the quality control criteria. The presence or absence of the analyte cannot be verified.
E	Reported result is an estimate because it exceeds the calibration range.
NAF	Not analyzed for.
NC	Not calculated.

\*Analogous to U. \*\*Analogous to UJ.

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

See previous section regarding verification and validation. Some elements of validation will be conducted as described in previous section. How the validation is conducted depends on which laboratory analyzes the samples.

### 13.4 Model quality assessment

Not applicable – no modeling done for this project.

# 14.0 Data Quality (Usability) Assessment

### 14.1 Process for determining project objectives were met

The Project Manager will determine whether the project objectives were met by determining whether the sampling and laboratory analyses met requirements described in this project plan.

Other staff may be consulted where their expertise can be of value in these determinations (e.g., quality assurance staff, laboratory staff). Characteristics of this determination will address the following:

- Sampling:
- Target #s of species of target size at target site in target season.
- Field data collected for 100% of cases the data are required.
- Post-field processing yields adequate numbers of composite samples
- Adequate budget for planned lab analyses.
- Lab Analysis:
- Successful analyses at 100% of goal.
- Successful verification and validation.
- All analyses meet MQOs and other needed QC.
- Data review
- Appropriate qualification or rejection of data based on defensible circumstances.
- Results make sense.

### 14.2 Treatment of non-detects

Non-detect values will usually be handled using one of two substitution methods, depending on the purpose of the analysis. Substitutions may be as follows:

- Substitute the reporting limit. Typically used for general characterization of the data to provide a high-level view of the results and where substituting the reporting limit does not compromise decisions related to regulatory actions.
- Substitute the value of zero. Typically used when results are used for comparison to Washington's water quality standards. The water quality standards require that the summing of certain results to obtain a "total" value, such as for "total PCBs", use only detected values for the addends that are being summed. Addends that are non-detects have their values set to zero for the summing process.

### 14.3 Data analysis and presentation methods

### **Data reduction**

Data from various sources will be compiled using MS products such as Excel and Word. All acceptable and appropriate lab and field results will be compiled in Excel tables from which further data reduction will occur. Individual tables are used for compiling data that originate

from different sources. These source tables are then used for data reduction efforts performed in different spreadsheets. The most common data sets will be:

- Field measurements of individual fish: species, total length, weight, capture location.
- Sample processing: data for every fish that is processed for use in composite sample.
- Laboratory results from MEL: sample and some QC results.
- Laboratory results from Contract Labs: sample and some QC results.

A final data set is compiled from and includes results from other data reduction efforts. The final data set for further analysis and reporting purposes will be a single Excel table that includes:

- Sample ID, location, species, collection date.
- Results and related parameter, method, and lab results for all target analytes.
- "Total" values for certain parameters (e.g., t-PCB, t-Chlordane, t-DDT, TCDD-TEQ).
- Average values of field measurements (length, weight, age) for all fish in a composite sample.

### **Calculation of "total" values**

As field and lab data are completed, data will be organized using various tabular and graphical formats for additional review, calculations, characterization and reporting. Results from some groups of target analytes are summed in order to account for their additive effects and simplicity of comparison to various criteria and other data. Parameters that are commonly summed include: PCBs, PBDEs, PCDD/Fs, DDTs, Chlordanes, and Endosulfans. Procedures for summing and handling qualified values such as non-detects will follow in-house guidance or be explained in reports.

For dioxins and furans (PCDD/Fs), the cumulative toxicity of the 17 most toxic congeners will be calculated using the international convention (Van den Berg et al., 2006) and expressed as the toxic equivalent (TEQ) to 2,3,7,8-TCDD. This TEQ is calculated by multiplying the result for each congener by its congener-specific Toxicity Equivalent Factor (TEF) and then summing the products (which are congener-specific TEQs) to obtain the 2,3,7,8-TCDD TEQ value. This value is also expressed as TCDD-TEQ.

### Data Analyses

Further analysis and reporting will proceed using Excel for data management and statistics, statistical software such as SYSTAT or R for data analyses, and Arc GIS for mapping. Common analyses are expected to include:

- Summary statistics.
- Evaluating whether target analytes are possible covariates to fish characteristics such as fish size, age, and lipids content.
- Plots and tables to identify exceedances of thresholds for protection of human health.
- Plots to compare contaminant concentrations among sampling sites and species.

- Plots of key parameters for temporal and spatial trends.
- Statistical tests and tabular summaries for temporal trends using hypothesis testing for determining differences between means or medians, such as the parametric two sample t-test and the non-parametric Mann-Whitney test.
- Statistical tests and tabular summaries for spatial trends will likely use the non-parametric Kruskal-Wallis single-factor ANOVA test.
- Maps showing magnitude of results for selected parameters at the sites sampled in one year or for statewide perspectives using results from multiple years.

## 14.4 Sampling design evaluation

The sampling designs for each year of sampling are expected to be adequate to meet most objectives most of the time. However, smaller sample numbers and higher variability than expected may render the sampling design to be less effective than desired in some cases. Such cases will likely manifest as the reduced ability to detect temporal and spatial trends of a desired magnitude for a given combination of location, species, and analyte. In most cases, the project will work with the quality and quantity of results available, and note in the report any impacts on attaining objectives. Post-hoc analyses of statistical power of the trend tests may be performed in order to inform future sampling design.

### 14.5 Documentation of assessment

Documents used for the data usability assessment will include a variety of notes and reports described above, such as:

- Field notes and laboratory Case Narratives.
- Verification and validation reports from laboratories and project staff.
- Worksheets and tables comparing results from field and QC samples to MQOs and other data quality indicators.

The Data Quality Review worksheet is one table referenced in the previous bullet which includes a place to record the overall decision about how to use laboratory results for each group of analytes. Further documentation of the data usability assessment will occur in the report Methods section.

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# 16.0 Appendices

# Appendix A. Fish Tissue Data Evaluation by Ecology and Health

Several state and federal agencies collect and evaluate fish tissue data in Washington State. These include Ecology, Health, Washington Department of Fish and Wildlife, the U.S. Environmental Protection Agency (EPA), and the U.S. Geological Survey. Tissue data are evaluated differently by these agencies because their mandates and roles are varied. These multiple evaluations often lead to confusion and misunderstanding among agencies and the public on how fish tissue data are used and interpreted. Adding to potential confusion are the numerous thresholds derived by different agencies to provide guidance for determining the risks of consuming contaminated fish and protecting public health.

Most tissue contaminant data from Washington fish and shellfish, regardless of who conducted the study, make their way to Health for evaluation regarding the safety of consuming fish. Health provides information about the heathy benefits of fish as well as advice regarding Fish Consumption Advisories at: <u>www.doh.wa.gov/CommunityandEnvironment/Food/Fish.aspx</u>.

The fish tissue data collected for the FFCMP and many other Ecology studies are evaluated primarily (1) to determine if the waterbodies are supporting designated uses in the water quality standards and (2) to provide tissue data results that can be used to determine potential risks to human health from consuming contaminated fish that may warrant further study and/or development of a fish consumption advisory.

Ecology determines whether water quality standards are met through the Policy 1-11 listing methodologies and prioritizes Clean Water Act Section 303(d) listings to begin the process to correct problems where standards are not met. Health and local health departments are responsible for weighing the potential risks to human health and developing fish consumption advisories in Washington. There is some overlap in these evaluations because the water quality standards that fish tissue data are compared to were developed to protect the beneficial uses of fish and shellfish harvest.

The following is an overview of how Ecology and Health evaluate fish tissue data to meet different needs.

### Washington State Water Quality Standards

Washington's water quality standards for the protection of human health from toxic contaminants were originally issued to the state through EPA's 1992 National Toxics Rule (NTR) codified in 40 Code of Federal Regulations 131.36. Ecology revised the water quality standards in October 2017 (Ecology, 2017). For toxic contaminants, Water Quality Program Policy 1-11 describes how numeric and narrative criteria are used to minimize the risk of health effects from exposure to contaminants in water and fish/shellfish obtained from surface waters.

Ecology is responsible for assessing water bodies in the state to meet federal requirements for an integrated report under Sections 303(d) and 305(b) of the CWA. Policy 1-11, Chapter 1, describes the methods for determining whether water quality standards are met and beneficial uses are protected. The assessed waters are grouped into categories that describe the status of water quality. Category 5 represents the 303(d) list, which comprises those waters that are in the polluted water category, for which beneficial uses– such as drinking, recreation, aquatic habitat, and industrial use – are impaired by pollution. Waterbodies in Category 5 require development of a water cleanup plan (such as a Total Maximum Daily Load, or TMDL). The water cleanup plan identifies the sources of pollution and a public involvement process which identifies actions to correct the sources of pollution. Ecology uses the TMDL program to control sources of the particular pollutant in order to bring the waterbody back into compliance with the water quality standards.

### **Risk Management Decisions for Fish Advisories**

Health uses an approach similar to that in EPA's Guidance for Assessing Chemical Contaminant Data for use in Fish Advisories Vol. 1-4 for assessing contaminants (EPA, 2000). These guidance documents provide a framework from which states can evaluate fish tissue data to develop fish consumption advisories. The framework is based on sound science and established risk management concepts such as:

- **Risk Assessment** involves calculating allowable meal limits based on known fish contaminant concentrations. These calculations are conducted for both non-cancer and cancer criteria using the appropriate Reference Dose (RfD) or Cancer Slope Factor (CSF), if available. These initial calculations are the starting point for evaluating contaminant data to determine whether a fish advisory is warranted. Additionally, known or estimated fish consumption rates help determine the potential magnitude of exposure and highlight the sensitive groups or populations that may exist due to elevated consumption rates.
- **Risk Management** includes (but is not limited to) consideration of contaminant background concentrations, reduction in contaminant concentrations through preparation and cooking techniques, known health benefits from fish consumption, contaminant concentrations, health risks associated with replacement foods, and cultural importance of fish. Other considerations are the possible health criteria associated with a contaminant, the strength or weakness of the supporting toxicological or sampling data, and whether effects are transient or irreversible.
- **Risk Communication** is the outreach component of the fish advisory. The interpretation of the data from the risk assessment and risk management components drives how and when the fish advisory recommendations are issued to the public, dependent on whether the message is targeted toward a sensitive group or a population or the general public. Health's dual objective is (1) how best to provide guidance to the public to increase fish consumption of fish low in contaminants to gain the benefits of eating fish, while (2) steering the public away from fish that have high levels of health-damaging contaminants.

## Appendix B. Target Fish Species

Table B-1. Characteristics of fish species that may be collected for the FFCMP.

Common name	Ecology Species Code	Scientific name	Habitat	Feeding	Water temp	Tolerance	Family name	Possible Hatchery or Transplant
Black crappie	BC	Pomoxis nigromaculatus	water column	invert/piscivore	warm	Т	Centrarchidae	Y
Bluegill	BG	Lepomis macrochirus	water column	invert/piscivore	warm	Т	Centrarchidae	Y
Bridgelip sucker	BLS	Catostomus columbianus	benthic	herbivore	cool	Т	Catostomidae	
Brook trout	BKT	Salvelinus fontinalis	hider	invert/piscivore	cold	I	Salmonidae	Y
Brown bullhead	BBH	Ameiurus nebulosus	hider	invert/piscivore	warm	Т	Ictaluridae	
Brown trout	BNT	Salmo trutta	hider	invert/piscivore	cold	I	Salmonidae	Y
Burbot	BUR	Lota lota	benthic	piscivore	cold	I	Gadidae	
Channel catfish	CC	lctalurus punctatus	benthic	invert/piscivore	warm	Т	Ictaluridae	Y
Chiselmouth	CLM	Arocheilus alutaceus	benthic	herbivore	cool	I	Cyprinidae	
Common carp	CCP	Cyprinus carpio	benthic	omnivore	warm	Т	Cyprinidae	
Cutthroat trout (Coastal) 1	CTTC	Oncorhynchus clarki clarki	water column	invert/piscivore	cold	S	Salmonidae	Y
Cutthroat Trout (Lahontan) 1	CTTL	Oncorhynchus clarki henshawi	water column	invert/piscivore	cold	S	Salmonidae	Y
Cutthroat Trout (Western) 1	CTTW	Oncorhynchus clarki lewisi	water column	invert/piscivore	cold	S	Salmonidae	Y
Grass carp	GCP	Ctenopharyngodon idella	benthic	herbivore	warm	Т	Ictaluridae	Y
Green sturgeon	GST	Acipenser medirostris	benthic	piscivore	cold	S	Acipenseridae	
Green sunfish	GS	Lepomis cyanellus	water column	invert/piscivore	warm	Т	Centrarchidae	
Kokanee salmon	KOK	Oncorhynchus nerka	water column	invertivore	cold	S	Salmonidae	Y
Lake trout	LKT	Salvelinus namaycush	benthic	piscivore	cold	S	Salmonidae	
Lake whitefish	LWF	Coregonus clupeaformis	water column	invertivore	cold	I	Salmonidae	
Largemouth bass	LMB	Micropterus salmoides	water column	piscivore	warm	Т	Centrarchidae	Y
Largescale sucker	LSS	Catostomus macrocheilus	benthic	omnivore	cool	Т	Catostomidae	
Longnose sucker <sup>2</sup>	LNS	Catostomus catostomus	benthic	invertivore	cold	I	Catostomidae	

Common name	Ecology Species Code	Scientific name	Habitat	Feeding	Water temp	Tolerance	Family name	Possible Hatchery or Transplant
Mountain sucker	MS	Catostomus platyrhynchus	benthic	herbivore	cool	I	Catostomidae	
Mountain whitefish	MWF	Prosopium williamsoni	benthic	invertivore	cold	I	Salmonidae	
Northern Pike	NOP	Esox lucius	water column	piscivore	cold	S	Esocidae	
Northern pikeminnow	NPM	Ptychocheilus oregonensis	water column	invert/piscivore	cool	Т	Cyprinidae	
Peamouth	PEA	Mylocheilus caurinus	water column	invertivore	cool	I	Cyprinidae	
Pumpkinseed	PMP	Lepomis gibbosus	water column	invert/piscivore	cool	Т	Centrarchidae	
Rainbow trout <sup>3</sup>	RBT	Oncorhynchus mykiss	hider	invert/piscivore	cold	S	Salmonidae	Y
Rock bass	RKB	Ambloplites rupestris	water column	invert/piscivore	warm	I	Centrarchidae	L
Salish Sucker <sup>2</sup>	SS	Catostomus catostomus	benthic	omnivore	cool	S	Catostomidae	
Sculpins	СОТ	Cottus sp.	benthic	invertivore	cool	Т	Cottidae	
Smallmouth bass	SMB	Micropterus dolomieui	water column	piscivore	cool	I	Centrarchidae	Y
Starry flounder	STF	Platicthys stellatus	benthic	invertivore	cold	S	Pleuronectidae	L
Tench	TCH	Tinca tinca	water column	invertivore	warm	Т	Cyprinidae	
Tiger Trout	тт	Salmo trutta X Salvelinus fontinalis	hider	invert/piscivore	cold	I	Salmonidae	Y
Walleye	WAL	Sander vitreus	water column	piscivore	cool	I	Percidae	Y
Warmouth	WM	Lepomis gulosus	water column	invert/piscivore	warm	Т	Centrarchidae	•
White crappie	WC	Pomoxis annularis	water column	invert/piscivore	warm	Т	Centrarchidae	Y
White sturgeon	WST	Acipenser transmontanus	benthic	invert/piscivore	cold	I	Acipenseridae	
Yellow bullhead	YBH	Ameiurus natalis	hider	invert/piscivore	warm	Т	Ictaluridae	
Yellow perch	YP	Perca flavescens	water column	invert/piscivore	cool	I	Percidae	

1 - Cutthroat trout: if uncertain of subspecies, just call it CTT (Oncorhynchus clarki). Subspecies usually haven't been distinguished in past work. EIM doesn't distinguish fish subspecies yet. (2008).

2 - Same species, Salish Sucker appears to be dwarf form of Longnose. Salish is found west of Cascade crest. The Longnose is found east of the Cascade crest. EIM doesn't distinguish different forms.

3 - Some RBT hybridize with CTT so that fish have some characteristics of both species. Note in field book if hybrids suspected.

Tolerance field describes overall pollution tolerance: S = sensitive, I = intolerant, T = tolerant

### Appendix C. Glossary, Acronyms, and Abbreviations

### **Glossary of General Terms**

**Clean Water Act:** A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

**Conductivity:** A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

**Designated uses:** Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained.

**Fish Tissue Equivalent Concentration (FTEC):** The FTEC is a tissue contaminant concentration used by Ecology to determine whether the designated uses of fishing and drinking from surface waters are being met. The FTEC is an interpretation of Washington's water quality criterion for a specific chemical for the protection of human health: the National Toxics Rule (40 CFR 131.36). Fish tissue sample concentrations that are lower than the FTEC suggest that the uses of fishing and drinking from surface waters are being met for that specific contaminant. Where an FTEC is not met (i.e., concentration of a chemical in fish tissue is greater than the FTEC), that water body is then placed into Category 5 during Washington's periodic Water Quality Assessment (WQA and 303d List). Category 5 listings become part of Washington's 303(d) list during the assessment process. The FTEC is calculated by multiplying the contaminant-specific Bio-Concentration Factor (BCF) times the contaminant-specific Water Quality Criterion found in the National Toxics Rule.

**Nonpoint source:** Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

**Point source:** Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

**Pollution:** Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to

(1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Reach: A specific portion or segment of a stream.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

**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.

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands

**Tissue Exposure Concentration (TEC):** The TEC is a tissue concentration that Ecology developed to represent exposure to a potentially harmful level of a pollutant through the consumption of fish or shellfish. The TEC was developed using parts of the EPA's human health criteria equations. When the concentration of a pollutant in composite samples of fish or shellfish is greater than a threshold related to the TEC, the designated use of harvest is considered impaired, indicating that the waterbody may not be meeting water quality standards for the State of Washington, and may be placed on the Clean Water Act 303(d) list.

**Total Maximum Daily Load (TMDL):** A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

**Turbidity:** A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

**Watershed:** A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

**303(d) list:** Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

**90<sup>th</sup> percentile:** An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90<sup>th</sup> percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

### Acronyms and Abbreviations

BMP	Best management practice
CRM	Certified Reference Material
CP	Chlorinated pesticides
CWA	Clean Water Act
DDT	dichloro-diphenyl-trichloroethane
Health	Washington State Department of Health
e.g.	For example
EA	Environmental Assessment (Program)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FFCMP	Freshwater Fish Contaminant Monitoring Program
GIS	Geographic Information System software
GPS	Global Positioning System
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NTR	National Toxics Rule
PBDE	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyls
PCDD/F	poly-chlorinated dibenzo-p-dioxins and dibenzofurans
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
SRM	Standard reference materials
TMDL	(See Glossary above)
USFS	U.S. Forest Service
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WCP	Water Cleanup Plan
WDFW	Washington Department of Fish and Wildlife

#### Units of Measurement

°C	degrees centigrade
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
mg	milligram
mg/Kg	milligrams per kilogram (parts per million)
mm	millimeter
ng/g	nanograms per gram (parts per billion)
ng/Kg	nanograms per kilogram (parts per trillion)
pg/g	picograms per gram (parts per trillion)
ug/g	micrograms per gram (parts per million)
ug/Kg	micrograms per kilogram (parts per billion)
WW	wet weight

### Quality Assurance Glossary

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

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

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

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

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

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

**Check standard:** A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an

obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

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

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

**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:** Is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e. data verification) to determine the analytical quality of a specific data set (EPA, 2002). It involves a detailed examination of the data package, using both professional judgment and objective criteria, to focus on particular data needs for a project. Data validation begins with the outputs from data verification. In practice, the extent of the validation effort is often characterized by "stages" (e.g., Stage 2b, Stage 3, Stage 4) relating to the increasing rigor of the evaluation (EPA, 2009).

Ecology considers four 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 analytical results from:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The Data Validation report generated at the end of the data validation process assigns qualifiers to indicate the quality of the laboratory results. These qualifiers include:

- No qualifier: analyte was present at the reported concentration.
- J (or a J variant): analyte was positively identified and the associated value is an estimate. The result may be biased high or low.
- N (or N variant): analyte was tentatively identified; the associated value is an estimate.

• REJ – data are rejected, cannot be used for intended purposes. (Kammin, 2010; Ecology, 2004).

**Data verification:** Is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements (EPA, 2002). Contractual requirements are often expressed in project plans as Measurement Quality Objectives (MQOs) such as precision, bias, and sensitivity.

**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).

**Laboratory Control Sample (LCS)/LCS Duplicate:** 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). Monitors lab's process for bias and precision.

**Lower Limit of Quantitation (LLOQ)**: The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence. The LLOQ must be  $\geq$  the lowest point in the calibration curve and is verified annually for organics.

**Matrix spike/Matrix Spike Duplicate:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias and precision errors 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).

**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 40 CFR 136, October 26, 1984 edition. The 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). In 2017 per SW-846 MDLs were eliminated for all 8000 series organics methods.

**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).

**Sample Detection Limit (SDL):** The MDL adjusted to reflect sample-specific actions such as dilution or the use of smaller aliquot sizes, or to report results on a dry-weight basis.

**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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