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Quality Assurance Project Plan

Measuring Mercury Trends in Freshwater Fish in Washington State

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Quality Assurance Project Plan

Measuring Mercury Trends in Freshwater Fish in Washington State

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2.0 Abstract

Mercury was chosen as the first pollutant to be addressed in the state's Persistent, Bioaccumulative, and Toxic (PBT) Reduction Strategy. The Washington State Departments of Ecology (Ecology) and Health developed a Mercury Chemical Action Plan (CAP) in 2003, which identified the need for improved understanding of mercury's behavior in the environment. As a result, Washington's Legislature provided funds for Ecology to begin long-term monitoring of mercury in freshwater environments in the state.

In 2005, Ecology created a long-term monitoring program with the goal of assessing temporal trends in mercury levels of freshwater fish throughout the state. The program selected 30 core sites statewide to monitor in rotation. Each year, Ecology collects 10 individual largemouth or smallmouth bass from six lakes for analysis of total mercury. Ecology returns to each set of lakes every five years to assess trends and determine if mercury levels are changing.

As of 2019, Ecology has carried out three rounds of sampling at each of the 30 sites since 2005. This project plan outlines the next five years of sampling (2020 through 2024), which will be the fourth collection from each site. In 2020, a paired fish muscle plug will be collected from one side of each individual bass sample to assess whether collection methods could be changed to this non-lethal method in future sampling years.

A secondary goal of this project is to provide information about mercury levels in fish species other than bass in order to help the Department of Health craft more informative recommendations for fish consumption advisories. When encountered, three composite samples of up to 2 additional species will be collected and analyzed for total mercury.

Results from each sampling year will be published in a short report annually. After the fourth round of sampling is complete (2024), a synthesis report will be written and goals of the program re-assessed.

3.0 Background

3.1 Introduction and problem statement

While mercury is a naturally occurring substance, human activity has increased the release of mercury into the environment. Consequences of this include increased health risks to humans and wildlife due to the persistent, bioaccumulative, and toxic (PBT) nature of this substance. Concerns about these risks have led governments at international, national, state, and local levels to recognize and address the problems associated with humanity's use and disposal of mercury.

In Washington, mercury was chosen as the first priority pollutant to be addressed in the state's PBT Reduction Strategy (Gallagher, 2000). This focus on mercury resulted in development of the Washington State Mercury Chemical Action Plan (CAP) (Peele et al., 2003). The Washington State Departments of Ecology (Ecology) and Health (DOH) developed the Mercury CAP with assistance from an advisory committee representing business, health, environmental, and local government organizations.

The Mercury CAP provides a thorough description of mercury in the environment including:

- Natural and anthropogenic sources.
- Occurrence and biogeochemical cycling.
- Mercury use and emissions in Washington.
- Summary of health effects and concerns.
- Fish consumption advisories in Washington due to mercury-contaminated fish.

Other information in the Mercury CAP addresses:

- Clean Water Act Section 303d listings of waterbodies impaired by mercury.
- Review of research projects looking at mercury in Washington.
- Regulatory structures and numerical criteria that address mercury.
- Recommendations for reducing mercury emissions in Washington.

One of the goals of the PBT Strategy and Mercury CAP was to develop information needed for understanding the behavior of PBTs in the environment and reaching decisions on measures to reduce PBTs. While several early studies helped to initially characterize mercury levels in Washington's environment, these studies and the Mercury CAP recognized and stated the need for a long-term commitment to monitoring mercury in the environment.

In 2005, the Legislature provided funds to begin long-term monitoring of mercury in the environment. This funding was provided to determine mercury levels in edible tissue from 10 individual fish of the same species (bass and/or walleye) from six sites per year for long-term trend characterization. Sampling at each of these sites were to be repeated every five years such that a total of 30 sites will be sampled over a five-year period.

The lack of a long-term monitoring effort for mercury in fish tissue hampered efforts to understand the scope of fish tissue contamination and develop reasonable expectations for managing mercury sources to reduce their levels in freshwater environments. This long-term monitoring program was created to help characterize mercury levels in fish across Washington State and also to determine whether those levels are increasing or decreasing over time.

The first 15 years of the long-term monitoring study were recently completed in 2019. Each of the 30 sites has been sampled three times. Starting in 2020, all sites will be re-sampled for a fourth time, over the next five years (2020 through 2024). This document is the plan for the fourth round of sampling as part of the long-term monitoring project "Mercury Trends in Fish".

3.2 Study area and surroundings

Thirty waterbodies across the state were selected for this long-term monitoring program. Figure 1 displays the study locations and sample dates over the next five years. The spatial extent of this project encompasses the entire state of Washington. Sites were selected based on the following criteria.

Primary Considerations

- Ability to collect target species at adequate size and numbers (e.g. boat access, min. fish length 10").
- Stability of fish community (e.g. target species likely to be there for decades, long-term Washington Department of Fish and Wildlife (WDFW) management, waterbody size).
- Historical issue with contamination (e.g. Roosevelt, Whatcom fish consumption advisories, 303d listing for Hg in tissue).
- Distance to local mercury point sources and urban areas (e.g. coal power plant, incinerators, other point sources).
- Statewide distribution to represent varied site and regional characteristics (e.g. urban, rural, agriculture, forestry, reference, lake, reservoir, river).

Secondary Considerations

- Ability to obtain info on fish community status, productivity, food chain length, and changes over time (e.g. WDFW surveys).
- Availability of historical data (e.g. sampled during 2002 screening study).
- Ability to obtain current/historical water quality data (e.g. DO profile, seasonal dynamics/stratification, reducing environment at sediment/water interface).
- Ability to track changes in watershed, lake management, etc. (e.g. info/help from lake management groups, etc.).
- Potential complement to other work with mercury (e.g. sediment cores).
- Ability to leverage sampling and data resources from other entities (federal sampling, WDFW surveys, academia/research driven water quality info).

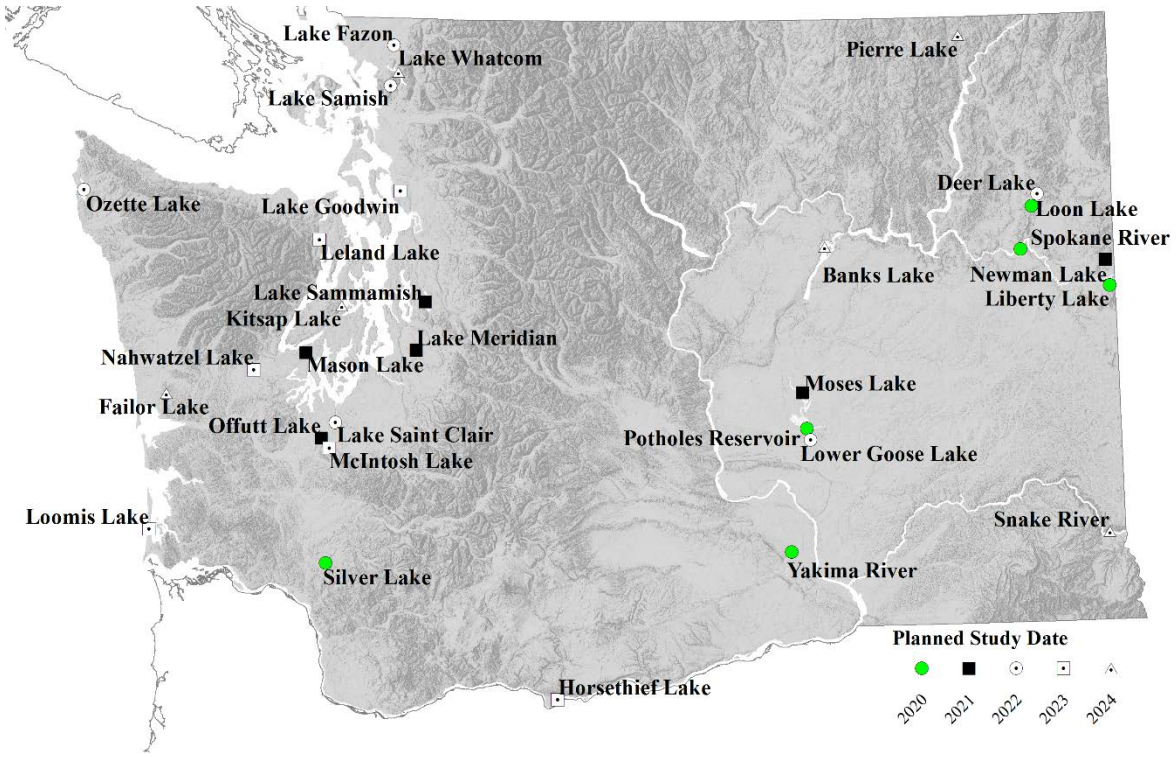

Figure 1. Map of larger study area.

Table 1 displays the 30 study locations, the counties they are located in, and physical characteristics of the watersheds. The selected study locations reflect a gradient of land and climate types, lake chemistry parameters, and physical watershed characteristics. Many of the sites in western Washington are located within forested, residential, and urban watersheds. Sites on the eastern side of the state range from arid grassland or sagebrush steppe to forested land watersheds.

Table 1. Study locations, counties, and physical characteristics.

Waterbody	County	Dominant Land Type	Elevation (ft)	Drainage Area (ac)	Surface Area (ac)	DA:SA ratio
Banks Lake	Grant	G, A	1,570	-	27,000	-
Deer Lake	Stevens	F, R	2,474	11,648	1,100	11
Failor Lake	Grays Harbor	F	117	3,130	65	48
Fazon Lake	Whatcom	F	128	621	31	20
Horsethief Lake	Klickitat	G	160	-	92	-
Kitsap Lake	Kitsap	F, R	156	1,747	250	7
Lake Goodwin	Snohomish	R, F	324	3,310	560	6
Lake Meridian	King	R, U	370	742	150	5
Lake Ozette	Clallam	F	29	49,600	7,300	7
Lake Sammamish	King	R, F	26	62,720	4,900	13
Lake Spokane	Spokane	F, R, U	1,536	3,947,500	45,000	88
Lake St. Clair	Thurston	R, F	73	9,280	88	105
Lake Whatcom	Whatcom	F, R	315	35,776	5,000	7
Leland Lake	Jefferson	F	190	3,650	110	33
Liberty Lake	Spokane	R, F	2,053	8,512	713	12
Loomis Lake	Pacific	W, F	17	922	170	5
Loon Lake	Stevens	R, F	2,381	9,024	1,130	8
Lower Goose Lake	Grant	G	856	-	50	-
Mason Lake	Mason	F, R	194	12,928	1,000	13
McIntosh Lake	Thurston	F, R	336	1,450	93	16
Moses Lake	Grant	U, G	1,046	1,971,200	6,800	290
Nahwatzel Lake	Mason	F	440	3,970	270	15
Newman Lake	Spokane	F, R	2,124	18,304	1,200	15
Offutt Lake	Thurston	R, O	230	1,728	200	9
Pierre Lake	Stevens	F	2,005	17,152	110	156
Potholes Reservoir	Grant	G A	1,046	25,008,800	28,000	893
Samish Lake	Whatcom	F, R	273	5,888	680	9
Silver Lake	Cowlitz	F	484	25,152	2,300	11
Snake River	Asotin	G A	700	-	-	-
Yakima River	Benton	G, A	410	6,120	-	-

R = residential, F = forested, G = grassland, A = agriculture, O = open space, U = urban, W= wetlands

3.2.1 History of study area

Several early studies described the extent and severity of mercury contamination of freshwater fish in Washington, many of which led to issuance of fish consumption advisories.

Fischnaller et al. (2003) examined mercury in bass and sediment from 20 sites across Washington. Samples of muscle tissue from bass confirmed that elevated levels of mercury were prevalent across Washington. The study recommended developing and implementing a long-term monitoring plan for mercury in fish, leading to the Mercury Trends in Fish project.

The Fischnaller et al. study found that mercury concentrations were positively correlated with fish size, increasing with fish age, weight, and length in about 90% of sites sampled. These findings were stated to be consistent with other studies, demonstrating that bioaccumulation of mercury occurs in upper trophic level predatory species, such as bass. A weak, positive correlation was found between mercury concentrations and lipids such that lipids analysis in future studies was deemed unnecessary.

This study was the basis of DOH's issuance of a statewide fish consumption advisory for large- and smallmouth bass (McBride, 2003). Many fish exceeded one or more criteria for protection of human health that were current at the time of writing. Forty-two (~23% of 185 fish) fish representing 14 (70% of 20 sites) sites exceeded the EPA Recommended Fish Tissue Criterion of 300 ug/kg wet weight (ww) (EPA, 2001). A single ten-year old fish from Samish Lake had a muscle tissue mercury level of 1,280 ug/kg ww. This result exceeded the National Toxics Rule criterion of 825 ug/kg ww (CFR, 2004) and FDA's Action Level of 1000 ug/kg ww (FDA, 1985). The Action Level criterion is used to remove fish from commercial markets.

Serdar et al. (2001) examined mercury concentrations in six different finfish species and one crayfish species through collection of 273 fish in Lake Whatcom. Mercury levels were particularly elevated in smallmouth bass. The Lake Whatcom fish tissue mercury data were used in development of a fish consumption advisory for Lake Whatcom. Serdar et al. (2001) recommended a monitoring program to routinely characterize mercury levels in fish throughout Washington.

Munn et al. (1995) investigated mercury and other metals in walleye, bass, and trout from Lake Roosevelt. Elevated mercury levels in walleye led DOH to issue a fish consumption advisory in Lake Roosevelt (USGS, 1997).

3.2.2 Summary of previous studies and existing data

Annual reports summarizing results of the first five years of sampling (2005 through 2009) for the Mercury Trends in Fish project were reported by Furl et al. (2007), Furl (2007), Furl and Meredith (2008), Furl et al. (2009), and Meredith et al. (2010). The next five years of sampling (2010-2014) were captured in annual reports with temporal trends assessed by comparing to the first round of sampling, and data collected by Fischnaller et al. (2003) when possible (Meredith and Friese, 2011; Mathieu and Friese, 2012; Mathieu et al., 2013b; Mathieu and McCall, 2015a).

In 2014, two cycles of fish sampling were completed for all waterbodies targeted in the study. During the first cycle from 2005 to 2009, ten bass were analyzed for mercury from six waterbodies annually, and then re-sampled five years later during the second cycle between 2010

and 2014. A synthesis report was written in 2014 to summarize trends observed over this first 10 years of the monitoring program (Mathieu and McCall, 2016).

Results for all trend tests as reported by Mathieu and McCall (2014) are displayed in Table 2. In total, collection goals were met and statistical analysis was possible for 26 of the 30 waterbodies. No statistical difference was observed in bass mercury concentrations between the first and second sampling visits for over half of the waterbodies (54%). Mercury levels in bass increased in 35% of waterbodies (9 out of 26). Three lakes (12%) showed decreases in mercury concentrations. The average percent change in estimated mercury values was 37.1% for sites showing an increase in mercury concentrations and -36.0% for the sites with decreases.

Table 2. Results of trends in bass mercury concentrations between the first and second sampling visits for the long-term monitoring program.

Date of First Sampling Visit	Date of Second Sampling Visit	Waterbody	Species	Trend in Hg_{bass}	Percent Change in Hg_{bass}	Co-variate	First Visit Hg_{bass}	Second Visit Hg_{bass}	Mean Fish Length (mm)
2005	2010	Liberty Lake	SMB	↑	34%	L	182	244	394
2005	2010	Loon Lake	LMB	=	---	L	249	260	430
2005	2010	Potholes Res.	SMB	=	---	L	107	134	381
2005	2010	Silver Lake	LMB	=	---	L	72	87	337
2005	2010	Yakima River	SMB	=	---	L	136	161	319
2006	2011	Meridian Lake	LMB	=	---	L	211	195	333
2006	2011	Moses Lake	SMB	=	---	L	28	29	337
2006	2011	Newman Lake	LMB	=	---	L	199	241	391
2006	2011	Offutt Lake	LMB	=	---	none	210	179	294
2006	2011	Lake Sammamish	LMB	↑	34%	L	247	330	380
2007	2012	Deer Lake	LMB	↑	22%	L	318	390	382
2007	2012	Lake Fazon	LMB	↑	25%	none	384	479	403
2007	2012	Lower Goose Lake	LMB	↓	-30%	L	322	225	402
2007	2012	Lake Ozette	LMB	=	---	L	526	470	317
2007	2012	Lake Samish	LMB	↑	46%	L	235	343	305
2007	2012	Lake St. Clair	LMB	↑	25%	A	422	526	362
2008	2013	Lake Goodwin	SMB	↑	49%	none	117	174	247
2008	2013	Leland Lake	LMB	↓	-34%	L	506	335	358
2008	2013	Loomis Lake	LMB	↑	55%	L	119	185	216
2008	2013	McIntosh Lake	LMB	=	---	A	129	101	301
2008	2013	Lake Nahwatzel	LMB	↓	-44%	L	353	197	255
2009	2014	Banks Lake	SMB	=	---	L	131	154	357
2009	2014	Failor Lake	LMB	↑	44%	L	61	88	259
2009	2014	Pierre Lake	SMB	=	---	none	201	179	345
2009	2014	Snake River	LMB	=	---	L	151	193	324
2009	2014	Lake Whatcom	SMB	=	---	L	403	370	367

L: length; A: age

Hg_{bass}: back-transformed least squares means from Bonferroni post-hoc tests, with Duan's Smearing estimator applied to correct for back-transformation bias (Helsel and Hirsch, 2002; Duan, 1983).

All variables were log10 transformed before analysis to achieve normality and homogeneity of variance.

Mercury accumulation in bass is determined by a complex set of factors, including the amount of mercury loading to the waterbody, the availability of that mercury to the trophic system (i.e., methylation), and food web dynamics. The 2014 report (Mathieu and McCall, 2016) and annual reports starting in the year 2010 address the temporal trends in respect to these mercury accumulation factors.

Watershed land uses and degree of development did not appear to explain mercury trends seen in the bass. Landscape changes assessed through GIS photo-imagery between the collection periods were qualitatively examined and did not reveal any apparent contributing factors.

Ecology has analyzed mercury in sediment cores collected from nine of the lakes in this study. Sediment cores from Lake St. Clair and Lake Goodwin showed increases in mercury concentrations and fluxes since the 1990s (Furl, 2007; Mathieu and McCall, 2015). Mercury levels in bass also increased in these lakes: by 33% in St. Clair and 52% in Goodwin. The consistent trend in both fish tissue and sediment fluxes suggests that recent increases in mercury loading may be at least partly responsible for the increase seen in bass concentrations in these two lakes. The trend in mercury concentrations in bass from Lake Offutt was also consistent with that of the sediment core collected there (Furl et al., 2009). Both fish tissue mercury levels and recent (since 1990s) sediment mercury concentrations and fluxes were unchanged in Lake Offutt.

Trend direction was inconsistent at the other six lakes with sediment core data. Sediment mercury concentrations and fluxes decreased since the 1990s at Loon and Ozette Lakes, yet mercury levels in bass showed no change (Furl and Meredith, 2008; Furl, 2007). Decreases were also seen in Lake Sammamish sediment concentrations and fluxes (Furl, 2007), whereas bass mercury concentrations increased over the recent five-year period. Conflicting trends were also seen at Deer, Samish, and Nahwatzel Lakes. Sediment mercury loading appears not to have been a key factor affecting fish tissue levels in these lakes. However, variation in mercury mobilization rates from the watershed can result in time lags ranging up to decades or longer until a response in fish mercury levels are seen (Munthe et al., 2007).

Correlations between percent change in bass mercury levels and variables potentially affecting mercury methylation were examined to explore patterns that may explain trends in fish tissue concentrations across the 26 waterbodies. Summer water samples collected in the corresponding years of fish collections at the waterbodies have been analyzed for dissolved organic carbon (DOC) and alkalinity. Water profile measurements of temperature, pH, conductivity, and dissolved oxygen (DO) were also taken. No relationships were found between the percent change in bass mercury levels and the difference in first and second visit water chemistry values, on a statewide scale. Water sampling occurred as a discrete sampling event in one year, whereas fish tissue samples are an integration of multiple years of exposure.

The difference in average annual precipitation values for the five-year period preceding fish collections did not correlate with percent change in bass mercury concentrations. Other factors, such as physical features of the waterbody (i.e., drainage area to surface area ratios, lake volume, elevation, etc.) also did not reveal any patterns related to mercury trends. Furthermore, geographic location did not appear to influence percent change in mercury levels, as correlations between percent change and latitude or longitude showed no relationship. However, a greater proportion of waterbodies on the west side of the state (7 out of 15) showed increased mercury concentrations in bass compared to the east side (2 out of 11). Figure 2 shows the trend in bass mercury concentrations across the statewide dataset.

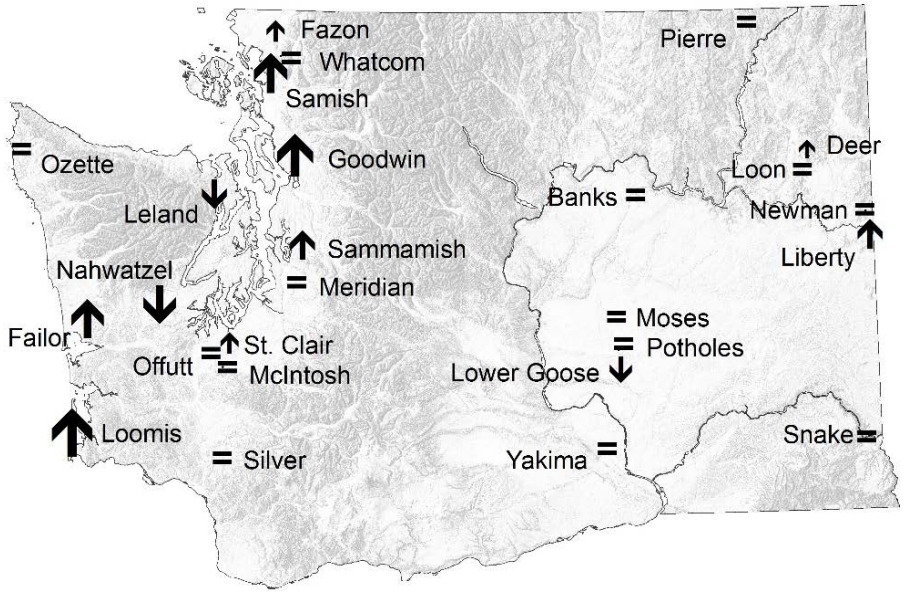

Figure 2. Temporal trends of bass mercury concentrations in a five-year time period.

Arrows indicate increase or decrease, with size of arrow proportional to the percent change.
An equals sign represents waterbodies where no significant difference was found.

3.2.3 Parameters and species of interest and potential sources

Fish fillet tissue will be analyzed for total mercury. Total mercury was the target analyte used in early fish tissue studies in Washington and over the first 15 years of this monitoring program, largely due to the relative simplicity and lower cost as compared to methylmercury. The EPA issued guidance to state fish contaminant monitoring programs to measure total mercury and to make the conservative assumption that all mercury is present as methylmercury so as to be most protective of human health (EPA, 2000). Methylmercury is the bioaccumulative and toxic form of mercury in fish, and accounts for up to 95% of the total mercury in edible fish tissue where it is associated with muscle proteins (Bloom, 1995; Driscoll et al., 1994). A more recent study by Lescord et al. (2018) found that methylmercury accounts for a lower percentage of the total mercury in younger and smaller forage fish species; however, for large-bodied species higher on the trophic chain such as walleye, they state that the assumption of 95% is appropriate.

Physical characteristics of fish are critical to help explain variability in tissue mercury levels and increase the sensitivity of trend analyses. The total length, weight, sex, and age will be determined for each fish analyzed for mercury. Fish condition indices and growth rates (Nielson, et al., 1983) may also be determined using size and age information.

While fish tissue mercury concentrations generally increase with size and age, there can be shifts in this relationship as the food source of fish changes throughout their life. Driscoll et al. (1994) reported shifts in the relationship between mercury and fish size in yellow perch from 16 Adirondack Lakes. A shift toward higher mercury concentrations in fish seems to occur as young fish shift to being more piscivorous. Growth dilution may occur in older, larger fish after a certain age as the rate of weight gain exceeds that of mercury uptake in the food. Thus older and faster growing fish may exhibit a decline in mercury concentrations.

Lipids will not be analyzed in individual fish based on the recommendation of Fischnaller et al. (2003) who found that lipids did not correlate well enough with mercury levels to be useful in accounting for variance in trends analyses. Review of other studies of mercury show that lipids were not analyzed even though studies were trying to discern spatial and temporal trends as well as sources of variability in fish tissue mercury.

Water chemistry parameters were originally measured at each study location for this project to better understand patterns dynamics and changes in fish tissue mercury levels over space and time. This data was helpful in explaining differences on a spatial scale among the study locations across the state over the first five years of sampling (Mathieu et al., 2013a). For instance, alkalinity, dissolved organic carbon, and chlorophyll explained some of the spatial variability in bass mercury levels comparing site to site. However, the water chemistry parameters were not explanatory when comparing temporal trends at a study location. The discrete sampling nature of the water chemistry parameters was not effective in tracking changes over time. For this reason, and to balance the resources involved in the sampling of water chemistry parameter, this additional sampling will no longer be done.

Target species

The target species for long-term trend monitoring are largemouth bass (*Micropterus salmoides*) and smallmouth bass (*Micropterus dolomieu*). These species are selected because of their known propensity to accumulate mercury, their widespread occurrence across Washington, and frequent targeting by recreational anglers. Historical data are available for bass at many sites investigated for mercury in fish (Fischnaller et al., 2003; Serdar et al., 2001). Walleye (*Sander vitreus*) were originally one of the target fish species for this project due to their abundance, popularity, and management as a fishery by WDFW. However, due to limited encounters with this species across the study locations, walleye have only been sampled from a few sites and will not be a target species over the next five years of sampling.

Target species where mercury will be determined in tissue from composite samples include many freshwater species in Washington that represent varied trophic levels (Table 3). These other species are included in the project so that DOH can better inform the public about risks and benefits of consuming species other than bass. The more popular fish species sought by anglers will be targeted for collection. Species in Table 3 are listed in general order of preference for collection.

Table 3. Target fish species for composite analysis.

Common name	Scientific name	Habitat	Feeding
Walleye	Sander vitreus*	water col.	piscivore
Rainbow trout	Oncorhynchus mykiss	hider	invert/piscivore
Cutthroat trout	Oncorhynchus clarki	water col.	invert/piscivore
Kokanee salmon	Oncorhynchus nerka	water col.	invertivore
Lake trout	Salvelinus namaycush	benthic	piscivore
Brook trout	Salvelinus fontinalis	hider	invert/piscivore
Yellow perch	Perca flavescens	water col.	invert/piscivore
Black crappie	Pomoxis nigromaculatus	water col.	invert/piscivore
White crappie	Pomoxis annularis	water col.	invert/piscivore
Pumpkinseed	Lepomis gibbosus	water col.	invert/piscivore
Bluegill	Lepomis macrochirus	water col.	invert/piscivore
Channel catfish	Ictalurus punctatus	benthic	invert/piscivore
Lake whitefish	Coregonus clupeaformis	water col.	invertivore
Common carp	Cyprinus carpio	benthic	omnivore
Rock bass	Ambloplites rupestris	water col.	invert/piscivore
Mountain whitefish	Prosopium williamsoni	benthic	invert/piscivore
Northern pikeminnow	Ptychocheilus oregonensis	water col.	invert/piscivore
Peamouth	Mylocheilus caurinus	water col.	invertivore
Brown bullhead	Ameiurus nebulosus	hider	invert/piscivore
Yellow bullhead	Ameiurus natalis	hider	invert/piscivore

3.2.4 Regulatory criteria or standards

Objectives for this study do not include assessment of regulatory compliance. While data generated from this study are entered into the database that the state uses to assess the water quality of waterbodies in the state, it is outside of the scope of this study for annual reports to include this assessment. However, to provide context for the annual sampling results, data will be compared to two methylmercury thresholds: Washington State's Water Quality criterion (WQC) for human health (40 CFR 131.45) that went into effect in 2016, and DOH's Screening Level (DOH SL) for fish consumption advisories. Both thresholds are based on the toxicological effects of methylmercury, the bioaccumulative and toxic form of mercury in fish tissue, while results from this study reflect total mercury.

Washington State's methylmercury WQC of 30 ppb is a tissue-based human health criterion based on a fish consumption rate of 175 g/day over a 70-year lifespan. This rate is representative of the average consumption of all fish and shellfish (including salmon and fish/shellfish eaten at restaurants, locally caught, imported, or obtained from other sources) for highly exposed populations that consume both fish and shellfish from Puget Sound waters. Washington State assesses waterbodies for impairment using all data collected from a waterbody over the period of time that the assessment cycle is addressing, using median concentrations of fish tissue composite samples (Ecology, 2018).

The DOH SL is a threshold DOH uses when developing fish consumption advisories, in addition to other factors. The DOH SL of 101 ppb is based on a general population consumption rate of 59.7 g/day, which the American Heart Association recommends for a healthy diet (two 8 oz fish meals per week). DOH uses the SL to provide advice to fish consumers in Washington, while the WQC is used to set National Pollutant Discharge Elimination System (NPDES) permit limits and assess waters, and represents full protection of the designated use of harvest.

Data exceeding these thresholds do not necessarily represent an impaired use or trigger a fish consumption advisory. State agencies use data, including data provided in this report, as part of an overall assessment of a waterbody, using an approach to address average exposures over a period of time.

4.0 Project Description

4.1 Project goals

The primary goal of this project is to characterize temporal trends of mercury levels in freshwater fish in Washington State. A secondary goal is to provide information about mercury levels in fish species other than bass to help DOH craft more informative recommendations for fish consumption advisories.

4.2 Project objectives

- Determine mercury concentrations in 10 individual fish from six sites per year on a five-year sampling frequency. Thirty different sites will be sampled over a single five-year period. Samples targeted include largemouth and smallmouth bass in comparable size ranges as collected in previous visits.
- Evaluate temporal trends of largemouth and smallmouth bass compared to previous sampling events for each site.
- In 2020, collect a fish muscle plug from one side of each individual bass for analysis of mercury. Compare the fish muscle plug concentrations to the paired (other side) homogenized fillet sample that serves as the primary sample for this project, and make recommendations on collection methods for the sampling years 2021 – 2024.
- Determine mercury concentrations in composite fillet samples of three to five individual fish from two other fish species present at sampling sites where bass are collected.

4.3 Information needed and sources

Sampling targets for each site will require assessment of previous samples collected from the waterbody by this monitoring program. Fish species and individual lengths, weights, and ages from previous sampling events will be reviewed prior to collection efforts. In the field, crews will attempt to collect the same species and sizes as previously documented. This data is included in final reports for each sampling year, as well as field notes and processing benchsheets kept with the project manager.

4.4 Tasks required

The tasks required to meet the project goals and objectives will be completed annually. The tasks include:

- Plan for field collection and write QAPP addendum if necessary.
- Coordinate with other staff in the Environmental Assessment Program to secure scientific collection permits to obtain freshwater fish samples.
- Schedule staff for sample collection in fall of each sampling year. Mid-September through mid-October should be targeted.
- Inventory, repair, purchase, and calibrate the equipment required for sampling.
- Complete field collections according to QAPP objectives and SOPs listed in this QAPP.
- Decontaminate equipment used to process and homogenize fish.
- Homogenize samples and facilitate delivery to lab for analysis.
- Review and assess data quality of laboratory results.
- Enter field and lab data into Environmental Information Management System (EIM).
- Analyze data and write annual report documenting results for the sampling year and temporal trends in fish mercury levels observed.
- Compare fish muscle plug mercury concentrations to the paired homogenized fillet mercury concentrations and make recommendation on future sampling protocols.

4.5 Systematic planning process

This document represents the systematic planning process for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 4 shows the responsibilities of those who will be involved in this project.

Table 4. Organization of project staff and responsibilities.

Staff (all EAP)	Title	Responsibilities
Jessica Archer SCS Phone: 360-407-6698	Client and SCS Manager	Clarifies scope of the project. Provides internal review of the QAPP addendum and final report. Approves the final QAPP addendum.
James Medlen Toxic Studies Unit SCS Phone: 360-407-6194	Client and Supervisor for the Project Manager	Clarifies scope of the project. Provides internal review of the QAPP addendum, and final report. Approves the final QAPP and addendums. Manages budget and staffing needs.
Callie Mathieu Toxic Studies Unit SCS Phone: 360-407-6965	Project Manager and Principal Investigator	Writes the original QAPP and final report. Coordinates with MEL and contract laboratory. Oversees field collections. Conducts QA review of data, analyzes and interprets data
Jakub Bednarek Toxic Studies Unit SCS Phone: 360-407-6765	Field Lead	Leads field collections, records field information, and sends samples to the laboratory. Enters data into EIM.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Arati Kaza Manager's Unit Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
SCS: Statewide Coordination Section
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
MEL: Manchester Environmental Laboratory

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.

All staff involved in this project are required to obtain training and then adhere to various task- and operation-specific procedures that are described in EAP's Safety Program. EAP 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. Staff assisting with processing and homogenizing fish will be trained by senior staff via on-the-job training and will be expected to follow EAP's SOP for resecting finfish (Sandvik, 2018a).

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

Tables 4 through 7 provide the organization of this study.

5.4 Proposed project schedule

The project schedule will be completed as outlined in Tables 5 through 7 below. Due dates in these tables reflect the first round of sampling – the 2020 sampling year. For future rounds of sampling, add one year to each date. Planning and field operations will occur during the first year and final reports will be completed the follow year.

Table 5. Schedule for completing field and laboratory work.

Task	Due date	Lead staff
Fish Collection	September-November 2020	Jakub Bednarek
Fish Tissue Processing	November 2020	Jakub Bednarek
Laboratory Analyses	December 2020	MEL
Lab Data to Project Manager	February 2021	MEL

Table 6. Schedule for data entry.

Task	Due date	Lead staff
EIM data loaded*	August 2021	Jakub Bednarek
EIM QA	September 2021	Callie Mathieu
EIM complete	October 2021	Jakub Bednarek

*EIM Project ID: HgFish20
EIM: Environmental Information Management database

Table 7. Schedule for final report.

Task	Due date	Lead staff
Draft to supervisor	June 2021	Callie Mathieu
Draft to client/ peer reviewer	July 2021	Callie Mathieu
Final draft to publications team	September 2021	Callie Mathieu
Final report due on web	November 2021	Publications staff

5.5 Budget and funding

Table 8 shows the estimated laboratory costs for this study. The additional costs for the non-lethal fish plugs are anticipated for 2020. After 2020, the feasibility of using this collection method will be assessed and a QAPP addendum will be written with the updated budget.

All funding is provided by the PBT Monitoring Program budget, which comes from the state toxics control account.

Table 8. Laboratory budget details.

Parameter	Sample Type	Number of Samples	Number of QA Samples*	Total Number of Samples	Cost Per Sample ($)	Lab Subtotal
Total Mercury	Primary project sample	96	20	116	$50	$5,800
Total Mercury	Non-lethal fish plug	60	12	72	$50	$3,600
					Total laboratory cost:	**$9,400**

*Number of QA samples include only those that are not free of charge with the analysis (laboratory duplicates, matrix spikes, matrix spike duplicates, and standard reference material).

6.0 Quality Objectives

6.1 Data quality objectives [1]

The quality objectives for this project are to collect a sufficient quantity and quality of data for use in long-term trend monitoring of mercury in freshwater fish fillet tissue. Ten individual fish per site were determined to be enough to detect long-term trends. The sample size of 10 individual fish per site were selected by balancing several factors: available staff and funding resources, achieving spatial coverage, and ability to detect trends. Earlier reviews by Ehinger (2002) and Yake (2002) evaluated variability introduced by covariates and effectiveness of sample size on trend detection and determined 10 individual fish provided the optimum balance of cost and ability to detect trends.

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

The MQOs for analytical data, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Table 9. The MQOs for laboratory control samples, method blanks, laboratory duplicates, matrix spikes, and matrix spike duplicates will be used by MEL as their acceptance limits and by the project manager to inform the data quality review. Recoveries of the standard reference material will be used only by the project manager in the overall assessment of data quality. MEL does not use acceptance limits for standard reference materials as part of their quality review of mercury analyses.

[1] DQO can also refer to ***Decision*** Quality Objectives. The need to identify Decision Quality Objectives during the planning phase of a project is less common. For projects that do lead to important decisions, DQOs are often expressed as tolerable limits on the probability or chance (risk) of the collected data leading to an erroneous decision. And for projects that intend to estimate present or future conditions, DQOs are often expressed in terms of acceptable uncertainty (e.g., width of an uncertainty band or interval) associated with a point estimate at a desired level of statistical confidence.

Table 9. Measurement quality objectives for mercury analysis.

Parameter	Matrix	Laboratory Control Samples (% recovery)	Laboratory Method Blanks	Laboratory Duplicates (RPD)	Matrix Spikes (% recovery)	Matrix Spike Duplicate (RPD)	Standard Reference Material (% recovery)	Reporting Limit
Mercury, total	Tissue	85-115	< MDL	≤ 20	75-125	≤ 20	75-125	0.017 mg/kg ww

RPD = relative percent difference; MDL = method detection limit; mg/kg ww = milligram per kilogram wet weight

6.2.1.1 Precision

Precision is a measure of variability among replicate measurements due to random error. The precision of mercury analyses will be assessed through laboratory duplicates and matrix spike duplicates. MQOs for relative percent difference of laboratory duplicate values and matrix spike duplicate recoveries is included in Table 9.

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 through analysis of laboratory control samples, matrix spikes, and standard reference materials. 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.

Table 9 outlines the MQOs for recoveries of laboratory control samples, matrix spikes, and standard reference materials.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Laboratory analysis sensitivity for this study is defined as the reporting limit. See Table 9 for the reporting limit for mercury analyses. This reporting limit reflects what MEL can achieve with the minimum required sample size (0.3 g for each sample). For the fish muscle plug portion of the 2020 sampling, we anticipate the plugs will yield 0.5 g of sample. If fish plug samples do not yield the 0.3 g minimum, the reporting limits will be raised due to limited sample size.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

The selected sampling and analytical methods should ensure that data are comparable over the life of the project. Where possible, fish for this study will be collected from the same area and be of a similar size range as fish previously collected for this project, at each study location. Standard Operating Procedures (SOPs) for field collections, sample processing, sample decontamination, and laboratory methods will be followed to ensure comparability across years of this long-term monitoring program. Potential changes in field and/or lab methods will be reviewed by the project manager to ensure comparability of results over time.

6.2.2.2 Representativeness

Fish samples are expected to be representative of conditions due to the timing and manner of their collection. Fish will be sampled in the fall of each year to coincide with other fish collection efforts by Ecology and other agencies. Fall sampling will also allow use of data statewide 2000/2001 bass mercury study by Fischnaller et al. (2003), of which 10 sites overlap with this long-term monitoring project. Fish will be collected from suitable habitats within the waterbody since fish collection techniques include shoreline (electrofishing) and open water habitats (gillnetting).

The target size range for individual bass will be determined by historical data from the site. The size range and individual sizes of the historical data set will be duplicated as best possible in new collections.

The minimum size for fish to be used in composite samples of non-trend fish species will be determined by considering what size could reasonably be expected to be kept by anglers. The 75% Rule recommended for composite samples by EPA (2000) will be used as a rough guide in selecting fish to retain for analyses of individuals (i.e. the length of the smallest fish should be at least 75% the length of the largest fish).

6.2.2.3 Completeness

The completeness goal for laboratory analytical data is 100%. Any loss of fish tissue data or inability to collect sufficient numbers will decrease the ability to detect trends at sites where data needs are not met. The completeness goal for field measurements is also 100%.

6.3 Acceptance criteria for quality of existing data

This study will collect new data as well as use historical data in trend analysis. Data collected over the first 15 years of this project, as well as data from Fischnaller et al. (2003), will be used in trend analyses. The quality of the historical data is documented in annual reports. Only data that met MQOs and were deemed usable for all purposes will be included in trend analyses.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

In 2005, Ecology began a long-term monitoring program with the primary goal of assessing temporal trends in mercury levels of freshwater fish throughout the state. Each year, Ecology collects 10 individual largemouth or smallmouth bass from six lakes for analysis of total mercury. Ecology returns to each set of lakes every five years to assess trends and determine if mercury levels in the edible fish tissue are increasing, decreasing, or staying the same. Additional species are also collected and analyzed as composites for a secondary goal of supporting fish consumption advisories.

7.1 Study boundaries

This study will collect bass and other fish samples from 30 waterbodies throughout Washington state. Thirty waterbodies were chosen as long-term monitoring sites based on practical constraints such as access and ability to collect adequate size and numbers of fish. Consideration was also given for whether sites have historical issues with contamination, the sites proximity to point sources, and statewide distribution of sites for general representativeness. Section 3.2 discusses the considerations made in site selection. The 30 waterbodies are listed in Table 1.

7.2 Field data collection

At each lake site, fish will be collected from suitable habitats throughout the entire waterbody. Field staff will attempt to capture bass along the shoreline of the waterbody using an electrofishing boat. Gill netting and angling in deeper areas may also be used in some waterbodies when electrofishing is unsuccessful. Study locations are entered into Ecology's EIM database as the centroid of sampling area. At the three river sites, samples will be collected within 2 river miles of the location stated in Table 10.

Table 10. Sampling sites for the river study locations.

River Study Location	Sampling Site
Lake Spokane	Spokane River downstream of Nine Mile Dam, River Mile 40.8
Snake River	Downstream of Clarkston, River Mile 132
Yakima River	Yakima River, 12 mi NW of Richland, River Mile 19

7.2.1 Sampling locations and frequency

Six sites per year will be sampled on a five-year rotation such that 30 sites will be completed every five years. Collections occur every fall, from mid-September through October, to ensure data is comparable to past sampling events. The fall sampling period was outlined in the original QAPP to coincide with other fish collection efforts by Ecology (e.g. Fischnaller et al., 2003).

The sampling design (number of samples and frequency) was selected based on the following considerations: sampling feasibility, analytical cost, and ability to detect trends. Yake (2002) estimated that analyzing 10 individual fish with variance due to fish length removed would be sufficient to detect a change (increase or decrease in mean fillet mercury concentrations) of 31% of the mean mercury value between two sample events. The review by Yake (2002) was based on detectable change as determined using a standard t-test. This program uses an ANCOVA

when appropriate to remove the variance of fish length. An ANOVA, akin to a t-test for multiple groups, is used when no covariates are present in the data.

7.2.2 Field parameters and laboratory analytes to be measured

The following field parameters will be recorded for each fish retained for analysis:

- Fish total length (mm)
- Fish weight (grams)
- Fish sex (M or F), determined during fish processing
- Fish age (year), determined by WDFW Fish Age Laboratory

The laboratory analyte, total mercury, will be measured in each fillet tissue sample

7.3 Modeling and analysis design

Not applicable.

7.4 Assumptions underlying design

This study assumes that observable trends in the concentration of mercury through resampling of 10 individual bass at target sites conducted on a 5-year cycle, can sufficiently represent the toxic burden of mercury in the upper trophic level of the program's selected waterbodies.

Earlier reviews during the planning process for this long-term monitoring program estimated that the study design would be sufficient to detect a trend of +/- 31%. This is close to what was observed over the second round of sampling for this program. Decreases and increases of mercury were detectable at a percent change of approximately 30 percent or greater. A more robust design would capture smaller trends, but the original project plan decided to balance resources with the ability to detect trends.

The statistical analyses conducted for each dataset will satisfy assumptions of the test chosen, such as homogeneity of variances, normality, random independent samples, and linearity of relationships (for analysis of covariance).

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

The nature of collecting fish from waterbodies presents logistical challenges. Field staff target the timing of fish collections to coincide with historical sampling events (fall season), when bass are likely to be encountered. However, specific species and size targets can be difficult to obtain during sampling events. Upon difficulty in collecting target species and sizes, field staff will attempt up to three sampling events at each site. Up to 10 bass meeting target lengths will be collected during each event; subsequent events will take into account fish already collected. Other species or sizes may be considered if targets are not encountered. The timing of fish collections cannot be moved to another season for this long-term monitoring study. Collection of fish during different seasons and at different life cycles introduces variability to a long-term dataset that cannot be accommodated.

Access has been secured for each of the 30 sampling sites, but ongoing access requires coordination with WDFW, counties, and city park staff at some sites. Fish collections generally occur at night; therefore, it is essential that the field lead identifies boat launches that may be locked at night and works with the appropriate staff to secure access. Site reconnaissance is done every year to help identify issues such as access or other potential logistical concerns.

Other issues can arise before or during sampling events, such as unsuitable weather conditions and/or equipment failure. Safety of the field crew is the most important factor in determining whether fish collections can be carried out. In cases of unsuitable weather, sampling will be postponed to another date within the window of collections. In cases of equipment failure, sampling will be postponed until the equipment is working properly. Good planning and scheduled boat and equipment maintenance ahead of the fishing season helps to ensure successful sampling events.

7.5.2 Practical constraints

Practical constraints for carrying out this long-term monitoring project include availability of staff resources. Trained field staff are necessary to assist the field lead with fish collections, as well as to process the fish prior to shipment to the laboratory. Retaining qualified staff to carry out this work is essential in continuing the project's long-term dataset.

A major practical constraint in 2020, and possibly future sampling years, is the delay of sampling due to COVID-19 restrictions. As of the time of writing this QAPP, Washington State is under various restrictions by counties, called "phases." Ecology has imposed field work restrictions, including restrictions on overnight travel, based on what phase the county the field work to be conducted is in. Sampling at five out of six study locations in 2020 involved overnight trips, and thus may not be feasible depending on county phases related to COVID-19 infection rates. Field collections will occur only if sampling is allowed from at least three of the six sites planned. Sites not approved based on COVID-19 restrictions will be sampled the following year. If at least three sites are not feasible due to restrictions in 2020, all sites will be postponed for sampling until 2021 and the rest of the five year schedule will be delayed subsequent sampling years.

7.5.3 Schedule limitations

Issues with obtaining and processing the target number of fish samples would lead to data gaps and a delayed annual report. Other impacts to completing the annual report include the time required of the project manager. Other projects may take priority of the project manager's time and can result in the delay of completed reports. Retaining support staff to assist with data management and report writing will help to keep the project schedule on time.

8.0 Field Procedures

8.1 Invasive species evaluation

Invasive species may be encountered during fish collections. Environmental ethics and Washington law prohibit the transportation of all aquatic plants, animals, and many noxious

weeds. Field staff for this project will follow protocols outlined in the Ecology Environmental Assessment Program's SOP to Minimize the Spread of Invasive Species (Parsons et al., 2018).

8.2 Measurement and sampling procedures

Fish collections

Tissue samples will be collected, preserved, and analyzed following procedures designed to meet data quality objectives of this project. Methods for the collection, handling, and processing of fish tissue samples for analysis will be guided by methods described in EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories (EPA, 2000) and EAP Standard Operating Procedure for Field Collection, Processing, and Preservation of Finfish Samples at the Time of Collection in the Field (Sandvik, 2018b). All equipment used in fillet homogenization will be cleaned following EAP Standard Operating Procedure for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2020). The procedures are outlined below.

Fish will be collected using a combination of methods including electrofishing, netting, and angling. Fish may also be collected through cooperative efforts with other agencies, such as the Washington Department of Fish and Wildlife (WDFW) fish population surveys. Upon capture in the field, fish will be identified to species level 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).

For the trend monitoring component at each site, 10 fish of largemouth or smallmouth bass will be collected and analyzed as individual samples for tissue mercury concentrations. For mercury characterization in two other species per site, adequate numbers of fish will be collected to form three composite samples of 3-5 fish per composite for each species. Field crews will use field notes from past years' sample collections from each study location as a guide for the current year's collection effort. Past field notes will guide species to target, fish sizes, and collection methods. Past field notes and electrofishing logs will also inform the current year's collection efforts on sampling areas and electrofishing settings.

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 zip-lock 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 a maximum of 24-72 hours and then they will be frozen to –20 C at Ecology facilities in Lacey, Washington.

Sample homogenization

Skin-on fillets will be used for individual fish and for most fish used in composite samples. Fish will be removed from the freezer, partially thawed, slime and scales removed, rinsed in tap water, and a final rinse in deionized water. Fish will then be filleted with the skin left on for most species. Skin will only be removed for scaleless species, like catfish or bullhead. Fillets will be cut into small cubes and passed three times through a Kitchen-Aid food grinder. The ground tissue will be homogenized by stirring to a consistent texture and color. Subsamples from the

homogenate will be placed into appropriate containers, frozen, and transported with ice to the laboratory for analyses. Excess homogenate will be placed into an appropriate container, labeled, and archived frozen at –20 C.

After fillets are removed, the sex of the fish will be determined and recorded. Species-appropriate structures (e.g. otoliths, scales, opercula) will be removed, cleaned, and sent to WDFW biologists who will determine the age of individual fish.

Non-lethal muscle plugs

In addition to whole-fish sampling, muscle plug biopsies will be collected from all bass samples in 2020 to assess a non-lethal method of monitoring mercury trends in fish. The success of muscle biopsy in fish tissue analysis has been well documented by other monitoring programs (Pearson 2000; Baker et al. 2004; Peterson et al. 2004). Using muscle plugs will benefit fish populations at our monitoring locations, create better justification for sampling permits with fish and wildlife agencies, and streamline field and processing operations by reducing equipment needs and resources. However, the small sample volume of a muscle plug may compromise lab measurement quality objectives (MQOs).

In 2020, we will conduct a side-by-side study to determine if muscle plug biopsies are adequate for meeting the goals of this project. We will collect muscle plugs from each bass being analyzed individually for this project, following the National Rivers and Streams Assessment operations manual protocols (EPA, 2013). Scales will be scraped away from a small portion of skin. Muscle tissue will be collected from the dorsal muscle section of the fish using an 8 millimeter disposable biopsy punch. Muscle plugs will be weighed and stored in a sterile glass scintillation vial and sealed to prevent moisture loss. Samples will be stored on ice up to 72 hours and frozen immediately thereafter at -20 degrees C. Muscle plugs will be given the station ID of the primary fillet sample, followed with “-MP”.

Each sample should yield approximately 0.5 grams of tissue. At least 0.3 grams are needed for laboratory analysis, with an additional 0.3 grams needed for laboratory QC tests (matrix spikes, matrix spike duplicates, and laboratory duplicates). Two biopsy punches will be collected from the largest three fish encountered to collect enough material for QC tests (one fish per 20 fish retained).

Muscle plug biopsies will only be collected for bass retained for analysis as individuals. At this time, species collected for composite analysis will be retained as the whole fish and no muscle plug biopsy analyzed. If the muscle plug biopsy collection method proves viable for the long-term monitoring component of this project, consideration may be given to composite species. The project manager will discuss this option with DOH to determine whether the new collection method would meet the needs for fish consumption advisory assessments.

8.3 Containers, preservation methods, holding times

Tissue samples will be stored, preserved, and transported following procedures designed to maintain the integrity, quality, and identification of the sample. Pre-cleaned sample containers will be obtained prior to field sampling efforts with containers for metals possessing Quality Assurance Certification from the supplier. Sampling containers, sample preservation, and holding times for tissue samples are described in Table 11.

Table 11. Sample containers, preservation, and holding times.

Parameter	Sample Type	Minimum Quantity Required	Container	Preservative	Holding Time
Mercury, total	Whole fillet ground	5 g	2 oz. precleaned glass jar with teflon lid, ESS	Freeze, -20 C	6 months
Mercury, total	Muscle plug	0.3 g	20 mL glass scintillation vial	Freeze, -20 C	6 months

This project will use a six-month holding time for tissue samples. The holding time is the period of time between sample collection and laboratory analysis. For fish tissue, this decision is based on review of varied opinions about the proper holding time for fish tissue samples and the practical need to store fish samples for extended periods in order to maximize efficiency of field and laboratory operations.

Nationally, the USGS's National Water Quality Assessment program uses six months as a holding time for biota (Crawford and Luoma, 1993). Bloom (1995) also states that biota samples for mercury analysis may be stored indefinitely when frozen. Ecology's Manchester Environmental Laboratory (MEL) SOP for mercury in fish tissue states a maximum holding time of 28 days from the date tissue is removed from the fish and ground or macerated. This project will aim to meet both holding times: six months from the time of collection and 28 days from the time of homogenization.

8.4 Equipment decontamination

All utensils used for processing tissue samples will be cleaned in order to prevent contamination of the sample. Decontamination of the utensils will follow the metals instructions in EAP Standard Operating Procedure for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2020). Utensils include disposable biopsy punch instruments, bowls, forceps, and knives of stainless steel, and tissue grinding appliances having plastic, wood, bronze, and stainless steel parts. All utensils for fish tissue sampling will be cleaned with the following procedure: soap (Liquinox) and hot water wash, hot tap water rinse, 10% nitric acid rinse, and a final deionized water rinse. Utensils will be air-dried and then packaged in aluminum foil until used. Fish will be filleted and tissues processed on aluminum foil that covers a nylon cutting board laid on the workbench. The foil will be placed such that fish contact only the dull side of the foil.

8.5 Sample ID

Individual fish retained during fish collections are assigned a unique fish field ID following the format of "YYY ##", where YYY = the three letter code for the species and ## = consecutive numbers starting with 01. For instance, the first largemouth bass recorded at a site would have a fish field ID of "LMB 01". After recording the fish weight and total length in field notebook, the fish field ID is written on a sample tag along, with the sampling site and collection date. The sample tag is then placed in between the two layers of foil wrapping the individual fish.

After homogenization, individual fish and composite samples are given a "station ID". The station ID consists of the following format: AAAYYY##, where AAA = three letter abbreviation for the sampling site, YYY = the three letter species code, and ## = consecutive numbers starting with 01. For instance, the first largemouth bass collected from Lake Whatcom to be processed will have a station ID of "WHALMB01." Station IDs will be written on the top of the laboratory analysis jar lid. Muscle plugs will be given the station ID of the primary fillet sample, followed with "-MP".

Each sample is assigned a unique lab sample number using the 7-digit MEL-assigned work order number, followed by a dash and a consecutive 2-digit number starting with -01. The 2-digit number will be assigned by the Project Manager (e.g., 1701015-19). MEL will assign a unique work order number for each sampling year after receiving the pre-sample notification form from the field lead each fall.

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 form will be used to serve as the chain of custody record. This form lists all laboratory sample IDs, station IDs, and the analyses required for each sample. 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 notes will be kept for each sampling event as described by SOP EAP009 (Sandvik, 2018b). Notes will be entered in a weather resistant field notebook. Pre-printed forms will be used if possible to facilitate recording of required info. The info recorded will include:

- Name of the project
- Field personnel
- Location, methods, and timing of fish sampling (e.g., boat electrofishing, gill netting, angling)
- Field measurements related to electrofishing (temperature, conductivity, electrofishing parameters)
- General weather conditions
- Estimates of species and sizes encountered not retained.
- Field ID, total length, weight, and species of fish samples collected.
- Any circumstances that may affect interpretation of results.
- Latitude and longitude coordinates, and their datum, will be obtained with a hand-held Global Positioning System device and use of maps.

Additionally, a fish processing bench sheet form will be used to record various data during processing, such as: processing date, processing crew, lab sample ID names, lab sample numbers, fillet weights, sex of individual fish, age structure container references, and any relevant comments.

8.8 Other activities

Annual training includes safety related and equipment operation training. Electrofishing training is conducted annually on the safe operation of electrofishing equipment and use of the electrofishing boat. The agency also requires current certifications in CPR/First Aid. Staff are required to complete training on Minimizing Spread of Invasive Species and Heat Stress annually.

Bottle orders will need to be coordinated with MEL prior to analysis. We will coordinate with MEL regarding sample delivery and analyses timeframes through submittal of the Pre-Sampling Notification form. We will also notify WDFW about delivery of aging structures for determining fish age.

The Field Lead will be responsible for coordinating the maintenance of the electrofishing boat, towing vehicle, backpack electrofishing unit, angling supplies, nets, and other related fishing gear. Consumables such as foil, bags, gloves, and decontamination reagents will need to be inventoried and ordered if necessary. Weighing and measuring devices will need to be checked and calibrated by the field lead as well.

The field lead will also work with other EAP staff to secure required Scientific Collection Permits necessary for sampling. For fish collection work throughout most of Washington, these permits are required by WDFW, National Marine Fisheries Service, and the United States Fish and Wildlife Service. Additional permits may be required by those having jurisdiction in some areas such as the National Park Service, tribes, cities, and county governments.

Staff scheduling and resource needs will be coordinated with Toxic Studies Unit and relevant EAP staff.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 12 presents laboratory measurement methods. MEL modification to analytical methods are documented in their Standard Operating Procedures.

Table 12. Measurement methods (laboratory).

Analyte	Sample Type	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
Mercury, total	Primary project sample	Tissue	96/ December	0.020 – 1.50 mg/kg ww	0.017 mg/kg ww	EPA 245.6	EPA 245.6; MEL SOP 720027
Mercury, total	Non-lethal fish plug	Tissue	60/ December	0.020 – 1.50 mg/kg ww	0.017* mg/kg ww	EPA 245.6	EPA 245.6; MEL SOP 720027

*The reporting limit of 0.017 mg/kg ww may not be met depending on amount of material provided to MEL. Smaller sample sizes will increase the reporting limit.

9.2 Sample preparation method(s)

Prior to delivering samples to MEL, staff will prepare samples by homogenizing tissues in the Ecology Headquarters laboratory. Sample homogenization is described in SOP EAP007, V1.2: Resecting Finfish Whole Body, Body Parts, or Tissue Samples (Sandvik, 2018a). Homogenized tissue will be put in lab approved sample jars and delivered to MEL for analysis.

Manchester Environmental Laboratory will prepare the homogenized tissue samples following EPA method 245.6 and any methods cited by that procedure. Alterations from this procedure are documented in MEL SOPs.

Due to the limited amount of sample size yielded from the muscle plug biopsies, those samples will not be homogenized in the lab.

9.3 Special method requirements

Not applicable. The analytic method required for this study is a standard EPA method.

For analysis of the muscle plug biopsies, if insufficient material is provided (<0.3 g) for analysis, the reporting limit will be raised accordingly. No other special method requirements are anticipated for the muscle plug biopsies, but any changes needed will be discussed with the project manager.

9.4 Laboratories accredited for methods

Manchester Environmental Laboratory holds accreditation for analysis of mercury following EPA Method 245.6 and will perform the analysis for this study.

10.0 Quality Control Procedures

Quality control (QC) procedures will include adherence to the field and lab SOPs. The field SOPs are outlined by Sandvik (2018a, b). Laboratory analyses will follow EPA Method 245.6 and MEL SOP#720027 Version 2.3. Situations that deviate from SOPs and this QAPP will be resolved using the guidance available, past field notes, and the experience of the Project Manager. Any deviations will be documented in project plan addendums if known in advance or in the project annual report.

10.1 Table of field and laboratory quality control

Field replicate samples for fish tissue will not be taken because 10 individual fish will be collected from each site; this sample size will be adequate to estimate the variability and a central tendency for tissue mercury level for that species and site.

Laboratory QC procedures will include various analyses such as calibration standards, lab control samples, lab control sample duplicates, matrix spikes, and standard reference materials, to evaluate the quality of data that are generated. Table 13 describes the type and frequency of lab QC samples. MEL will provide the project manager with case narratives describing sample holding times, instrument calibrations, and results of QC tests.

With each laboratory batch, MEL will analyze one Standard Reference Material 1946 (Lake Superior fish tissue) from the National Institute of Standards and Technology as a regular sample. This reference material has a mean total mercury concentration of 433 ug/Kg ww with an approximate 95% Confidence Interval of +/- 9 ug/Kg.

Table 13. Quality control samples, types, and frequency.

Parameter	Laboratory Control Samples	Laboratory Control Sample Duplicate	Laboratory Method Blanks	Matrix Spikes	Matrix Spike Duplicates	Standard Reference Material
Mercury	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch

Batch = up to 20 samples

Each type of QC sample listed above have MQOs associated with it (Section 6.2) that will be used to evaluate the quality and usability of the results.

10.2 Corrective action processes

MEL will follow the corrective action processes outlined in EPA Method 245.6 and MEL SOP#720027 Version 2.3. The project manager will work with MEL staff to examine data that fall outside of QC criteria. The project manager will determine whether data should be re-analyzed, rejected, or used with appropriate qualification. Decisions will be documented in the project annual report.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

All field data and observations will be recorded on waterproof paper kept in field notebooks. Staff will transfer information contained in field notebooks to Excel spreadsheets after they return from the field. This manual transfer of field data to electronic spreadsheets will be reviewed by the project manager for accuracy and any errors will be addressed.

Manchester Environmental Laboratory will provide data electronically in EIM format via the Laboratory Information System (LIMS). Field and laboratory data for the project will be entered into Ecology's EIM system and the EIM data entry will be independently verified for accuracy by another member of the project team following standardized EAP procedures for QC of data entry.

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

11.2 Laboratory data package requirements

Manchester Environmental Laboratory will provide the electronic data deliverable described above, which will include results of samples and QC tests. The laboratory will also provide a case narrative documenting the condition of samples upon receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests. Narratives will address any problems encountered with analyses, corrective actions taken, changes to the referenced method, and explanations of data qualifiers. The MEL sample coordinator will send the project manager the case narrative via email, as well as copies of signed chain of custody forms.

11.3 Electronic transfer requirements

Laboratory data generated by MEL will be entered into the Laboratory Information Management System (LIMS) by MEL staff. The LIMS electronically transfers the data in an EIM deliverable format to the Project Manager. The format of data deliverables is typically a comma separated values (CSV) table. CSV format is generally readable by most common data analysis and management tools such as Excel.

11.4 EIM/STORET data upload procedures

Lab and field data will be entered into Ecology's EIM database following detailed internal EAP guidance and procedure documents. An EIM Study ID will be created for each sampling year following the convention 'HgFish' plus the last two digits of the sampling year. In 2020, the EIM Study ID for this project will be HgFish20.

11.5 Model information management

Not applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No audits are planned for the field procedures, sampling process, or other components outside of the analytical laboratory. The laboratory conducting sample analyses is 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

Short annual reports will be generated to describe results for the year of sampling. Every five years, a larger synthesis report will be written to describe results of the overall program.

Annual reports will address the following elements:

- Abstract
- Background
- Methods
- Results
- Fish Tissue Mercury Relationships
- Temporal Trends
- Discussion
- Conclusions
- Recommendations
- References

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

Data verification is defined as "the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements" (EPA, 2002). Data verification will take place after each field collection event before leaving the site. Laboratory generated data will be verified by MEL staff when data are entered into LIMS. Data will also be verified during the data archival step where data are loaded to EIM. The verification steps will establish quality level that meets credibility requirements needed for informing decisions.

13.1 Field data verification, requirements, and responsibilities

Field data are generated at the time of sample collection and during sample processing at Ecology's Headquarters lab. Field notes, maps, labels, and any other field data generated should be verified by the field lead to ensure accuracy and completeness. During fish tissue homogenization, sample processing bench sheets, lab analysis and tracking sheets, age structure labelling, and other notes will be verified by the field lead and project manager for legibility, completeness, and errors.

Where errors or omissions in the data are found, the source of the data (e.g. field sampling personnel) will be consulted to determine the correct value or form of the data in question. Corrections will be made where possible. If correction cannot be made, additional information will be noted to explain the error. If necessary, data will be qualified or rejected from use based on verification.

After field data are entered into EIM, EAP's internal EIM Data Review Procedure checks 10% of the data to ensure it was entered correctly.

13.2 Laboratory data verification

Laboratory data verification examining the data for errors, omissions, and compliance with QC acceptance criteria are reviewed by qualified staff at MEL before they are entered into the LIMS. MEL will include a case narrative that discusses whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions. The case narrative will also define qualifiers and the reason for their use and will be released to the project manager. Laboratory staff may be consulted in order to review QC data that are normally retained by MEL.

The project manager is responsible for the final acceptance of the project data. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered. Accuracy of data entered into EIM will be verified by someone other than the data engineer per the Environmental Assessment Program's EIM data entry business rules.

13.3 Validation requirements, if necessary

Independent validation will not be required for this project.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will determine data usability by assessing whether data meet the MQOs outlined in Section 6 and Table 7. Data will either be accepted, accepted with qualification, or rejected and re-analysis considered. Results of usability assessment will be included in the project annual report.

14.2 Treatment of non-detects

Non-detects are rarely encountered in the bass mercury dataset. Only six samples out of 829 (0.7%) from this project as of 2019 have been non-detects for mercury at a reporting limit of 17 ug/kg ww. In the rare case of non-detects, the non-detected result will be omitted from analysis.

14.3 Data analysis and presentation methods

The project annual report will present mercury concentrations for individual fish at each lake. Summary statistics will be presented in the project annual report along with relationships between fish characteristics such as weight, age, length, and mercury concentration. Mercury concentrations of composite samples will also be presented.

Data for this project are intended to observe trends in bass mercury concentrations over time. Analysis of covariance (ANCOVA) is used to determine differences in fish mercury concentrations among sampling years at an individual study location. Because mercury increases with age and size of fish, a covariate is used to control for the variability. Fish length, fish weight, or fish age may be used as the covariate, depending on the strongest relationship. For datasets lacking significant mercury-to-size or age relationships (for any of the collection years), the project manager will assess the most suitable analysis method, if any. In some cases, this may be an analysis of variance (ANOVA) while including only fish of similar or overlapping sizes.

Least squares means from either ANCOVA or ANOVA results will be back-transformed and corrected for transformation bias with Duan's Smearing estimator (Duan, 1983; Helsel et al., 2020) and these values are given as "estimated mercury levels" in the annual reports. The magnitude of change in bass mercury concentrations between sampling years will be calculated as the percent change in estimated mercury levels.

To compare the muscle plug biopsy values to the primary fillet sample values, we will follow guidance by Helsel et al. (2020) for paired samples statistical tests.

14.4 Sampling design evaluation

The sampling design for this project strikes a balance between statistical power and cost. Ten samples per site allows us to detect statistically significant trends over time. The distribution of sites throughout Washington provides a representative sample of areas of interest.

14.5 Documentation of assessment

The project annual report will present findings, interpretations, and an assessment of data usability for the sampling year.

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16.0 Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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

Anthropogenic: Human-caused.

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.

Reach: A specific portion or segment of a stream.

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.

Acronyms and Abbreviations

e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
i.e.	In other words
LIMS	Laboratory information management system
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NTR	National Toxics Rule
PBT	Persistent, bioaccumulative, and toxic substance
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SRM	Standard reference materials
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife

Units of Measurement

Ft	feet
G	gram, a unit of mass
mm	millimeter
mg	milligram
mg/kg	milligrams per kilogram (parts per million)
mL	milliliter
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).

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

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

Examples of data types commonly validated would be:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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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