Quality Assurance Project Plan

Screening Survey of Mercury Levels in Edible Fish Tissue from Selected Lakes and Rivers of Washington State

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July 2002

Waterbody Numbers:
Banks Lake (WA-42-9020), Black Lake (WA-23-9010), Bonaparte Lake (WA-49-9050), Deer Lake (WA-59-9040), Duck Lake (WA-22-9030), Fazon Lake (WA-01-9020), Fish Lake (WA-45-9040), Loomis Lake (WA-24-9040), Lake Meridian (WA-09-9160), Moses Lake (WA-41-9250), Newman Lake (WA-57-9020), Offutt Lake (WA-13-9110), Okanogan River (WA-49-1040), Palmer Lake (WA-49-9270), Lake Samish (WA-03-9160), Lake Terrell (WA-01-9120), Upper Long Lake (WA-04-9040), Vancouver Lake (WA-28-9090), Walla Walla River (WA-32-1010), Lake Whatcom (WA-01-9170)

Ecology EIM Number: PAND0001

Approvals

Approved by:	October 8, 2002
Mike Gallagher, PBT Coordinator	Date
Approved by:	October 1, 2002
Steve Fischnaller, Project Manager, Toxics Studies Unit	Date
Approved by:	October 1, 2002
Paul Anderson, Principal Investigator, Toxics Studies Unit	Date
Approved by:	October 1, 2002
Dale Norton, Unit Supervisor, Toxics Studies Unit	Date
Approved by:	October 1, 2002
Will Kendra, Section Manager, Watershed Ecology Section	Date
Approved by:	October 8, 2002
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	October 2, 2002
Cliff Kirchmer, Ecology Quality Assurance Officer	Date

Abstract

In recent years, several studies have documented mercury at levels of concern in freshwater fish from several waterbodies in Washington State. However, limited information is available on the statewide distribution and magnitude of mercury in edible freshwater fish tissue. Additional information is lacking on environmental factors that may influence the uptake of mercury into freshwater fish.

To address these data gaps, the Washington State Department of Ecology Environmental Assessment Program (EA Program) will collect and analyze fish, sediment, and water samples from eighteen lakes and two rivers statewide. The target species will be bass due to their wide distribution and tendency to bioaccumulate mercury. Muscle fillet from each bass will be analyzed separately for total mercury. Surface sediments from three locations in each lake will be analyzed for total mercury. Additionally, a single sample of water will be collected from each lake, approximately one meter off the bottom, and analyzed for alkalinity and hardness. Conductivity, dissolved oxygen, and pH will be measured in the field. Visibility of surface waters will be measured using a Secchi disk.

Data generated from this study will be used in conjunction with existing data to evaluate the need for additional consumption advisory studies and aid in designing a long-term monitoring program for mercury. A final project report will be prepared to present and discuss the study findings.

Background and Problem Statement

Historically, studies investigating mercury contamination and bioaccumulation in muscle tissue of small mouth bass (SMB) and large mouth bass (LMB) have found elevated concentrations (Table 1).

Table 1. Historical Data for Mercury in Muscle Tissue.

Waterbody	Species	Tissue	Year	# Fish	Maximum Concentration ug/Kg ww	Study
Lake Whatcom	SMB	Muscle	2000	95	1840	Lake Whatcom
Yakima River	Northern Pike Minnow	Muscle	1984		780	BWMP
Yakima River	Mountain Whitefish	Muscle	1984		640	BWMP
Black Lake	LMB	Muscle, skin off	1989	4	540	10 Lakes Study
Duwamish River	Northern Pike Minnow	Muscle	1984		530	BWMP
Klickitat River	Spring Chinook	Muscle, skin on	1997		510 J	CRITFIC
Lake Whatcom	Yellow Perch	Muscle	2000	5	475	Lake Whatcom
Yakima River	SMB	Muscle, skin on	1998		470	CRITFIC
Lake Whatcom	Brown Bullhead	Muscle	2000	3	444	Lake Whatcom
Lake Roosevelt	SMB	Muscle, skin off	1995	5	620	USGS, 1994
Columbia River	White Sturgeon	Muscle, skin off	1998	1	380	CRITFIC
Snake River	Largescale Sucker	Muscle, skin on	1998		370	CRITFIC
Lake Roosevelt	Walleye	Muscle, skin off	1995	24	364	USGS, 1994
Ward Lake	LMB	Muscle, skin off	1992		350 J	Lake Toxics
Yakima River	Largescale Sucker	Muscle, skin on	1998		350	CRITFIC
Lake Samish	LMB	Muscle	1989	5	270	10 Lakes Study
Yakima River	Channel Catfish	Muscle, skin on	1998		270	CRITFIC
Yakima River	Bridgelip Sucker	Muscle	1984		250	BWMP
Columbia River	Channel Catfish	Muscle, skin on	1997		240	CRITFIC
Lake Crescent	Cutthroat Trout	Muscle	1989	2	220	10 Lakes Study
American Lake	Rock Bass	Muscle	1989	5	220	10 Lakes Study
Columbia River	Largescale Sucker	Muscle, skin on	1997		220	CRITFIC
Icicle Creek	Spring Chinook	Muscle, skin on	1997		220	CRITFIC
Snake River	Steelhead	Muscle, skin on	1997		210	CRITFIC
Lake Roosevelt	Rainbow Trout	Muscle, skin off	1995	6	202	USGS, 1994

LMB = Large Mouth Bass; SMB = Small Mouth Bass; USGS = United States Geological Survey

J = Estimated Concentration; CRITFIC = Columbia River Inter-Tribal Fish Commission

In humans, chronic mercury poisoning may occur when fish are frequently ingested that contain elevated levels of mercury. As bioaccumulation of this heavy metal occurs in a human, and tissue levels rise, metabolic and neurological damages may result. The biological half-life of mercury in humans is about 70 days (Clinical Diagnosis 1974).

Humans of all ages are susceptible to chronic mercury poisoning; however, women of child-bearing age who may become pregnant and children under six years of age are especially susceptible (DOH 2001). Mercury poisoning may harm the developing nervous system in fetuses and children under six years of age, permanently affecting the ability to learn. Adults exposed to high levels of mercury can also suffer from central nervous system problems and adverse effects on the cardiovascular system (DOH 2001).

The U. S. Environmental Protection Agency (EPA) has developed two criteria for total mercury levels in fish muscle tissue. The established EPA National Toxics Rule human health criterion for mercury of 825 µg/kg (Serdar et al., 2001) will be used to evaluate data obtained by this study. A revised criterion for levels of total mercury in fish muscle tissue has been proposed at 300 µg/kg (EPA 2002). This new criterion is based on the average rate of consumption of freshwater and estuarine fish by recreational fishers, and will be discussed in the final report.

Historical studies provided reliable results but are difficult to compare because of a lack of standard study design. Some studies incorporated skin and others did not (Table 1).

Many of these studies resulted in fish consumption advisories released by the Washington State Department of Health (DOH, Table 2).

Table 2. **Summary of Mercury Advisories Released by the Washington State Department of Health.**

Location	Nearest Community	Species Affected
Eagle Harbor	Bainbridge Island	All shellfish including crab and all bottom fish
Indian Island	Port Townsend	All shellfish
Lake Roosevelt	Grand Coulee	Walleye, whitefish, sturgeon
Lake Whatcom	Bellingham	Smallmouth bass, yellow perch
Sinclair Inlet	Bremerton	All shellfish including crab and all bottom fish including rockfish

The Lake Whatom study of mercury in edible fish tissue investigated the extent of contamination of several species of fish including bass. Overall mercury concentrations in SMB averaged 490 µg/kg (wet), with a maximum concentration of 1,840 µg/kg (USGS 1995). All other species collected were contaminated with some amount of mercury over a range of 50–200 µg/kg (wet).

The Lake Roosevelt study detected mercury in walleye fillets with a mean concentration of 280 µg/kg wet (Serdar et al., 2001). Other species sampled in Lake Roosevelt generally had lower concentrations of mercury. Data from the study resulted in a fish consumption advisory and a 303(d) listing of the lake for mercury in tissue (Ecology 2000). Fish from both Lake Whatcom and Lake Roosevelt were found to contain mercury; however, the Lake Whatcom fish were found to have levels above the EPA National Toxics Rule human health criterion of 825 µg/kg (Serdar et al., 2001).

Data from the Lake Whatcom and Lake Roosevelt studies as well as data from other studies indicate that long lived species and species high on the trophic scale tend to have higher concentrations of mercury (Table 2). Higher concentrtions of mercury are usually found in these types of fish due to the ability of methylmercury to bioaccumulate and biomagnify in the muslce tissue of fish and other aquatic organisms. Large and small mouth bass are both long lived and are predators high on the trophic scale. Both species have been found to accumulate particularily high concentrations of mercury in their tissue and were chosen as the target species for this study because of this characteristic and their wide distribution.

Due to the small number of spatially dispersed lakes, limited information is available on the distribution and magnitude of mercury in edible fish tissue statewide. In addition, regional information is lacking regarding other factors that might influence the uptake of mercury into freshwater fish. Some evaluation of the correlation between age, weight, and length to mercury concentrations has been performed for Washington. However, this evaluation was limited to a single study done on Lake Whatcom. Even with the preceding evalutaion there is still a lack of data to evaluate correlations of mercury levels with other variables such as sex, age, and lipid content.

As a result of the lack of information and the potential threat to human and environmental health, mercury was chosen by Ecology's Persistent Bioaccumulative Toxins (PBT) program to be the first chemical for the development of an action plan. The chemical action plan, which is still in development, will have two goals of equal importance. The two goals are:

1. Virtual elimination of the use and release of anthropogenic mercury in Washington State.

2. Minimize human exposure to anthropogenic mercury.

In order to evaluate the effectiveness of the chemical action plan at reducing mercury in the environment, a long-term monitoring plan will need be put in place. As a part of the long-term monitoring plan, a trend monitoring component is being developed by the Washington State Toxics Monitoring Program. This study will attempt to provide the data necessary to develop a baseline for a monitoring program that will help evaluate the risk to consumers who are eating contaminated fish.

Data from this study will also be provided to the DOH. Currently, Washington State does not have a mercury criterion for edible fish tissue that is used to trigger consumption advisories. Instead, DOH issues advisories on a case-by-case basis. The use of the case-by-case approach for health assessment has prevented DOH from declaring a specific tissue concentration that would trigger a health advisory. DOH may use data from this study to develop a statewide health advisory for freshwater fish consumption.

Project Description

In order to address the lack of information on fish tissue concentrations, the EA Progam will collect and analyze game fish from 18 lakes and 2 rivers distributed statewide. The target species for this work will be SMB and LMB due to their wide distribution and capacity to bioaccumulate mecrcury. The target catch is 10 bass from each waterbody. Muscle fillets from each bass will be analyzed separately in order to remove the variance due to length, while maintaining a moderate sampling difficulty (Yake 2002). To evaluate other factors affecting mercury uptake, surface sediments from three locations in each lake will be analyzed for total mercury (Håkanson et al.,1988). A single water sample will be collected at each lake approximately one meter off the bottom and analyzed for conventional water quality parameters, including field analysis of pH, dissolved oxygen, water temperature, and conductivity. Secchi disk depth will be used to measure visibility in surface waters. Hardness and alkalinity will be analyzed by the laboratory.

Project objectives are as follows:

- Provide regional screening level data on mercury concentrations in edible fish tissue (LMB and SMB) from freshwater areas of Washington State. Data generated from this study will be used in conjunction with existing data to evaluate the need for additional consumption advisory studies and aid in designing a long-term monitoring program for mercury.

- Increase the body of data needed to evaluate correlations of mercury levels with other variables such as fish length, weight, sex, age, and lipid content. This information is needed to help design the long-term trend monitoring component of the Washington State Toxics Monitoring Program and evaluate the effectivness of the PBT mercury action plan at reducing mercury levels in the environment.

- Collect additional information on potential factors that affect mercury uptake in fish (i.e. water chemistry, surface sediment mercury concentrations, and watershed characteristics).

Responsibilities

Ecology Manchester Environmental Laboratory (MEL)
Stuart Magoon (360-871-8801) is the director of MEL and is responsible for coordinating analysis services for the project at MEL.

Ecology Quality Assurance
Cliff Kirchmer (360-407-6455) is the quality assurance officer for Ecology. He will review this Quality Assurance Project Plan (QA Project Plan) to ensure that it meets Ecology quality standards and be available to provide assistance with the evaluation of QA/QC data for the project.

Ecology Toxics Studies Unit
Steve Fischnaller (360-407-7168) is the project manager. He will be responsible for overall project management, QA Project Plan preparation, field sampling, data analysis, and preparation of a final report. He will also coordinate with the PBT program for presentation of project information to interested groups.

Paul Anderson (360-407-7548) is the principal investigator. He is responsible for field sampling, assisting with data analysis, preparing a final report, and obtaining collection permits. He will also be responsible for data entry into the Environmental Information Management (EIM) system.

Schedule

QA Project Plan Approved for Sampling	September 2002
Sample Collection	September to October 2002
Sample Preparation	September to October 2002
Laboratory Analysis Complete	November 2002
Draft Report	December 2002
Final Report	February 2003
Data Entered in EIM System	February 2003

Study Design

Sampling of edible fish tissue in LMB and SMB for mercury concentrations will occur in the early fall of 2002. Samples will be collected from 20 waterbodies distributed statewide among the four Department of Ecology regions (Northwest, Southwest, Central, and Eastern). The four regions and 18 proposed lakes and two rivers are shown in Figure 1. Approximately five water-bodies will be sampled in each region. Waterbodies will be selected for sampling based on consideration of the following factors:

1. Evidence or high probability for mercury uptake in fish. Sampling will not be conducted in waterbodies that already have adaquate mercury data on fish tissue (i.e. >10 individual tissue samples).

2. Proximity to potential sources of mercury.

3. Availability of target species.

4. Availability of public lake access and/or presence of a recreational fishery.

5. Ability to obtain scientific collection permit.

6. Availability of water quality and watershed characteristic information.

For each waterbody, the goal will be to collect ten individual fish of one species, either largemouth (Micropterus salmoides) or smallmouth (Micropterus dolomieu) bass. A minimum of five individual fish will be needed for an adequate sample. The first ten bass of either species that exceed a minimum size of ten inches will be retained for analysis. Ten inches was selected as the minimum size to provide adquate tissue for chemical analysis. It also is just under the miminum size most anglers prefer to catch (quality length) based on work conducted by WDFW in Lake Whatcom (Gabelhouse 1984).

Fish tissue samples will be obtained through a combination of new tissue collections and analsysis of fish from ongoing EA Program studies (Okanogan River Total Maximum Daily Load [TMDL], Walla Walla River TMDL, and the Washington State Toxics Monitoring Program [WSTMP]). The list of 20 waterbodies proposed for inclusion in the study is shown in Table 3. A minimum of five individual bass are available from the lakes that have already been sampled. New scientific collection permits from WDFW will be needed for sites not covered by existing programs. A number of the sites can be covered under existing programs or in some cases collection activities that are planned by the WDFW. For those sites not covered under existing activities, permits will need to be obtained from WDFW. A list of proposed and complete lakes is shown in Table 3. There are 18 lakes and two rivers proposed for study of mercury; ten lakes have not been sampled for bass and 11 lakes have already had fish tissue collected and analyzed.

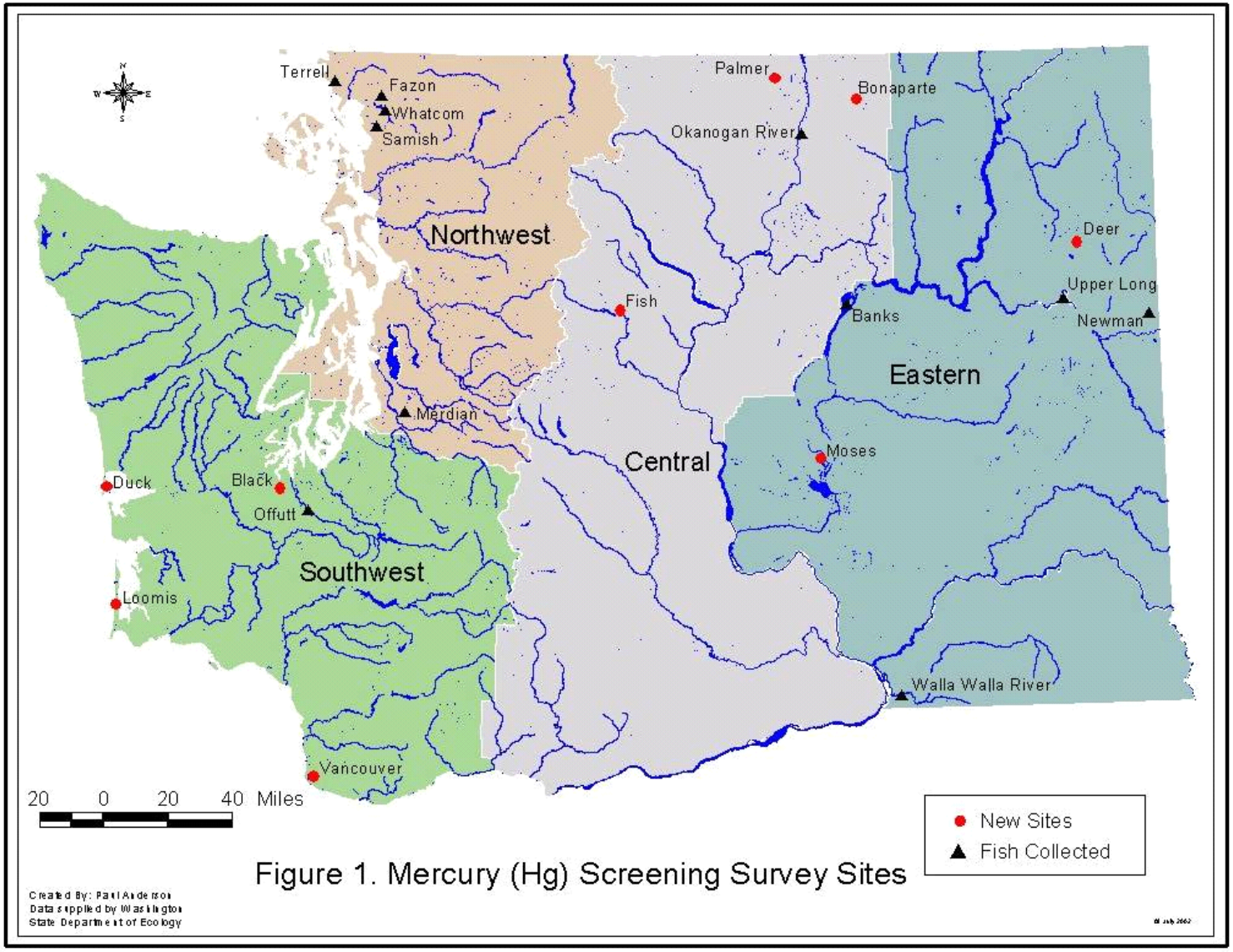

Figure 1. Mercury (Hg) Screening Survey Sites

Surface sediments (top 2 cm) will be collected and analyzed for total mercury from three locations in each of the 20 waterbodies adjacent to where fish samples are collected. These data will be used to estimate the mean mercury concentration in surface sediments from the fish collection area. In addition to sediment samples, water quality data will be collected at each of the 20 waterbodies. A single water column sample will be collected one meter off the bottom and analyzed for alkalinity and hardness. Field measurements for dissolved oxygen, temperature, pH, conductivity, and secchi disk depth will also be collected. Previous studies have indicated significant negative correlations between water quality parameters and mercury accumulation in certain fish species (Håkanson et al.,1988; Rose et al., 1999). Negative correlations have also been shown between concentrations of mercury in sediment and fish tissues. Additional lake area and available watershed information will be reviewed to see if correlations are present with observed mercury concentrations in fish tissue.

Table 3. New Sites and Sites Where Fish Have Been Collected for Mercury Screening Survey in Edible Fish Tissue.

Region	Species	Fish Collected	Study	County
Southwest				
Duck	LMB	NO	WSTMP	Grays Harbor
Loomis	LMB	NO	WSTMP	Pacific
Vancouver	LMB	NO	WSTMP	Clark
Black	LMB	NO	WSTMP	Thurston
Offutt	LMB	YES	WSTMP	Thurston
Eastern				
Newman	LMB	YES	WSTMP	Spokane
Moses	SMB,LMB	NO	WSTMP	Grant
Deer	SMB,LMB	NO	WSTMP	Stevens
Walla Walla River	SMB	YES	Walla Walla River TMDL	Walla Walla
Upper Long	SMB,LMB	YES	Metals/PCBs in Long Lake	Spokane
Central				
Palmer	SMB,LMB	NO	WSTMP	Okanogan
Fish	SMB,LMB	NO	WSTMP	Chelan
Bonaparte	SMB	NO	WSTMP	Okanogan
Okanogan River	SMB,LMB	YES	Okanogan River TMDL	Okanogan
Banks	LMB	YES	WSTMP	Grant
Northwest				
Whatcom	SMB	YES	WSTMP	Whatcom
Fazon	LMB	YES	WSTMP	Whatcom
Terrell	LMB	YES	WSTMP	Whatcom
Samish	LMB	YES	WSTMP	Whatcom
Meridian	LMB	YES	WSTMP	King

SMB = Smallmouth Bass; LMB = Largemouth Bass

WSTMP = Washington State Toxics Monitoring Program

* Will be used if needed (backup)

Quality Objectives

A summary of measurement quality objectives for all parameters is shown in Table 4.

Table 4. Measurement Quality Objectives.

Parameter	Bias	Precision (RSD)	Accuracy	Required Reporting Limit
Fish Tissue				
Mercury	10%	10%	30%	5 µg/kg, wet
Lipids	N/A	N/A	N/A	0.10%
Sediment				
Mercury	10%	10%	30%	5 µg/kg, wet
TOC	N/A	10%	N/A	0.1% Carbon
Water				
pH	N/A	±0.1 pH units	±0.2 pH units	±0.1 pH units
Temperature	N/A	±0.2 ˚C	±0.4 ˚C	±0.1 ˚C
Dissolved Oxygen	N/A	±0.06 mg/L	±0.12 mg/L	±0.2 mg/L
Conductivity	N/A	±20 µmhos/cm	±40 µmhos/cm	±1% of Reading
Secchi Disk Depth	N/A	±0.5 m	±1.0 m	N/A
Alkalinity	5%	5%	15%	10 mg/L
Hardness	5%	10%	25%	1 mg/L

Representativeness will be achieved by individually analyzing each fish to obtain estimates of mercury concentration for each location. A sample size of ten individual fish will be used to provide 95% confidence intervals about the mean (Yake 2002). In addition to the 95% confidence interval, a sample set of ten individually analyzed fish will remove variance due to length and other population shifts between sampling events (Yake 2002). Individually analyzed fish also retain information about the population that would be obscured by sample compositing. Waterbodies will be selected based on five considerations explained in the study design. The waterbodies selected for sampling will be evenly distributed as much as possible across the four Department of Ecology regions (Northwest, Southwest, Eastern, and Central). Sediment samples will be collected in locations that are adjacent to fish collection sites.

Completeness will be improved by detailed field preparation, following sample collection methods outlined in field procedures, and using care in transporting samples. The laboratory and the laboratory courier will be notified in advance of a sampling event to ensure recommended holding times be met.

Comparability of the results will be ensured by using standard and consistent methods for all sampling events. Sample collection and field procedures will be the same for each sampling effort and are consistent with current and historic methods used for sampling fish tissue for mercury concentrations.

Field Procedures

Scientific Collection Permits

Scientific collection permits will be acquired prior to collecting fish. Washington's Department of Fish and Wildlife issues permits for any collection activities in the state. For areas inhabited by fish listed under the Endangered Species Act (ESA), fish will be collected under the appropriate permit (National Marine Fisheries Service for anadromous species or the U. S. Fish and Wildlife Service for inland species). Approximately three to six months are needed for these federal agencies to process applications for scientific collection permits. For federal permits, we will be able to utilize permits obtained under the WSTMP, which were issued in late summer of 2002.

Permits are needed because ESA-listed species may be encountered during collection activities. The collection methods used (electrofishing primarily) may disturb or harass listed species and is considered "take" under ESA. There are currently 15 species or stocks of anadromous fish in Washington waters that are listed or are proposed for listing as endangered or threatened. The Bull Trout (Salvelinius confluentes) is listed as threatened in Washington and other northwest states. These species or stocks collectively inhabit large areas of Washington; therefore, the project collection efforts, to the extent possible, will focus on areas where federal collection permits are not needed.

Sampling Methods

Fish will be collected using a combination of techniques based on permit requirements, including hook and line and fike net and electrofishing. Methods for collection, handling, and processing of fish tissue samples will be guided by methods described in EPA (2000). Upon capture in the field, fish will be placed in a live tank and identified to species. Only target species will be retained; non-target species will be released. Fish that are retained will be inspected to ensure that they are acceptable for further processing (e.g. proper size, no obvious damage to tissues, skin intact). Fish selected for retention will be stunned by a blow to the head with a dull object, rinsed in ambient water to remove foreign material from their exterior, weighed, and their fork and total length measured. Individual fish will then be double-wrapped in aluminum foil (dull side in), lableled, and placed in large plastic or zip-lock bags. All fish will be assigned unique identification numbers. All fish samples will be placed in coolers on ice and transported to the EA Program storage facilities and frozen at -18˚C within 24-48 hours. Chain-of-custody procedures will be used with all samples. Fish locations will be identified in the field with a hand held GPS unit.

Sediment samples will be collected using a 0.05 m^2 stainless steel ponar grab. A grab will be considered acceptable if: (1) it is not overfilled with sediment, (2) overlying water is present and not excessively turbid, (3) the sediment surface is relatively flat, and (4) the desired depth of penetration (>2cm) has been achieved. After siphoning off overlying water, the top 2-cm of sediment from each individual grab will be removed with a stainless steel spoon, placed in a stainless steel bowl, and homogenized by stirring. Sediments in contact with the side walls of

the grab will not be retained for analysis. Sub-samples of the homogenized sediment will be placed in 4-oz. glass jars with Teflon lid liners, that have been cleaned to EPA QA/QC specifications for mercury (EPA 1990). Separate sub-samples of sediment will also be placed in 2-oz glass jars for total organic carbon (TOC) analysis.

Only pre-cleaned sampling equipment and sample containers will be used to collect, manipulate, and store the sediments. Sampling equipment will be pre-cleaned by washing with Liquinox® detergent followed by sequential rinses with hot tap water, 10% Baker Instra-Analyzed® nitric acid rinse, and deionized water rinse. The sampling equipment will then be allowed to air dry and wrapped in aluminum foil (dull side in) until used in the field. The same cleaning procedure will be used to clean the grab before going into the field. Between sampling locations, cleaning of the grab will consist of thoroughly brushing with on-site water. If oil or visible contamination is encountered, the grab will be cleaned between samples with a deteregent followed by a rinse with on-site water.

Care should be taken with operating the vessel in shallow water so as not to disturb and affect the sediments being sampled. Sample containers will be placed in polyethylene bags to further reduce the possibility of cross-contamination. All samples will be placed on ice immediately after collection.

Water samples will be collected using a Kemmer sampler. Samples will be collected by slowly lowering the sampler to one foot off the bottom. Water will be collected at one point during each sampling event and used to measure alkalinity and hardness. Secchi depth, pH, conductivity, DO, and temperature will be measured in the field, while hardness and alkalinity will be sent to MEL for analysis.

Dissolved oxygen, pH, temperature and conductivity will be measured using a calibrated hydro lab. Water turbidity will be measured using a Secchi disk. Sample location coordinates will be determined in the field with a Magellan GPS 320 global positioning receiver. Recommended sample bottles, preservatives, and holding times for all parameters are listed in Table 5.

Table 5. Recommended Sample Containers and Preservation.

Parameter	Sample Container	Preservation	Holding Time
Fish Tissue			
Mercury	glass/Teflon lid liner, 4 oz.	-18˚C Frozen	28 days
Sediment			
Mercury	glass/Teflon lid liner, 4 oz.	4˚C	28 days
TOC	glass/Teflon lid liner, 2 oz.	4˚C	28 days
Water			
Alkalinity	Polyethylene, 500 mL	4˚C	14 days
Hardness	acidified bottles, 125 mL	4˚C, HNO_3, <pH 2	6 months

Sample containers in sealed plastic bags will be placed into coolers and cooled with ice. Glass sample containers will be protected from breakage by wrapping each in bubble-wrap. Chain-of-custody procedures will be used for all samples. After collection, samples will be stored in a refrigerator at the Ecology headquarters building and then transported to the Ecology MEL the next business day by sample courier.

MEL personnel will observe the condition of the shipped water samples and make note of any samples that are leaking, not cold, or have other problems. Upon receipt of water samples, laboratory personnel will complete all paperwork required to track the shipment and log in the samples. Water samples will be stored at MEL at 4 ± 2°C, until they are extracted and analyzed.

Tissue Preparation

Muscle tissue of up to ten fish will be indivually analyzed for mercury at the laboratory. Fillet resection will be performed at the Ecology headquarters building by removing foil from the partially thawed specimen and then removing the fillet with a stainless steel fillet knife or stainless scalpel. Care will be taken to avoid puncturing internal organs. Fish scales, otoliths, and opercules will be extracted from individual fish and sent to a WDFW biologist contracted to determine fish age from these structures. Fish tissue will also be extracted and anlayzed for percent lipids.

Tissue will be homoginized with three passes through a Kitchen-Aid® food processor or non-contaminating hand held grinder. Ground tissue will be thoroughly mixed following each pass through the grinder. All equipment used for tissue preparation will be vigorously washed with Liquinox® detergent followed by sequential rinses in hot tap water, 10% Baker Instra-Analyzed® nitric acid rinse, and deionized water rinse. This decontamination procedure will be repeated between the processing of each sample. Fully homogenized tissue from each specimen will be placed in 4-oz. glass jars with Teflon lids cleaned for metals per USEPA Office of Solid Waste and Emergency Response Directive #9240.0-05. Samples will then be stored at -18ºC until analysis. Excess muscle tissue will be placed into appropriate containers, labeled, and archived frozen at -18˚C. All fish will be processed within the 28 day holding time.

Laboratory Procedures

Tissue, sediment, and water samples will be analyzed at MEL. A summary of analytical methods and matrices by parameter is presented in Table 6. Projected costs for all analytical methods are presented in Table 7.

Table 6. Summary of Parameters and Analytical Methods for Each Matrix.

Parameter	Matrix	Analytical Method	Method Detection Limit
Fish Tissue			
Mercury	Fish Tissue	CVAA, EPA Method 245.6*	3 µg/kg, wet
Lipids	Fish Tissue	Gravimetric	.02%
Sediment			
Mercury	Sediment	CVAA, EPA Method 245.5*	3 µg/kg, wet
TOC	Sediment	Combustion/CO_2 Generation	0.1% Carbon
Water			
pH	Water	Field-Hydrolab	0.2 pH unit
Temperature	Water	Field-Hydrolab	0.1 ˚C
Dissolved Oxygen	Water	Field-Hydrolab	0.2 mg/L
Conductivity	Water	Field-Hydrolab	1% of Reading
Secchi Disk Depth	Water	Secchi disk	
Alkalinity	Water	EPA Method 310.2	5 mg/L
Hardness	Water	ICP 2340B	1 mg/L

CVAA = Cold Vapor Atomic Absorption

TOC = Total Organic Carbon

ICP = Inductively Coupled Plasma

MEL = Manchester Environmental Laboratory
* = Lower Method Detection Limit Obtained with New Instrumentation

Table 7. Sample Numbers and Analytical Costs for Mercury Screening Study.

Analysis	Number of Samples	Number QA Samples	Total Number of Analysis	Dollars/Sample	Subtotal
Fish Tissue					
Mercury	100	20	120	55	6,600
Lipids	100	5	105	82	8,610
Age	110	N/A	100	10	1,100
Sediment					
Mercury	60	15	75	30	2,250
TOC	60	3	63	33	2,079
Water					
pH	20	1	21	Field	-
Dissolved Oxygen	20	1	21	Field	-
Conductivity	20	1	21	Field	-
Secchi Depth	20	-	20	Field	-
Alkalinity	20	1	21	14	294
Hardness	20	1	21	12	252
				Total	**$21,085**

QA = 1 Field Duplicate for Every 20 Samples, Hg = 1 MS/MSD Set for Every 20 Samples

Quality Control Procedures

Quality control procedures include the use of field replicates, field method blanks, and spike and duplicate spike samples. A summary of quality control procedures are presented in Table 8.

Table 8. Quality Control Procedures for Field and Laboratory.

	Field	Laboratory		
Parameter	**Replicates**	**Check Standards (SRM)**	**Matrix Spikes and Duplicates**	**Method Blank**
Fish Tissue				
Mercury	1/20 Samples	1 Duplicate/Batch*	1 Set/20 Samples	3
Lipids	1/20 Samples	N/A	N/A	N/A
Age	N/A	N/A	N/A	N/A
Sediment				
Mercury	1/20 Samples	1Duplicate/Batch*	1 Set/20 Samples	3
TOC	1/20 Samples	N/A	N/A	N/A
Water				
pH	1/20 Samples	N/A	N/A	N/A
Dissolved Oxygen	1/20 Samples	N/A	N/A	N/A
Conductivity	1/20 Samples	N/A	N/A	N/A
Alkalinity	1/20 Samples	N/A	N/A	N/A
Hardness	1/20 Samples	N/A	N/A	N/A

*Not to exceed 3

SRM = Standard Reference Material (DORM-2 Dogfish Muscle)

Bias from interference or matrix effects will be assessed through analysis of matrix spikes and standard reference materials. The target quality control limits for matrix spike recoveries are 75-125% for mercury. Bias due to calibration will be assessed from the mean recoveries of lab control sample analyses.

Precision of the data will be assessed through the analysis of matrix spike duplicates as well as lab and field duplicate samples. The data quality objective for precision is a relative percent difference (RPD) of 15%.

The use of field instruments will follow manufacturer's calibration and operating procedures. Commercial standards will be used for calibrating pH and conductivity instruments.

Laboratory quality control procedures routinely used by MEL will be sufficient for this project. Should problems with samples or analyses arise, MEL will confer with the project lead about the nature and need for corrective actions.

Three method blanks will be prepared during the course of the study by rinsing surfaces of foil and instruments that come in contact with fish tissue and sediment. Composite rinsate will be collected and analyzed for mercury.

Data Management Procedures

Field notes will be kept for each sampling event. Notes will be entered into a field notebook including date and time, sampling personnel, general sampling location, and latitude/longitude coordinates of fish collection, general weather conditions, method of sampling, fish species collected, weights and lengths for individual specimens, and results from field measurements. Additional notes will be taken when samples are processed and submitted for laboratory analysis, including type of tissue, laboratory identification numbers, and laboratory analyses requested. The sex of individual fish will be determined during tissue processing. After completion of the project, field data will be entered into the Environmental Information Management (EIM) system. After laboratory data has been reviewed, resulting qualified data will also be entered into EIM. All data will be entered in EIM before, or soon after, the final report is complete.

Data Review and Validation

Project data generated in the field or received from the laboratory will be tabulated and verified. Field measurements will be reviewed by the project lead for quality and the results summarized in narrative form. Water quality data will be verified by MEL staff according to the requirements of the method. The water quality data will then be sent to the project lead accompanied by written quality assurance reviews from MEL staff. Data from the lab will then be reviewed by the project lead. Results from field and laboratory measurements will be entered into the Ecology EIM database.

Data Quality Assessment

Once data have been reviewed, verified, and validated, the project lead will compare the results to the Data Quality Objectives (DQOs) specified in this QA Project Plan to determine if the DQOs were obtained. If the results are satisfactory, statistical tools will be used to assess among-site comparisons of mercury levels in edible fish tissue and correlations to fish age and mercury in sediment. Results from QA samples will be compared to identify potential error between sites and sample events. Resulting data will be given to the Washington State Department of Health for review and use.

Reporting

A report for the screening survey of mercury levels in edible fish tissue will by prepared by the project manager. The final project report will include the following:

- A map and latitude/longitude information for all samples collected.
- A summary of field data collected including species type, length, weight, and water quality conditions.
- A summary of analytical data for fish tissue, sediments, and water quality.
- Comparison of fish tissue results for mercury to regulatory guidelines for the protection of human health. The Department of Health will also review the fish tissue data generated from this study.
- Comparison of mercury concentrations in sediment to historic freshwater sediment quality values.
- Comparison between fish weight and mercury, fish length and mercury, and fish age and mercury relationships in tissue from each waterbody.
- Comparison to historical mercury data for fish tissue in Washington.
- Comparison of observed correlations of mercury concentrations with other factors such as sediment concentrations, water quality, and lake size.
- Recommendations for follow-up work if needed.

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