Quality Assurance Project Plan

Mercury Screening in Lake Ozette Sockeye

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Cover photo: Sockeye salmon (Oncorhynchus nerka)

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October 2010

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Signatures are not available on the Internet version.
W2R - Waste 2 Resources Program
EAP - Environmental Assessment Program
EIM - Environmental Information Management system

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Abstract

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance (QA) Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This QA Project Plan describes the analysis of mercury in Lake Ozette Sockeye salmon. Lake Ozette sockeye were collected by Makah Fisheries from the Umbrella Creek broodstock during the fall of 2009. Both fillet and whole body samples will be analyzed to characterize mercury concentrations. Results will be compared to applicable consumption criteria and other published data on sockeye.

Background

Introduction

Considerable attention has been given to mercury contamination of aquatic food webs due to its biomagnification potential, widespread environmental prevalence, and toxicity to humans and wildlife. In Washington, mercury was chosen as the first pollutant to be addressed in the state's Persistent and Bioaccumulative Toxics (PBT) Reduction Strategy (Gallagher, 2000). This focus on mercury resulted in development of the *Washington State Mercury Chemical Action Plan* (Peele, 2003).

As a result of the *Chemical Action Plan*, long-term fish tissue monitoring was initiated in 2005 (Seiders, 2006). To date, five years (2005-2009) of statewide tissue monitoring (30 sites) has been completed (Furl et al., 2007; Furl, 2007; Furl and Meredith, 2008; Furl et al., 2009; Meredith et al., 2010).

The highest concentrations of mercury in individual bass have been found at Lake Ozette located in the northwest corner of Washington's Olympic Peninsula (Figure 1) in the Olympic National Park.

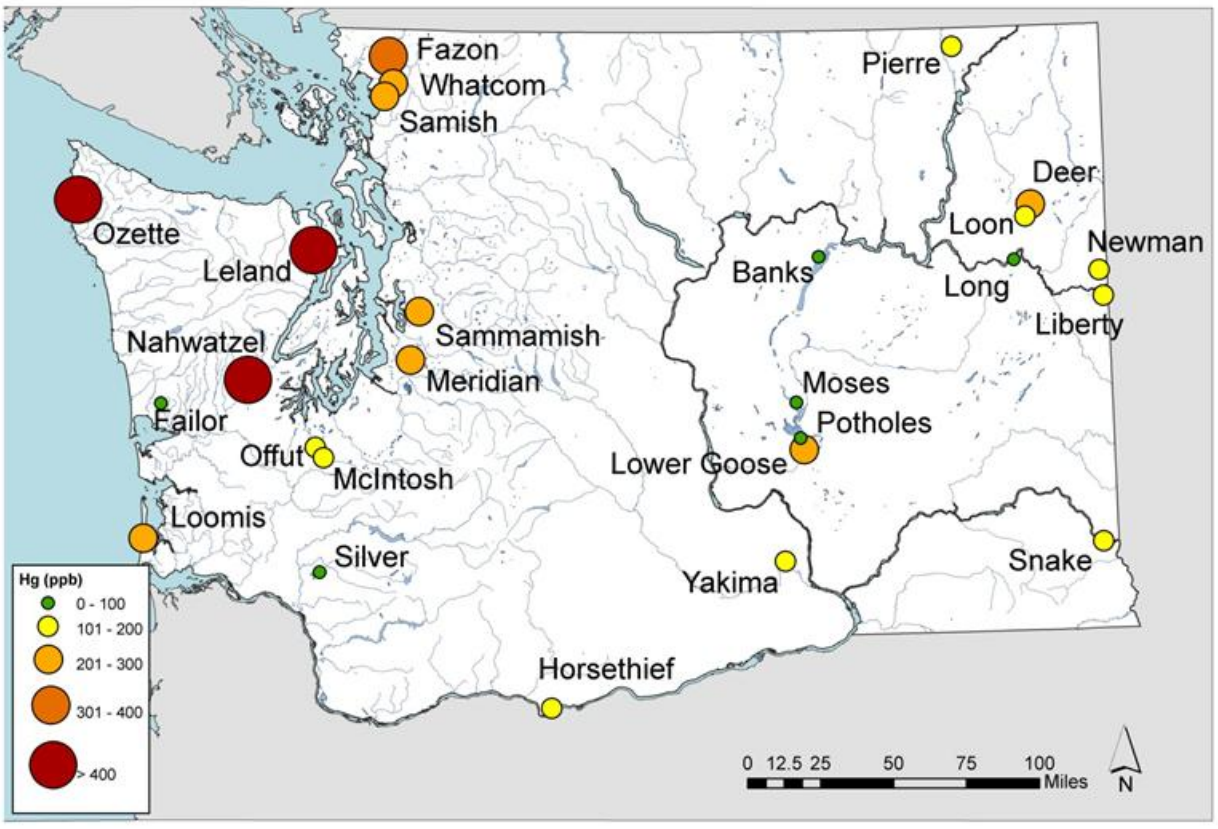

Figure 1. Normalized mercury concentrations in bass as part of the mercury trends monitoring project 2005-2009.

In order to further investigate biological contamination at Lake Ozette, sockeye (*Oncorhynchus nerka*) from Lake Ozette will be analyzed for mercury concentrations.

Lake Ozette Sockeye

The Lake Ozette sockeye are one of six sockeye salmon "evolutionarily significant units" present in Washington State. In March 1999 Lake Ozette sockeye were listed as a threatened Evolutionarily Significant Unit under the Endangered Species Act. It was concluded that the species was likely to become endangered in the foreseeable future if present conditions continue. Over the past decade considerable research has been conducted and much has been written about the causes of the declining population. The following information was collected from the recovery plan and limiting factors analysis (Haggerty et al., 2008 and 2009, respectively).

Historical accounts of Lake Ozette Sockeye escapement are sparse but, based on a 1940s estimate, several thousand fish are believed to have returned. In 1949, annual harvest by Makah Fisheries reached an estimated high of over 17,000. Since the mid-1990s Lake Ozette sockeye escapements have averaged around 2000 with low years dropping to a few hundred. Hatchery operations have supported Lake Ozette sockeye restoration efforts since 1983. Currently, broodstock are collected from Umbrella Creek and fry/fingerlings are released to Big River and Umbrella Creek.

Life History

Lake Ozette sockeye return from mid-April through mid-August primarily as four-year-old adults. Their early return to the lake (peak returns are in late May to early June) precludes them from being intercepted by commercial efforts aimed at the Fraser River sockeye. The fish hold in Lake Ozette for two to ten months prior to spawning in November and December. Fish spawn in three tributaries (Umbrella Creek, Big River, and Crooked Creek) and two beaches (Olsen's Beach and Allen's Beach). Fry emergence and dispersal in the lake occur from February to May. Juvenile Lake Ozette sockeye rear in the lake for one summer before immigrating to sea during their second spring.

Limiting Factors Analysis

Several factors have been suggested for the causes of the Lake Ozette sockeye declines. Key among them is the loss of adequate spawning grounds due to excessive sedimentation. The most important factors responsible for the decline are thought to include:

- Loss of adequate quality and quantity of spawning habitat.
- Predation and disruption of natural predator-prey relationships.
- Introduction of non-native fish and plant species.
- Past over-exploitation in fisheries.
- Poor marine survival.
- Synergistic and cumulative effects of these factors.

Lake Ozette

Located within the coastal strip of the Olympic National Park 5 km from the Pacific Ocean, Lake Ozette is the third largest natural lake in Washington State. The lake has a surface area of 29.5 km^2 and an average depth of 40 m (Bortleson et al., 1976) (Figure 2). The National Park Service owns 15% of the 118 km^2 watershed while over 80% of the watershed is zoned as commercial forest land. Climate in the watershed can be characterized as temperate coastal-marine, resulting in mild winters and cool summers. Average annual precipitation in the area is in excess of 250 cm (≈100 inches) per year with greater than 80% occurring between October and April.

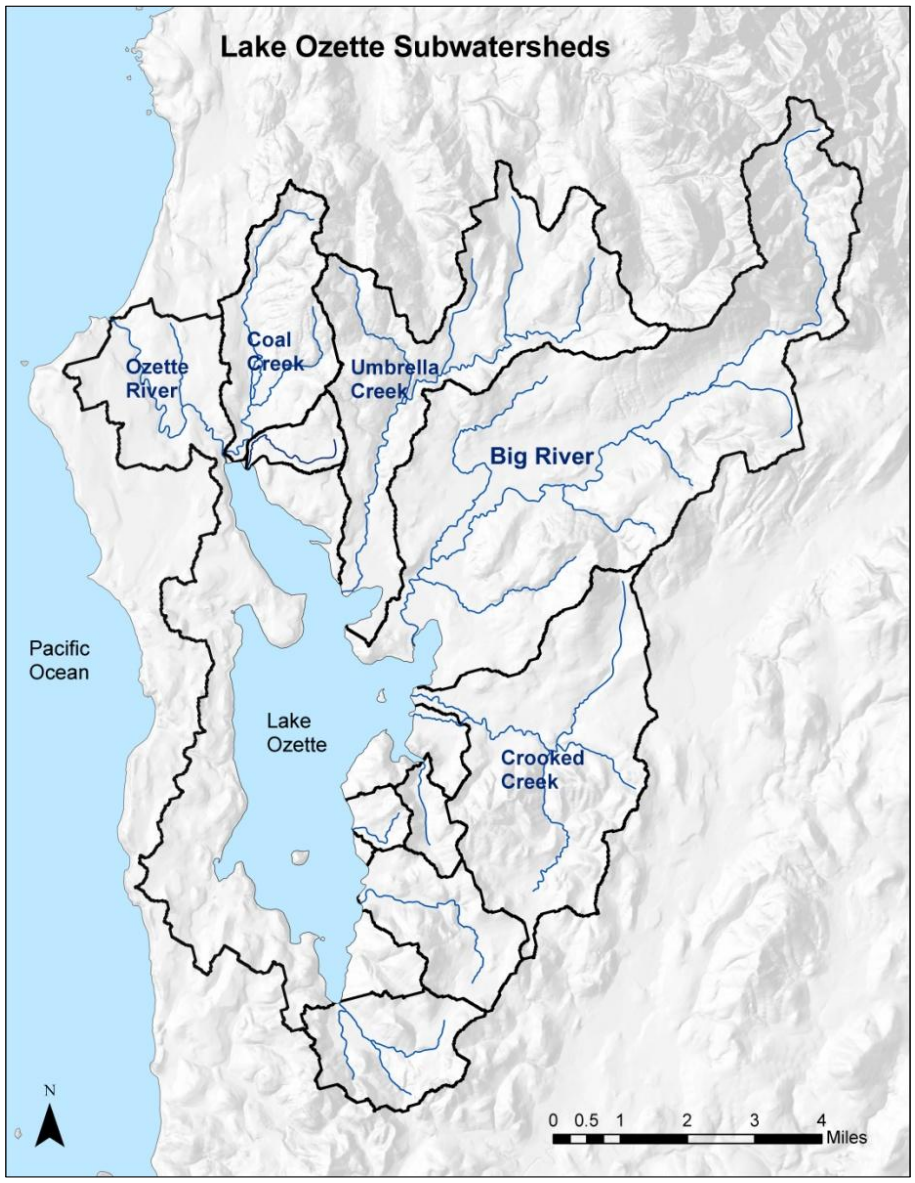

Figure 2. Lake Ozette watershed.

Mercury Studies

Several mercury studies (fish, wet deposition, sediment, streams) have been conducted in and near Lake Ozette over the last several years. Below are brief descriptions of their findings.

Fish

Fish from Lake Ozette were collected and analyzed for mercury in two previous Ecology studies:

- *Mercury Trends:* During the fall of 2007, Furl and Meredith (2008) analyzed ten individual largemouth bass and composite samples (3-5 fish) of northern pikeminnow and yellow perch.
- *Washington State Toxics Monitoring Program:* During the fall of 2004, Seiders et al. (2007) analyzed composite samples (3-5 fish) of cutthroat trout, northern pikeminnow, yellow perch, and largemouth bass.

As previously mentioned, mercury concentrations in fish tissues from Lake Ozette are among the highest recorded in the state. Figure 3 is a cumulative frequency graph of all bass collected as part of the mercury trends monitoring program plotted against values from Lake Ozette bass.

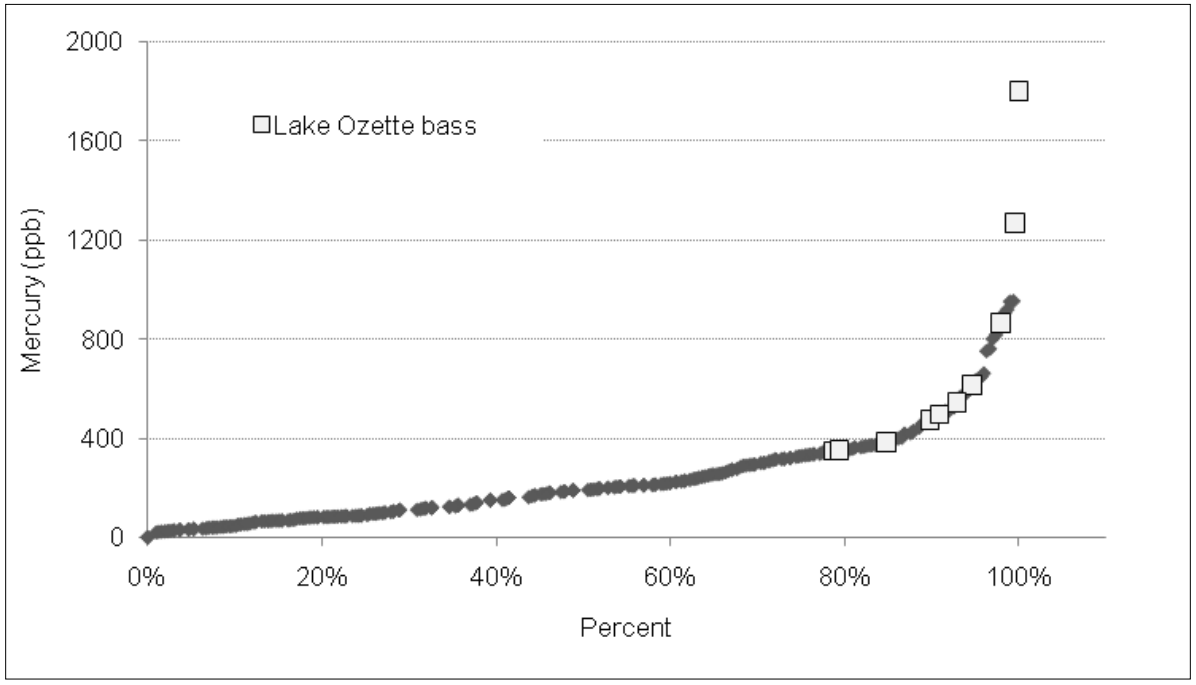

Figure 3. Cumulative frequency of bass concentrations from the mercury trends monitoring project 2005-2009.

Wet deposition

Currently, mercury wet deposition measurements are being made at two Washington State Mercury Deposition Network (MDN) collection sites. The Makah station (WA03) is located 15 km from the north end of Lake Ozette and has been operating since March 2007. The second station is located in Seattle approximately 180 km from Lake Ozette. Results from the stations indicate mercury wet deposition rates are similar at Lake Ozette and Seattle (≈ 6 ug/m^2/yr) despite much greater precipitation at the WA03 (≈ 3 fold) (http://nadp.sws.uiuc.edu/MDN/).

Sediment

Ecology collected a single deep sediment core from Lake Ozette in 2006 to measure mercury trends over time at Lake Ozette. Dates were applied to the sediment core using ^{210}Pb measurements, and mercury was analyzed in 1-cm intervals (Furl, 2007b). Furl et al. (2010) applied the constant rate of supply dating model to the core in order to estimate changing sedimentation rates and calculate mercury fluxes. Results showed mercury flux rates increasing abruptly after 1950, coinciding with increased lake sedimentation. Current mercury flux rates estimated from the upper portion of the sediment core are approximately 200 µg/m^2/yr.

Streams

Speciated mercury was examined in three streams in (Umbrella and Palmquist Creeks) and adjacent to (background site west of the lake) the Lake Ozette watershed to investigate the role of land use on mercury export from Lake Ozette sub-drainages (Furl and Meredith, 2010 in prep). Total mercury concentrations were high and methylmercury values were low in streamwater in comparison to a nationwide study conducted by the USGS.

Project Description

Ecology will conduct a one-time screening study to examine total mercury concentrations in Lake Ozette Sockeye. Resident fish from Lake Ozette have been previously identified as containing elevated mercury levels. Total mercury was chosen as opposed to methylmercury (the bioaccumulative form) since over 95% of mercury present in fish is methylmercury. Fish were collected during the fall/winter 2009 from Umbrella Creek broodstock.

Specific objectives of the study are to:

- Examine mercury concentrations in whole fish and fillet samples.
- Compare Lake Ozette sockeye mercury concentrations to sockeye values shown in literature.
- Compare results of the study to various human consumption criteria.

Organization and Schedule

The following people will contribute to this project. All are employees of the Washington State Department of Ecology.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies W2R - RTT Phone: (360) 407-7398	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Chad Furl Toxics Studies Unit SCS Phone: (360) 407-6060	Author/ Project Manager/ Principal Investigator	Writes the QAPP. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Tanya Roberts Toxics Studies Unit SCS Phone: (360) 407-7392	EIM Data Engineer	Enters data into EIM.
Dale Norton Toxics Studies Unit SCS Phone: (360) 407-6765	Unit Supervisor	Provides internal review of the QAPP. Approves the budget and approves the final QAPP.
Robert F. Cusimano WOS Phone: (360) 407-6596	Section Manager	Reviews the project scope and budget and tracks progress. Reviews the draft QAPP and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

SCS - Statewide Coordination Section.
QAPP - Quality Assurance Project Plan.
EIM - Environmental Information Management database.
WOS - Western Operations Section.

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Sample processing completed	October 2010	Chad Furl
Laboratory analyses completed	December 2010	
Environmental Information System (EIM) database		
EIM user study ID	cfur0008	
Product	Due date	Lead staff
EIM data loaded	January 2011	Tanya Roberts
EIM quality assurance	March 2011	Michael Friese
EIM complete	April 2011	Tanya Roberts
Final report		
Author lead / Support staff	Chad Furl	
Schedule		
Draft due to supervisor	January 2011	
Draft due to client/peer reviewer	February 2011	
Final (all reviews done) due to publications coordinator (Joan)	March 2011	
Final report due on web	April 2011	

Quality Objectives

Manchester Environmental Laboratory (MEL) is expected to meet all quality control requirements of the analytical methods being used for this project. The measurement quality objectives (MQOs) for all analyses being conducted for this project are shown in Table 3. Each quality control test will be run once per sample batch.

Table 3. Measurement quality objectives.

Parameter	Method Blank	Control Sample	Matrix Spike	Sample Duplicate
Mercury	< 17 ug/kg	85 - 115%	75 - 125%	< 20% (RPD)

Sampling Process Design (Experimental Design)

Twenty- eight Lake Ozette sockeye were retained from the Umbrella Creek broodstock by Makah Fisheries for mercury analyses. All 28 fish will be measured for mercury in whole body samples (minus eggs in females). A subset of ten of these fish will be measured for mercury in fillets. The fillet samples will be split equally between male and female. For this subset of ten, whole body concentrations will be calculated using a mass balance equation.

Sample Processing

Fish tissue samples will be prepared following adapted guidelines from the EA Program's *Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples* (Sandvik, 2006). Fish will be removed from the freezer and partially thawed before processing. Fish will be rinsed with tap water followed by a deionized water rinse.

Fillet tissue will be passed through a Kitchen-Aid food grinder three times mixing the tissue after each pass. Whole fish and carcass (fillet already removed) samples will be prepared the same as fillet composites using a Hobart commercial meat grinder. The weight of the whole fish, fillet, and carcass will be recorded in order to perform the mass balance formula (on fish sampled for fillets). Subsamples of the homogenate will be placed into laboratory-provided clean glass jars. Samples will be refrozen, assigned a MEL identification number, and shipped to the laboratory for analysis. Excess homogenate will be labeled and archived at -20° C at Ecology Headquarters.

All utensils will be cleaned before processing to prevent contamination of samples. Utensils include resecting tools, scalpels, bowls, spoons, and blender parts having plastic, wood, bronze, and stainless steel parts. The cleaning procedure will include: hand-wash with soap (Liquinox) and hot tap water, hot tap water rinse, 10% nitric acid rinse, and a final deionized water rinse. Fish processing will be carried out on the dull side of aluminum foil covering a nylon cutting board. New foil and clean processing utensils will be used for each sample. All staff will wear nitrile gloves during tissue processing.

Measurement Procedures

All samples will be measured using EPA Method 245.6 *Determination of Mercury in Tissues by Cold Vapor Atomic Absorption Spectrometry*. Briefly, a tissue sample is digested with sulfuric and nitric acid followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is reduced and measured with cold vapor atomic absorption.

A budget for the project is included below (Table 4).

Table 4. Project budget.

Sample type	Number of samples	Cost per sample	Total Costs
Whole body	28	48	1344
Fillet	10	48	480
			$1,824

Quality Control Procedures

Laboratory

Laboratory quality control procedures will include various analyses such as calibration standards, lab control samples, matrix spikes, and duplicate analyses to evaluate the quality of data that are generated. MQOs are listed under *Quality Objectives*.

Costs include 50% discount for MEL.

Data Management Procedures

All processing notes will be stored with the field lead. Notes and observations will be transferred to Microsoft Excel spreadsheets.

Analytical data from MEL will be provided in an electronic format. MEL staff will verify all data before sending case narratives to the project manager. Reviewed analytical data will be entered into Ecology's Environmental Information Management system (EIM) database. EIM data entry is conducted following formal Ecology guidelines. Data entered into EIM are reviewed by the project manager, data entry staff, and an independent reviewer.

Audits and Reports

MEL participates in routine audits of their laboratory facilities, capabilities, and analytical performance. Results of audits are available upon request.

A technical report will be prepared from data collected for the project. A draft technical report will be ready for supervisor review in January 2011. A final Ecology report is anticipated to be completed by April 2011. See *Organization and Schedule* within this QA Project Plan for a complete project timeline.

Finalized project data will be entered into EIM by April 2011.

Data Verification

MEL will review all analytical data generated for the project. MEL will verify that all laboratory procedures outlined in the QA Project Plan were followed and provide their findings to the project manager in a case narrative. Parameters reviewed by MEL include, but are not limited to: acceptability of holding times, instrument calibration, procedural blanks, spiked samples, precision data, laboratory control samples, and assigned data qualifiers.

The project manager and MEL staff will examine the complete data record and determine whether results are acceptable as specified in the QA Project Plan.

The results of field and laboratory quality control samples will be reviewed in order to determine if MQOs were met. Estimates of accuracy and precision will be based on laboratory quality control. Data will be accepted, accepted with qualifiers, or rejected at the discretion of the project manager.

Data Quality (Usability) Assessment

The quality of the data will be determined based on whether project objectives can be met using the verified data. The entire data package will be assessed by the project manager to determine the usability of the data for screening Lake Ozette sockeye for mercury levels. The final report will provide detail on data quality and usability.

References

Bortleson, G., N. Dion, J. McConnell, and L. Nelson, 1976. Reconnaissance Data on Lakes in Washington: Clallam, Island, Jefferson, San Juan, Skagit, and Whatcom Counties. Water-Supply Bulletin 43, Vol. 1.

Furl, C., 2007a. Measuring Mercury Trends in Freshwater Fish in Washington State: 2006 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-043. www.ecy.wa.gov/biblio/0703043.html.

Furl, C., 2007b. History of Mercury in Selected Washington Lakes Determined from Age-Dated Sediment Cores: 2006 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-019. www.ecy.wa.gov/biblio/0703019.html.

Furl, C., K. Seiders, D. Alkire, and C. Deligeannis, 2007. Measuring Mercury Trends in Freshwater Fish in Washington State: 2005 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-007. www.ecy.wa.gov/biblio/0703007.html.

Furl, C. and C. Meredith, 2008. Measuring Mercury Trends in Freshwater Fish in Washington State: 2007 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 08-03-027. www.ecy.wa.gov/biblio/0803027.html.

Furl, C., C. Meredith, and M. Friese, 2009. Measuring Mercury Trends in Freshwater Fish in Washington State: 2008 Sampling Results. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/biblio/0903045.html.

Furl, C.V., J.A. Colman, and M.H. Bothner, 2010. Mercury sources to Lake Ozette and Lake Dickey: Highly contaminated remote coastal lakes, Washington State, USA. Water Air and Soil Pollution, 208:275-286.

Furl, C. and C. Meredith, 2010. Speciated Mercury in Surface Waters from Streams in the Lake Ozette Catchment. Washington State Department of Ecology, Environmental Assessment Program. Olympia, WA. In preparation.

Gallagher, M., 2000. Proposed Strategy to Continually Reduce Persistent Bioaccumulative Toxics (PBTs) in Washington State. Washington State Department of Ecology, Olympia, WA. Publication No. 00-03-054. www.ecy.wa.gov/biblio/0003054.html.

Haggerty, M.J. et al., 2008. Proposed Recovery Plan for Lake Ozette Sockeye Salmon. NOAA's National Marine Fisheries Service. Northwest Office. www.nwr.noaa.gov/Salmon-Recovery-Planning/Recovery-Domains/Puget-Sound/Ozette-Plan.cfm.

Haggerty, M.J., A.C. Ritchie, J.G. Shellberg, M.J. Crewson, and J. Jalonen, 2009. Lake Ozette Sockeye Limiting Factors Analysis. Prepared for the Makah Indian Tribe and NOAA Fisheries in Cooperation with the Lake Ozette Sockeye Steering Committee, Port Angeles, WA. www.mhaggertyconsulting.com/Lake_Ozette_Sockeye.php.

Meredith C., Furl, C., and Friese, M., 2010. Measuring Mercury Trends in Freshwater Fish in Washington State: 2009 Sampling Results. Washington State Department of Ecology, Environmental Assessment Program, Olympia, WA. In preparation

Peele, C., 2003. Washington State Mercury Chemical Action Plan. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-001. www.ecy.wa.gov/biblio/0303001.html.

Sandvik, P., 2006. Standard Operating Procedure for Resecting Finfish Whole Body, Body Parts, or Tissue Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP No. EAP007. www.ecy.wa.gov/programs/eap/quality.html.

Seiders, K., 2006. Quality Assurance Project Plan: Measuring Mercury Trends in Freshwater Fish in Washington State. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-103. www.ecy.wa.gov/biblio/0603103.html.

Seiders, K., C. Deligeannis, and P. Sandvik, 2007. Washington State Toxics Monitoring Program: Contaminants in Fish Tissue from Freshwater Environments in 2004 and 2005. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/biblio/0703024.html.

Appendix. Glossary, Acronyms, and Abbreviations

Glossary

Broodstock: A group of sexually mature individuals kept for hatchery breeding.

Escapement: The number of fish arriving at a natal stream or river to spawn.

Fry: Young salmon.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
ESA	Endangered Species Act
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBT	Persistent, bioaccumulative, and toxic substance
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedures

Units of Measurement

µg/Kg	micrograms per kilogram (parts per billion)
ww	wet weight