



DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Lake Ozette Watershed PBT Monitoring: Speciated Mercury in Stream Surface Waters

October 2009

Publication No. 09-03-129

Publication Information

This plan is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0903129.html.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, CFUR0006.

Ecology's Project Tracker Code for this study is 10-127.

Waterbody Numbers:

Lake Ozette WA-20-9040; LLID#: Palmquist Creek 1246592481574; Umbrella Creek 1246336481251.

Author and Contact Information

Chad Furl and Callie Meredith
P.O. Box 47600
Environmental Assessment Program
Washington State Department of Ecology
Olympia, WA 98504-7710

For more information contact: Carol Norsen, Communications Consultant
Phone: 360-407-7486

Washington State Department of Ecology - www.ecy.wa.gov/

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

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

To ask about the availability of this document in a format for the visually impaired, call Carol Norsen at 360-407-7486.

Persons with hearing loss can call 711 for Washington Relay Service.

Persons with a speech disability can call 877- 833-6341.

Quality Assurance Project Plan

Lake Ozette Watershed PBT Monitoring: Speciated Mercury in Stream Surface Waters

October 2009

Approved by:

Signature:

Holly Davies, Client, Reducing Toxic Threats, Waste 2 Resources

Date: October 2009

Signature:

Carol Kraege, Section Manager, Reducing Toxic Threats, Waste 2 Resources

Date: October 2009

Signature:

Chad Furl, Author and Project Manager and Principal Investigator, TSU, SCS, EAP

Date: October 2009

Signature:

Callie Meredith, Co-Author and EIM Data Engineer, TSU, SCS, EAP

Date: October 2009

Signature:

Dale Norton, Unit Supervisor, TSU, SCS, EAP

Date: October 2009

Signature:

Will Kendra, Section Manager, SCS, EAP

Date: October 2009

Signature:

Robert F. Cusimano, Section Manager, Western Operations Section, EAP

Date: October 2009

Signature:

Stuart Magoon, Director, Manchester Environmental Laboratory, EAP

Date: October 2009

Signature:

Bill Kammin, Ecology Quality Assurance Officer

Date: October 2009

Signatures are not available on the Internet version.
SWFAP – Solid Waste and Financial Assistance Program.
TSU – Toxics Studies Unit
SCS – Statewide Coordination Section
EAP - Environmental Assessment Program.
EIM - Environmental Information Management system.

Table of Contents

	<u>Page</u>
List of Figures and Tables.....	3
Abstract.....	4
Background.....	5
Introduction.....	5
Lake Ozette.....	6
Project Description.....	11
Organization and Schedule.....	12
Quality Objectives.....	14
Sampling Process Design (Experimental Design).....	15
Sampling Procedures.....	17
Collecting Mercury Samples.....	17
Measuring Additional Parameters.....	17
Measurement Procedures.....	19
Sample Preparation.....	19
Chemical Analysis.....	19
Quality Control Procedures.....	21
Field.....	21
Laboratory.....	21
Budget.....	22
Data Management Procedures.....	23
Audits and Reports.....	23
Data Verification.....	24
Data Quality (Usability) Assessment.....	24
References.....	25
Appendix. Glossary, Acronyms, and Abbreviations.....	28

List of Figures and Tables

Page

Figures

Figure 1. Average mercury concentrations in standard size (356 mm) bass measured in statewide mercury trends monitoring studies, 2005-2008.	5
Figure 2. Study area location and land uses in the Lake Ozette watershed.	6
Figure 3. Ozette River watershed, Lake Ozette watershed, and major Lake Ozette subwatersheds.	7
Figure 4. Mercury concentrations and lengths of freshwater fish analyzed by Ecology’s 2007 Mercury Trends Monitoring and 2004 Exploratory Monitoring Studies.	8
Figure 5. Cumulative frequency of all mercury in freshwater fish tissue data available in Ecology’s EIM database.	9
Figure 6. Study sites, drainage areas, and sampling locations.	15

Tables

Table 1. Mercury wet deposition and precipitation data collected from Washington State MDN stations in 2007 and 2008.	10
Table 2. Organization of project staff and responsibilities.	12
Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.	13
Table 4. Measurement quality objectives for laboratory analyses.	14
Table 5. Lowest concentrations of interest for analytes.	14
Table 6. Physical and land use characteristics of study site subwatersheds.	16
Table 7. Container types, sample sizes, and matrices of samples.	17
Table 8. Sample preservation, storage, and holding times for each analyte.	19
Table 9. Expected range of results, detection limits, and methods.	20
Table 10. Field quality control procedures.	21
Table 11. Laboratory quality control procedures.	21
Table 12. Laboratory cost estimates.	22

Abstract

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

Ecology will measure total mercury and methylmercury in surface water samples in three streams in, and adjacent to, the Lake Ozette watershed: Palmquist Creek, Umbrella Creek, and an unnamed reference creek. Sampling will occur monthly from September 2009 through March 2010.

The goal of the study is to determine concentrations and fluxes of total mercury and methylmercury in streams draining different land uses. Palmquist and Umbrella Creeks flow into Lake Ozette's north end; their drainage areas have undergone extensive logging. The unnamed reference stream is located in an adjacent watershed which has remained relatively pristine.

Measurements of total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), pH, dissolved oxygen, specific conductivity, and temperature will also be collected during each sampling event.

Background

Introduction

Mercury contamination of aquatic food webs is a widespread global phenomenon with mercury levels found in remote aquatic ecosystems rendering fish unsuitable for consumption (Fitzgerald et al., 1998). Anthropogenic mercury emissions as a result of coal combustion and waste incineration have severely altered the natural mercury cycle. After mercury is emitted to the atmosphere, it can be transported globally before being deposited, depending on its chemical speciation (Schroeder and Munthe, 1998). Once deposited, mercury can undergo transformation to methylmercury which is the bioaccumulative form found in fish.

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

As a result of the CAP, long-term fish tissue monitoring was initiated in 2005 (Seiders, 2006). To date, four years (2005 - 2008) of statewide tissue monitoring (24 sites) has been completed (Furl et al., 2007; Furl, 2007; Furl and Meredith, 2008; Furl et al., 2009b). The highest concentrations of mercury in fish tissues have been found at Lake Ozette located in the northwest corner of Washington's Olympic Peninsula (Figure 1) in the Olympic National Park.

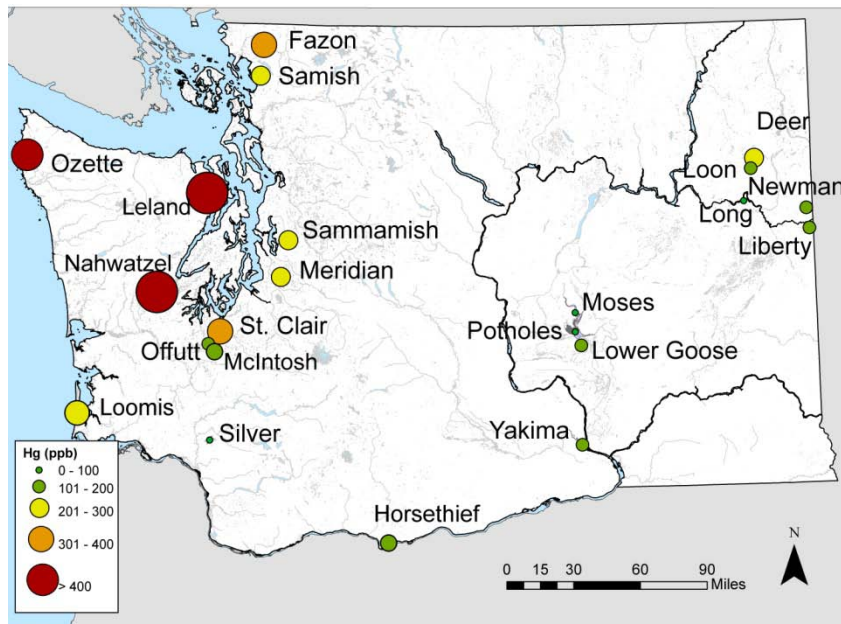


Figure 1. Average mercury concentrations in standard size (356 mm) bass measured in statewide mercury trends monitoring studies, 2005-2008.

Causes of the elevated mercury concentrations in fish tissues at Lake Ozette are currently unknown. Based on an age-dated sediment core and historical land-use analysis, Furl et al. (2009a) hypothesized increased sedimentation due to logging in the lake's watershed has greatly increased the net flux of total mercury to the lake. It is currently unknown whether land-use practices have had the same effect on methylmercury export from upland areas to the lake.

To further investigate the role of forest practices in mediating total mercury and methylmercury delivery to Lake Ozette, speciated mercury in whole water samples will be measured in two of the tributaries to Lake Ozette and in one stream with an undisturbed watershed in an adjacent drainage.

Lake Ozette

Background

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 km² and an average depth of 40 m (Bortleson et al., 1976) (Figure 2). The National Park Service owns 15% of the 118 km² watershed while over 80% of the watershed is zoned as commercial forest land.

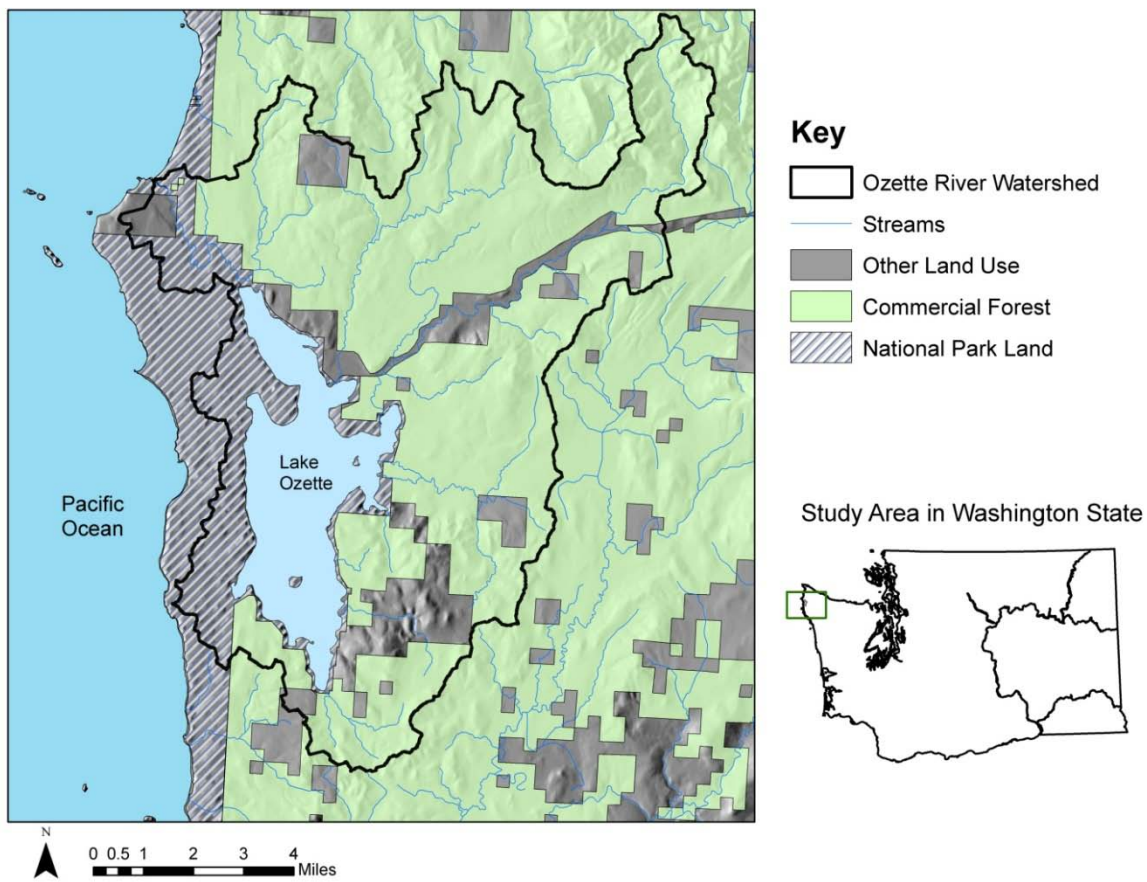


Figure 2. Study area location and land uses in the Lake Ozette watershed.

Approximately 60% of the Lake Ozette watershed drains to the lake by three large creeks: Big River, Crooked Creek, and Umbrella Creek (Figure 3). In addition to the three main inflows, numerous unnamed perennial streams contribute surface water to Lake Ozette. The lake is drained into the Pacific Ocean by the Ozette River at the lake's north end. The average lake level is 10 m above sea level; watershed elevations range up to 580 m. Watershed geology consists of glacio-fluvial deposits situated between resistant marine deposited sedimentary rocks. Human population of the Lake Ozette watershed is estimated to be less than 100 (Haggerty et al., 2007).



Figure 3. Ozette River watershed, Lake Ozette watershed, and major Lake Ozette subwatersheds.

Forests within the watersheds can be classified as a coastal temperate rainforest. The watersheds are dominated by coniferous species, and commercial logging is the primary land-use activity. The nearest urban population centers are Seattle, Washington and Vancouver, British Columbia (Canada). Seattle is located approximately 180 km to the east of Lake Ozette.

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. Fog drip is also believed to be a large contributor to ground surface precipitation. Air flows from the west occur greater than 50% of the time at the nearest weather station, 20 km south of Lake Ozette (Haggerty et al. 2007).

Mercury Monitoring

Fish Tissue

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 10 individual largemouth bass and composite samples (3-5 fish) of northern pikeminnow and yellow perch.
- *WSTMP*: 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 are among the highest recorded in the state. Figure 4 is a scatterplot of mercury concentration versus fish length for the two studies. Figure 5 is a cumulative frequency graph of all mercury in freshwater fish tissue data in Ecology's Environmental Information Management (EIM) system ($n = 1,934$).

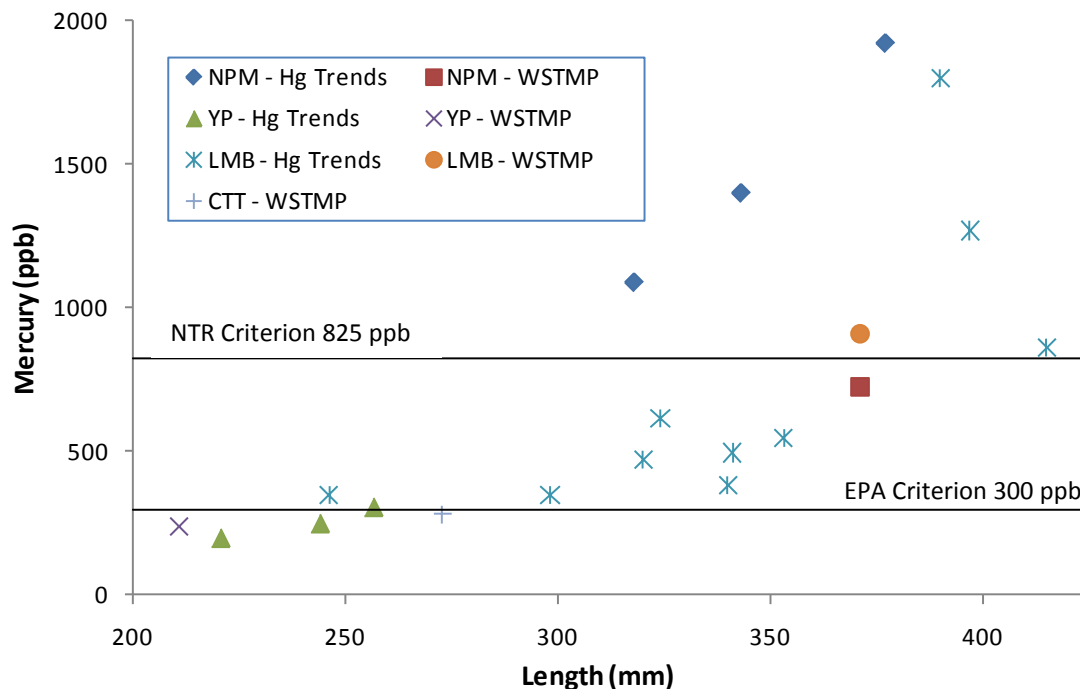


Figure 4. Mercury concentrations (ppb) and lengths (mm) of freshwater fish analyzed by Ecology's 2007 Mercury Trends Monitoring (Hg Trends) and 2004 Exploratory Monitoring (WSTMP) Studies.

NPM = Northern Pikeminnow; YP = Yellow Perch; LMB = Largemouth Bass; CTT = Cutthroat Trout.

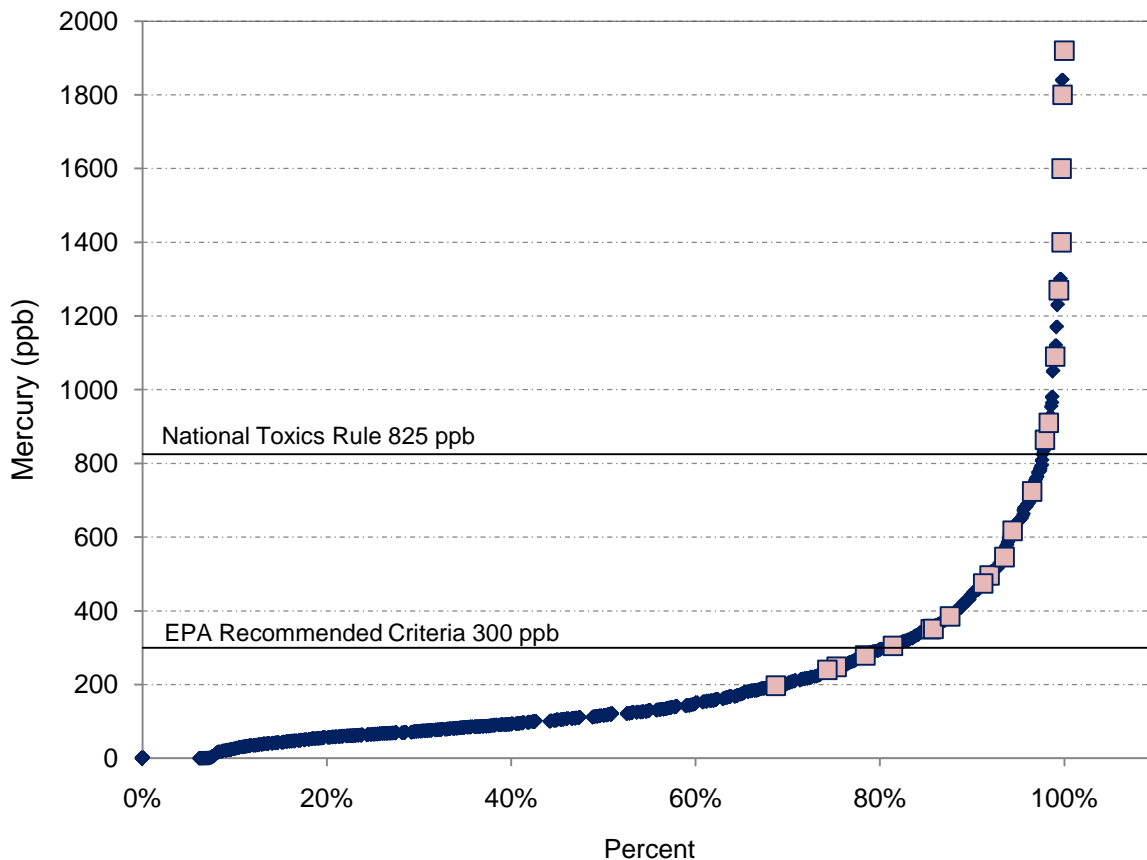


Figure 5. Cumulative frequency of all mercury in freshwater fish tissue data available in Ecology's EIM database (n = 1,934). *Squares represent data points from Lake Ozette.*

Atmospheric

Ecology is collecting ongoing mercury wet deposition measurements at two Washington State Mercury Deposition Network (MDN) collection sites. The Makah station 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 and Lake Dickey. Wet deposition measurements have been conducted at the Seattle station since 1996.

Mercury wet deposition and precipitation values for the two MDN stations are presented in Table 1 (March 2007 – December 2008). The Makah station measured slightly higher mercury deposition than the Seattle station over the first 12 months of its operation. Over the same time period, precipitation at the Makah station was nearly three times greater than the Seattle station. Wet deposition values for the 10 month period starting in March 2008 were similar at both stations. Precipitation ratios between sites were similar to the first year of monitoring (2007) although the sites have received much less precipitation.

Results from the first 22 months of mercury wet deposition monitoring found similar deposition rates at Lake Ozette and Seattle. Deposition rates are closely tied to rainfall. Over the sampling period, the Seattle site received approximately 40% of the rainfall collected at the Ozette station.

Table 1. Mercury wet deposition and precipitation data collected from Washington State MDN stations in 2007 and 2008.

MDN Station	March 2007 – February 2008 (12 months)		March 2008 – December 2008 (10 months)	
	Wet Deposition ($\mu\text{g}/\text{m}^2$)	Precipitation (cm)	Wet Deposition ($\mu\text{g}/\text{m}^2$)	Precipitation (cm)
WA03 – Makah	7.59	223	4.31	101
WA13 - Seattle	6.55	77	4.88	38

Atmospheric monitoring of mercury was conducted at Cheeka Peak 20 km from the north end of Lake Ozette from May 2001 – May 2002 (<http://research.uwb.edu/jaffegroup/modules/archive/>). Concentrations of elemental mercury were found to be generally consistent with the Northern Hemisphere background ($1.7 \text{ ng}/\text{m}^3$) (Weiss-Penzias et al., 2003).

Atmospheric concentrations in the Seattle metro area averaged $2.5 \text{ ng}/\text{m}^3$ over a two-year period from 1994-1995 (Bloom et al., 1995).

Sediment Cores

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, 2007). Furl et al. (2009a) 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 $200 \text{ ug}/\text{m}^2/\text{yr}$.

During this period of rapid increases in sedimentation and mercury fluxes (1950 – present), the percent of primary forest in the watershed was reduced from nearly 100% to approximately 20%.

Environmental Conditions

Several studies have described physical, chemical, and biological conditions present in Lake Ozette, its drainage area, and stream surface waters entering the lake (Bortleson and Dion, 1979; Meyer and Brenkman, 2001; Haggerty et al., 2009). The majority of these studies have been aimed at identifying the causes of reduced Pacific Salmon returns.

Meyer and Brenkman (2001) collected water quality data in Lake Ozette and in six tributaries to the lake from September 1993 to October 1994. Water quality conditions in the lake generally appeared to be favorable for salmonids. Elevated turbidity levels were observed in Big River and Umbrella Creek during storm events. The authors attributed degraded water quality in tributaries to the lake's eastern shoreline to extensive timber harvest in the watershed.

Haggerty et al. (2009) summarized data pertaining to the factors limiting the survival and productivity of Lake Ozette sockeye. The document provides extensive descriptions of lake and tributary water quality.

Project Description

Ecology's Environmental Assessment Program will conduct a one-time study to measure total mercury and methylmercury in whole water samples from three streams in and adjacent to the Lake Ozette watershed. Sampling will be conducted at Palmquist and Umbrella Creeks which enter Lake Ozette at its northern end, draining extensively logged landscapes. An unnamed creek flowing to the Pacific Ocean through a pristine landscape adjacent to Lake Ozette will also be sampled. Total mercury and methylmercury are being monitored in response to the elevated fish tissue concentrations found in Lake Ozette.

Goals of the study are to assess mercury loading from different land-uses.

Specific objectives of the study are to:

- Determine if total mercury and methylmercury loads are different in streams from logged and unlogged drainages.
- Evaluate whether significant methylmercury production is occurring in upland areas of the watershed.
- Assess correlations between total mercury/methylmercury with TOC, DOC, TSS, and other conventional water quality parameters.

Frontier Geosciences (FGS) will analyze total mercury and methylmercury using methods adapted from EPA 1631E and EPA 1630, respectively.

Ecology's Manchester Environmental Laboratory (MEL) will perform TOC, DOC, and TSS analysis.

Organization and Schedule

The following people are involved in this project (Table 2). All are employees of the Washington State Department of Ecology.

Table 2. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Holly Davies SWFAP 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	Project Manager and Principal Investigator	Writes the QAPP. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Callie Meredith Toxics Studies Unit, SCS Phone: (360) 407-6965	Field Lead and EIM Data Engineer	Oversees field sampling and transportation of samples to laboratory, records field information, and enters data into EIM.
Michael Friese Toxics Studies unit, SCS Phone: (360) 407-6737	Field Assistant	Helps collect samples and records field information.
Tanya Roberts Toxics Studies Unit, SCS Phone: (360) 407-7392	Field Assistant	Helps collect samples and records field information.
Dale Norton Toxics Studies Unit, SCS Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6698	Section Manager for the Study Area	Reviews the project scope and budget, 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.

SWFAP – Solid Waste and Financial Assistance Program.

EAP – Environmental Assessment Program.

SCS – Statewide Coordination Section.

QAPP – Quality Assurance Project Plan.

EIM – Environmental Information Management system.

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	March 2010	Callie Meredith
Laboratory analyses completed	April 2010	
Environmental Information System (EIM) database		
EIM user study ID	CFUR0006	
Product	Due date	Lead staff
EIM data loaded	September 2010	Callie Meredith
EIM QA	October 2010	Tanya Roberts
EIM complete	November 2010	Chad Furl
Final report		
Author lead / Support staff	Chad Furl / Callie Meredith	
Schedule		
Draft due to supervisor	July 2010	
Draft due to client/peer reviewer	August 2010	
Draft due to external reviewer(s)	September 2010	
Final (all reviews done) due to publications coordinator	October 2010	
Final report due on web	November 2010	

Quality Objectives

MEL and FGS are 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 4. MQOs for this project were established to minimize uncertainties in contaminant concentrations.

Table 4. Measurement quality objectives for laboratory analyses.

Analysis	Method Blank	Laboratory Control Sample	Duplicates	Matrix Spikes
Total Mercury	≤ 0.5 ng/L	75-125%; RPD ≤ 25	RPD ≤ 25	75-125%; RPD ≤ 25
Methylmercury	≤ 0.05 ng/L	70-130%; RPD ≤ 25	RPD ≤ 25	70-130%; RPD ≤ 25
TOC	< 1 mg/L	80-120%	80-120%	75-125%
DOC	< 1 mg/L	80-120%	80-120%	75-125%
TSS	-	80-120%	80-120%	-

RPD – Relative percent difference.

The lowest concentrations of interest for each parameter are listed in Table 5. Based on a review of studies analyzing speciated mercury in similar waterbodies, analyzing down to these levels should be sufficient to accurately quantify the majority of analytes in most samples.

Table 5. Lowest concentrations of interest for analytes.

Analysis	Lowest Concentration of Interest	Laboratory
Total Mercury	.50 ng/L	FGS
Methylmercury	.05 ng/L	FGS
TOC	1 mg/L	MEL
DOC	1 mg/L	MEL
TSS	1 mg/L	MEL

Sampling Process Design (Experimental Design)

Locations for the three sampling sites along with their delineated sub-watersheds (drainages) are displayed in Figure 6.

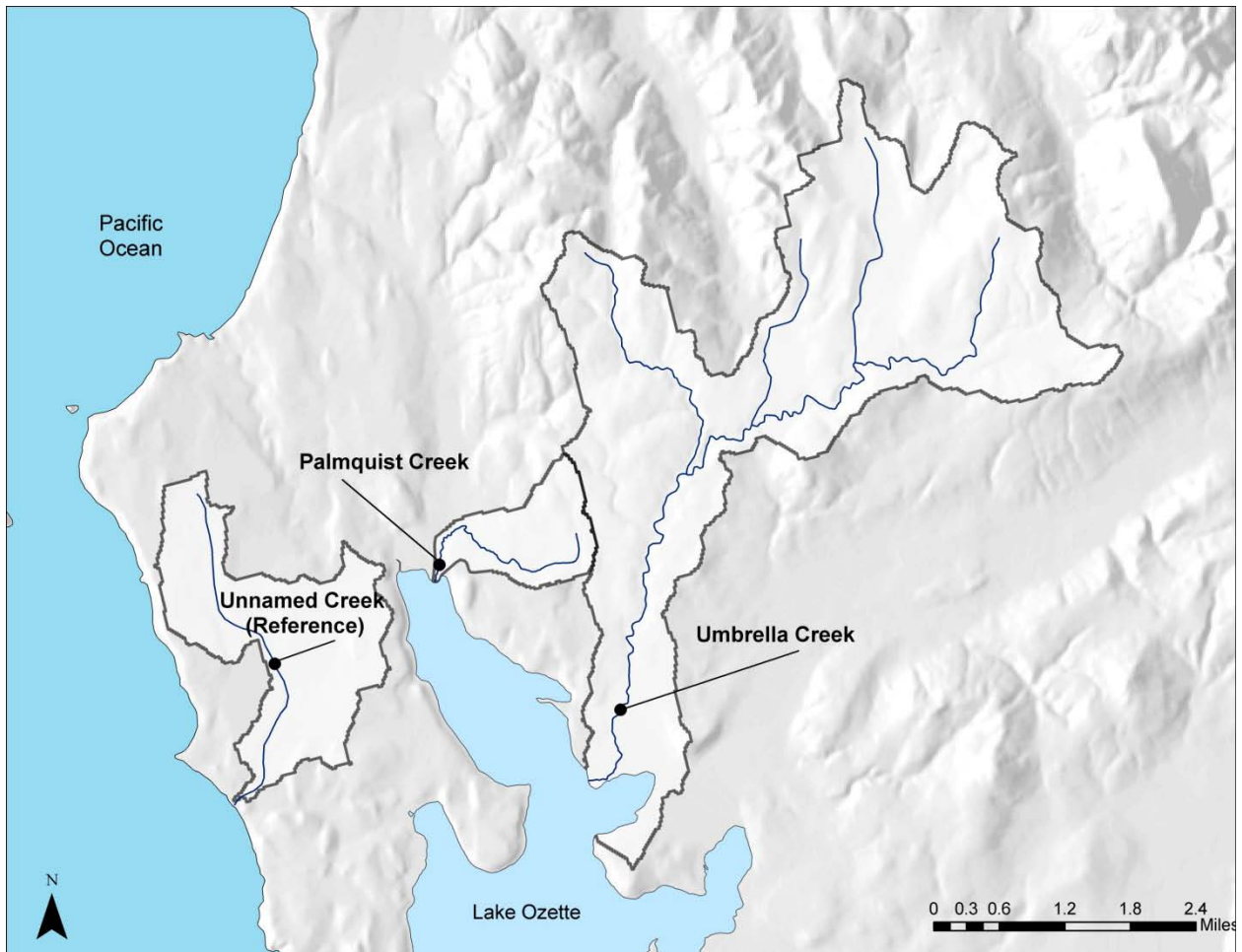


Figure 6. Study sites, drainage areas, and sampling locations (black dots).

Ecology will retrieve whole water samples approximately monthly from September 2009 – March 2010 to examine patterns under a wide range of streamflows. In addition to monthly sampling, two high-flow collections are anticipated. Water samples will be analyzed for total mercury, methylmercury, TOC, DOC, and TSS. In addition to the lab analyses, pH, dissolved oxygen, specific conductance, and flow will be measured in the field during sampling events.

The three streams chosen for sampling provide a range of sub-watershed sizes and land-use activity.

- Umbrella Creek is the third largest tributary to Lake Ozette draining more than 10 mi², and was chosen to characterize mercury loading from one of Ozette's major sub-drainages.

- Palmquist Creek and the reference creek are considerable smaller (draining 1.00 and 1.26 mi², respectively) and were chosen due to their similarity in sub-watershed size and wetland density.

The Umbrella Creek and Palmquist Creek sub-watersheds have undergone extensive historical logging with > 90% of their area designated as commercial forest.

Table 6 displays physical and land-use data for the study sites. Coordinates of sampling locations will be recorded in the field.

Table 6. Physical and land use characteristics of study site subwatersheds.

Study area	Drainage area at sampling point (sq. mi.)	Drainage area of total sub-watershed (sq. mi.)	Minimum basin elevation (ft)	Maximum basin elevation (ft)	Area with slope > 30% (% of watershed)	Mean annual precipitation (in)	Wetland area (% of watershed)	Land use (% of watershed)		
								Commercial forest	National park	Residential or retail
Umbrella Creek	10.61	11.71	61	1170	6.3	93	3.1	93	0	0
Palmquist Creek	1.00	1.01	54*	738	0.15*	83*	3.1	95	6.5	3.2
Unnamed Creek (reference)	1.26	2.97	83	251	0	105	2.7	0	100	0

* Estimated

Monthly values for mercury concentrations and fluxes (concentration * flow) will be compared between all three sites to examine differences resulting from drainage size and land-use. Comparisons between Palmquist Creek and the reference creek will provide the most relevant data concerning land use due to their similar size. Additionally, total mercury concentrations will be compared to acute and chronic water quality criteria (2.1 and 0.12 ug/L, respectively) (WAC, 2006).

Sampling Procedures

Collecting Mercury Samples

Ecology will collect water samples using modifications of EPA Method 1669 and Ecology's standard operating procedure (SOP) for *Collection and Field Processing of Metals Samples* (Ward, 2007).

Water samples will be collected by wading into the approximate thalweg of the stream and dipping a capped bottle beneath the surface of the water. While the bottle is submerged, the cap will be unscrewed allowing the bottle to be filled. The bottle will then be turned upside down (mouth of the bottle facing the bottom of the stream) and lifted to just above the water's surface to drain the bottle. The sample jar will be rinsed in this manner three times before taking the sample. To take the sample, the bottle will be submerged to half the depth of the stream allowing it to fill without disturbing the substrate. The filled bottle will be removed from the stream, and a small amount of water will be poured from the bottle to allow room for the preservative before being capped.

If streams become unwadeable during high flows, samples will be collected from the bank or bridge by attaching the bottle to a pole using a stainless steel clamp. Bottle rinsing will be conducted from the bank in the same manner described above prior to attaching the sample bottle to the pole. Care will be taken to ensure sample water does not contact the pole device prior to entering the bottle.

Field personnel will wear shoulder-length nitrile gloves beneath new wrist-length powder free vinyl gloves for each sample collection in order to avoid contamination.

Measuring Additional Parameters

DOC, TOC, and TSS samples will be collected from the same locations as mercury samples immediately after mercury sampling. Water samples will be collected as described above by manually dipping the bottle or using the pole sampling device. Table 7 includes information on sample containers.

Table 7. Container types, sample sizes, and matrices of samples.

Analyte	Jar Type	Sample Size	Matrix
Total Mercury	500-mL I-Chem class 200 glass	500 mL	whole water
Methylmercury	250-mL I-Chem class 200 glass	250 mL	whole water
DOC	60-mL poly	50 mL	filtered water; 0.45 um pore size
TOC	60-mL poly	51 mL	whole water
TSS	1000-mL poly	1000 mL	whole water

Conductivity and pH will be measured at each site following a modification of Ecology's Environmental Assessment (EA) Program's *Standard Operating Procedures for Hydrolab® DataSonde® and MiniSonde® Multiprobes* (Swanson, 2007).

Flow for Palmquist Creek and the reference stream will be measured and calculated according to the EA Program's *Standard Operating Procedure for Estimating Streamflow* (Sullivan, 2007). Flow data for Umbrella Creek will be estimated using an instream staff gage. Makah Fisheries management has developed a rating curve for the gage.

Air and water temperature will be continuously measured by data logging tidbits.

Measurement Procedures

Sample Preparation

Samples will be acidified in the field and immediately shipped to the laboratory after collection. Sample holding times and preservation methods are listed in Table 8.

Table 8. Sample preservation, storage, and holding times for each analyte.

Analyte	Preservation Technique	Storage	Holding Time
Total Mercury	HNO ₃ to < 2 pH	≤ 6°C	28 days
Methylmercury	HNO ₃ to < 2 pH	≤ 6°C	28 days
TOC	1:1 HCL to < 2 pH	≤ 6°C	28 days
DOC	1:1 HCL to < 2 pH	≤ 6°C	28 days
TSS	-	≤ 6°C	7 days

Chemical Analysis

Mercury Analysis

Total mercury is analyzed by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). The method is a modified version of EPA 1631E.

Methylmercury (CH₃Hg) is analyzed by distillation, aqueous ethylation, purge and trap, desorption, and CVAFS. The method is a modified version of EPA 1630.

Both methods FG069 and FG070 for analysis of total mercury and methylmercury, respectively, are available from the laboratory.

Other Parameters

TOC and DOC are calculated from the difference between total carbon and inorganic carbon. The two carbon components are detected by a non-dispersive infrared gas analyzer. Solids are determined by the residue left after evaporation and subsequent oven drying. MEL methods are available upon request.

Table 9 presents information on the analyses of samples for the project.

Table 9. Expected range of results, detection limits, and methods.

Analysis	Number of Samples	Expected Range of Results	Detection Limits	Reporting Limits	Analytical Method
Total Mercury	36	.50 ng/L - 70 ng/L	.0770 ng/L	.50 ng/L	FG069 - CVAFS
Methylmercury	36	.05 ng/L - 3.0	.0192 ng/L	.05 ng/L	FG070 - CVAFS
TOC	36	1 - 10 mg/L	NA	1 mg/L	SM5310B
DOC	36	1 - 5 mg/L	NA	1 mg/L	SM5310B
TSS	33	1 - 1000 mg/L	NA	1 mg/L	SM2540D

FG – Frontier Geosciences.

CVAFS – cold-vapor atomic fluorescence spectrometry.

SM – standard method.

Quality Control Procedures

Field

Field variability and contamination will be assessed using replicate sampling and blanks, respectively (Table 10). Replicates will be taken in succession with their source sample for approximately 10% of the sampling events using the same sampling techniques.

Table 10. Field quality control procedures.

Analyte	Replicates	Field Blanks
Total Mercury	3	3
Methylmercury	3	3
TOC	3	3
DOC	3	3
TSS	3	0

Field blanks will be collected by transferring lab-certified, mercury-free water from a full bottle to an empty bottle in the field. The quality control procedure will test for contamination from field staff, precipitation, and the atmosphere.

Replicates and field blanks will be spaced approximately equally over the 7-month sampling period, September 2009 – March 2010.

Laboratory

Table 11 lists the lab quality assurance (QA) procedures and the frequency they are performed.

Table 11. Laboratory quality control procedures.

Analysis	Method Blank	LCS	Analytical Duplicate	Matrix Spike	Lab
Total Mercury	-	1/ batch*	1/ batch	1/ batch*	FGS
Methylmercury	-	1/ batch*	1/ batch	1/ batch*	FGS
TOC	1/ batch	1/ batch	1/ batch	1/ batch	MEL
DOC	1/ batch	1/ batch	1/ batch	1/ batch	MEL
TSS	1/ batch	1/ batch	1/ batch	-	MEL

* Samples run as duplicates.

For total mercury laboratory control samples (LCSs), a 200x dilution of standard reference material with a certified value of 16.01 mg/L is analyzed. For methylmercury, LCSs consist of a blank spike at 2.0 ng/L. Control samples along with matrix spikes are analyzed as duplicates.

MEL staff will review data generated by FGS for accuracy, completeness, and adherence to quality objective guidelines set forth in this QA Project Plan.

Budget

Costs for the project are presented in Table 12.

Table 12. Laboratory cost estimates.

Item	No. of samples	No. of QA samples*	Cost per sample	Lab	Costs
Total Mercury	27	6	70	FGS	2,310
Methylmercury	27	6	140	"	4,620
Blank water		3	35	"	105
High QA data package~	-	-	-	"	1,055
MEL Surcharge¥	-	-	-	MEL	2,023
TOC	27	6	33	"	1,089
DOC	27	6	35	"	1,155
TSS	27	3^	11	"	330
Equipment	-	-	-	-	780
Total					\$13,467

* replicates and blanks.

~ 15% surcharge of FGS sample costs.

¥ 25% surcharge of FGS total.

^ replicates only.

Costs for TOC, DOC, and TSS include a 50% discount for Manchester Laboratory.

Data Management Procedures

Field data will be recorded on waterproof paper and checked for legibility and completeness. All field data will be stored with the field lead. Field notes and observations will be transferred to Microsoft Excel (Microsoft, 2007) spreadsheets.

Analytical data from MEL and FGS 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 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 and FGS laboratories participate 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 July 2010. A final Ecology report is anticipated to be completed by November 2010. See *Organization and Schedule* within this QA Project Plan for a complete project timeline.

Finalized project data will be entered into EIM by November 2010.

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 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 the analysis of total mercury and methylmercury in the streams sampled. The final report will provide detail on data quality and usability.

References

- APHA, AWWA, and WEF, 1998. Standard Methods for the Examination of Water and Wastewater 20th Edition. American Public Health Association, Washington, D.C.
- Bloom, N., Prestbo, E., Tokos, J., Kuhn, E., and von der Geest, E., 1995. Distribution of Mercury Species in the Pacific Northwest Atmosphere. Presented at the Mercury Deposition and Cycling Symposium, 210th ACS Meeting, 1995.
- Bortleson, G., Dion, N., McConnell, J., and Nelson, L., 1976. Reconnaissance Data on Lakes in Washington: Clallam, Island, Jefferson, San Juan, Skagit, and Whatcom Counties. Water-Supply Bulletin 43, Vol. 1.
- Bortleson, G. and N. Dion, 1979. Preferred and observed conditions for sockeye production in Ozette Lake and its tributaries, Clallam County, Washington.
- Ecology, 1993. Field Sampling and Measurement Protocols for the Watershed Assessments Section. Washington State Department of Ecology, Olympia, WA. Publication No. 93-e04. www.ecy.wa.gov/biblio/93e04.html.
- Fitzgerald, W., Engstrom, D., Mason, R., and Nater, E., 1998. The Case for Atmospheric Mercury Contamination in Remote Areas. Environmental Science and Technology, 32(1), 1-7.
- Furl, C., 2007. 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., Seiders, K., Alkire, D., and Deligeannis, C., 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 Meredith, C., 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., Colman, J., and Bothner, M., 2009a. Mercury Sources to Lake Ozette and Lake Dickey: Highly Contaminated Remote Coastal Lakes Washington USA. Water, Air, and Soil Pollution. 10.1007/s11270-009-0165-y.
- Furl, C., Meredith, C., and Friese, M., 2009b. Measuring Mercury Trends in Freshwater Fish in Washington State: 2008 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-045. www.ecy.wa.gov/biblio/0903045.html.
- Gallagher, M., 2000. Proposed Strategy to Continually Reduce Persistent Bioaccumulative Toxins (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., Ritchie, A.C., Shellberg, J.G., Crewson, M.J., and Jalonen, J., 2009. Lake Ozette Sockeye Limiting Factors Analysis: Draft 8_1. Prepared for the Makah Indian Tribe and NOAA Fisheries in Cooperation with the Lake Ozette Sockeye Steering Committee, Port Angeles, WA.

Janisch, J., 2006. Standard Operating Procedure for Determining Global Position System Coordinates, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP013. www.ecy.wa.gov/programs/eap/quality.html.

Joy, J., 2006. Standard Operating Procedure for Grab sampling – Fresh water, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. www.ecy.wa.gov/programs/eap/quality.html.

Lombard, S. and Kirchmer C., 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030. www.ecy.wa.gov/biblio/0403030.html.

MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Meyer, J. and Brenkman S., 2001. Status Report on the Water Quality of Lake Ozette and Potential Human-related Impacts on Salmonids. Unpublished report to Olympic National Park.

Microsoft, 2007. Microsoft Office XP Professional, Version 10.0. Microsoft Corporation.

Ott, W., 1995. Environmental Statistics and Data Analysis. Lewis Publishers, New York, NY.

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.

Schroeder, W. and Munthe, J., 1998. Atmospheric Mercury – An Overview. Atmospheric Environment, 32(5), 809-822.

Seiders, K., Deligeannis, C., and Sandvik, P., 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.

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.

Sullivan, L., 2007. Standard Operating Procedure for Estimating Streamflow, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP024. www.ecy.wa.gov/programs/eap/quality.html.

Swanson, T., 2007. Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html.

WAC 173-201A, 2006. Water Quality Standards for Surface Waters in the State of Washington Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/laws-rules/ecywac.html.

Ward, W.J., 2007. Collection and Field Processing of Metals Samples, Version 1.3. Washington State Department of Ecology, Olympia, WA. SOP Number EAP029. www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_029MetalsSampling.pdf.

Weiss-Penzias, P., Jaffe, D., McClintick A., Prestbo, E., and Landis, M., 2003. Gaseous Elemental Mercury in the Marine Boundary Layer: Evidence for Rapid Removal in Anthropogenic Pollution. *Environmental Science and Technology*, 37, 3755-3763.

Appendix. Glossary, Acronyms, and Abbreviations

Analyte: Water quality constituent being measured (parameter).

Anthropogenic: Human-caused.

Bioaccumulative pollutants: Pollutants that build up in the food chain.

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

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Flux: Amount that flows through a unit area through a unit time.

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the n th root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Hyporheic: The area beneath and adjacent to a stream where surface water and groundwater intermix.

Methylmercury: A form of organic mercury that is easily bio-accumulated in mercury.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Salmonid: Any fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

Scatterplots: A plot of pairs of values of a set of bivariate (two-variable) data.

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

Speciated mercury: Refers to multiple chemical forms of mercury (e.g., Hg^{+0} , Hg^{+1} , Hg^{+2} , organic mercury).

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

Thalweg: The deepest and fastest moving portion of a stream.

Total mercury: Includes all speciated forms of mercury.

Total suspended solids (TSS): Portion of solids retained by a filter.

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

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

Whole water sample: An unfiltered water sample.

Acronyms and Abbreviations

Ecology	Washington State Department of Ecology
DOC	Dissolved organic carbon
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FGS	Frontier Geosciences
Hg	Mercury
LLID	Latitude Longitude ID
MDN	Mercury Deposition Network
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NTR	National Toxics Rule
PBT	Persistent, bioaccumulative, and toxic chemical
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedures
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WSTMP	Washington State Toxics Monitoring Program

Units of Measurement

cm	cubic meters
km	kilometer, a unit of length equal to 1,000 meters.
m	meter
mm	millimeter
ng/L	nanograms per liter (parts per trillion)
ppb	parts per billion
ug/Kg	micrograms per kilogram (parts per billion)
µg/m	micrograms per meter