Land-Use Effects on Export and Retention of Mercury in the Lake Ozette Watershed

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For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

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
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Cover photo: Ozette River, November 2009.

Land-Use Effects on Export and Retention of Mercury in the Lake Ozette Watershed

by

Chad Furl and Callie Meredith

Toxics Studies Unit
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

Waterbody Number: Lake Ozette – WA-20-9040

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Abstract

Eight sampling events were conducted at three streams in and adjacent to the Lake Ozette watershed from September 2009 through March 2010 to assess the effects of land use on mercury export. The sites included two logged watersheds, Palmquist and Umbrella Creeks, which flow into the north end of Lake Ozette, and an unlogged reference site, Tea Creek, which is 1.5 miles west of Lake Ozette. Water samples were analyzed for total mercury, methylmercury, total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS).

Total mercury ranged from 2.15 – 12.80 ng/L among the three creeks. DOC, TSS, and stream discharge had the strongest correlations with total mercury. Total concentrations followed a pattern of Tea>Palmquist>Umbrella. Median concentrations in all three creeks were elevated (> 80^{th} percentile) when compared to a U.S. Geological Survey (USGS) nationwide survey of 236 rivers and streams.

Methylmercury concentrations ranged from < 0.05 – 2.36 ng/L and did not follow a consistent pattern among sites. Unlike total mercury, median methylmercury concentrations were lower than those typically encountered in the USGS nationwide survey.

Differences in water quality characteristics (DOC, TSS, pH) encountered between the three creeks hampered cross-comparisons of the mercury data. However, median total mercury and methylmercury fluxes (mg/hr/km^2) were highest in Umbrella Creek. Total mercury and methylmercury fluxes differed little between the logged watershed of Palmquist Creek and the pristine watershed of Tea Creek.

Yearly total mercury flux estimates at Umbrella Creek indicated an elevated watershed yield (15.6 µg/m^2/yr). Mercury retention in the watershed was very low (≈ 35%). Particulates appear to be an important mode of transport at Umbrella Creek allowing for large episodic export events.

Acknowledgements

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Introduction

Background

Methylmercury is highly bioaccumulative in aquatic food webs and can be concentrated a million fold or more in fish species at the top of the food chain (Peele, 2003). Over the past 5 years (2005-2009), the Washington State Department of Ecology (Ecology) has conducted long-term monitoring of mercury in fish tissues (30 sites) (Furl et al., 2007; Furl, 2007a; Furl and Meredith 2008; Furl et al., 2009a; Meredith et al., 2010) (Appendix A).

The highest mercury concentrations in individual bass measured as part of the mercury monitoring program were found at Lake Ozette (Figure 1). Elevated fish tissue concentrations similar to those encountered at Lake Ozette were also recorded by USGS at Lake Dickey approximately 5 miles east of Lake Ozette (Furl et al., 2010).

Causes of the elevated mercury concentrations in fish tissues at these two remote coastal lakes are unknown. Based on age-dated sediment cores and historical land-use analysis of the Lake Ozette watershed, Furl et al. (2010) hypothesized that increased sedimentation due to logging has greatly increased the net flux of total mercury to these lakes. Recent total mercury fluxes in sediment cores (≈ 200 µg/m^2/yr) from these lakes are among the highest in Washington State (Furl, 2007b; Furl, 2008; Furl et al., 2009b; Furl and Roberts, 2010).

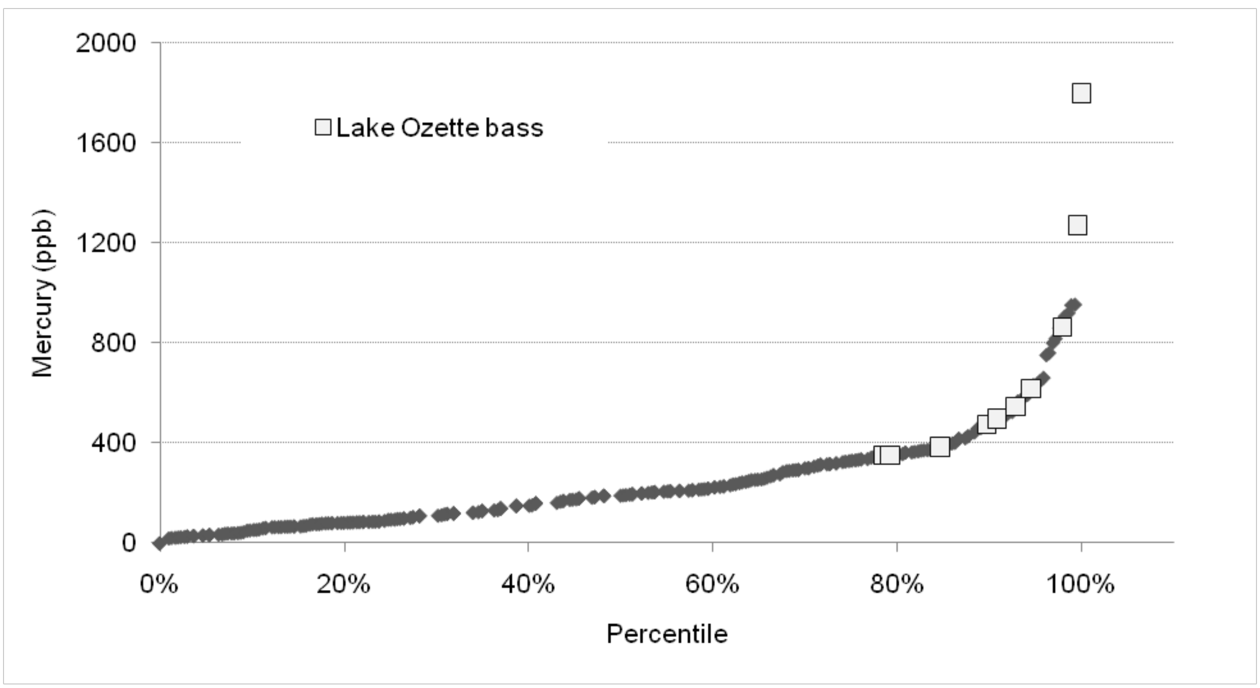

Figure 1. Lake Ozette Bass Concentrations Plotted with Individual Bass Collected Statewide as Part of the Mercury Trends Monitoring Program, 2005 - 2009.

Goals and Objectives

To further investigate the role of forest practices in mediating total mercury and methylmercury yields to Lake Ozette, Ecology's Environmental Assessment Program conducted a one-time study to measure speciated mercury in whole water samples from three streams in and adjacent to the Lake Ozette watershed.

During 2009 and 2010, sampling was conducted at Palmquist and Umbrella Creeks, which enter Lake Ozette at its northern end. Both of these creeks drain logged areas. An unnamed creek (hereafter referred to as Tea Creek) flowing to the Pacific Ocean through a pristine landscape adjacent to Lake Ozette was chosen as a reference site.

Goals of the study were to assess speciated (total and methyl) mercury concentrations and loads from different land uses.

Specific objectives of the study were to:

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

Methods

Study Design

Locations for the three sampling sites along with their delineated watersheds are displayed in Figure 2.

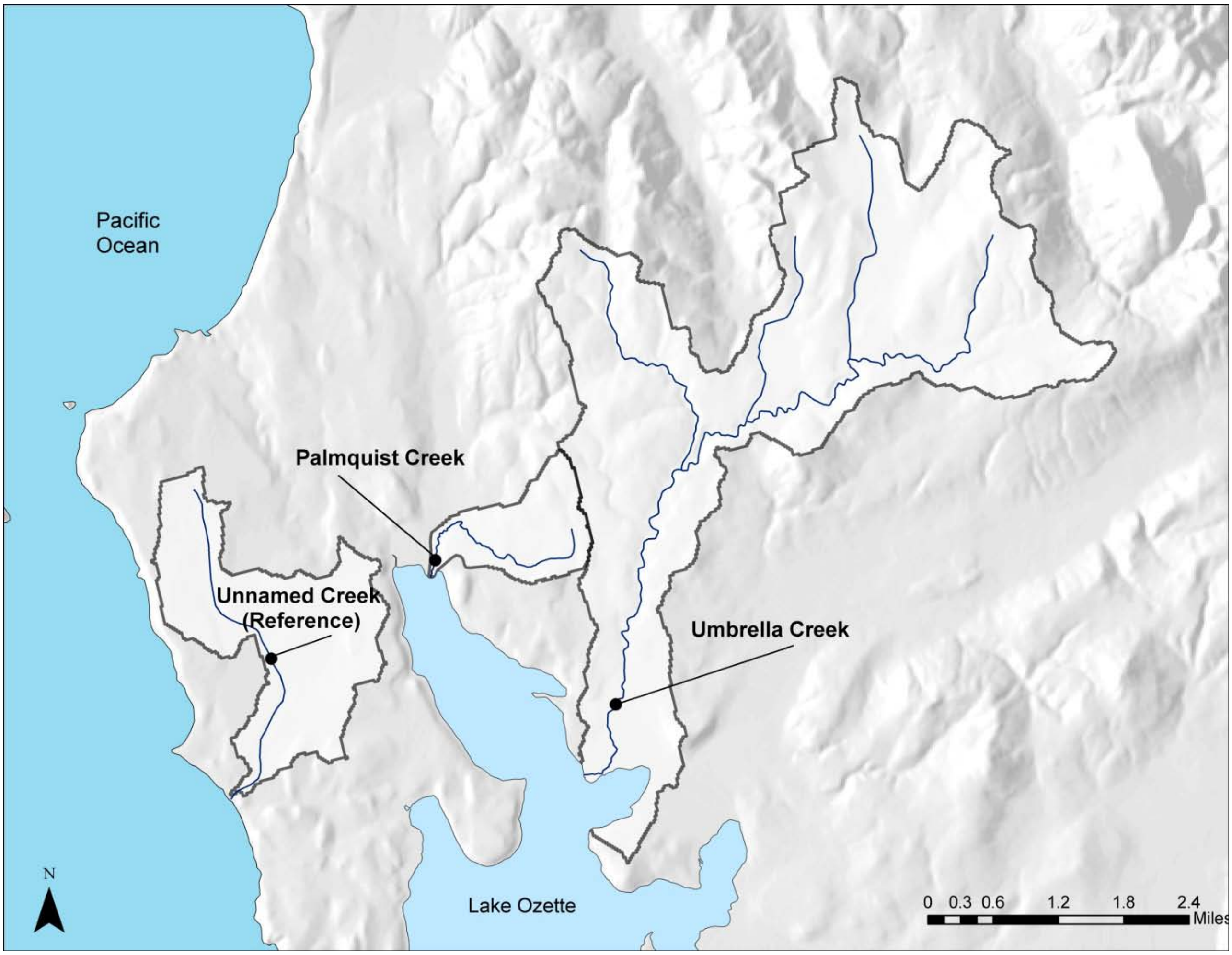

Figure 2. Study Sites, Drainage Areas, and Sampling Locations, 2009 – 2010. (black dots).

Whole water samples were collected monthly from September 2009 – March 2010. In addition to routine monitoring, one additional high-flow storm event was sampled. Water samples were analyzed for total mercury, methylmercury, TOC, DOC, and TSS. Field measurements included pH, dissolved oxygen, specific conductance, and flow.

The study was conducted following a Quality Assurance (QA) Project Plan (Furl and Meredith, 2009). The QA Project Plan provides additional commentary on Lake Ozette and previous mercury studies conducted within and near the lake, such as fish, sediment core, and atmospheric deposition studies.

Site Selection

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

- Umbrella Creek is the third largest tributary to Lake Ozette draining more than 10 mi^2. It was chosen to characterize mercury loading from one of Ozette's major sub-watersheds.
- Palmquist Creek and the reference creek (Tea Creek) are considerably smaller (draining 1.00 and 1.26 mi^2, respectively). They were chosen due to their similarity in watershed size and wetland density.

The Umbrella Creek and Palmquist Creek watersheds have undergone historical logging with > 90% of their watershed area designated as commercial forest. Table 1 displays physical and land-use data for the study sites.

Site Descriptions

While located within a short distance of each other, the three sampling sites and their watersheds each contain unique environmental settings. A brief discussion of the watersheds follows. A detailed account of Umbrella Creek and other major sub-watersheds is provided by Haggerty et al. (2009).

Palmquist Creek

Palmquist Creek was accessed along the Hoko-Ozette Road approximately 0.5 mile east of the Olympic National Park (ONP) ranger station. A detailed account of logging within the watershed is not readily available; however, the majority of the area is zoned as commercial forest (≈ 95%). The catchment area at the sampling point is slightly smaller than the reference creek and considerably steeper (ranging from 47 – 738 ft) (Table 1). Wetland density was estimated as approximately 3%.

Umbrella Creek

Umbrella Creek was sampled along the Hoko-Ozette Road approximately two miles east of the ONP ranger station at the Makah Fisheries Management (MFM) gaging station. Umbrella Creek is the third largest tributary to Lake Ozette and provides spawning grounds for the threatened Lake Ozette sockeye. A detailed account of environmental conditions within Umbrella Creek can be found in Haggerty et al. (2009) and Ritchie and Bourgeois (2009 draft). Additionally, the ONP collected water quality data at the creek for 16 months (Meyer and Brenkman, 2001).

The stream originates at Elk Lake where it flows south-southwest until joined by the West Branch Umbrella Creek before draining to Umbrella Bay. Umbrella Creek has experienced the most rapid road building and most complete removal of original forest of any Lake Ozette sub-watershed (Ritchie and Bourgeois, 2009 draft) and delivers large episodic sediment loads. Other studies examining this creek have identified harmful levels of turbidity and other deteriorating habitat conditions (Meyer and Brenkman, 2001; Ritchie and Bourgeois, 2009 draft; Herrera, 2006).

Tea Creek (unnamed reference creek)

An unnamed creek dubbed "Tea Creek" was sampled as the reference location. The site was accessed along the ONP Sandpoint Trail approximately 1.5 miles southwest of the ONP ranger station located at the northern end of the lake. The catchment area has very low relief (≈ 95% between 80 – 200 ft) and is located entirely within the backcountry area of ONP. Modern commercial logging has not occurred within the watershed. Wetland density was estimated as approximately 3% of the watershed. No information is available on groundwater movement through the watershed; however, the soil remained considerably moist in areas surrounding the stream throughout the sampling period with respect to the other two sites. During the two highest flows sampled, water exceeded the banks.

Table 1. Physical and Land-Use Characteristics of Study Site Watersheds.

Study Area	Drainage Area at Sampling Point (sq. mi.)	Total Sub-watershed Area (sq. mi.)	Minimum Basin Elevation* (ft)	Maximum Basin Elevation (ft)	Area with Slope > 30% (% of watershed)	Mean Annual Precipitation (inches)	Wetland Area (% of watershed)^	Land Use (% of watershed)		
								Commercial Forest	National Park	Residential or Retail
Palmquist Creek	1.00	1.01	47	738	0.15	83	3.1	95	6.5	3.2
Umbrella Creek	10.61	11.71	61	1170	6.3	93	3.1	93	0	0
Unnamed "Tea" Creek (reference)	1.26	2.97	83	251	0	105	2.7	0	100	0

* Estimated from USGS Topography Maps.
^ Estimated from U.S. Fish and Wildlife Service's National Wetland Inventory.

Field Methods

Water sampling was conducted using modifications of Environmental Protection Agency (EPA) Method 1669 and Ecology's standard operating procedure (SOP) for *Collection and Field Processing of Metals Samples* (Ward, 2007). Pre-cleaned I-Chem® class 200 glass sample bottles (500 mL for total mercury and 250 mL for methylmercury) were used for sampling. Frontier Geosciences provided bottles, field blank reagent water, and preservatives (hydrochloric acid) meeting their Quality Control requirements.

Samples were collected by wading into the approximate thalweg of the stream and dipping an uncapped bottle beneath the surface of the water. After the bottle was filled, it was 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 sample jar was rinsed in this manner three times before taking the sample. To take the sample, the bottle was submerged to half the depth of the stream, allowing it to fill without disturbing the substrate. The filled bottle was removed from the stream, and a small amount of water was poured off from the bottle to allow room for 1 mL of hydrochloric acid (for methylmercury only) before being capped. Samples were double bagged in laboratory-provided poly bags and immediately cooled.

Umbrella Creek became unwadeable several times during high flows. During these high-flow events, samples were collected from the bank by attaching the bottle to a pole using a pre-cleaned stainless steel clamp. Bottle rinsing was conducted from the bank in the same manner as described above prior to attaching the sample bottle to the pole. Care was taken to ensure sample water did not contact the pole device prior to entering the bottle.

Field personnel wore shoulder-length nitrile gloves beneath new wrist-length, powder-free vinyl gloves for each sample collection to avoid contamination.

TSS, TOC, and DOC samples were all taken from the same location as mercury samples by hand dipping or using the pole device. DOC samples were field filtered.

pH and flow measurements were taken following the Environmental Assessment Program's SOPs (Swanson, 2007; Sullivan, 2007, respectively).

Laboratory Methods

Mercury Analysis

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

Methylmercury (CH_3Hg) was analyzed by distillation, aqueous ethylation, purge and trap, desorption, and CVAFS. The method is a modified version of EPA 1630.

Both method FG069 and FG070 for analysis of total mercury and methylmercury, respectively, are available from Frontier Geosciences.

Other Parameters

TOC, DOC, and TSS analyses were performed by Ecology's Manchester Environmental Laboratory (MEL). TOC and DOC were calculated from the difference between total carbon and inorganic carbon in whole and field-filtered water samples, respectively. The two carbon components were detected by a non-dispersive infrared gas analyzer. For TSS measurements, solids were determined by the residue left after evaporation and subsequent oven drying. The MEL methods are available upon request.

Data Quality

MEL prepared case narratives describing the quality of the analytical data. The narratives include a description of results, laboratory quality assurance, and special issues encountered during analysis. Case narratives are available upon request.

Data quality was good for each of the 5 laboratory parameters measured. Due to the small batch sizes (3-7 samples/ event), some of the associated quality control (QC) tests for mercury were run on samples not collected as part of the Lake Ozette project. Average values for QC tests by parameter are shown in Table 2. Measurement quality objectives (MQOs) and complete results for all QC tests are located in Appendix F.

Table 2. Average Quality Control Results.

Analyte	LCS (% recovery)	LCSD (RPD)	Lab Duplicates (RPD)	MS (% recovery)	MSD (RPD)	Field Blanks	Field Replicates (RPD)
Mercury	99	3	7	102	3	< LOQ	9
Methyl-mercury	102	11	11	111	6	< LOQ	6
TOC	98	-	2	99	-	< LOQ	2
DOC	100	-	1	102	-	< LOQ	1
TSS	99	1	9	-	-	-	40*

*Only one pair of samples were both > LOQ. Source sample = 3 mg/L, replicate = 2 mg/L.
LCS: Laboratory Control Sample.
LCSD: Laboratory Control Sample Duplicate.
MS: Matrix Spike.
MSD: Matrix Spike Duplicate.
RPD: Relative Percent Difference.
LOQ: Limit of Quantitation.

Total Mercury and Methylmercury

Laboratory control samples, laboratory duplicates, and field replicates met MQOs in all instances. A single matrix spike recovery for methylmercury was outside acceptance limits (140%). No adjustments were made since all other QC for the batch was acceptable. All total mercury matrix spikes were recovered acceptably.

Total mercury concentrations > LOQ were measured in one of the field blanks. No adjustments were required since the field blank contamination was far below (<1/10) levels measured in environmental samples.

Measurements for total and methylmercury were corrected by subtracting the mean of the method blanks. Very low levels were detected in some of these blanks.

Organic Carbon and Total Suspended Solids

QC measurements for organic carbon measurements met MQOs in all instances. All TSS QC measurements met MQOs with the exception of a single field replicate (source sample = 3 mg/L, replicate = 2 mg/L; RPD 40%). Full results are included in Appendix F.

Data Calculations

Yearly Watershed Yield and Watershed Retention

Daily total mercury concentrations were modeled using the linear relationship between discharge and concentration at Umbrella Creek. Mean daily discharges at the creek were obtained from Makah Fisheries Management. Appendix E displays the linear relationship along with a residuals plot.

The product of modeled concentration values and mean daily discharge was used to calculate a daily mercury flux for Umbrella Creek. Daily flux values were summed over the period of 4/1/2009 – 3/31/2010 to estimate yearly watershed mercury yield. The yearly sum was normalized to watershed size and expressed on an area basis (µg/m^2/yr).

Mercury wet deposition values from the Makah Mercury Deposition Network station (http://nadp.sws.uiuc.edu/mdn/) were used to calculate deposition within the Umbrella Creek watershed over the same yearly period as fluxes (4/1/2009 – 3/31/2010). Total deposition was estimated as 4 times wet deposition as suggested by Grigal (2002) for forested landscapes. Retention estimates were calculated from the difference of inputs and outputs, ignoring volatilization.

Yearly watershed yields and retentions were not calculated for Palmquist or Tea Creeks due to the lack of continuous flow monitoring and poor linear relationships between stream discharge and mercury concentrations at those sites.

Results and Discussion

Sample Collection and Tributary Flows

Eight samples were collected approximately monthly from the 3 study sites. Provisional stream discharge data for Umbrella Creek during the sampling period (September 2009 – March 2010), along with the sampling events, are shown in Figure 3. Long-term data for this gage are not available. Figure 4 displays sampling events plotted on a year-long flow duration curve (April 2009 – March 2010) for Umbrella Creek. Rainfall data at the Ozette ranger station are shown in Appendix D.

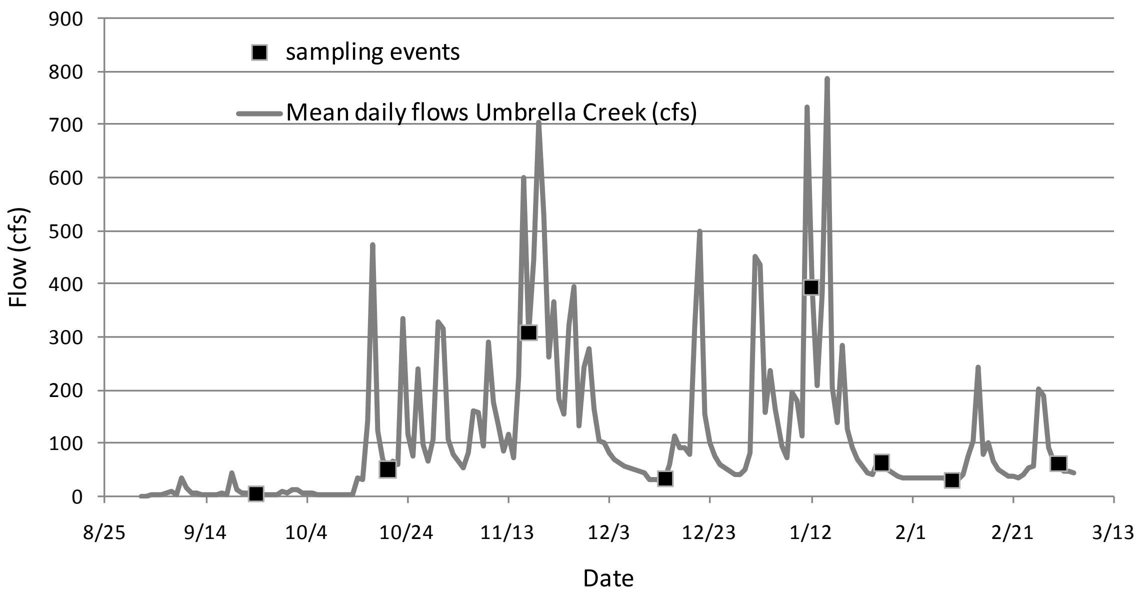

Figure 3. Sampling Events Plotted against Mean Daily Flows, September 2009 – March 2010.

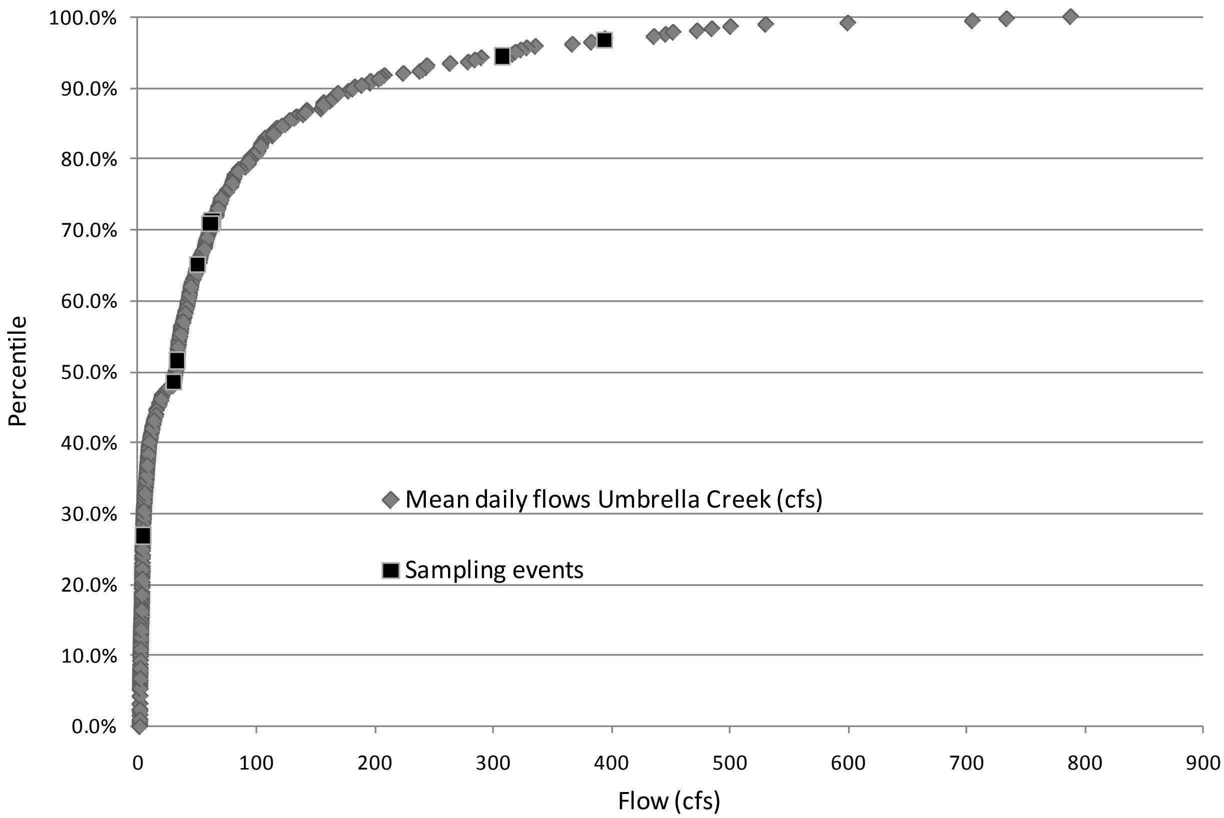

Figure 4. Sampling Events Plotted on a Year-long Flow Duration Curve, April 2009 – March 2010.

All samples were collected on steady or falling limbs of the hydrograph (Figure 3). This has important implications for interpreting the mercury data, as numerous studies have indicated peak concentrations occur during periods of rising flow (Shanley et al., 2008; Brigham et al., 2009; Balogh et al., 2003).

The distribution of samples on the flow duration curve indicates high flows were effectively captured during the November 17 (95^{th} percentile) and January 12 (97^{th} percentile) sampling events. The remaining samples were collected between 25^{th} to 75^{th} percentile flows.

Figure 5 displays instantaneous flows measured at all three sites during sampling events.

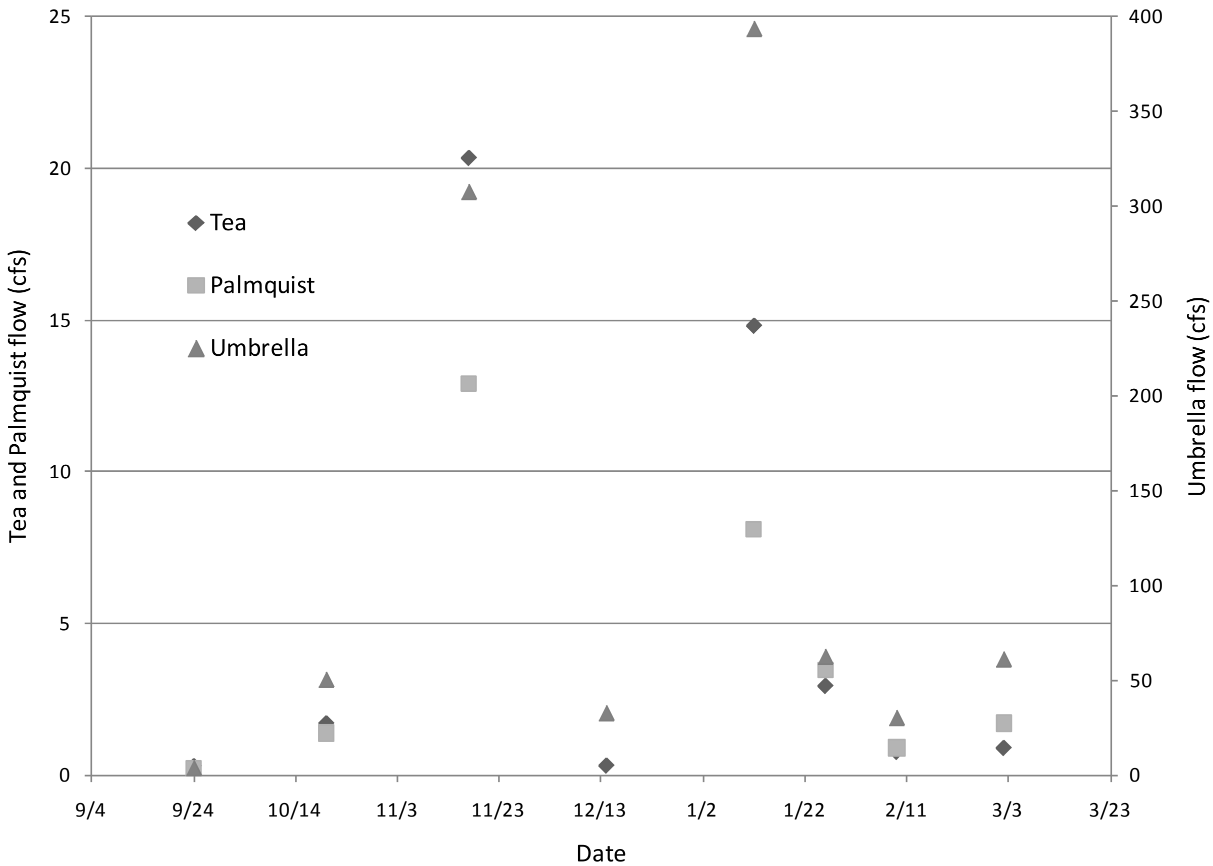

Figure 5. Instantaneous Flows Measured during Sampling Events, 2009 – 2010.
Flows at Umbrella Creek represent daily average flow, collected by MFM.

Flows at Tea and Palmquist Creeks followed a similar directional pattern to Umbrella Creek measurements. Maximum flows at Tea and Palmquist Creeks were recorded during the first high-flow sampling event (November). Peak flows at Umbrella Creek were recorded during the mid-January sampling event.

Discharge measurements at Palmquist Creek were influenced by lake stage (negative flow rate) during the December sampling event. Our estimated elevation for the sampling site was 47 feet above sea level. Long-term lake stage data collected by various entities (USGS, ONP, MFM) show stage can vary from 31 – 41 feet above sea level (Haggerty et al., 2009). Peak lake stage was likely reached during December after heavy rainfall throughout November (Appendix D). We do not believe any other Palmquist discharge values were affected by lake stage.

Total Mercury and Methylmercury Concentrations

Concentrations for each of the 8 sampling events are plotted in Figures 6 and 7. A statistical summary of total and methylmercury concentrations is provided in Appendix C.

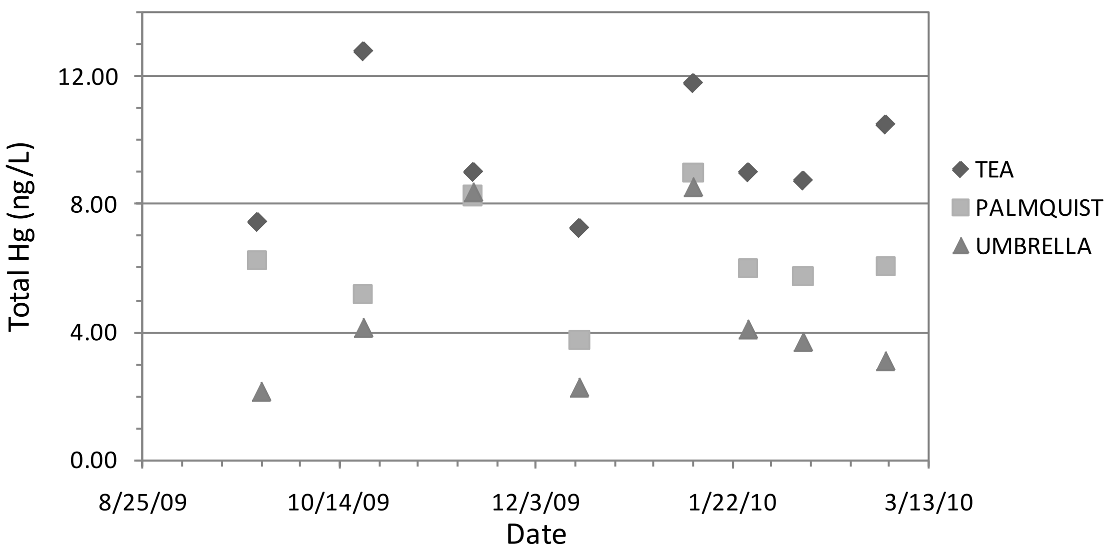

Figure 6. Total Mercury Concentrations.

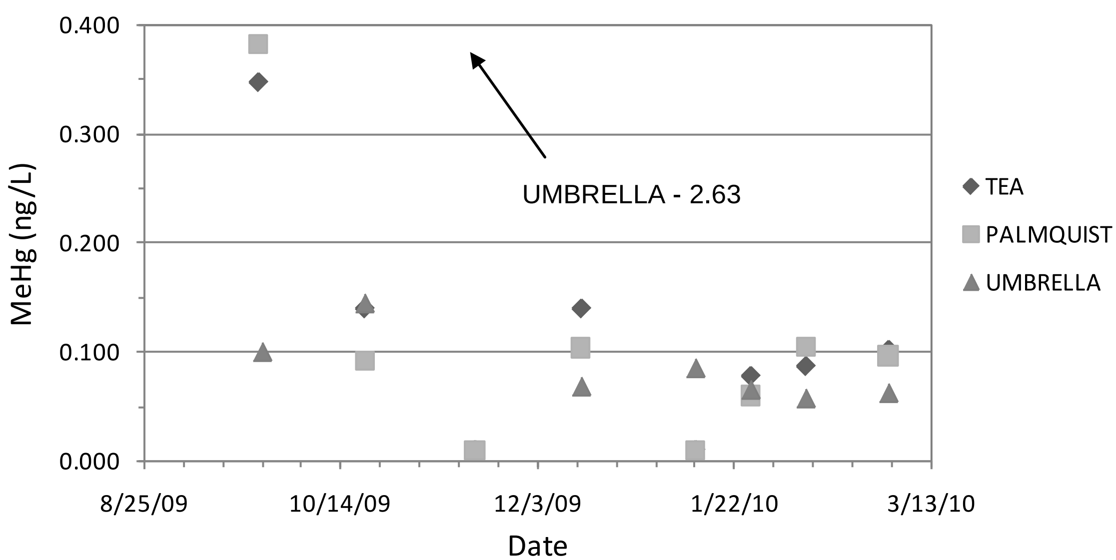

Figure 7. Methylmercury Concentrations.

Total mercury concentrations followed a consistent pattern of Tea>Palmquist>Umbrella. For methylmercury, there was no consistent pattern between the creeks. The majority of methylmercury concentrations (≈ 70%) were found within the range of 0.057 – 0.145 ng/L.

Numerous studies have described speciated mercury concentrations in lakes and streams worldwide. Recently, the USGS reported findings on speciated mercury from 352 streams and rivers draining mined and unmined sites across the entire U.S. Figure 8 presents results for total and methylmercury from the unmined sites of the USGS study (n = 236), along with median values from the current study.

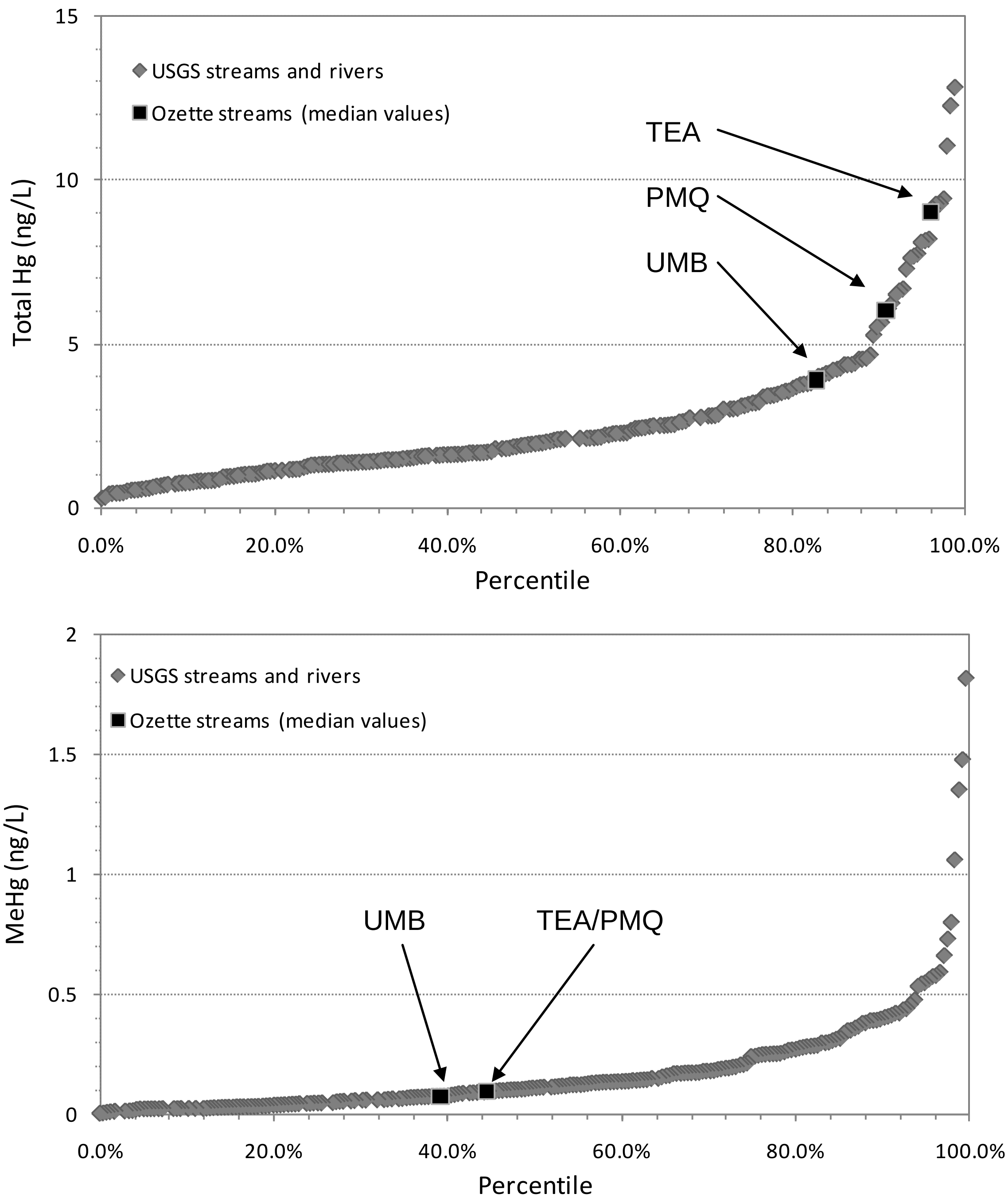

Figure 8. Median Total Mercury and Methylmercury Concentrations Plotted Against Values Recorded by a Nationwide River and Stream Study (n = 236)
(Adapted from Scudder et al., 2009).

Total mercury concentrations at the Ozette study streams (median = 6.80 ng/L) were above the 80^{th} percentile for concentrations recorded as part of the national survey (median = 1.90 ng/L). However, individual samples much greater (> 50 ng/L) than those recorded from the Ozette streams have been found in more intensively sampled waterbodies (Shanley et al., 2008; Balogh et al., 2003).

Methylmercury concentrations in streamwater do not appear elevated, with the exception of a single value from Umbrella Creek (2.63 ng/L). Other concentrations recorded at Lake Ozette streams (median = 0.090 ng/L) were similar to values collected as part of the nationwide study (median = 0.11 ng/L). Additionally, Krabbenhoft et al. (2007) reviewed available literature and found that most surface waters had methylmercury concentrations in the range of 0.04 – 0.8 ng/L, consistent with the USGS nationwide study.

The highest methylmercury concentration (2.63 ng/L) was recorded at Umbrella Creek during the first high-flow event (sampled on 11/17/2009). Concentrations were approximately 7 times greater than the next highest value, and only one sample measured higher in the nationwide survey by Scudder et al. (2009). The sample was taken during sockeye spawning in Umbrella Creek which may have influenced the value. In a study of the Woods River System in Bristol Bay Alaska, Baker et al. (2009) found smolts exported an average of 12% of mercury imported by their parental spawning class. Currently, Ecology is planning on assessing mercury concentrations in Lake Ozette sockeye collected by MFM (Furl, 2010)

Water Quality Criteria

Surface water quality standards for total mercury established by Chapter 173-201A WAC, *Water Quality Standards For Surface Waters Of The State Of Washington,* list chronic and acute criteria as 12 and 2,100 ng/L, respectively. Figure 9 displays a cumulative frequency of concentrations recorded at all three sites along with the chronic standard.

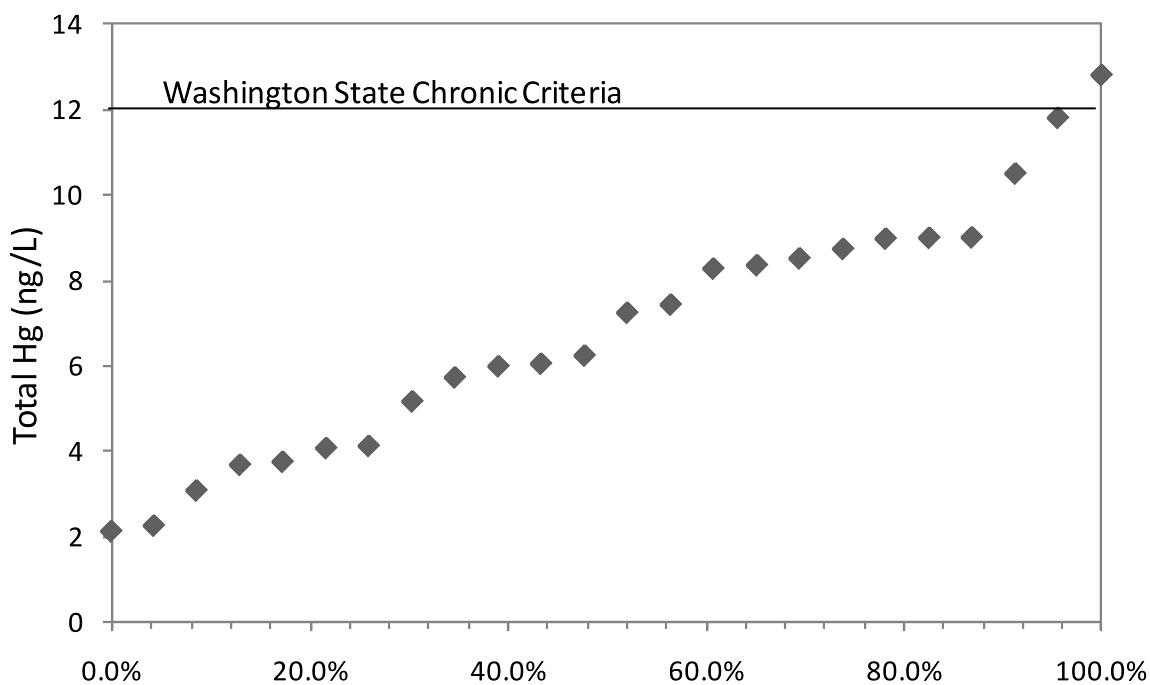

Figure 9. Total Mercury Concentrations from All Lake Ozette Streams Plotted with Washington State Surface Water Chronic Exposure Criteria (12 ng/L).

Chronic values were violated in a single sample from Tea Creek. All values were well below acute criterion (2,100 ng/L).

Ancillary Parameters

In addition to streamflow, TSS, DOC, and pH are all parameters known to have a large effect on mercury mobility and cycling (e.g., Lawson and Mason, 2001; Balogh et al., 2003; Nelson et al., 2007). Large gradients in these measures related to differing topography and local environmental conditions were recorded among the three locations. Brief descriptions of these ancillary parameters at each of the streams are included below. Table 3 provides descriptive statistics on the measures, and the complete data are included in Appendix B.

Table 3. Summary Statistics of Ancillary Laboratory Measurements.

	TSS (mg/L)			DOC (mg/L)			pH		
	Tea	Palmquist	Umbrella	Tea	Palmquist	Umbrella	Tea	Palmquist	Umbrella
Median	< 1	< 1	1.3	27.9	13.1	4.4	4.66	5.98	6.86
Average*	< 1	2.5	12.9	28.2	13.0	4.2	4.55	5.86	6.77
Range	NC	ND - 7	ND - 49	21.8 - 42.0	7.8 - 15.5	2.3 - 5.7	4.26 - 4.81	5.32 - 6.13	6.40 - 6.94

* ND: (non-detect) set to 0.5 for TSS calculations.
NC: not calculated.

Total Suspended Solids

Total suspended solids were less than the detection limit (1 mg/L) in all samples from Tea Creek. Concentrations at Palmquist and Umbrella Creeks varied in relation to flow (PMQ $r^2 = 0.52$; UMB $r^2 = 0.97$), with the highest concentrations found at Umbrella Creek. Values greater than detection limits (1 mg/L) at both creeks were recorded under both moderate-flow and high-flow conditions.

The MFM have sporadically measured turbidity since 2005 at the Umbrella Creek flow gage. Figure 10 presents Umbrella Creek turbidity data measured from February – October 2005 (Haggerty et al., 2009).

While turbidity and TSS relationships can vary widely between streams, the above graph illustrates several exceedances over 100 NTU. It is also well reported that Umbrella Creek can deliver significant sediment loads to Lake Ozette over a short period of time (Ritchie and Bourgeois, 2009 draft). During the study period, much higher TSS values likely occurred than were captured by our two high-flow sampling events taken on falling limbs of the hydrograph.

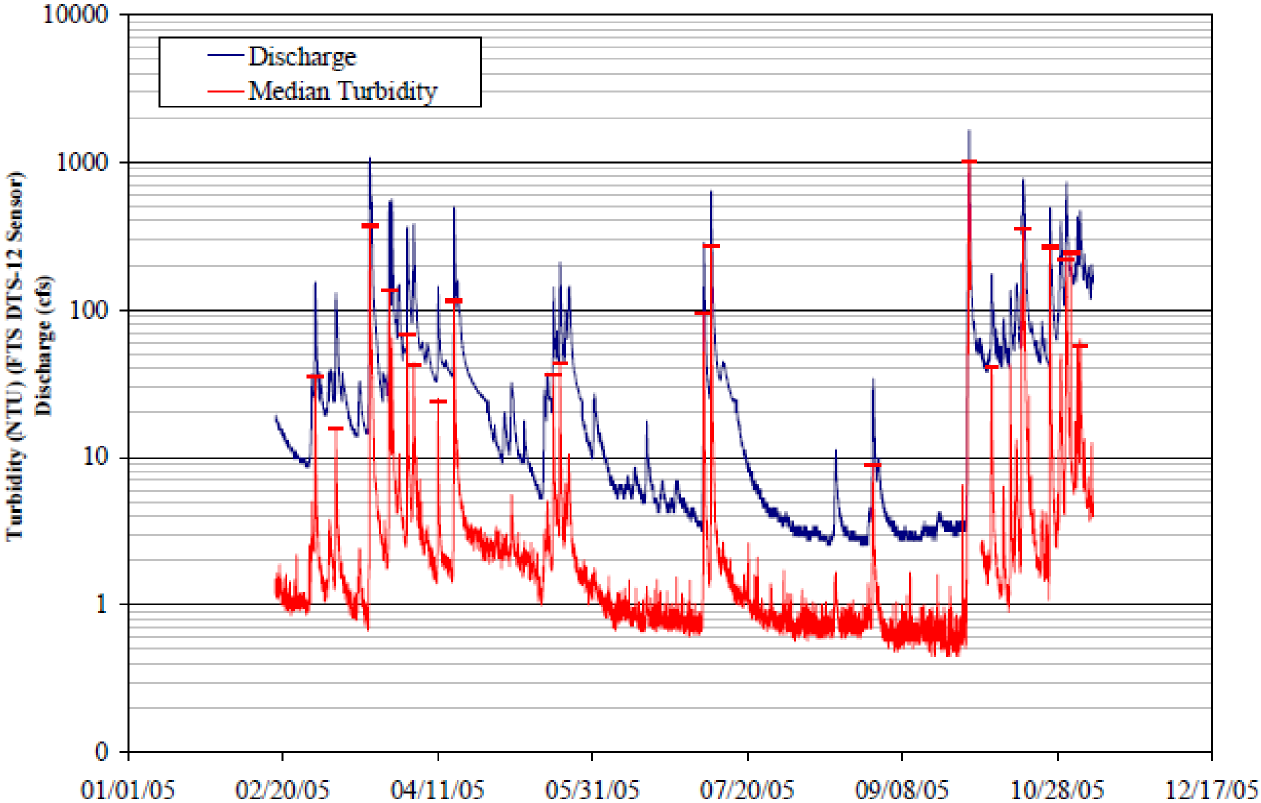

Figure 10. Preliminary Results from Continuous Turbidity Readings and Provisional Stream Discharge for Umbrella Creek.

Haggerty et al., 2009 – unpublished MFM data. Horizontal bars represent turbidity peaks.

Organic Carbon

Measures for dissolved and total organic carbon were similar in all instances (DOC = TOC), even under periods of increased TSS. A very large gradient was found in DOC samples across the streams following the pattern of Tea>Palmquist>Umbrella. Median DOC concentrations at Tea Creek were over 6 times greater than Umbrella Creek. The large differences in DOC content among the sites are important for interpreting results due to the strong complexes between mercury and DOC (Grigal, 2002).

pH

pH measures indicated all three streams were acidic. Variances similar to those found in DOC and TOC were recorded in pH following a pattern of Tea<Palmquist<Umbrella. Our mean pH at Umbrella Creek agreed with values collected by Meyer and Brenkman (2001) over a 16-month period. Again, the large difference in pH must be considered when interpreting mercury data due to the known effect of lower pH values enhancing mercury methylation (Xun et al., 1987).

Correlations with Mercury Concentrations and Ancillary Parameters

Pearson correlations were examined for relationships between speciated mercury and other ancillary parameters (pH, flow, DOC, and TSS). Parameters were log_{10} transformed to improve the normality of the data and analyzed as a single group and by individual streams. Table 4 presents correlation coefficients.

Table 4. Pearson Correlations for Ancillary Measures and Total Mercury and Methylmercury.

	All streams		Tea		Palmquist		Umbrella	
	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
pH	**-0.781**	0.308	-0.388	**0.860**	**-0.720**	**0.921**	**-0.724**	-0.655
Flow	-0.220	-0.104	0.520	**-0.935**	0.690	**-0.967**	**0.901**	0.454
DOC	**0.830**	-0.142	0.460	0.549	**0.822**	-0.494	**0.799**	0.524
TSS	0.200	0.251	-	-	**0.728**	-0.439	**0.945**	0.666

Bolded values indicate $p < 0.05$ on 2 tail.

DOC and pH displayed strong and significant correlations with total mercury across the "all streams" grouping. The "all streams" correlations are highly affected by the large environmental gradients found within the ancillary parameters. Commonalities between the streams analyzed individually provide a better means for identifying controls on mercury.

DOC and flow had strong positive relationships with total mercury concentrations within each stream. TSS and total mercury had positive correlations at Umbrella and Palmquist Creeks. These relationships are not surprising and have been reported with other stream studies (e.g., Brigham et al., 2009; Shanley et al., 2008; Balogh, 2003).

Mercury's strong affinity for humic acids (found in DOC) partially explains the greater concentrations recorded at Tea Creek where shallow subsurface flow paths through rich organic matter transport mercury to the stream. The more channelized, steeper watersheds of Palmquist and Umbrella Creeks likely have much shorter retention times in terrestrial systems leading to lower DOC content.

Several reports have documented greater mercury concentrations under periods of high flow and high turbidity, particularly on the rising limb of the hydrograph. This relationship was found at Umbrella and Palmquist Creeks and indicates terrestrial sources of particulate mercury are important.

There were no strong relationships between methylmercury and the ancillary parameters apparent between all three streams. Methylmercury did not vary inversely with pH in the "all streams" group as one might expect with such large pH gradients.

Unlike total mercury, methylmercury concentrations correlated inversely with flow at Tea and Palmquist Creeks. The highest concentrations for both waterbodies were recorded during the lowest flows of the study period (September). During the two high-flow events, methylmercury concentrations at both creeks were below detection limits. This suggests methylmercury is produced within the hydrologically connected wetlands and the stream channel itself, and terrestrial runoff results in a dilution of concentrations. While higher methylmercury concentrations coupled with higher flows have been reported (Shanley et al., 2008), streams from other studies have exhibited an inverse relationship as seen here (Brigham et al., 2009). This underscores the importance of the effects local site conditions have on mercury cycling.

Methylmercury concentrations at Umbrella Creek did not have a similar response to flow as the other two streams. Concentrations remained fairly constant across a range of flow conditions with the exception of the anomalously high value (2.63 ng/L) taken during the first high-flow event.

Mercury Fluxes and Stream Comparisons

Total mercury and methylmercury fluxes on an area basis (mg/hr/km^2) for each of the creeks are displayed in Figures 11 and 12.

Total mercury fluxes at the sites ranged from 0.03 – 12.44 mg/hr/km^2 following the pattern of Umbrella>Tea>Palmquist. Fluxes at Tea Creek were only slightly greater than Palmquist Creek. Total fluxes at all three creeks were generally less than 1 mg/hr/km^2 with the exception of the two high-flow events.

Methylmercury fluxes followed a similar pattern to total fluxes. Fluxes at Tea and Palmquist Creeks were less than 0.01 mg/hr/km^2. The highest fluxes were at Umbrella Creek where median values were approximately 3 fold greater than Tea and Palmquist (Appendix C).

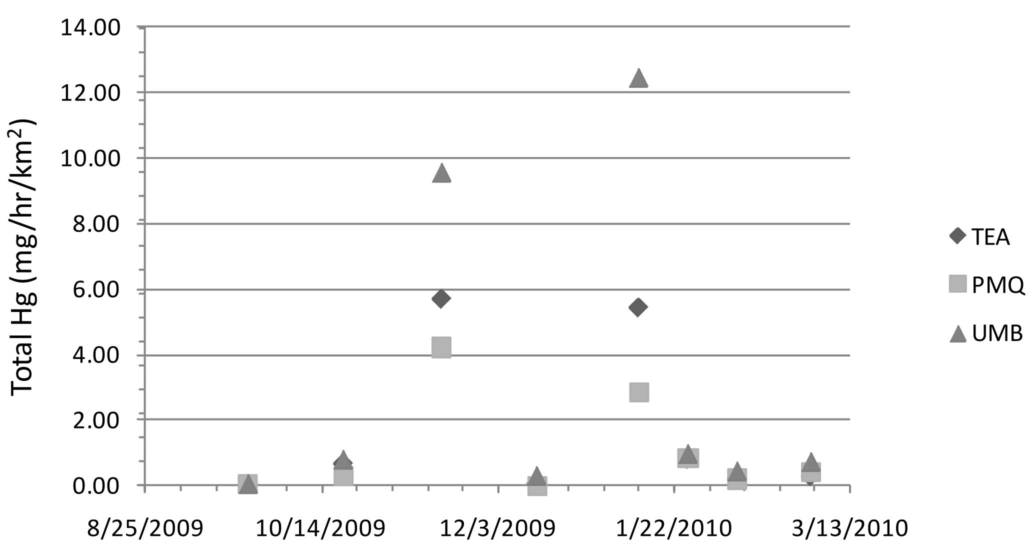

Figure 11. Total Mercury Fluxes (mg/hr/km^2).

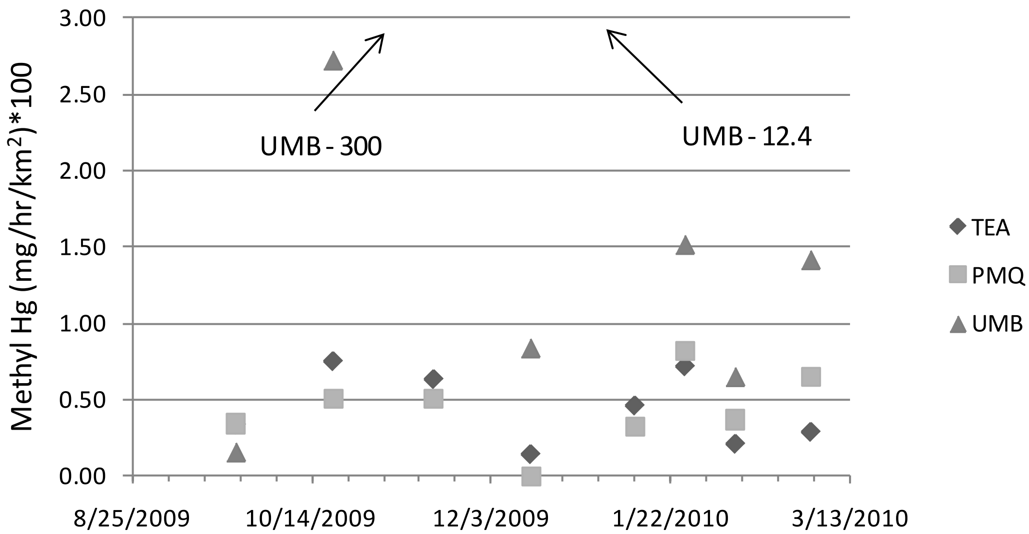

Figure 12. Methylmercury Fluxes $(mg/hr/km^2)$*100.

Umbrella Creek Yearly Mercury Flux and Watershed Retention

Yearly total mercury flux (4/1/2009 – 3/31/2010) at Umbrella Creek was estimated as 15.6 $\mu g/m^2/yr$. Estimates were not made at Palmquist and Tea Creeks due to a lack of continual flow monitoring and weaker relationship between flow and total mercury concentration.

The watershed yield estimated at Umbrella Creek is much higher than most values reported in literature. In a review of 121 studies covering a range of watershed sizes, Grigal (2002) found a mean annual total mercury flux of 1.7 $\mu g/m^2/yr$. Seventy-five percent of the values were in the range of 1 – 3 $\mu g/m^2/yr$ (Figure 13).

In a study of small forested headwater catchments, Shanley et al. (2008) estimated a yearly flux of 54.4 $\mu g/m^2/yr$ from a stream in Puerto Rico. The authors attributed the high export in the catchment to frequent landslides in the watershed mobilizing mercury. A total flux similar to Umbrella Creek (15.9 $\mu g/m^2/yr$) was recorded in a forested catchment in industrialized central Europe (Schwesig and Matzner, 2001).

Total mercury deposition in the Umbrella Creek watershed was estimated as 24.12 $\mu g/m^2/yr$ (6.03 wet; 18.09 dry) from 4/1/2009 – 3/31/2010. Using this total deposition estimate, watershed retention was estimated as approximately 35% with 65% being exported via runoff. This mercury retention rate is low. Total mercury export in excess of wet deposition is rare. Ignoring volatilization, watersheds typically retain 70-95% of wet deposition and > 90% of total deposition (Grigal, 2002; Shanley et al., 2008; Nelson et al., 2007). Our export estimates show that total mercury yields from Umbrella Creek are approximately 2.5 times greater than precipitation inputs. Adding in dry deposition estimates shifts the balance to a net retention scenario (35%).

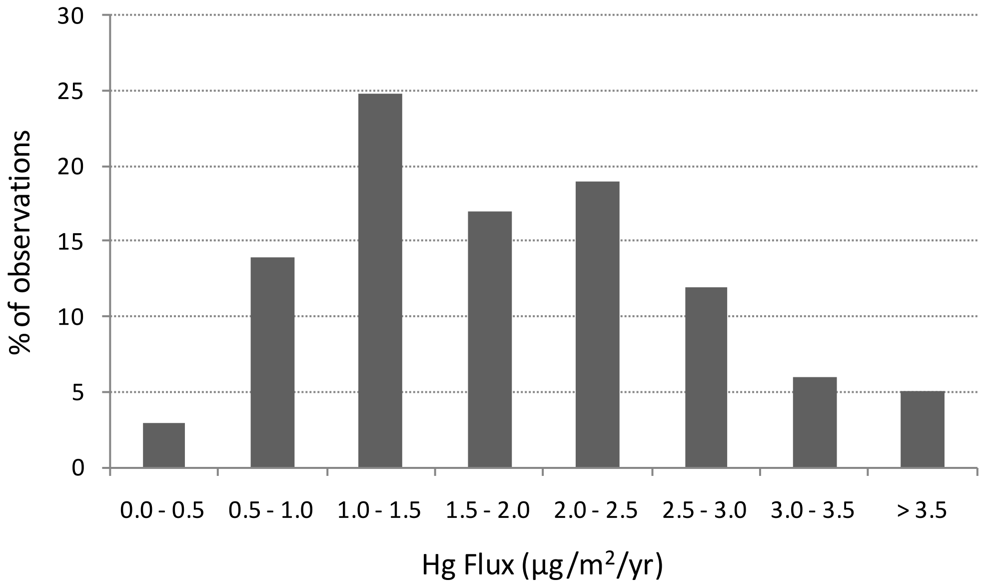

Figure 13. Yearly Mercury Export Values from Selected Drainages.
(Adapted from Grigal, 2002.)

DOC and particulates are the most important factors altering mercury retention rates in a watershed (Grigal, 2002). In watersheds with insignificant DOC concentrations, particulates are the primary mode of transport. In Umbrella Creek, particulate mercury transport appears to be the primary means of export to the lake. DOC concentrations are low relative to the other two creeks, and total mercury concentrations displayed a strong positive relationship with TSS.

The phenomena of higher concentrations during periods of elevated TSS and flow allows for large loads of mercury to be delivered to the lake in short time periods. In the yearly flux model for Umbrella Creek (15.6 $\mu g/m^2/yr$), ≈ 50% of the total load was delivered in 15 days. This is congruent with what is known about sediment delivery dynamics in the Umbrella Creek watershed. Ritchie and Bourgeois (2009 draft) estimated the Umbrella Creek delta has grown by 2.4 hectare since 1950. Additionally, very large sediment delivery events (≈ 50 cm) from Umbrella Creek have been documented (Ritchie and Bourgeois, 2009 draft).

Role of Land Use in Mercury Exports

Several studies have indicated logging within a watershed can increase mercury export and lead to elevated concentrations in downstream biota (Garcia and Carignan, 1999, 2000; Porvari et al., 2003; Sorensen et al., 2009; Skyllberg et al., 2009; Munthe and Hultberg, 2004). The primary mechanisms for increased loads after logging are from larger water yields, higher instream DOC concentrations, increased particulate transport, and changed hydrological pathways to streams.

It is difficult to quantify the impact of logging on mercury exports at the study sites considering their unique environmental settings (i.e., differences in pH, DOC, TSS, and mean watershed slope). While instantaneous fluxes ($mg/hr/km^2$) were highest at Umbrella Creek, values differed little between Tea and Palmquist.

Considering the several-fold increase in sedimentation rates at Lake Ozette over the past 50 years (Furl et al., 2010; Ritchie and Bourgeois, 2009 draft; Herrera, 2006) and the importance of particulate mercury transport, it seems reasonable to conclude that alterations in the watershed landscape have increased mercury export from terrestrial surfaces surrounding the lake. The very high mercury yield ($\mu g/m^2/yr$) and low retention rates at Umbrella Creek support this conclusion.

It should also be noted that total mercury concentrations were high at all three creeks even in the absence of logging at Tea Creek. While concentrations were highest at Tea Creek, the dominant form of transport was through DOC mobilization and not particulates. Continual flow monitoring allowing for yearly area-based export and retention estimates at Tea and Palmquist Creeks would be useful.

Many of the studies describing mercury exports from logged watersheds have also noted increases in methylmercury exports. Researchers have suggested forestry practices enhance methylmercury production by raising soil temperature, increasing the supply of readily available carbon, and raising the water table depleting soils of oxygen.

With the exception of the single high value from Umbrella Creek, methylmercury concentrations were modest at all three streams in the present study. This is somewhat unexpected considering the presence of wetlands and elevated fish tissue concentrations in the lake. An evaluation of methylmercury concentrations within the lake itself should be considered to determine where the primary zone of methylation is occurring.

Summary and Conclusions

A total of eight sampling events were conducted at three streams in and adjacent to the Lake Ozette watershed from September 2009 – March 2010 to assess the effects of land use on mercury export. The sites included two logged watersheds, Palmquist and Umbrella Creeks, which flow into the north end of Lake Ozette, and an unlogged reference site (Tea Creek) sampled near the Sandpoint Trail in the Olympic National Park. Water samples were analyzed for total mercury, methylmercury, TOC, DOC, and TSS.

Total mercury concentrations in the creeks ranged from 2.15 – 12.80 ng/L. DOC, TSS, and stream discharge had the strongest correlations with total mercury. Total concentrations followed a pattern of Tea>Palmquist>Umbrella. Median concentrations in all three creeks were elevated (> 80^{th} percentile) when compared to a USGS nationwide survey of 236 rivers and streams.

Methylmercury concentrations ranged from < 0.05 – 2.36 ng/L. Concentrations did not follow a consistent pattern. Median values were highest at Tea and Palmquist Creeks (approx. 0.1 ng/L). Unlike total mercury values, median methylmercury values were lower than concentrations typically encountered in a USGS nationwide survey. The highest methylmercury concentration recorded was collected from Umbrella Creek during a high-flow event. The sample was well elevated above other methylmercury concentrations recorded during the study.

A large gradient in environmental measures (DOC, TSS, and pH) encountered between the three creeks hampered cross-comparisons of the mercury data. However, median total mercury and methylmercury fluxes ($mg/hr/km^2$) were highest in Umbrella Creek. Total and methylmercury fluxes differed little between the logged watershed of Palmquist Creek and the pristine watershed of Tea Creek.

Yearly total mercury flux estimates at Umbrella Creek indicated an elevated watershed yield ($15.6\ \mu g/m^2/yr$) when compared to values reviewed in literature. Mercury retention in the watershed was very low (≈ 35%). Particulates appear to be an important mode of transport at Umbrella Creek, allowing for large episodic pulses of mercury to the lake.

Recommendations

As a result of this 2009 – 2010 study, the following recommendations are made:

- Evaluate seasonal methylmercury concentrations in the Lake Ozette water column. Methylmercury concentrations were generally low in streams entering the lake, and the lake could serve as the primary area of methylation.

- Conduct continuous flow monitoring in creeks when evaluating mercury loads.

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Appendices

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Appendix A. Mercury Trends Fish Monitoring Sites, 2005 - 2009.

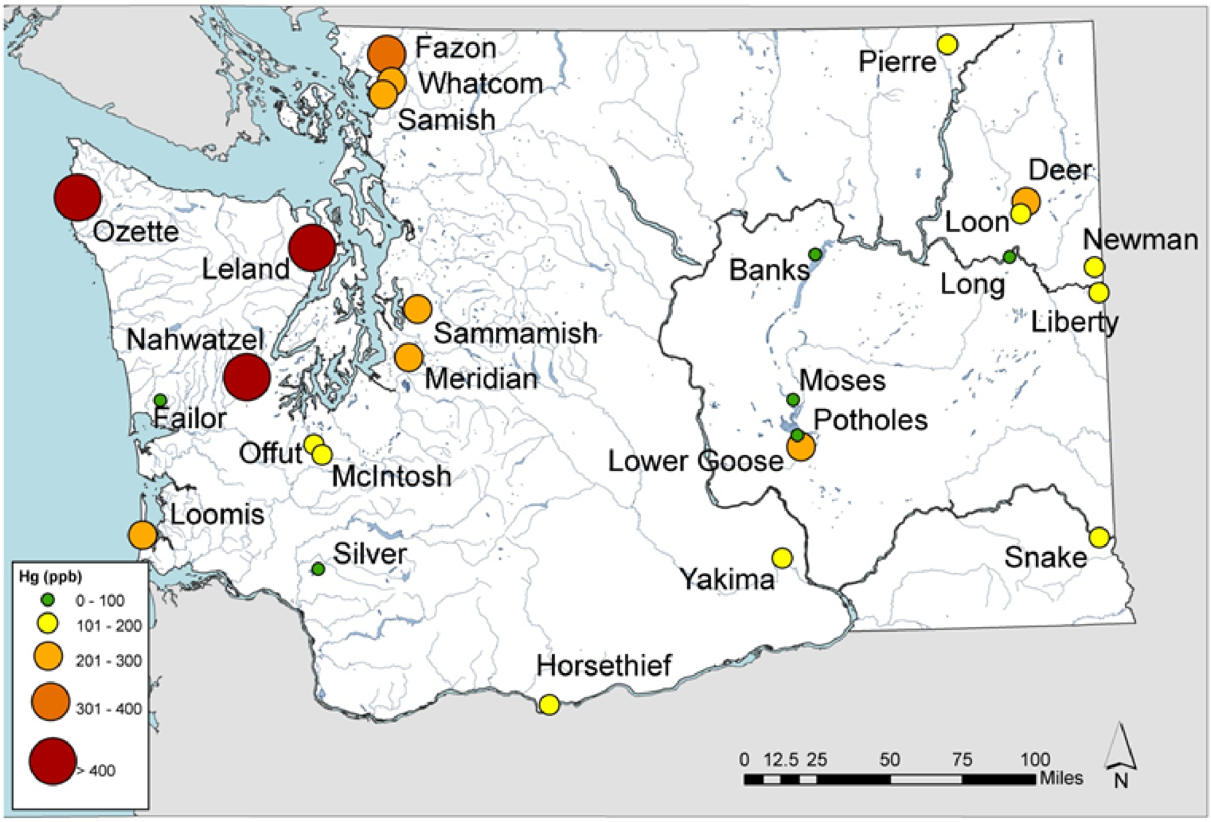

Figure A-1. Standard-size (356 mm) Bass Concentrations in Study Lakes, 2005 – 2009.

Appendix B. Project Data

Table B-1. Project Data.

Work order	Lab #	Station	Date of sample	pH	Temp (º C)	Cond (µs/cm)	Flow (cfs)	DO (mg/L)	THg (ng/L)	MeHg (ng/L)	DOC (mg/L)	TOC (mg/L)	TSS (mg/L)
909069	01	Tea	9/23/09	4.81	12.2	74	0.31	8.0	7.44	0.348	30.7	30.7	ND
909069	02	Palmquist	9/23/09	6.08	12.8	45	0.23	8.6	6.25	0.383	12.2	12.6	5
909069	03	Umbrella	9/24/09	6.94	13.2	97	4.03	9.0	2.15	0.100	3.4	3.5	ND
910059	01	Tea	10//09	4.59	10.1	54	1.72	7.8	12.80	0.140	42.0	42.1	ND
910059	02	Palmquist	10//09	5.85	10.3	42	1.39	9.8	5.18	0.092	14.7	14.8	1
910059	03	Umbrella	10//09	6.95	11.0	60	50.59	10.1	4.14	0.145	5.4	5.4	3
911042	01	Tea	11/17/09	4.17	8.5	52	20.32	9.1	9.01	ND	22.5	22.0	ND
911042	02	Palmquist	11/17/09	5.32	8.7	29	12.91	10.2	8.28	ND	15.0	14.7	7
911042	03	Umbrella	11/17/09	6.4	8.3	29	307.75	-	8.36	2.630	5.7	4.9	47
912039	01	Tea	12/14/09	4.8	2.8	28	0.33	11.0	7.25	0.140	21.8	21.1	ND
912039	02	Palmquist	12/14/09	6.02	2.5	33	-1.07	16.2	3.77	0.104	7.8	7.7	ND
912039	03	Umbrella	12/14/09	6.78	3.0	61	32.99	12.6	2.28	0.068	2.3	2.3	ND
1001037	01	Tea	1/12/10	4.26	8.8	29	14.80	9.0	11.80	ND	23.4	23.7	ND
1001037	02	Palmquist	1/12/10	5.44	8.7	19	8.10	10.4	8.98	ND	15.5	15.9	5
1001037	03	Umbrella	1/12/10	6.58	8.6	26	393.69	10.9	8.52	0.085	5.0	4.8	49 J
1001074	01	Tea	1/26/10	4.32	7.0	39	2.95	9.9	9.00	0.078	26.4	25.8	ND
1001074	02	Palmquist	1/26/10	5.93	7.0	24	3.45	10.8	6.00	0.060	13.7	13.7	ND
1001074	03	Umbrella	1/26/10	6.93	7.1	35	62.68	10.0	4.09	0.065	5.0	4.9	2
1002041	01	Tea	2/9/10	4.75	5.6	40	0.78	9.8	8.74	0.087	29.5	27.7	ND
1002041	02	Palmquist	2/9/10	6.13	5.9	2.8	0.89	11.5	5.74	0.105	12.4	12.3	ND
1002041	03	Umbrella	2/9/10	6.63	6.6	55	30.46	12.0	3.70	0.057	3.7	3.7	ND
1003040	01	Tea	3/2/10	4.72	7.9	23	0.91	9.4	10.50	0.102	29.3	29.2	ND
1003040	02	Palmquist	3/2/10	6.08	9.8	26	1.70	10.7	6.06	0.097	12.5	12.7	ND
1003040	03	Umbrella	3/2/10	6.93	9.8	42	61.36	11.2	3.10	0.062	3.4	3.5	ND

ND: Non-detect   J: Estimate

Appendix C. Mercury Data Summaries

Table C-1. Summary Statistics for Total and Methylmercury Concentrations.

Total Mercury (ng/L)				
	Tea	Palmquist	Umbrella	All streams
Average	9.57	6.28	4.54	6.80
Median	9.01	6.03	3.90	6.75
Range	7.25 - 12.80	3.77 - 8.98	2.15 - 8.52	2.15 - 12.80
Methylmercury (ng/L)				
	Tea	Palmquist	Umbrella*	All streams*
Average	0.114	0.108	0.402 (0.083)	0.208 (0.103)
Median	0.095	0.095	0.077 (0.068)	0.090 (0.087)
Range	ND - 0.348	ND - 0.383	0.057 - 2.63	ND - 2.63
Percent Methylmercury				
	Tea	Palmquist	Umbrella*	All streams*
Average	1.3%	1.9%	6.1% (2.5%)	3.0% (1.9%)
Median	1.0%	1.7%	2.5% (2.0%)	1.6% (1.6%)
Range	0.1 - 4.7%	0.1 - 6.1%	1.0 - 31.5%	0.1 - 31.5%

* Parentheses excludes methylmercury outlier (2.63).

Table C-2. Hourly Total and Methylmercury Fluxes (mg/hr/km^2) during Sampling Events. (Note methylmercury units.)

Date	Total Mercury (mg/hr/km^2)			Methylmercury (mg/hr/km^2)*100		
	Tea	Palmquist	Umbrella	Tea	Palmquist	Umbrella
9/23/2009	0.07	0.06	0.03	0.34	0.34	0.15
10/20/2009	0.69	0.28	0.78	0.75	0.50	2.72
11/17/2009*	5.73	4.21	9.55	0.64	0.51	300.28
12/14/2009	0.07	-	0.28	0.14	-	0.83
1/12/2010*	5.46	2.86	12.44	0.46	0.32	12.42
1/26/2010	0.83	0.81	0.95	0.72	0.81	1.51
2/9/2010	0.21	0.20	0.42	0.21	0.37	0.64
3/2/2010	0.30	0.41	0.71	0.29	0.65	1.41
Average	1.67	1.26	3.14	0.44	0.50	40.00
Median	0.49	0.41	0.74	0.40	0.50	1.46

* Methylmercury non-detects were estimated as 0.01 ng/L, 1/5 the value of reporting limits.

Appendix D. Rainfall at Ozette Ranger Station, April 2009 - March 2010

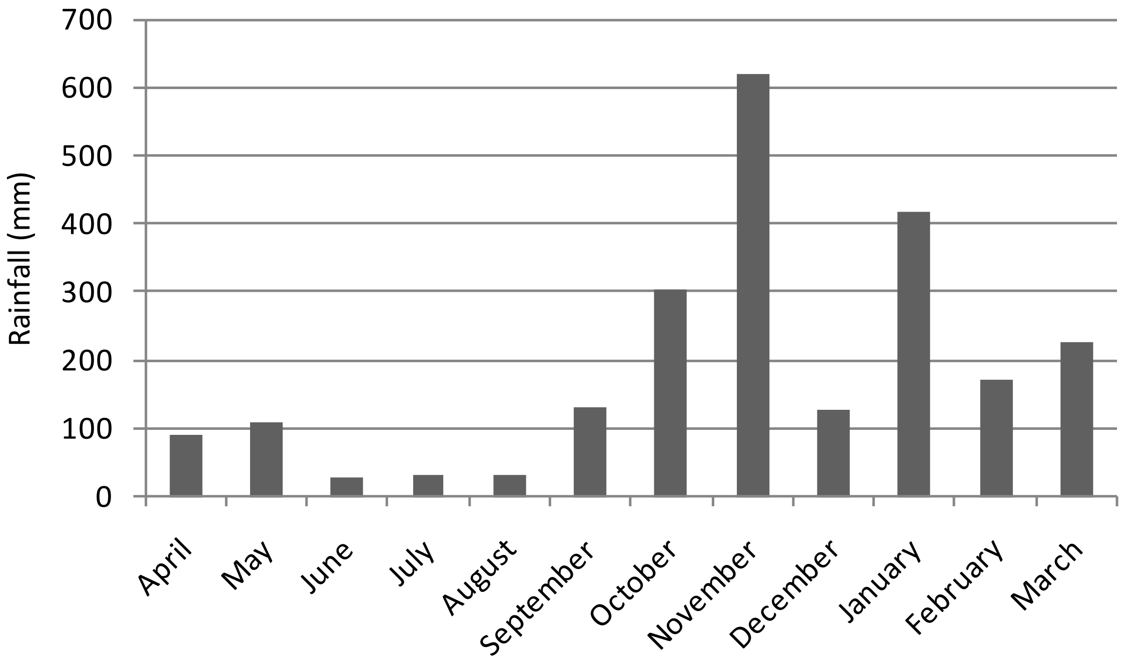

Figure D-1. Rainfall at Ozette Ranger Station, 4/01/09 – 3/31/10.

Appendix E. Umbrella Creek Total Mercury Concentration Modeling

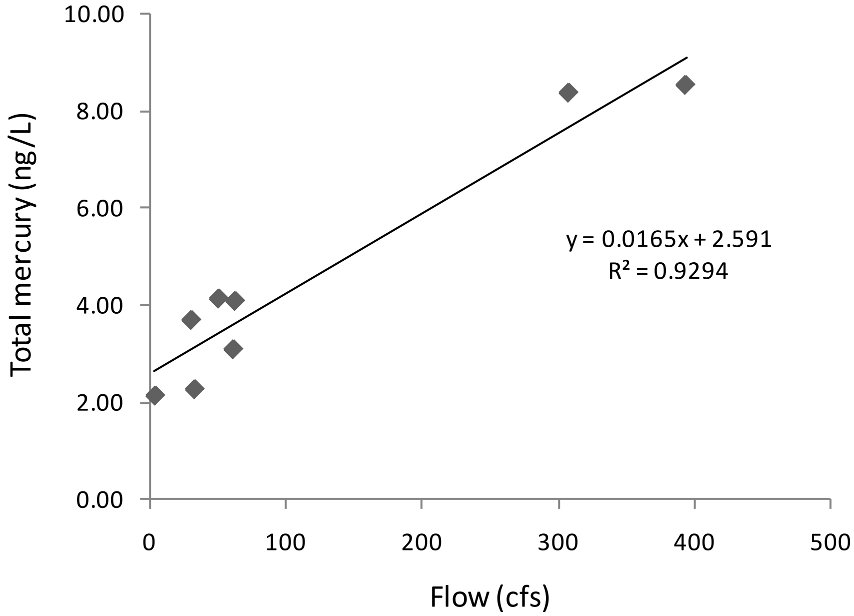

Figure E-1. Linear Relationship between Total Mercury Concentration and Flow.

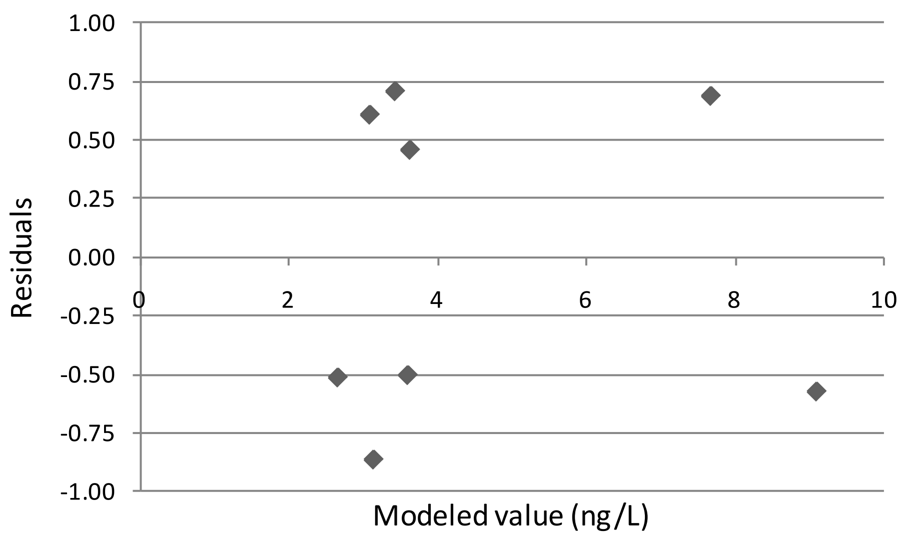

Figure E-2. Residuals Plot for Linear Regression Shown in Figure E-1.

Appendix F. Quality Assurance Data

Table F-1. Measurement Quality Objectives.

Analysis	Method Blank	LCS (%)	Duplicates (%)	Matrix Spikes (%)
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	RPD ≤ 25	75-125
DOC	< 1 mg/L	80-120	RPD ≤ 25	75-125
TSS	-	80-120	RPD ≤ 25	-

LCS: Laboratory Control Sample.
RPD: Relative Percent Difference.

Field Replicates

Table F-2. Total and Methylmercury.

Work order	Lab #	Field ID	Date of sample	THg (ng/L)	RPD (%)	MeHg (ng/L)	RPD (%)
910059	01 04	TEACRK	10/20/09	12.80 12.00	6.5	0.140 0.138	1.4
	02 05	PMQCRK		5.18 5.88	12.7	0.092 0.083	10.3
	03 06	UMBCRK		4.14 3.43	18.8	0.145 0.157	7.9
912039	01 04	TEACRK	12/14/09	7.25 7.25	0.0	0.140 0.143	2.1
	02 05	PMQCRK		3.77 3.89	3.1	0.104 0.095	9.0
	03 06	UMBCRK		2.28 2.22	2.7	0.068 0.068	0.0
1002041	01 04	TEACRK	2/9/10	8.74 8.49	2.9	0.087 0.085	2.3
	02 05	PMQCRK		5.74 5.42	5.7	0.105 0.094	11.1
	03 06	UMBCRK		3.70 2.90	24.2	0.057 0.061	6.8
				Average	8.5		5.7

Table F-3. Ancillary Lab Parameters.

Work order	Lab #	Field ID	Date of sample	DOC (mg/L)	RPD (%)	TOC (mg/L)	RPD (%)	TSS (mg/L)	RPD (%)
910059	01 04	TEACRK	10/20/09	42.0 41.9	0.2	42.1 41.0	2.6	1 U 1	NC
	02 05	PMQCRK		14.7 14.8	0.7	14.8 14.5	2.0	1 1 U	NC
	03 06	UMBCRK		5.4 5.4	0.0	5.4 5.7	5.4	3 2	40.0
912039	01 04	TEACRK	12/14/09	21.8 21.1	3.3	21.1 20.7	1.9	1.0 U 1.0 U	NC
	02 05	PMQCRK		7.8 7.8	0.0	7.7 7.7	0.0	1.0 U 1.0 U	NC
	03 06	UMBCRK		2.3 2.3	0.0	2.3 2.4	4.3	1.0 U 1.0 U	NC
1002041	01 04	TEACRK	2/9/10	29.5 30.3	2.7	27.7 27.6	0.4	1.0 U 1.0 U	NC
	02 05	PMQCRK		12.4 12.5	0.8	12.3 12.3	0.0	1.0 U 1.0 U	NC
	03 06	UMBCRK		3.7 3.6	2.7	3.7 3.7	0.0	1.0 U 1.0 U	NC
				Average	1.2		1.8		40.0

U: Not detected at concentration shown.
NC: Not calculated.

Field Blanks

Table F-4. Field Blanks for all Parameters.

Work order	Lab #	Station	Field ID	Date of sample	THg (ng/L)	MeHg (ng/L)	DOC (mg/L)	TOC (mg/L)
910059	07	Blank	OZEBLK	10/20/09	0.50 U	0.050 U	1.0 U	1.0 U
912039	07	Blank	OZEBLK	12/14/09	0.50 U	0.050 U	1.0 U	1.0 U
1002041	07	Blank	OZEBLK	2/9/10	0.16	0.050 U	1.0 U	1.0 U

U: Not detected at concentration shown.

Lab Duplicates

Table F-5. Lab Duplicates.

Work Order	Lab Number	Analyte	Sample Concentration (ng/L)	Duplicate Concentration (ng/L)	RPD (%)
0909069	F910062-DUP1	MeHg	ND	ND	NC
0910059	F910159-DUP1		0.092	0.097	5.0
0911042	F912007-DUP1		ND	ND	NC
0912039	F912095-DUP1		0.185	0.161	13.9
1001037	F001069-DUP1		ND	ND	NC
	F001091-DUP1		ND	0.054	NC
1001074	F002045-DUP1		ND	ND	NC
1002041	F002083-DUP1		1.202	1.055	13.0
1003040	F003057-DUP1		0.136	0.122	11.0
				Average	10.7
0909069	F910124-DUP1	THg	1.59	1.71	7.5
0910059	F911095-DUP1		12.04	14.2	16.4
0911042	F911156-DUP1		51.33	49.24	4.2
0912039	F912135-DUP1		3.77	3.98	5.5
1001037	F001092-DUP1		155.6	155.6	0.0
1001074	F002115-DUP1		4.78	4.57	4.5
1002041	F002114-DUP1		1166	1122	3.9
1003040	F003148-DUP1		7.11	6.41	10.4
				Average	6.5
0909069	B091237-DUP1	TOC	1.1	1.1	1
0910059	B09K045-DUP1		2.4	2.3	5
0911042	B09K231-DUP1		2.9	2.9	1
0912039	B09L201-DUP1		1U	1U	NC
1001037	B10A105-DUP1		1.7	1.7	2
1001074	B10B089-DUP1		1.6	1.6	0.7
1002041	B10B098-DUP1		1.6	1.6	3
1003040	B10C111-DUP1		4	4	0.2
				Average	1.8
0909069	B091236-DUP1	TSS	18	19	7
	B091236-DUP2		5	4	9
0910059	B09J234-DUP1		16	17	8
	B09J234-DUP2		29	32	11
	B09J260-DUP1		64	71	11

Work Order	Lab Number	Analyte	Sample Concentration (ng/L)	Duplicate Concentration (ng/L)	RPD (%)
	B09J260-DUP2	TSS	14	14	0.08
	B09J260-DUP3		134	137	2
0911042	B09K198-DUP1	TSS	122	122	0.004
	B09K198-DUP2		573	648	12
	B09K198-DUP3		374	347	8
0912039	B09L143-DUP1		41	47	13
	B09L143-DUP2		22	25	9
1001037	B10A102-DUP1	TSS	30	30	0.4
	B10A102-DUP2		310	316	2
	B10A102-DUP3		307	309	0.6
1001074	B10A187-DUP1	TSS	18	20	9
	B10A187-DUP2		19	20	6
1002041	B10B097-DUP1	TSS	13	29	73
	B10B097-DUP2		5	5	12
1003040	B10C033-DUP1	TSS	222	226	2
	B10C033-DUP2		99	100	0.4
	B10C033-DUP3		307	294	4
				Average	9.2
1003040	B10C110-DUP1	DOC	26	26.4	1
				Average	1.0

ND: Not detected.
NC: Not calculated.

Matrix Spike Matrix Spike Duplicates

Table F-6. Matrix Spikes and Matrix Spike Duplicates.

Work Order	Lab Number	Analyte	Sample Concentration (ng/L)	Spike Added (ng/L)	MS Concentration (ng/L)	MS Recovery (%)	RPD (%)
0909069	F910062-MS/MSD1	MeHg	ND	2.00	2.02	101	4.68
					1.93	96.3	
0910059	F910159-MS/MSD1		ND	2.00	2.37	119	12.4
					2.10	105	
0911042	F912007-MS/MSD1		0.197	2.00	2.36	108	2.39
					2.42	111	
0912039	F912095-MS/MSD1		0.275	2.00	2.53	113	1.53
					2.57	115	
	F912095-MS/MSD2		0.155	2.00	2.37	111	1.02
					2.35	110	
1001037	F001069-MS/MSD1		ND	2.00	2.30	115	6.07
					2.44	122	
	F001091-MS/MSD1		0.028	2.00	2.46	122	13.8
					2.83	140	
1001074	F002045-MS/MSD1		ND	2.00	2.18	109	5.57
					2.06	103	
1002041	F002083-MS/MSD1		ND	2.00	2.11	106	2.7
					2.17	109	
1003040	F003057-MS/MSD1		ND	2.00	2.18	109	8.7
					2.00	99.9	
					Average	111.21	5.89
0909069	F910124-MS/MSD1	THg	3.87	10.20	15.88	118	6.48
					14.88	108	
	F910124-MS/MSD2		165600.00	510000.00	695800.00	104	0.714
					700700.00	105	
0910059	F911095-MS/MSD1		12.76	21.00	35.71	109	0
					35.71	109	
0911042	F911156-MS/MSD1		51.33	102.00	174.50	121	5.53
					165.20	112	
0912039	F912135-MS/MSD1		7.25	20.40	27.78	101	0
					27.78	101	
1001037	F001092-MS/MSD1		172.10	400.00	575.50	101	2.36
					562.10	97.5	
	F001092-MS/MSD2		24.92	51.00	73.75	95.7	0

Work Order	Lab Number	Analyte	Sample Concentration (ng/L)	Spike Added (ng/L)	MS Concentration (ng/L)	MS Recovery (%)	RPD (%)
					73.75	95.7	
1001074	F002115-MS/MSD1	THg	14.37	20.00	34.11	98.7	0.788
					33.84	97.3	
	F002115-MS/MSD2		6.00	20.00	25.99	99.9	1.22
					26.30	102	
1002041	F002114-MS/MSD1		211.60	1010.00	1198.00	97.6	4.64
					1254.00	103	
1003040	F003148-MS/MSD4		6.06	20.40	23.35	94.6	12
					28.59	110	
	F003148-MS/MSD5		30.79	102.00	139.90	107	8.94
					128.00	95.3	
	F003148-MS/MSD6		45.01	204.00	240.40	95.8	7.88
					260.20	105	
	F003148-MS/MSD7		3.29	12.75	15.05	92.2	0
					15.05	92.2	
	F003148-MS/MSD8		4.14	25.50	29.31	98.7	0.837
					29.56	99.7	
					Average	102.23	3.43
0909069	B091237-MS1	TOC	0.9	2.50	3.40	99	
0910059	B09KO45-MS1		5.2	2.50	7.70	98	
0911042	B09K231-MS1		2.9	2.50	4.70	100	
0912039	B09L201-MS1		0.6	2.50	3.10	99	
1001037	B10A105-MS1		3.4	2.50	5.60	86	
1001074	B10B089-MS1		1.6	2.50	4.20	104	
1003040	B10C111-MS1		4	2.50	6.70	108	
					Average	99.1	
1003040	B10C110-MS1	DOC	18.8	2.50	21.40	102	
					Average	102.0	

MS: Matrix Spike.
ND: Not detected.

Laboratory Control Samples/ Laboratory Control Sample Duplicates

Table F-7. Laboratory Control Samples/ Laboratory Control Sample Duplicates.

Work Order	Lab Number	Analyte	Spike Added (ng/L)	LCS Concentration (ng/L)	LCS Recovery (%)	RPD (%)
0909069	F910062-BS/BSD1	MeHg	2.000	2.195	110.0	12.7
				1.933	96.7	
0910059	F910159-BS/BSD1		2.000	2.242	112.0	2.2
				2.194	110.0	
0911042	F912007-BS/BSD1		2.000	1.974	98.7	0.7
				1.989	99.4	
0912039	F912095-BS/BSD1		2.000	2.032	102.0	19.1
				1.678	83.9	
1001037	F001069-BS/BSD1		2.000	1.856	92.8	24.4
				2.372	119.0	
	F001091-BS/BSD1		2.000	2.212	111.0	1.2
				2.186	109.0	
1001074	F002045-BS/BSD1		2.000	1.642	82.1	13.4
				1.878	93.9	
				Average	101.5	10.5
0909069	F910124-BS/BSD1	THg	15.679	15.740	100.0	1.3
				15.940	102.0	
	F910124-BS/BSD2		5.000	5.080	102.0	2.3
	F910124-BS/BSD3			5.080	102.0	
	F910124-BS/BSD4			4.990	99.7	
0910059	F911095-BS/BSD1		15.679	15.490	98.8	3.3
				16.010	102.0	
0911042	F911156-BS/BSD1		15.679	15.880	101.0	1.3
				16.090	103.0	
0912039	F912135-BS/BSD1		15.679	15.810	101.0	0.8
				15.930	102.0	
1001037	F001092-BS/BSD1		15.679	15.160	96.7	0.0
				15.160	96.7	
	F001092-BS/BSD2		5.000	4.800	96.1	2.6
	F001092-BS/BSD3			4.680	93.6	
1001074	F002115-BS/BSD1		15.679	14.810	94.4	4.0
				15.420	98.3	
	F002115-BS/BSD2		5.000	4.740	94.8	3.3
	F002115-BS/BSD3			4.900	98.0	
1002041	F002114-BS/BSD1		15.679	15.890	101.0	0.8

Work Order	Lab Number	Analyte	Spike Added (ng/L)	LCS Concentration (ng/L)	LCS Recovery (%)	RPD (%)
		THg		16.020	102.0	
1003040	F003148-BS/BSD1		15.679	15.950	102.0	9.1
				14.560	92.9	
				Average	99.1	2.6
0909069	B091237-BS1	TOC	5.000	4.900	98.0	
0910059	B09K045-BS1		5.000	4.900	99.0	
0911042	B09K231-BS1		5.000	5.000	99.0	
0912039	B09L201-BS1		5.000	4.900	98.0	
1001037	B10A105-BS1		5.000	4.900	98.0	
1001074	B10B089-BS1		5.000	5.000	99.0	
1002041	B10B098-BS1		5.000	4.900	97.0	
1003040	B10C111-BS1		5.000	4.800	95.0	
				Average	97.9	
0909069	B091236	TSS	49.900	48.000	97.0	
0910059	B09J234-BS1		50.300	50.000	99.0	
	B09J260-BS1		50.100	51.000	102.0	
	B09J260-BS2		50.100	53.000	105.0	
0911042	B09K198-BS1		50.600	52.000	102.0	
0912039	B09L143-BS1		50.000	49.000	99.0	
1001037	B10A102-BS1		50.100	51.000	102.0	
1001074	B10A187-BS1		51.500	51.000	98.0	
1002041	B10B097-BS1		50.200	49.000	98.0	
1003040	B10C033-BS1		50.000	48.000	96.0	
				Average	99.8	
0909069	B091237-BS1	DOC	5.000	4.890	98.0	
0910059	B09K046-BS1		5.000	4.920	98.0	3.0
	B09K046-BSD1		5.000	5.090	102.0	
	B09K112-BS1		5.000	4.910	98.0	0.3
	B09K112-BSD1		5.000	4.930	99.0	
0911042	B09K230-BS1		5.000	4.950	99.0	0.7
	B09K230-BSD1		5.000	4.980	100.0	
0912039	B10A002-BS1		5.000	5.170	103.0	2.0
	B10A002-BSD1		5.000	5.050	101.0	
1001037	B10A100-BS1		5.000	4.940	99.0	0.0
	B10A100-BSD1		5.000	4.940	99.0	
1001074	B10B090-BS1		5.000	4.930	99.0	0.1

Work Order	Lab Number	Analyte	Spike Added (ng/L)	LCS Concentration (ng/L)	LCS Recovery (%)	RPD (%)
	B10B090-BS1D	DOC	5.000	4.930	99.0	
1002041	B10B090-BS1		5.000	4.930	99.0	0.1
	B10B090-BSD1		5.000	4.930	99.0	
	B10B098-BS1		5.000	4.870	97.0	
1003040	B10C110-BS1		5.000	4.930	99.0	
				Average	99.3	0.9

LCS: Laboratory Control Sample.

Appendix G. Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

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

Biota: Flora (plants) and fauna (animals).

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: A measure of the amount of oxygen dissolved in water.

Export: Delivery of a substance from terrestrial surfaces in the watershed to a downstream environment.

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

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

Parameter: Water quality constituent being measured (analyte). 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.

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

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

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

Speciated mercury: Total mercury and methylmercury.

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

Total suspended solids (TSS): The suspended particulate matter in a water sample as retained by a filter.

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.

Acronyms and Abbreviations

Cond	Conductivity
DO	Dissolved oxygen
DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GIS	Geographic Information System software
Hg	Mercury
MeHg	Methylmercury
MEL	Manchester Environmental Laboratory
MFM	Makah Fisheries Management
MQO	Measurement quality objective
ONP	Olympic National Park
PBT	Persistent, bioaccumulative, and toxic substance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
THg	Total mercury
TOC	Total organic carbon
TSS	Total suspended solids
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft	feet
g	gram, a unit of mass
km	kilometer, a unit of length equal to 1,000 meters.
mg	milligrams
mg/hr	milligrams per hour
ng/L	nanograms per liter (parts per trillion)
$\mu g/m^2/yr$	micrograms per m^2 per year