



Quality Assurance Project Plan

Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores

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Abstract

The Washington State Legislature provided funding in 2005 to the Washington State Department of Ecology (Ecology) *Persistent, Bioaccumulative and Toxics (PBT) Reduction Strategy* to develop a long-term monitoring program for mercury in freshwater systems. The primary objective of this project is to evaluate mercury deposition through the use of age-dated sediment cores.

All lakes in Washington are likely being impacted by the global pool of atmospheric mercury. Selection of lakes to include in the study will be based on potential impacts from local sources of mercury and other issues of importance to local and state environmental managers. A total of three lakes will be evaluated each year of the study.

During the summer of 2006, Ecology will collect sediment cores and surface sediments from (1) Lake Ozette, located in the northwest corner of the Olympic Peninsula, (2) Lake Sammamish in east King County, and (3) Clear Lake in southeast Thurston County. The three selected lakes will reflect potential impacts from the trans-Pacific transport of mercury from Asia, a large urban/industrial/residential area of Seattle, and the only coal-fired power plant in Washington State, respectively.

Cores will be age dated using lead²¹⁰ techniques. Sediment analysis will include total mercury, total lead, lead²¹⁰, total selenium, total organic carbon, and grain size.

Background

Mercury is a naturally occurring element and also a persistent toxin. The bulk of atmospheric mercury due to natural sources is from volcanic eruptions and ocean emissions (USGS, 2000a). In addition to natural sources, mercury is released into the air and water from anthropogenic (human-caused) sources like coal-fired power plants, cement kilns, medical incinerators, and other industries.

According to the United States Environmental Protection Agency (EPA), natural sources of mercury account for about one-third of the global source pool (EPA, 1997), although a high level of uncertainty was identified with this estimate. The uncertainty of EPA's estimate is largely due to the amount of mercury circulating around the earth released years ago when mercury was common in industrial, commercial, and even residential products and processes. These anthropogenic sources are estimated to account for the remaining two-thirds.

Natural sources tend to emit mercury in the elemental form. A significant fraction of mercury discharged from coal-fired plants, the largest anthropogenic source in the United States (NESCAUM, 2003), is ionic and particulate-bound mercury. These latter two forms of mercury are much more likely to be deposited locally or regionally through wet and dry deposition.

Mercury has been linked to brain, neurological, and kidney damage, so limiting anthropogenic sources is important to human health (ATSDR, 1999).

In efforts to reduce human exposure to long-lasting toxins that bioaccumulate in tissue, a *Persistent, Bioaccumulative Toxins (PBT) Reduction Strategy for Washington State* (Gallagher, 2000) was developed by the Washington State Department of Ecology (Ecology) in 2000. Mercury was the first priority pollutant chosen by the state to be addressed under the PBT strategy, resulting in development of a *Washington State Mercury Chemical Action Plan* (Peele et al., 2003).

In 2005 the Washington State Legislature funded a long-term monitoring program for mercury in freshwater. Two lines of investigation were identified for study.

1. One study will investigate mercury trends in fish tissue (Seiders, 2006; www.ecy.wa.gov/pubs/0603103.pdf) by collecting and analyzing fish from six lakes around the state each year. The study will evaluate temporal and spatial patterns of mercury in fish tissue.
2. A second study, described in this Quality Assurance (QA) Project Plan, will evaluate mercury deposition. Historical and recent mercury deposition in lake sediments will be evaluated by collecting sediment cores and surface sediments from lakes around the state potentially impacted by sources of mercury.

Other Studies on Mercury in Sediment Cores

Very few sediment core studies have been conducted to study mercury trends in Washington lakes. Ecology, in cooperation with the U.S. Geological Survey (USGS), conducted a study of Lake Whatcom, collecting one sediment core from each of the lake's three basins. Norton (2004) reported that core profiles suggest mercury concentrations began to increase from background levels around 1900 in Lake Whatcom. Mercury steadily increased in the lake, reaching peak levels between 1987 and 1995. Results suggest that mercury concentrations in sediments have leveled off or may be decreasing.

A companion study was conducted by the USGS (Paulson, 2004) in cooperation with the Whatcom County Health Department. A total of five additional Whatcom County lakes were evaluated for mercury trends by use of sediment cores. The additional studied lakes included Lake Terrell, Lake Samish, Baker Lake, Wisner Lake, and Fazon Lake. Paulson reported mercury concentrations in dated sediment core samples indicated that increases in mercury sedimentation were largest in the first half of the 20th century. Most of the increases in mercury sedimentation occurred before major facilities emitting mercury to the atmosphere began operating in Whatcom County. This finding suggests the general global source pool of mercury resulting from the industrial revolution was responsible for a significant amount of the loading to the lakes during the first half of the 20th century.

In this study, Paulson found decreases in mercury for recently deposited sediments in both Samish Lake and Fazon Lake. Terrell Lake had increasing levels of mercury up through 1958, but levels between 1968 and 1989 remained fairly constant, while the levels over the last eight years were slightly lower. Wisner Lake appeared to have disturbances in the sediment record, and Baker Lake's core was unable to reach native sediment prior to impounding, so these two lakes were not interpreted.

The USGS (USGS, 2000b) conducted a national study of 56 lakes. Lake Washington and Lake Ballinger north of Lake Washington were included in the study. Sediment cores were dated, and chemical analysis consisted of toxics substances and metals. Study data suggest Lake Washington sediment concentrations may have been influenced by the ASARCO copper smelter located in Ruston, Washington near Tacoma. Mercury concentrations increased above background in the early 20th century. Between 1930 and 1970, levels appeared to be fairly constant and then began to fall. Lake Ballinger's mercury sediment record was only taken back to the 1960s. The trend data showed increases through the 1990s, although the sources causing the increases are not currently known.

Project Description

Goal and Objectives

The goal of this study is to determine the historical trends of mercury deposition in sediments from lakes throughout Washington State. The specific objectives are to:

- Evaluate mercury deposition trends in lake sediments in different areas of the state by analysis of age-dated sediment cores from three Washington lakes per year.
- Determine recent mercury deposition in lakes by sampling and analysis of surface sediments to help select lakes for the companion study of mercury trends in freshwater fish (Seiders, 2006).

Study Site Selection

The extent of the study area includes all of Washington State. Three lakes will be selected for sediment coring and collection of surface sediments each year of the project. In year one, study lakes will be selected from the west side of the state. In year two, lakes from eastern Washington will be selected. Subsequent years of the study will include a mix of both western and eastern Washington lakes each year.

Selection of lakes for coring will be based on proximity to mercury sources and potential influences including both local deposition and global transport. When targeting specific sources, lakes as close as possible to the emission of mercury will be evaluated for inclusion to the study. Recent information on airborne mercury from power plant emissions has suggested soluble forms may be scrubbed from the atmosphere and deposited within days, close to the source (Lubick, 2006).

Below is a list of the primary and secondary considerations for inclusion of lakes to the study.

Primary

- Statewide coverage
- Proximity to known mercury sources
- Lake depositional patterns
- A developed access for Ecology's sampling platform

Secondary

- A review of results from the previous years coring
- Results from other mercury studies, including Ecology's mercury in fish study
- Discussions with regional resource managers
- Potential for undisturbed sediments
- Physical features of the lake and drainage
- Results to fill data gaps

Selection of lakes will be finalized in May of the study year. In the first year of the study, lakes will include Lake Ozette, Lake Sammamish, and Clear Lake (see Figure 1).

1. Lake Ozette, located in the northwest corner of the Olympic Peninsula, was selected to represent background levels (global sources) of mercury in lake sediments for Washington State. Results from Lake Ozette will reflect mostly the global trans-pacific transport of mercury from a lake largely isolated from local industrial or urban impacts.
2. Lake Sammamish, located adjacent to the Seattle metropolitan area, will be included to provide information on mercury deposition near a large urban/industrial area.
3. Clear Lake, in southeast Thurston County, reflects impacts due to a coal-fired power plant. TransAlta located near Centralia is currently the only coal-fired power plant in Washington State.

The overall plan is to sample three lakes per year for five years. At the end of five years the program will be re-evaluated. It may be decided at the end of five years that the study will be modified or that the companion fish and sediment studies be combined.

Waterbody Descriptions

Lake Ozette

The most westerly lake in the continental United States and the third largest natural lake in Washington State, Lake Ozette is located in the northwest corner of the Olympic Peninsula, within the coastal strip of the Olympic National Park. Lake Ozette is in Water Resource Inventory Area (WRIA) 20. Roughly a mile and one half from the Pacific Ocean in western Clallam County, Lake Ozette is about 21 miles from the nearest town, Sekiu. Situated in the remote northwest region of the Olympic Peninsula, the lake is generally isolated from impacts from urban/industrial centers of the Puget Sound basin.

Eight miles long by five miles wide, the lake has a surface area of 11.6 square miles and drainage area of 77.5 square miles. Lake Ozette is a deep lake with a mean depth of 130 feet and a maximum depth of 320 feet. A number of surface water flows contribute to the lakes volume, with the largest including Big River, Crooked Creek, Umbrella Creek, South Creek, and Siwash Creek. Numerous smaller named and unnamed perennial and ephemeral streams also contribute to the total input to the lake. Outflow is to the Pacific Ocean by way of Ozette River discharging from the lake's north end.

Land use in the basin is dominated by forest land at 83%. The lake surface accounts for about 16% of the basin area, while residential use is almost non-existent and agriculture is an estimated 1% (Bortleson et.al., 1976a).

Lake Sammamish

Lake Sammamish is a natural lake located about four miles east of Lake Washington in King County, within WRIA 8. Situated at the western edge of the Cascade foothills, the lake is surrounded by several suburbs of Seattle including Issaquah, Sammamish, Bellevue, and Redmond. Elliot Bay and central Puget Sound are about 11 miles from the east lakeshore. Impacts to the lake are likely from the well-established urban area surrounding the lake, in addition to the industrial areas of King County, Seattle, and the historical releases from ASARCO, the copper smelter in Ruston near Tacoma.

Just over eight miles long, the lake averages a little less than one mile wide, with a surface area of 7.6 square miles and a drainage area of 98.4 square miles. Lake Sammamish is a fairly deep lake with a mean depth of 58 feet and a maximum depth of 105 feet (Moshenberg, 2004). Issaquah Creek is the primary tributary to Lake Sammamish, contributing about 70% of the surface water (KCDNR, 1999). Other larger surface water inflows to the lake include Tibbetts Creek and George Davis Creek. A number of smaller named and unnamed perennial and ephemeral streams also contribute to the total input to the lake. Outflow from the lake is to the north into the Sammamish River, draining into Lake Washington's north end.

Land use within the basin is estimated at 40.7% for urban development, 55.8% for mixed forest/vegetative land, and the remaining 3.5% in surface water (Moshenberg, 2004).

Clear Lake

Located in the southeast corner of Thurston County, in the Bald Hills region, this small natural lake is within WRIA 11. Clear Lake is generally without obvious urban/industrial impacts, although located to the northeast of TransAlta, a large coal-fired power plant. Clear Lake is roughly 11 miles from the nearest town, Yelm to the northwest, and about two miles from both the Deschutes River to the south and west, and the Nisqually River and the Pierce County line to the north and east.

About one mile long by one half mile wide, the lake has a drainage area of 2.61 square miles and a surface area of 181 acres. This fairly shallow lake has a mean depth of 19 feet and a maximum depth of 25 feet. There are few surface water inputs contributing to the lake, but at least one perennial unnamed tributary. Outflow is to the north into Toboton Creek, discharging to the Nisqually River.

Land use in the basin is dominated by forest/vegetative land at 87%. The lake surface accounts for 10% of the basin area, while residential suburban land use is only about 3% of the basin. There is no agriculture within the basin. (Bortleson et al., 1976b).

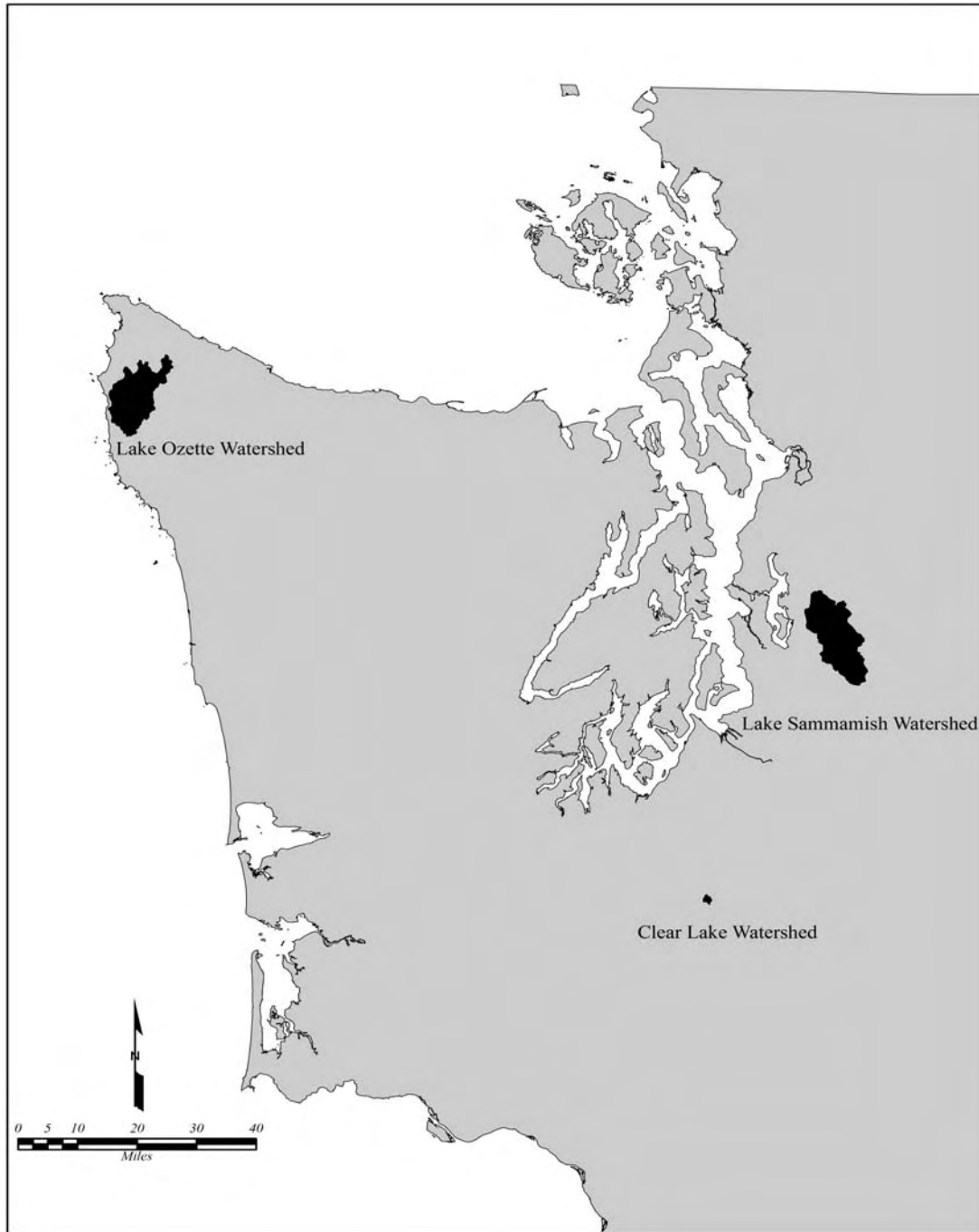


Figure 1. Lakes Selected for Year 1 of the Statewide Mercury Deposition Study.

Organization, Schedule, and Laboratory Budget

Organization

Name	Ecology Affiliation	Role	Phone Contact Information
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SWFAP-HQ = Solid Waste & Financial Assistance Program – Ecology Headquarters

HWTRP-HQ = Hazardous Waste & Toxics Reduction Program – Ecology Headquarters

EAP-WES-TSU - Environmental Assessment Program – Watershed Ecology Section – Toxics Studies Unit

Schedule

Environmental Information System (EIM) Data Set	
EIM data engineer	Brandee Era-Miller
EIM User Study ID	RCOO0007
EIM study name	Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores
EIM completion due	April 2007
Final Report	
Report author lead	Randy Coots
Schedule	
Draft report due to supervisor	January 2007
Draft report due to client/peer	February 2007
Final report due	April 2007

Budget

Estimated laboratory costs for the project are shown in Table 1. All analysis will be conducted at Manchester Environmental Laboratory except radio-dating and grain size. Analyses for radio-dating and grain size will be conducted by an accredited laboratory contracted by Manchester Laboratory.

The laboratory budget for this project is estimated at \$13,290 per year (Table 1). The estimate reflects a 50% discount for analysis conducted at Manchester Laboratory.

Table 1. Summary of the Estimated Annual Laboratory Cost for the Mercury Deposition Study.

Parameter	Cost Per Sample	Number of Samples ¹	Number of QC Samples	Total Number of Samples	Subtotal
Total Mercury	\$40	33	4	37	\$1480
Total Lead	\$44	30	3	33	\$1452
Lead ²¹⁰	\$195 ²	30	3	33	\$6435 ³
Total Selenium	\$40	3	1	4	\$160
Grain Size	\$100	3	3	6	\$600 ³
Total Organic Carbon	\$39	33	3	36	\$1404
25% Manchester Surcharge:					\$1759
Total Cost:					\$13,290

1 = Sample number includes quality control (QC) samples for the project.

2 = Includes calculation of sedimentation rates and age dating.

3 = Additional 25% surcharge is added for contracting services provided by Manchester.

Quality Objectives

Quality objectives for the study are to provide data of sufficient quality, minimize uncertainty, and produce results comparable to data from other recent studies. Meeting these objectives will require careful planning, sampling, measurements, and quality control (QC) procedures described within this plan. A goal of the study is to collect QC samples at a minimum frequency of 10%.

Measurement Quality Objectives

Manchester Laboratories, and laboratories contracted by Manchester Laboratory for analysis of study samples, are expected to meet QC requirements of methods selected for the project. Other equivalent analytical methods may be employed after consultation with the project lead. Table 2 shows the measurement quality objectives (MQOs) and the lowest concentration of interest for the analytical methods selected. Lowest concentrations of interest are those concentrations low enough to meet project objectives within budget limits.

Table 2. Measurement Quality Objectives for the Study of Mercury in Sediment Cores from Selected Washington Lakes.

Parameter	Accuracy (% of True value)	Precision (Duplicate RPD)	Bias (% of True value)	Lowest Concentration of Interest
Total Organic Carbon	-	25	-	1%
Grain Size	-	25	-	0.1%
Total Mercury	± 40% SRM	25	± 40% LCS	0.005 mg/Kg, dry
Total Lead	± 40% SRM	25	± 40% LCS	2 mg/Kg, dry
Total Selenium	± 40% SRM	25	± 40% LCS	0.5 mg/Kg, dry
Lead ²¹⁰	-	25	-	1dpm*/g

RPD = relative percent difference

SRM = standard reference material

LCS = laboratory control samples

*dpm = disintegrations per minute

MQOs may be difficult to achieve for results near the limits of detection. Relative accuracy will decrease when concentrations are near reporting limits and are subject to discretion depending on the results relative to the detection limits. These data will be reviewed by Manchester Laboratory for compliance with criteria. Data qualification will be applied where necessary.

Sampling Process Design

Sediment cores will be collected to evaluate historical trends in mercury deposition and sedimentation rates to lakes around Washington State.

The study area includes all of the state. Three lakes will be sampled each year of the study. Lakes in western Washington will be sampled in year one, while lakes in eastern Washington will be sampled in year two. Subsequent years will have a mix of both east- and west-side lakes. Selection will be based on proximity to known sources and an effort to sample as many different types of areas around the state as possible. Comparisons of sediment core results from various areas of the state will help form a statewide picture of mercury deposition.

In the initial year of the study, sediments will be collected from Lake Ozette on the Olympic Peninsula, Lake Sammamish near the city of Seattle, and Clear Lake in southeast Thurston County.

Because deep locations in lakes should give the best chance of sampling fine sediments in undisturbed areas, cores will be collected at the deepest point possible in each lake (see the Appendix). Bathymetric maps of each lake were reviewed to determine the best area for sample collection.

Analyzing discrete sediment layers from core samples will show the history of mercury deposition. These data, coupled with other information, may be used to predict future concentrations in sediment deposits over time.

Sediment cores will be dated using two methods. Analyzing core sediments for lead²¹⁰ and stable lead as markers allows for a weight of evidence approach (Norton, 2004) to determine sedimentation rates for cores from each lake. Following is a brief description of the two methods:

1. Lead²¹⁰ is primarily formed in the atmosphere, as a decay product of radon gas (²²²Rn). After formation, lead²¹⁰ adsorbs to aerosol particles and is deposited on the surface of land and water. After particulates settle to the bottom of a waterbody, they are incorporated into the sediments. With constant rates of both sedimentation and lead²¹⁰ deposition, and a known half-life for lead²¹⁰, sedimentation rates and date of deposition can be estimated by measuring lead²¹⁰ activity of different depths from a core. Small amounts of ²²²Rn are also present in the sediments. Subtracting this other source of ²²²Rn from the total gives the excess lead²¹⁰, an amount added to the water column from atmospheric sources. By plotting lead²¹⁰ as a function of depth, the slope of the line represents the rate of sedimentation (Schell and Nevissi, 1980).
2. A similar method will be used to assign dates using stable lead. The first appearance of elevated stable lead values in lake sediments occurred in western Washington between 1920 and 1940 (Yake, 2001). With the addition of tetraethyl-lead to gasoline, and possible low-level increases from the ASARCO smelter in Ruston near Tacoma, the peak for stable lead is typically expected around 1975. Sedimentation rates based on stable lead will be determined

by dividing the accumulated mass sedimentation at the mid-point of the interval the peak was found by 31 years (2006 – 1975). The peak will be defined as the mid-point of the sections that values are within 10% of the highest value.

A Wildco 13 cm x 13 cm x 50 cm box core will be used for collecting sediment cores. One centimeter horizons will be sub-sampled from the cores. Horizons will be analyzed for mercury, lead²¹⁰, total lead, and total organic carbon (TOC). Horizons not initially analyzed will be archived for potential analysis at a later date.

The companion study of mercury in fish tissue (Seiders, 2006) proposes collection of surface sediments at sites where fish will be evaluated. In an effort to help the companion study make future lake selections for sampling fish, an additional surface sediment sample will be collected along with the core sample. Core samples have a limited amount of sediments available for analysis from 1 cm horizons. The additional surface samples will be composites of three separate grabs from the top 2 cm by a 0.1 m² van Veen grab sampler. This composite surface sample will also be more comparable with other Ecology sediment studies and other future collection efforts from lakes.

The additional surface sediment sample will be analyzed for mercury, selenium, grain size, and TOC only. Selenium will be included in analysis of the surface sediments. Studies have recently suggested selenium may bind methyl mercury and make it less available to biology.

Sediment sample locations and their associated coordinates are shown in the Appendix.

Sampling Procedures

All sediment stations will be located by differentially corrected Global Positioning System (GPS) systems and recorded in field logs. Specific positioning accuracy is ± 3 meters for the GPS system. Station position relative to significant on-shore structures will also be recorded.

Sediment Cores

Sediment cores will be collected using Ecology's 26-foot research vessel, the RV Skookum, in September 2006. To collect sediment cores, a Wildco stainless steel box corer fitted with a 13 cm x 13 cm x 50 cm acrylic liner will be used. Sedimentation rates reported for several Washington lakes ranged from 0.04 to 0.52 cm/yr (Yake, 2001; Norton, 2004; Coots and Era-Miller, 2005; Serdar, 2003). Based on these rate estimates, the corer will need to reach as close to maximum penetration depth of 50 cm as possible to ensure at least a 100-year record on more productive lakes.

After retrieving the core, overlying water will be carefully siphoned off and the acrylic liner removed from the corer. The sediment-filled liner will be placed on an extruder table outfitted with a gear-driven piston to push sediments up and out of the liner. Sediment layers will be sliced with thin aluminum plates to a uniform thickness of 1 cm. The acrylic liner allows for a maximum of 50 layers per core, though similar sediment core studies of Washington lakes have only been able to retrieve between 25 and 45 1-cm layers (Norton, 2004; Coots and Era-Miller, 2005). Materials in contact with the liner will be excluded from the sample. Each sample layer will be transferred to 8-oz glass jars, placed in plastic bags, and stored in coolers on ice until laboratory processing.

Sediment age will be estimated by analyzing layers for the radioisotope lead²¹⁰ and total lead (Yake, 2001). Sub-samples will be selected for analysis that represent (1) recent conditions (top layer), (2) background conditions which are used to calibrate the lead²¹⁰ dating (bottom layer), and (3) a more concentrated selection of layers in the upper core, with wider spacing between layers moving down through the core. Any significant visual markers in the cores (ash layer) will be recorded in field books. Layers not selected for chemical analysis will be archived frozen for possible analysis later.

Sediment layers selected for analysis will be homogenized prior to dividing for analysis. Homogenized sediments will be split into sub-samples for analysis of mercury (2-ounce glass jars); total organic carbon (2-oz. glass jars); and total lead (2-oz. glass jars), and lead²¹⁰ (polystyrene containers) for dating. A minimum of 20 grams of material will be sub-sampled for each analysis. Samples not immediately analyzed will be kept at Ecology headquarters frozen under chain-of-custody procedures.

Utensils used in collection and manipulation of core samples will be washed thoroughly with tap water and Liquinox detergent, followed by sequential rinses of hot tap water, de-ionized water, and finally, 10% nitric acid. Equipment will then be air dried and wrapped in aluminum foil until used in the field. The same cleaning procedure will be used on the corer prior to going into the field. New acrylic liners will be used for each sediment core, pre-cleaned by washing

thoroughly with tap water and Liquinox detergent, followed by sequential rinses of hot tap water and de-ionized water. To avoid cross-contamination between sample stations, the corer will be thoroughly brushed down with on-site water at the next sample location prior to collection of the subsequent sample.

Surface Sediments

In addition to core samples, one composite surface sediment sample will be collected. To the extent possible, surface sediment sampling methods will follow PSEP (1996) protocols. Surface sediments will be taken immediately following collection of the core samples from the same location, using a 0.1 m² stainless steel van Veen grab. Surface sediment collection will be located within a 10-meter circle of the sediment core, established with the differentially corrected GPS.

Surface sediment samples will be a composite of three grabs from each lake. Following collection of each sediment grab, an evaluation of acceptability will be made. Information about each sediment grab will be recorded in the field log. A grab will be considered acceptable if it is not overfilled, overlying water is present but is not overly turbid, the sediment surface appears intact, and the grab reached the desired sediment depth.

Overlying water will be siphoned off prior to sub-sampling. Equal volumes of the top 2-cm of sediment will be removed from each of the three separate grabs per composite. Stainless steel spoons and bowls will be used for sub-sampling and to homogenize sediments from each station to a uniform consistency and color. Debris on the sediment surface, or materials contacting the sides of the van Veen grab, will not be retained for analysis.

All equipment used to collect surface sediments will be pre-cleaned using the procedure described above for sediment cores. All equipment will be air dried and wrapped in aluminum foil until used in the field. The same cleaning procedure used on sample equipment will be used on the grab prior to going into the field. To avoid cross-contamination between sample stations, the grab will be thoroughly brushed down with on-site water at the next sample location.

Surface sediment samples will be placed in coolers on ice immediately following collection, and transported to Ecology's Manchester Environmental Laboratory. Requirements for containers, preservation, and holding times are listed in Table 3. The chain-of-custody will be maintained throughout the sampling and analysis process.

Table 3. Containers, Preservatives, and Holding Times for Sediment Samples.

Analyte	Container ¹	Preservation	Holding Time
Total Mercury	Certified 2-oz Glass, Teflon Lid Liner	Cool to 4° C	28 Days
Lead ²¹⁰	Polystyrene	Freeze, -18° C Cool to 4° C	na
Total Lead	2-oz Glass	Freeze, -18° C Cool to 4° C	2 Years 6 Months
Total Selenium	2-oz Glass	Freeze, -18° C Cool to 4° C	6 Months
Total Organic Carbon	2-oz Glass or Polyethylene	Freeze, -18° C Cool to 4° C	6 Months 14 Days
Grain Size	Glass or Polyethylene	Cool to 4° C	6 Months

¹ = Containers will be obtained from Manchester Laboratory.

na = Not applicable

Measurement Procedures

All project samples will be analyzed at Manchester Laboratory or a contractor arranged by Manchester. Table 4 presents a list of the number of samples to be analyzed, the expected range of results, desired reporting limits, method description, and analytical method. Manchester and contract laboratories may use other appropriate methods following consultation with the project lead.

Table 4. Analytical Methods for the Statewide Mercury Trends in Lakes Study.

Analysis	Number of Samples ¹	Expected Range of Results	Reporting Limit	Method Description	Analytical Method
Total Mercury	37	0.005-0.50 mg/Kg, dry	0.005 mg/Kg, dry	CVAA	EPA 245.5; MEL SOP ²
Lead ²¹⁰	33	1.0-15.0 dpm/g	1 dpm/g	Gamma Detection	EPA 901.1
Total Lead	33	2-500 mg/Kg dry	2 mg/Kg, dry	ICP ⁴ - MS	EPA 200.8
Total Selenium	4	0.5-200 mg/Kg dry	0.5 mg/Kg, dry	ICP - MS	EPA 200.8
TOC	36	0.1% - 35%	0.1%	Combustion NDIR	PSEP Protocol
Grain Size	6	1% - 100%	1%	Sieve and Pipette	PSEP Protocol

1 = Includes QA samples.

2 = MEL modifications to analytical methods are documented in their Standard Operating Procedures.

3 = Disintegrations per minute/gram.

4 = Inductively coupled argon plasma.

TOC = Total organic carbon

EPA = U.S. Environmental Protection Agency

MEL = Manchester Environmental Laboratory

PSEP = Puget Sound Estuary Program

Quality Control Procedures

Field

No field quality control samples will be collected for this study.

Laboratory

Manchester Laboratory routinely runs laboratory control samples which will be satisfactory for the purposes of this project. The laboratory will follow standard operating procedures as described in the *Quality Assurance Manual for the Washington State Department of Ecology Manchester Environmental Laboratory* (MEL, 2001). Laboratory quality control samples to be analyzed for this project are presented in Table 5.

Table 5. Laboratory Quality Control Samples for the Mercury Trends in Sediment Cores Study.

Analysis	Method Blanks	Check Std./ LCS	MS/MSD	Duplicates
Total Mercury	1/batch	1/batch	1/batch ¹	1/batch
Total Lead	1/batch	1/batch	1/batch	1/batch
Total Selenium	1/batch	1/batch	1/batch ¹	1/batch
Total Organic Carbon	1/batch	1/batch	--	1/batch
Grain Size	--	--	--	1/batch

1 = ERA Priority Pollutant Inorganic lot #247 - a soils standard reference material (SRM). One per batch for the surface sediment samples.

As an indication of bias due to sample preparation, check standards and laboratory control samples (LCS) which contain a known amount of analyte will be analyzed. Analytical precision will be estimated by analysis of laboratory duplicates (split samples). Matrix spikes/matrix spike duplicates indicate bias due to matrix effects and provide an estimate of the precision of results.

Data Management Procedures

All field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets after return from the field. Data entries will be independently verified for accuracy by another member of the project team.

The case narratives included in the data package from Manchester Laboratory will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory quality control results will also be included in the data package. This will include results for laboratory blanks, surrogate recoveries, laboratory duplicates, and matrix spikes. The information will be used to evaluate data accuracy and determine if the projects measurement quality objectives were met.

Field and laboratory data for the project, including contract laboratory data, will be entered into Ecology's Information Management (EIM) system. Laboratory data will be downloaded directly to EIM from Manchester's data management system (LIMS). Data reports from contract laboratories used for the project will be delivered in Excel spreadsheets formatted for input to the EIM system.

Audits and Reports

Manchester Laboratory participates in performance and system audits of their routine procedures. Results of these audits are available by request. A draft report of the study findings will be completed by the project lead in February 2007 and a final report in April 2007. The report will include, at a minimum, the following:

- A map showing all sampling locations and any other pertinent features in the study area.
- Coordinates of each sample site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Results of mercury analysis related to recommended standards.
- Summary tables of the chemical and physical data.
- An evaluation of significant findings which will include mercury trends and sedimentation rates, and comparison of mercury levels between lakes presented in tables and shown on figures.
- Complete set of chemical and physical data and Manchester quality assurance review as an appendix.

Upon study completion, all project data will be entered into Ecology's EIM system. Public access to electronic data and the final report for the study will be available through Ecology's internet homepage (www.ecy.wa.gov).

Data Verification and Validation

Data Verification

Manchester Laboratory's standard procedures for data reduction, review, and reporting will meet the needs of the project. Data packages, including quality control results for analysis conducted by the laboratory and others, will be assessed by laboratory staff. Manchester Laboratory will provide a written report of their data review. This report will include discussion verifying that (1) measurement quality objectives were met, (2) analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions. All data generated from the project will be entered into the EIM database.

Data Validation

The project lead will be responsible for data validation and acceptance of project data. For data analyzed by outside laboratories, Manchester Laboratory will be responsible for data validation. The complete data package, along with the laboratory's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

Data Quality (Usability) Assessment

After the project data have been reviewed, verified, and validated, the project lead will determine if the data are of sufficient quality to make decisions for which the study was conducted. Data from the laboratory's quality control (QC) procedures – as well as results from laboratory blanks, surrogate recoveries, laboratory duplicates, and matrix spikes/matrix spike duplicates – will provide information to determine if measurement quality objectives (MQOs) have been met. Laboratory and quality assurance staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. Relative accuracy generally decreases when concentrations are near reporting limits and will be subject to discretion depending upon the results relative to the detection limits. Manchester's standard operating procedure for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. Laboratory QC results will be reviewed for the determination, which includes assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and success of laboratory QC samples meeting control limits.

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Appendix. Sediment Core Locations

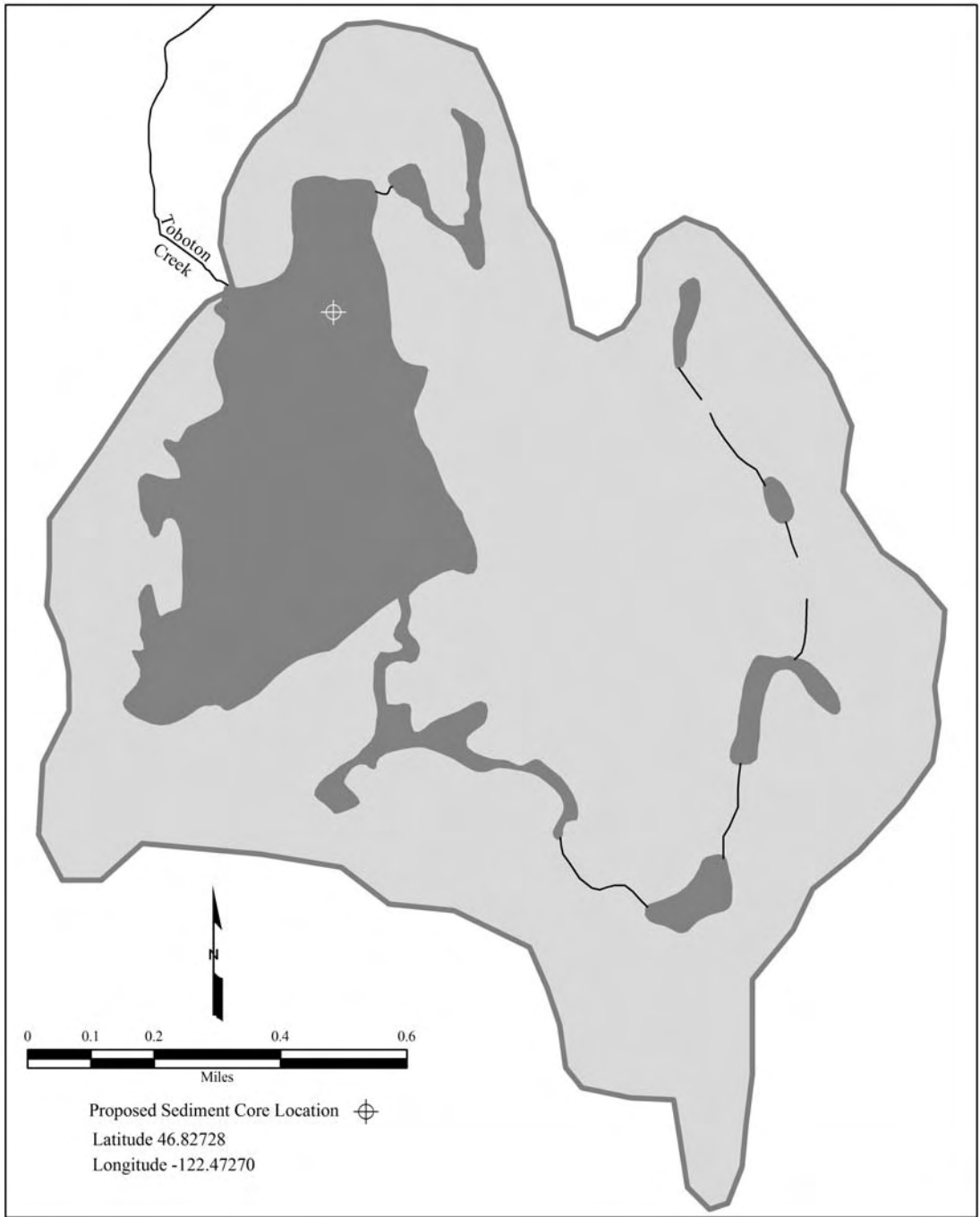


Figure A-1. Clear Lake and Watershed Showing Proposed Sediment Core Location.

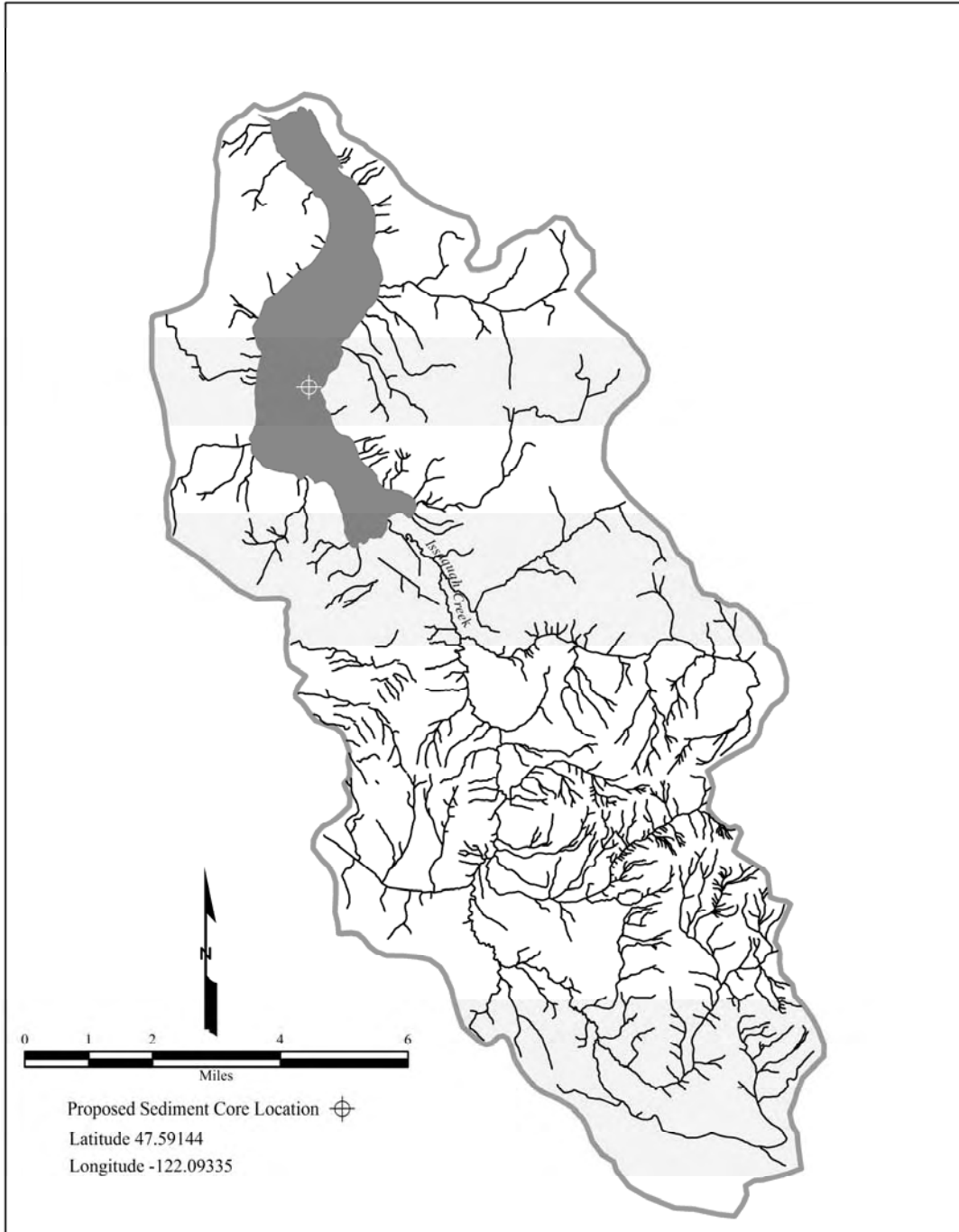


Figure A-2. Lake Sammamish and Watershed Showing Proposed Sediment Core Location

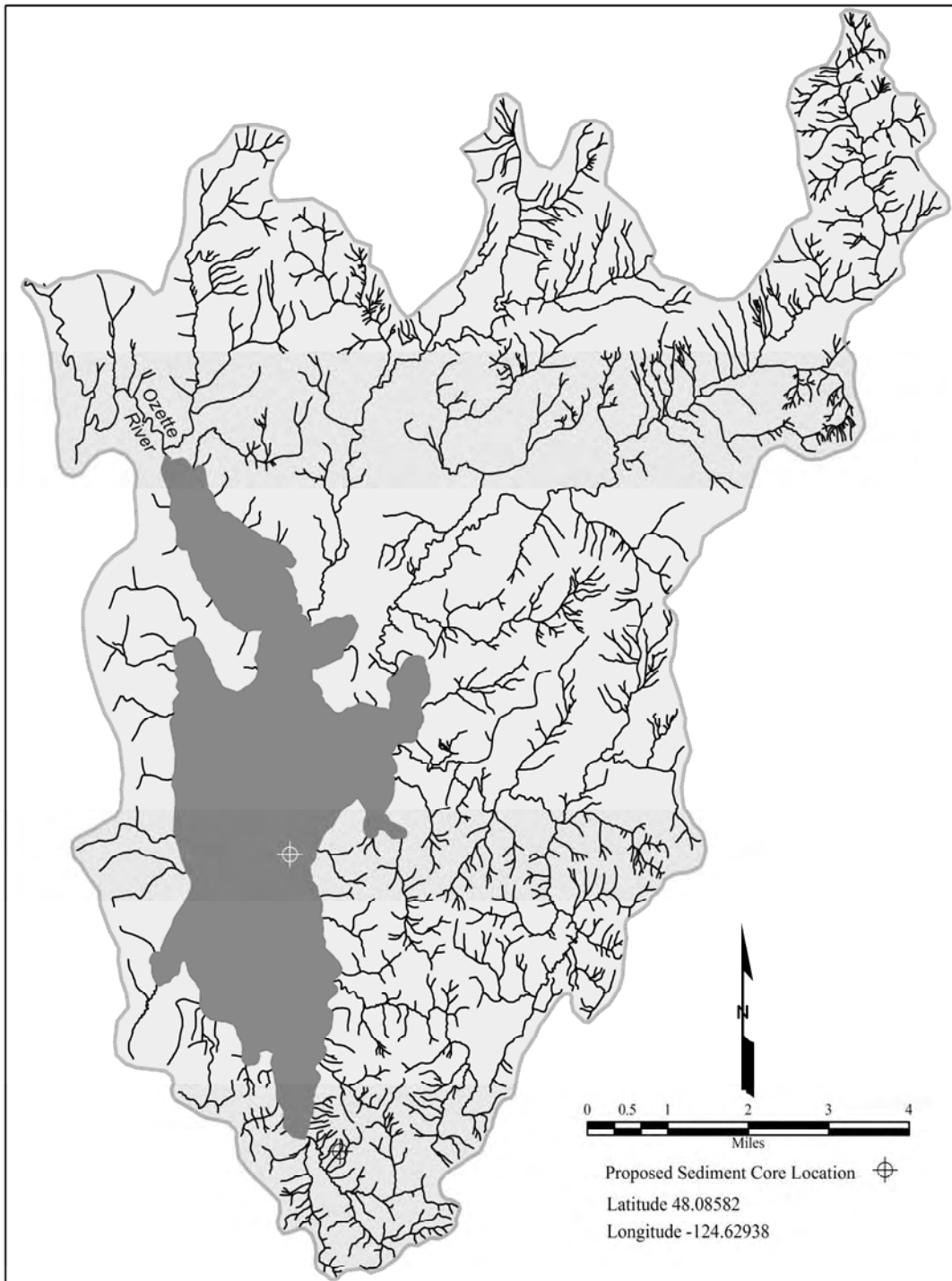


Figure A-3. Lake Ozette and Watershed Showing Proposed Sediment Core Location