# History of Mercury in Selected Washington Lakes Determined from Age-Dated Sediment Cores: 2007 Sampling Results

May 2008

Publication No. 08-03-012

DEPARTMENT OF
ECOLOGY
State of Washington

# Publication Information

This report is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0803012.html

Data for this project are available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, cfur0002.

Ecology's Project Tracker Code for this study is 06-501-02-02.

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Cover photo: Sediment core taken at Walupt Lake in August 2007.

# History of Mercury in Selected Washington Lakes Determined from Age-Dated Sediment Cores: 2007 Sampling Results

*by*
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April 2008

Latitude/Longitude ID Numbers:
Walupt Lake - 1214608464179
Loon Lake - 1176213480448
Wannacut Lake - 1195170488835

Waterbody Numbers:
Walupt Lake - WA-26-9140
Loon Lake - WA-59-9130
Wannacut Lake - WA-49-9350

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# Abstract

In 2005 the Washington State Legislature provided funding to the Washington State Department of Ecology (Ecology) to develop a long-term monitoring program for mercury in freshwater systems. Mercury is the first pollutant to be studied under the state's *Persistent, Bioaccumulative, Toxic Chemicals (PBT) Reduction Strategy*.

This report presents results of the second year of using age-dated sediment cores to evaluate mercury deposition. During August 2007, Ecology collected sediment cores and surface sediments from three lakes: Walupt (Lewis County), Loon (Stevens County), and Wannacut (Okanogan County).

Sediment cores were analyzed for $^{210}$lead, total lead, and mercury; dates were applied to the sediment core using the constant rate of supply (CRS) model. Surface grab samples were analyzed only for mercury.

The *Walupt Lake* sediment core displayed an overall decreasing trend in mercury dry concentrations; however, dates were not applied to the core due to a poor $^{210}$lead signal.

*Loon Lake* sediments have received little mercury contamination over the past 50 years. Mercury flux rates peaked in the mid-1990s at 22 ug/m$^2$/yr and are currently at 15 ug/m$^2$/yr. The flux rate decline detected at Loon Lake is attributed to reduced sedimentation, not reduced atmospheric loading.

*Wannacut Lake* sediments were severely contaminated with lead and mercury from mining activity in the lake's catchment from the late 1800s to 1940. A peak mercury flux of 361 ug/m$^2$/yr was measured in 1932. Contamination stopped abruptly after mining activity ceased within the lake's drainage, and mercury levels dropped accordingly. Flux rates at Wannacut Lake are currently 10 ug/m$^2$/yr.

Mercury concentrations and flux rates are low for all three lakes. The low flux rates can be attributed to the distance of the lakes from human-caused point sources, rural catchments, and low sedimentation.

# Acknowledgements

The author of this report would like to thank the following people for their contribution to this study:

- Fritz Wolff with the Washington State Department of Natural Resources for historical information on Okanogan mining.
- John Colman with the U.S. Geological Survey, and Amy Lavoie with the U.S. Environmental Protection Agency, for help with sample collection and analysis.
- Washington State Department of Ecology staff:
    - Patti Sandvik, Randy Coots, Brenda Nipp, Brandee Era-Miller, Callie Meredith, and Carolyn Lee for help with sample collection, sample processing, and data management.
    - Manchester Environmental Laboratory staff for their help and dedication to analytical services: Leon Weiks, Sarah Sekerak, Dean Momohara, Stuart Magoon, Pam Covey, and others.
    - Dale Norton for guidance and review of the project plan and report drafts.
    - Randy Coots for reviewing the draft report.
    - Joan LeTourneau and Cindy Cook for formatting and editing the final report.

# Introduction

Human exposure to biologically methylated forms of mercury (methylmercury) has prompted governments and health groups to seek ways to reduce exposure to this highly toxic chemical. Mercury contamination is a widespread global phenomena with toxic levels found in remote aquatic ecosystems rendering fish unsuitable for consumption. Mercury is transported and deposited to all reaches of the earth via the atmosphere where it can undergo transformation to methylmercury (Rudd, 1995).

Anthropogenic (human-caused) releases of mercury have severely altered the natural mercury cycle. Sediment core records have indicated that anthropogenic mercury inputs to sediments have increased by a factor of 2-8 (Engstrom and Swain, 1997). Currently, the largest point source of anthropogenic mercury in Washington State is the TransAlta coal-fired power plant in Centralia (USEPA, 2006).

In Washington State, a *Draft Strategy to Continually Reduce Persistent, Bioaccumulative, Toxic Chemicals (PBTs) in Washington State* (Gallagher, 2000) was developed by the Washington State Department of Ecology (Ecology) in 2000. Mercury was the first chemical 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).

A portion of the monitoring project created under the PBT strategy is aimed at learning more about the spatial and temporal trends of mercury in Washington lake sediments. Paleolimnological studies have been a popular way of investigating historical rates of mercury deposition to lake sediments (Gallagher et al., 2004; Kamman and Engstrom, 2002; and Engstrom et al., 2007). Coring studies allow for examination of trends and evaluation of current mercury increases over pre-industrial levels.

The goal of the study is to evaluate historical trends in mercury accumulation statewide through the use of age-dated sediment cores. A complete project plan for the statewide sediment coring effort is described in detail by Coots (2006).

In the second year of this study (2007), Ecology collected and analyzed three single deep sediment cores to determine mercury flux rates to sediments. The three lakes studied in 2007 are Walupt (Lewis County), Loon (Stevens County), and Wannacut (Okanogan County).

## Sediment Core Studies in Washington

Several freshwater sediment coring studies have been conducted for mercury in Washington lakes.

In the first year (2006) of the current study, Ecology examined cores from three lakes in western Washington: Sammamish, Ozette, and St. Clair. Mercury concentrations have significantly declined at Lake Sammamish since the 1940s, while Lake Ozette has experienced a leveling off

of mercury loading, with possible slight declines over the last decade. Mercury levels in sediments at Lake St. Clair have increased during the past 15-20 years (Furl, 2007).

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 mercury concentrations began to increase from background (natural) levels around 1900, steadily increasing in the lake until peaking between 1987 and 1995. Results suggest that mercury concentrations in sediments have leveled off or may be decreasing.

USGS (Paulson, 2004) conducted a companion study in cooperation with the Whatcom County Health Department. Sediment cores were taken from five additional Whatcom County lakes: Terrell, Samish, Baker, Wiser, and Fazon.

Paulson reported that increases in mercury loading were largest in the first half of the 20$^{th}$ century. Most increases in mercury sedimentation occurred before major facilities emitting mercury to the atmosphere began operating in Whatcom County. Paulson concludes that the global reservoir was responsible for the majority of mercury deposition to the lakes during the first half of the 20$^{th}$ century.

The USGS (Van Metre et al., 2004) conducted a national sediment coring study of 56 lakes including Lake Washington and Lake Ballinger. Study data reveal that Lake Washington sediment concentrations were largely influenced by local sources. Mercury concentrations increased substantially above background levels in the early 20$^{th}$ century. Between 1930 and 1970, levels appeared to be fairly constant and then began to fall. The Lake Ballinger sediment core was dated only back to the 1960s. The trends data showed increases to the early 1990s and then decreasing values in more recent years.

Ecology (Yake, 2001) conducted a literature review of the use of sediment cores as a means to track persistent pollutants in Washington State. A total of 11 marine and freshwater studies were reviewed for a variety of contaminants.

## Site Descriptions

Figure 1 displays the locations of the lakes, their bathymetry, and exact coring locations. Table 1 contains information on the catchment area, lake morphology, and precipitation.

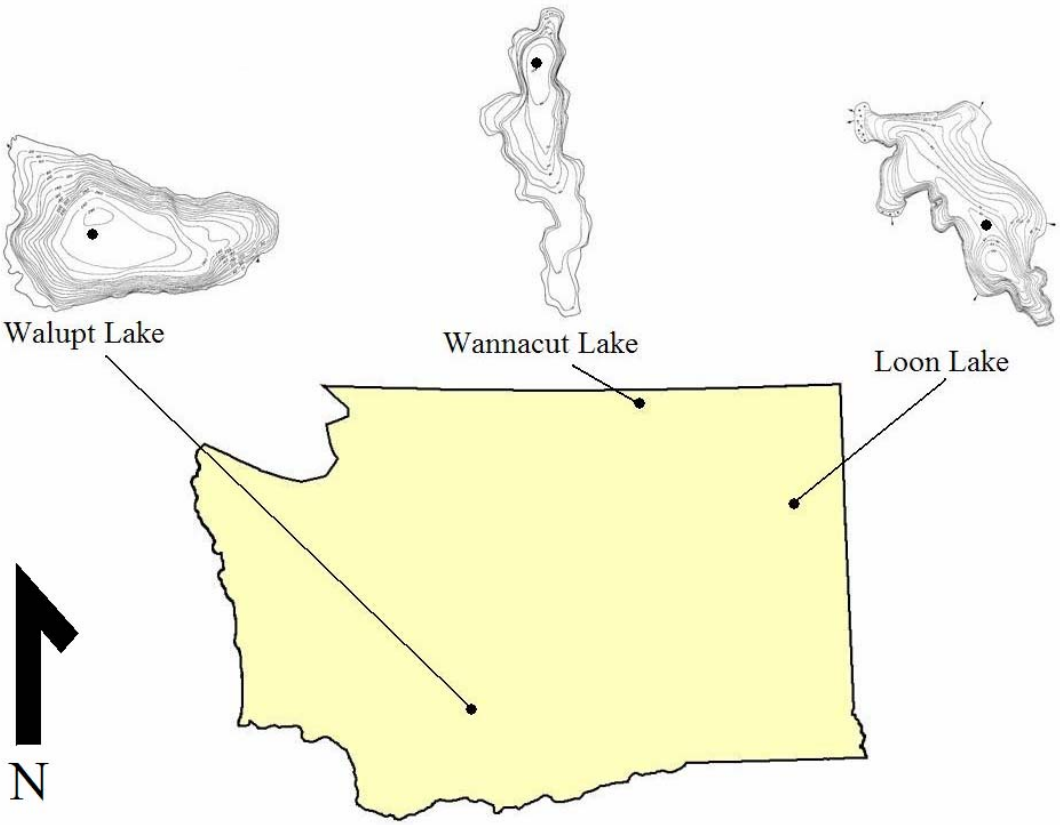


Figure 1. 2007 study lakes.

Table 1. Physical and climatic data for the three study lakes.

| | Walupt | Loon | Wannacut |
|---|---|---|---|
| Surface Area (ac) | 350 | 1100 | 410 |
| Drainage Area (ac) | 8768 | 9024 | 12,200 |
| Volume (ac-ft) | 62,000 | 52,000 | 23,000 |
| Maximum Depth (ft) | 300 | 100 | 160 |
| Mean Depth (ft) | 180 | 46 | 55 |
| DA:SA Ratio[1] | 25.1 | 8.2 | 29.8 |
| Precipitation[2] (mm) | 1637 | 576 | 373 |
| Altitude (ft) | 3926 | 2381 | 1857 |

[1] Drainage Area to Surface Area Ratio.
[2] Precipitation Data provided by PRISM, www.prism.oregonstate.edu/

**Walupt Lake**

Walupt Lake (in Lewis County) is located high in the Cascades 2.5 miles west of the pacific crest within the Gifford Pinchot National Forest. Mt. Adams is located 14.5 miles to the south of the lake, and Mt. St. Helens is 37.5 miles southwest of the lake. Soils in the area are comprised mostly of stony forest soils underlain by igneous rock. Land use in the area is dominated by relatively undisturbed forests with a single road and a campground in the drainage area.

The lake is fed by small ephemeral streams during snow melt and drained by Walupt Creek at its northwestern end. The lake was selected for coring to assess whether natural emissions from Mt. St. Helens (37.5 mi upwind) resulted in elevated lake loading of mercury.

**Loon Lake**

Loon Lake (in Stevens County) is located approximately 30 miles north of Spokane within the Northern Rockies ecoregion. Soils in the area consist of humus rich topsoil underlain by sedimentary and metamorphic rock. Land use within the lake's drainage consists of agricultural, residential, and undisturbed areas. The lake's shore is lined with houses with the exception of a wetland area at the northwest corner of the lake. The lake is fed by small ephemeral streams during snow melt and large storm events. Water is released from the lake through the wetland area.

Loon Lake was chosen for coring to assess mercury loading in a remote area of eastern Washington.

**Wannacut Lake**

Wannacut Lake (in Okanogan County) is located in the Okanogan Highlands at the eastern edge of the North Cascades. Soils in the area consist of shallow humus rich topsoil underlain by igneous rock. Approximately 12 houses are located along the shore, and the remaining drainage area is largely unproductive with a few farms. The lake is fed intermittently during snow melt and has no outlet.

Three major mining operations along with concentrating mills are known to have occurred in the lake's catchment. The bulk of mining activity occurred between 1900 – 1940 (Huntting, 1956; and Spedden, 1939.). The lake was selected to characterize the effects of hard rock mining in a lake catchment on mercury fluxes.

# Methods

## Field Methods

At Loon and Wannacut Lakes, cores were collected using a Wildco stainless steel box corer containing a 13cm x 13cm x 50cm acrylic liner. At Walupt Lake, a gravity corer with a circular 6.5cm diameter acrylic liner was used to collect the core sample. Sediment sampling devices, and other tools coming into contact with sediments, were prepared for sampling in the laboratory with the following sequential cleaning process: Liquinox detergent hot water wash, nitric acid rinse, and de-ionized water rinse. Sampling equipment was air dried and wrapped in foil until use in the field. The cleaning process was also conducted between lakes. Sampling devices were washed with ambient lake water after coming in contact with sediments until a suitable sample was obtained.

At Loon and Wannacut Lakes, cores were collected from deep areas of the lakes using the 26' research vessel *Skookum* (Figure 1). The core at Walupt Lake was collected using a pontoon raft outfitted with an A-frame to raise and lower the sampling device. An attempt was made to collect cores from the deepest area of the lakes. Core samples preserving the sediment water interface, while providing enough depth to date sediments to pre-anthropogenic influence, were obtained. Samples were processed immediately upon retrieval by sectioning the core into 1cm intervals using an extruding device.

Single surface sediment grab samples were collected near the coring locations using a 0.1m² stainless steel van Veen following the Environmental Assessment Program's standard operating procedure for freshwater sediment sampling (Blakley, 2008). The quality of sediment grabs was interpreted by the preservation of a sediment water interface. The top 2cm of the grab sample was removed after overlying water had been siphoned away.

In the field, all sediments were placed in 8oz I-Chem jars with Teflon-lined lids, stored in zip plastic bags, and placed on ice in coolers. Samples remained in coolers for no more than 48 hours before being frozen at Ecology headquarters at -20°C.

All field work was conducted in August 2007.

## Sample Preparation and Analysis

### $^{210}$Pb and Total Lead

Sediment age and accumulation rates were determined for the cores by measuring $^{210}$Pb radioactivity along with total Pb in 9 to 11 samples per core. Samples chosen for analysis were composites of equal amounts from two 1cm intervals for Loon and Wannacut Lakes. The Walupt Lake core was sectioned into 3cm and 4cm intervals. Samples near the top of the core were tested at a high density where $^{210}$Pb activity is at its greatest, and spread out further deeper in the core. Samples analyzed for $^{210}$Pb were homogenized with utensils cleaned in the same

manner as sampling equipment and placed in polystyrene jars provided by Test America Richland. Analysis was performed using gamma spectroscopy for 1000 minutes per sample.

At Loon and Wannacut Lakes, a portion of the $^{210}$Pb sample composite was also tested for total Pb. Total Pb samples were placed in a pre-cleaned 2oz I-Chem jar with a Teflon-lined lid before being shipped to Ecology's Manchester Environmental Laboratory. Analysis was conducted using EPA Method 200.8, ICP: mass spectrometry. The sediment core logs describing sample analyses are located in Appendix A.

## Mercury

Mercury was measured in selected 1cm horizons throughout the core and used to calculate total flux to sediments. A total of 13 to 15 mercury samples were chosen from 1cm horizons spread throughout the core, with a greater number of horizons analyzed at the top of the core.

Mercury samples were unfrozen, homogenized, and placed in 2oz pre-cleaned I-Chem jars before being sent to Manchester Laboratory for analysis. Sediments were digested in aqua regia for 2 minutes at 95°C. Potassium permanganate was then added, and the sample was oxidized for an additional 30 minutes at 95°C. Mercury was then reduced with stannous chloride to elemental mercury and measured with conventional cold vapor atomic adsorption. All laboratory measurements for mercury followed EPA method 245.5.

## Data Quality

Manchester Environmental Laboratory prepared case narratives describing data quality for all analytical data. The narratives include a description of results, laboratory quality assurance, and special issues encountered during analysis.

### $^{210}$Pb

Thirty samples were measured for $^{210}$Pb activity by Test America Richland. Sample counts were done in two batches, and quality control measures for each batch consisted of one laboratory control sample, one method blank, and one duplicate. Control samples were recovered at an average of 108.5%, method blanks were not detected above 0.45 pCi/g, and duplicates had an average relative percent difference (RPD) of 6.8%. All samples were measured to a detection limit of at least 0.45 picocuries/gram (pCi/g).

### Total Lead

Laboratory quality control for total Pb consisted of laboratory control samples, method blanks, and duplicates. Matrix spikes and lab duplicates were recovered at acceptable levels (<10%). No method blanks had detections above the reporting limit (0.005 mg/kg). A single result from Loon Lake was qualified as an estimate and excluded from analysis.

**Total Mercury**

Laboratory quality control for mercury consisted of matrix spikes, laboratory control samples, and method blanks. All quality control tests were reported within data quality objectives with the exception of one matrix spike duplicate. The source sample for the failed duplicate was qualified as an estimate and excluded from analysis. Eight archived mercury samples from Wannacut Lake were measured past the 28-day holding time. Samples were qualified as estimates but still included in the analysis of the Wannacut core. All laboratory measurement quality objectives, along with the results of laboratory quality assurance tests, can be found in Appendix B.

## Sedimentation Modeling and Calculations

The constant rate of supply (CRS) model was applied to the $^{210}$Pb measurements to estimate dates and varying sedimentation rates throughout the core (Appleby and Oldfield 1978). The model works by measuring the difference in supported and unsupported $^{210}$Pb in sediment horizons. Supported $^{210}$Pb is represented by the small amount of the precursor gas $^{222}$Rn (Radon) that is captured in soils. Unsupported $^{210}$Pb represents atmospherically deposited $^{210}$Pb resulting from the decay of $^{222}$Rn that escapes into the atmosphere and is estimated by subtracting supported $^{210}$Pb from total $^{210}$Pb. Using the known half-life (22.3 years) of $^{210}$Pb and the amount of the unsupported isotope, the rate of sedimentation and the date of formation can be calculated for approximately the last 150 years (Van Metre et al., 2004; Charles and Hites, 1987).

Supported $^{210}$Pb present in the study cores was estimated as the amount present at deep intervals where it appeared to no longer decline (Figure 2). Sediment dry mass (g/cm$^2$) was calculated from percent solids data obtained from total Pb and mercury measurements made at Manchester Laboratory. Estimates on percent solids were extrapolated where data did not exist. An assumed sediment density of 2.7 g/cm$^3$ was used based on other Washington State coring studies (Paulson, 2004).

The Mt. St. Helens ash layer (1980) and the 1975 peak of total Pb (Yake 2001) were used as independent measures where available to confirm the efficacy of the $^{210}$Pb-derived sedimentation rates applied to the cores.

Mercury flux rates (ug/m$^2$/yr) were calculated as the product of sediment mass accumulation rates (SMARs) and dry weight mercury concentrations:

Dry Weight Concentration (ng/g) * SMAR (g/cm$^2$/yr) * 10 = Mercury Flux Rate (ug/m$^2$/yr)

The results estimate net deposition to the lake. Flux rates normalize the variance involved with interpreting dry weight concentrations under varying sedimentation.

Several horizons were analyzed for mercury without an accompanying $^{210}$Pb measurement. Dates were assigned to these measurements by working back in time from the most recent $^{210}$Pb-derived date using an estimated interval SMAR modeled from the $^{210}$Pb sedimentation curve along with the mass of the interval:

$$Date_i = Date_{Pb} - (cum_i/SMAR_i)$$

Where

$Date_i$ = deposition date of sample without $^{210}$Pb measurements.

$Date_{Pb}$ = date assigned to the bottom of the interval last measured for $^{210}$Pb.

$Cum_i$ = cumulative mass from $Date_i$ to midpoint of sample i.

$SMAR_i$ = interval SMAR for sample i estimated from the $^{210}$Pb-derived SMAR curve.

# Results and Discussion

## Sedimentation Rates

Figure 2 displays the $^{210}$Pb activity in the three sediment cores on a logarithmic scale.

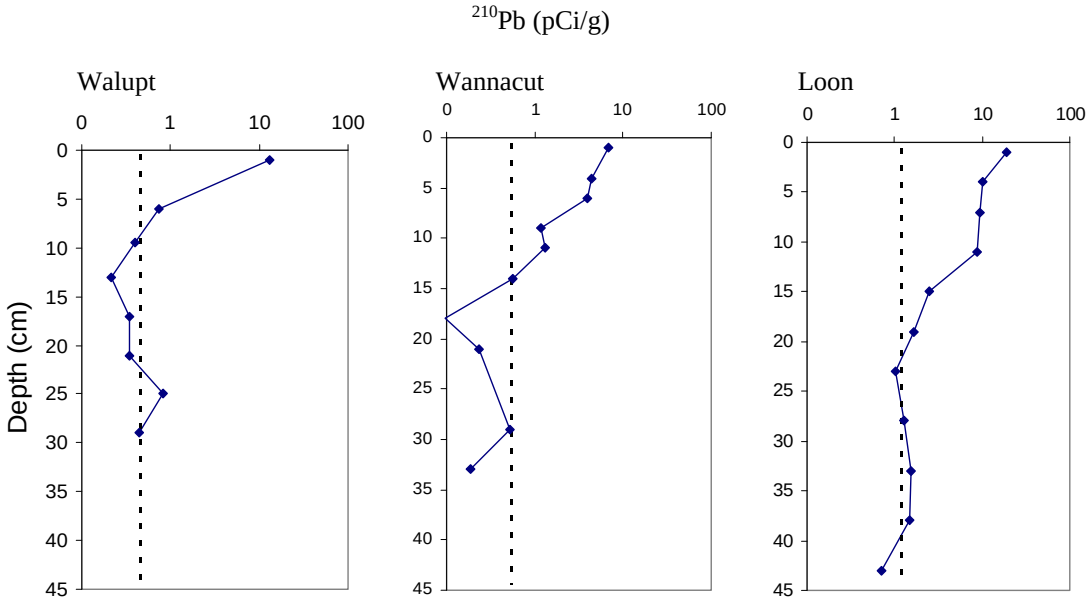


Figure 2. $^{210}$Pb activity plotted against depth. (The dashed line indicates supported $^{210}$Pb.)

Data for $^{210}$Pb at Walupt Lake was deemed unusable for the CRS model after the unsupported $^{210}$Pb signal disappeared beneath the ash layer (>2cm) from the Mt. St. Helens eruption of 1980. The $^{210}$Pb activity versus depth profile (Figure 2) resembles an isotope with a much shorter half-life such as $^{7}$Be (Beryllium) (half-life of 53 days).

Percent solids data from the sediment changed abruptly beneath the ash layer, suggesting sediments under the ash layer were subjected to compaction from the weight of the ash. Horizons near the bottom of the 31cm core taken from Walupt Lake are thought to contain extremely old sediments (> 500 years) due to the effects of compaction. A constant sedimentation rate was calculated based on sedimentation since 1980.

Supported $^{210}$Pb levels are shown in Table 2 along with estimated yearly unsupported $^{210}$Pb fluxes to sediments. Unsupported $^{210}$Pb fluxes calculated from measured data normally fall within 0.2 – 1.0 pCi/cm$^2$/yr (Oldfield and Appleby, 1984). The lower than expected value at Wannacut Lake (0.1314 pCi/cm$^2$/yr) could be indicative of sediment focusing at the coring site.

Table 2. Estimated supported $^{210}$Pb in sediments and yearly unsupported $^{210}$Pb fluxes.

| Lake | Supported $^{210}$Pb (pCi/g) | Unsupported $^{210}$Pb Flux (pCi/cm$^2$/yr) |
|---|---|---|
| Walupt | 0.4669 | - |
| Wannacut | 0.5415 | 0.1314 |
| Loon | 1.1954 | 0.3528 |

Sedimentation rates along with their estimated dates are plotted in Figure 3. The data point marked with a box on the $^{210}$Pb sedimentation curve marks the last CRS model sedimentation rate. Sedimentation rates beneath these points do not vary.

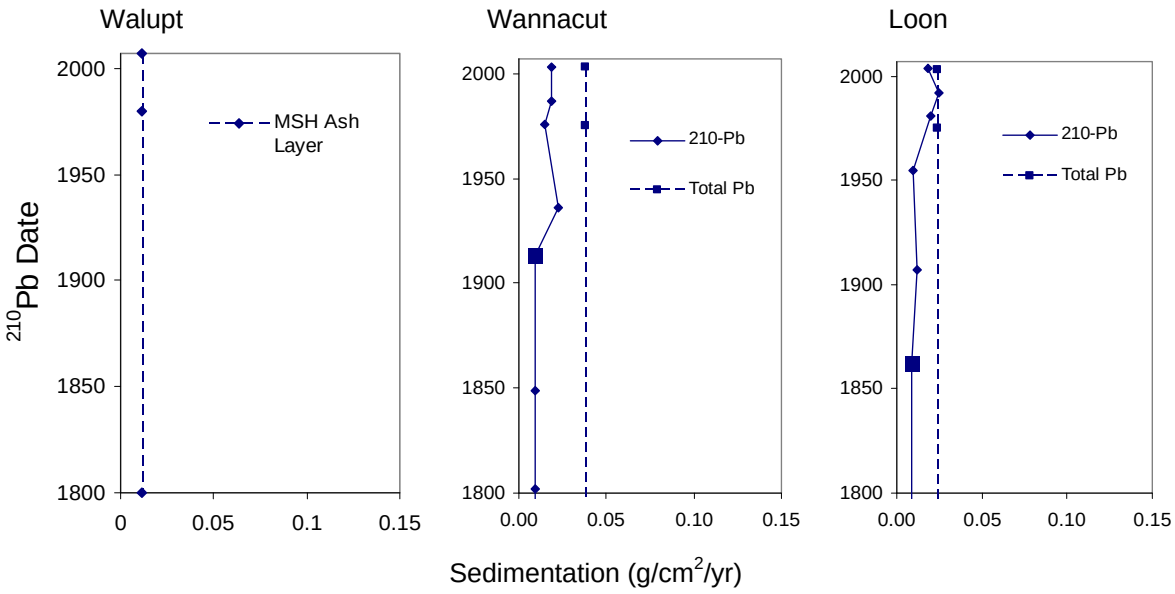


Figure 3. Sedimentation rates along with date estimates for 2007 coring sites.

Low sedimentation rates are a reflection of the small and infrequent hydrological inputs to all three of the lakes. Sedimentation rates for 2006 study lakes (Ozette, Sammamish, and St. Clair) were 2-5 times higher. Timing of sedimentation spikes and decreases match well with residential development at Loon Lake (Snarski et al., 2007) and known mining activity at Wannacut Lake (Huntting, 1956; and Spedden, 1939).

## Mercury Concentrations and Fluxes

Mercury flux rates to the study lakes were low with the exception of the period when Wannacut Lake was directly affected by mining activity in the catchment (late 1800s – 1940). Flux rates at the three lakes ranged from 88 – 259 ug/m$^2$/yr. Post-1970 flux rates for the study lakes were under 25 ug/m$^2$/yr, and the most recent fluxes were 15 ug/m$^2$/yr or less. Table 3 contains summary data on mercury fluxes, dry concentrations, and flux trends. The remainder of the section is a brief discussion of the core data from each lake.

Table 3. Mercury flux and dry weight concentration data for the study lakes.

| Lake | Total Hg Range (ng/g) | Total Hg Grab Sample (ng/g) | Modern Flux ($ug/m^2/yr$) (year) | Flux Peak ($ug/m^2/yr$) (year) | Flux Trend |
|---|---|---|---|---|---|
| Walupt | 11 - 75 | 118 | 3.1 (1980-2007) | 8.3 (-) | Decreasing |
| Wannacut | 5U - 1580 | 1130 | 10.5 (2003) | 361.0 (1936) | Decreasing |
| Loon | 15 - 90 | 98 | 15.1 (2004) | 22.4 (1993) | Decreasing |

## Walupt Lake

Mercury concentrations were low (11 ng/g – 75 ng/g) and similar to Loon Lake. A constant sedimentation rate was calculated based on the dry mass of the two centimeters of sediment that had accumulated since the 1980 Mt. St. Helen eruption. A mercury flux rate of 3.1 $ug/m^2/yr$ was calculated since 1980.

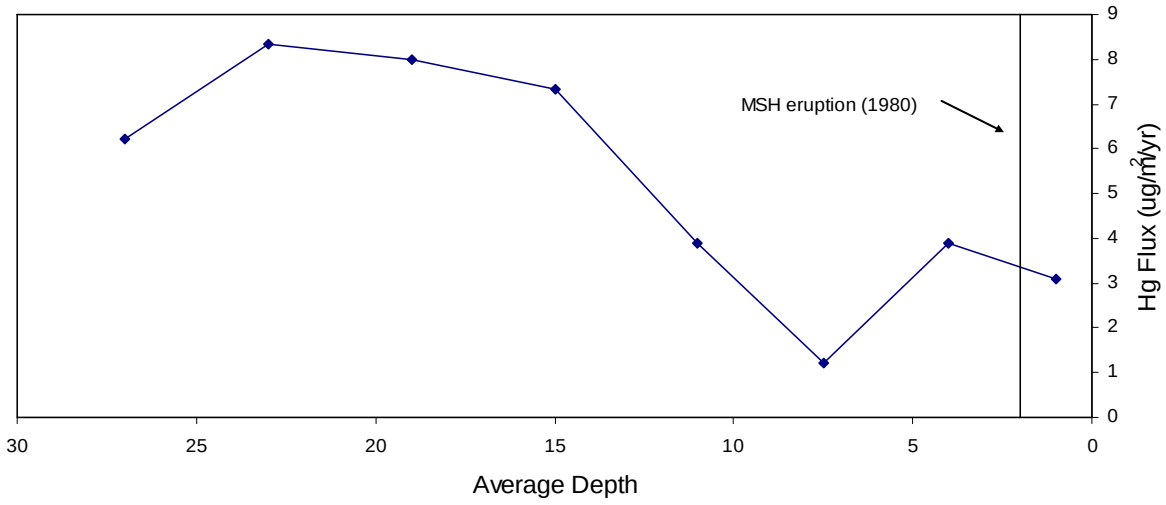


Figure 4. Walupt Lake mercury flux versus depth (flux rates calculated using constant sedimentation).

Mercury fluxes deep in the core are elevated over current estimates. The deepest four mercury measurements (all >15cm in depth) had an average flux of 7.5 $ug/m^2/yr$. The sources of the increased mercury fluxes deep within the core are unclear without the benefit of dates. The elevated mercury levels could be a recorded signal of the elevated global and regional mercury pollution occurring after 1800.

Based on the constant SMAR and dry mass measured since the eruption of 1980, sediments at a depth of 15cm would be at minimum several hundred years old, pre-dating anthropogenic pollution. This would implicate Mt. St. Helens as a pollution source several hundred years earlier. However, no additional fall debris was encountered past the 1980 eruption despite a known record of frequent volcanic activity, the most recent during the Goat Rocks period 1800-1857. During the Goat Rocks period, tephra (volcanic rock fragments) was carried northeastward (in the same direction as Walupt Lake) and found as far away as Montana (Crandell, 1987).

## Loon Lake

Loon Lake mercury flux rates were low (< 25 ug/$m^2$/yr) and followed a typical mercury signature to other lakes of similar latitude in North America not directly affected by point sources (Engstrom et al., 2007). Flux rates began increasing at the turn of the 20$^{th}$ century and peaked in the early 1990s. The most recent flux rate indicates a slight decline from the maximum.

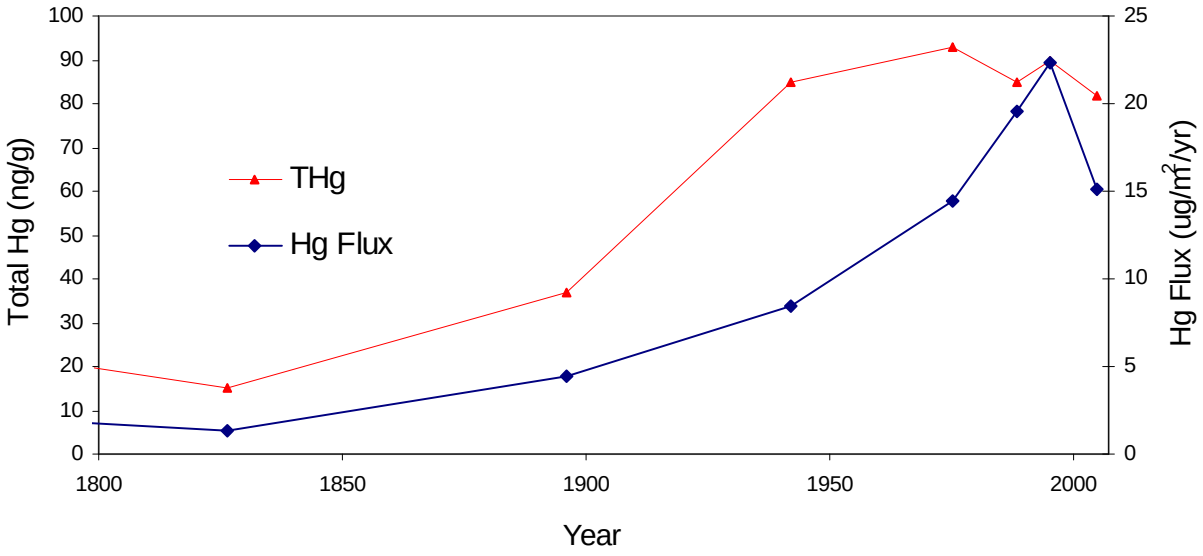


Figure 5. Mercury flux rates and concentrations with estimated dates for Loon Lake.

The decline in recent mercury fluxes appears to be closely tied to catchment activity based on the similarity of sedimentation (Figure 3) and flux profiles. Since the 1950s, mercury concentrations have remained fairly constant (82 – 93 ng/g), yet the flux rate profile (and sedimentation profile) display a sharp peak with recent declines. It appears that the sediment source contributing to the lake contains equal or slightly smaller amounts of mercury to the pre-existing sediment matrix and any changes in flux are tied to sedimentation rates. Since catchment activity and sedimentation appear to control mercury flux rates, it is difficult to discern changes in atmospheric deposition.

## Wannacut Lake

Wannacut Lake was heavily impacted by mining activity within the lake's catchment. Three major mines and concentrating mills seeking mostly gold were operated within the drainage from the late 1800s – 1940. Metals contamination to lake sediments occurred from seasonal overflows of flooded mine shafts and tailings from the mills (Huntting, 1956; and Spedden, 1939). The mine's impacts on lake sediments were revealed through abrupt spikes in lead, mercury, and sedimentation rates. Additionally, sediment varves (layers) well preserved deep in the core were disrupted during the mining period.

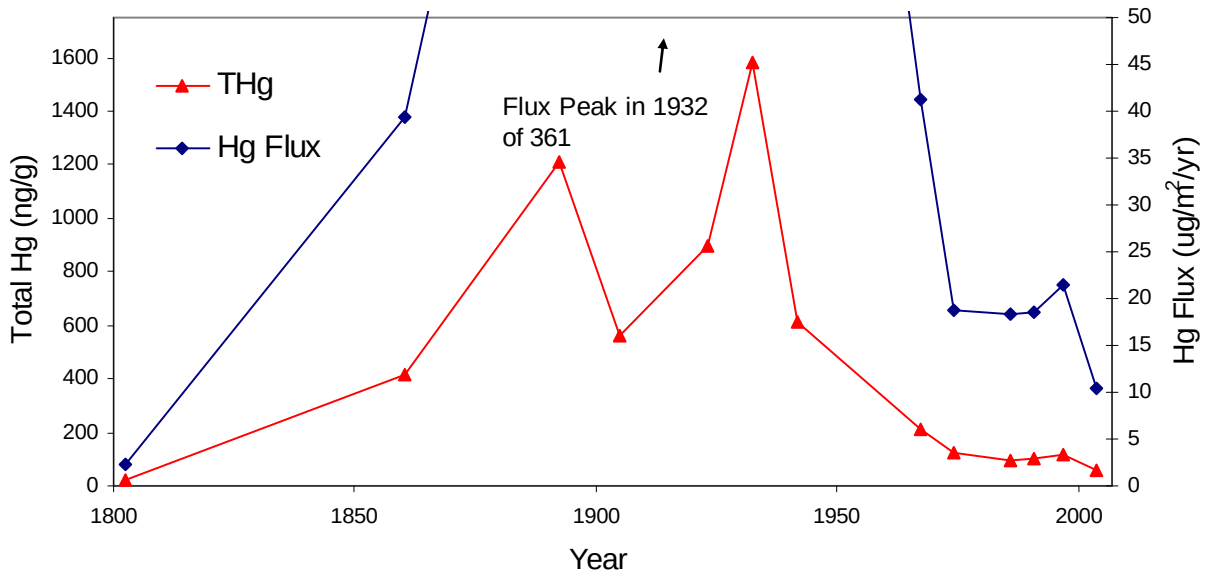


Figure 6. Mercury flux rates and concentrations with estimated dates for Wannacut Lake.

Mercury concentrations post-1970 have similar concentrations and trends to Loon Lake. Changes in sedimentation rates in the upper core are not an issue at Wannacut Lake. Sedimentation rates have only slightly increased since the mid-1970s and have remained constant since the late 1980s. Changes in flux rates are marked by similar changes in concentration values. Lowered flux rates at Wannacut Lake are the result of lowered mercury inputs into the lake, not changes in sedimentation. This indicates reduced atmospheric deposition to the lake since the late 1990s. Declines in atmospheric mercury deposition since the mid-1990s measured by sediment cores have been documented in remote Minnesota lakes and attributed to reduced regional pollution (Engstrom and Swain, 1997).

## Grab Samples

Grab samples did not match well with upper core concentrations at Wannacut and Walupt Lakes. Elevated concentrations from Wannacut Lake are believed to be the result of different sediment sampling techniques (ponar versus box corer). The sediments at Wannacut Lake were not able to support the weight of the ponar. When grabs were retrieved, sediments repeatedly filled the ponar full to the mesh screen, mixing the upper layer with deeper sediments.

## Comparison to 2006 Cores

Mercury flux rates along with varying sedimentation rates were developed for the 2006 study lakes (Ozette, Sammamish, St. Clair) and can be found in Figure 7 and Appendix C (Furl, 2007). Previously, only mercury concentrations (ng/g) were reported, and sediment ages were based on a single sedimentation rate.

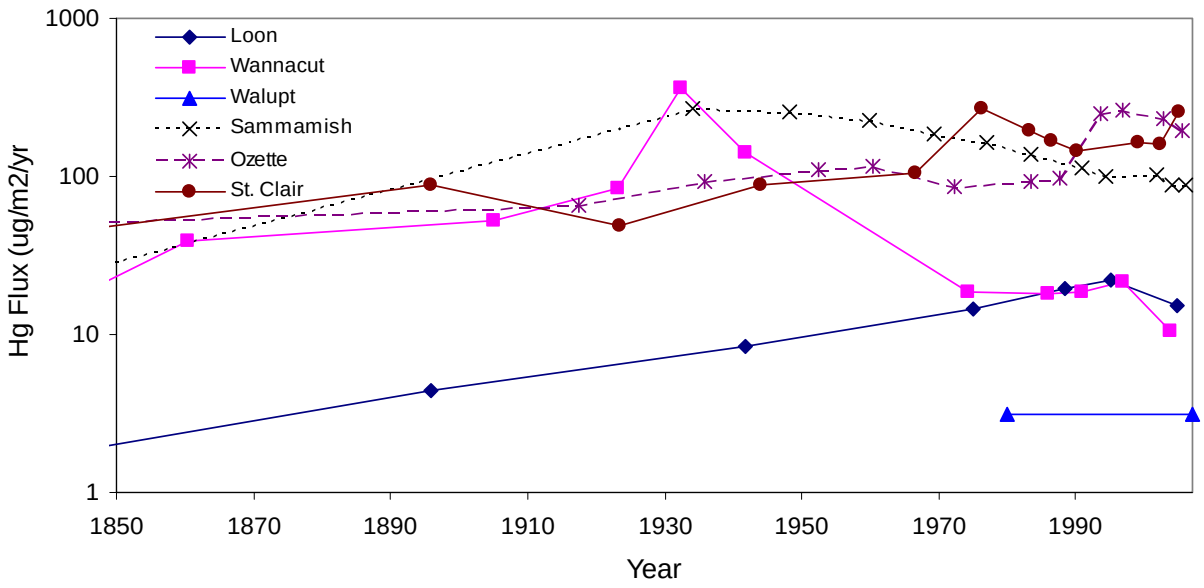


Figure 7. Mercury flux rates (ug/m$^2$/yr) for 2006 and 2007 study lakes. (Note logarithmic scale)

Mercury fluxes to sediments were low in the 2007 study lakes. The three lakes have similar flux rates to other remote locations in North America (Engstrom et al., 2007; Kamman and Engstrom, 2002). Average flux rates for sediments in the 2007 study lakes were 10 ug/m$^2$/yr compared to 181 ug/m$^2$/yr in the 2006 study lakes (Table 4). This large difference is a accredited to: (1) rapid removal of mercury from anthropogenic sources which are primarily found in western Washington; (2) mercury's affinity for water and wet deposition as means for the primary removal of mercury from the atmosphere; and (3) the effects of urbanization (and other catchment disturbances) on sedimentation rates.

Table 4. Recent mercury flux rates (ug/m$^2$/yr) for 2006 and 2007 lakes.

| 2007 | | | 2006 | | |
|---|---|---|---|---|---|
| Loon | Wannacut | Walupt | Sammamish | Ozette | St. Clair |
| 15.07 | 10.452 | 3.108 | 87.914 | 196.036 | 258.68 |

# Conclusions

This study was the second year of a five-year project evaluating present and historical mercury trends in Washington State. Sediment cores were collected from three Washington lakes: Walupt, Loon, and Wannacut.

The *Walupt Lake* sediment core displayed an overall decreasing trend in mercury concentrations; however, dates were not estimated for the core due to a poor $^{210}$lead signal. Mercury emissions from Mount St. Helens appear to have had little impact if any on lake sediments.

*Loon Lake* sediments have received low mercury inputs over the past 50 years, and recent flux rates indicate a decline. Mercury flux rates peaked in the mid-1990s at 22 ug/m$^2$/yr and are currently at 15 ug/m$^2$/yr. Concentrations have remained nearly constant since the 1950s ranging from 82 – 93 ppb. The flux rate decline experienced at Loon Lake is attributed to reduced sedimentation.

*Wannacut Lake* sediments were severely contaminated with lead and mercury from mining activity that occurred in the lake's catchment from the late 1800s to 1940. A peak mercury flux of 361 ug/m$^2$/yr was measured in 1932. Peak mercury concentrations during this time period measured 1,580 ng/g. Contamination stopped abruptly after mining activity ceased within the lake's drainage, and mercury levels dropped accordingly. Flux rates at Wannacut Lake have experienced recent declines and are currently 10 ug/m$^2$/yr.

All three sites are currently receiving low mercury fluxes and have similar flux rates to other remote locations in North America. A general trend of near-surface flux declines was also observed in the cores. At Walupt and Wannacut Lakes, the declines appear to be a function of declines in atmospheric loading. Change in Loon Lake atmospheric fluxes are unrecognizable due to the effects of mercury sedimentation from the catchment.

Contamination sources to all three lakes are dominated by global and regional activity. The low flux rates can be attributed to the lake's distance from human-caused point source mercury pollution, rural catchments, and low sedimentation.

# Recommendations

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

- Analyze $^{210}$lead in at least three of the first five horizons to enhance resolution of date estimates and source identification.
- Examine the effects of erosion caused by catchment activity on mercury fluxes to lake sediments.
- Avoid analyzing sediment intervals for $^{210}$lead without an accompanying mercury measurement.
- Analyze $^{210}$lead and total lead in 1-cm intervals.
- Discontinue collecting surface sediment grabs.

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# Appendices

Appendix A. Sediment Core and Surface Sediment Data

Appendix B. Quality Assurance Data

Appendix C. 2006 Study Lakes Mercury Flux Profiles

Appendix D. Glossary and Acronyms

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# Appendix A. Sediment Core and Surface Sediment Data

Table A1. Walupt Lake core sectioning, collected August 17, 2007.

| Section (cm intervals) | Dating Analysis | Sample ID | Lab ID |
|---|---|---|---|
| 0-1 | Pb-210, Hg, TOC | Walupt2 | 354545 |
| 1-2 | | | |
| 2-3 | -- | -- | -- |
| 3-4 | -- | -- | -- |
| 4-5 | Pb-210, Hg, TOC | Walupt5 | 354548 |
| 5-6 | | | |
| 6-7 | | | |
| 7-8 | | | |
| 8-9 | Pb-210, Hg, TOC | Walupt6 | 354549 |
| 9-10 | | | |
| 10-11 | | | |
| 11-12 | Pb-210, Hg, TOC | Walupt7 | 354550 |
| 12-13 | | | |
| 13-14 | | | |
| 14-15 | | | |
| 15-16 | Pb-210, Hg, TOC | Walupt8 | 354551 |
| 16-17 | | | |
| 17-18 | | | |
| 18-19 | | | |
| 19-20 | Pb-210, Hg, TOC | Walupt9 | 354552 |
| 20-21 | | | |
| 21-22 | | | |
| 22-23 | | | |
| 23-24 | Pb-210, Hg, TOC | Walupt10 | 354553 |
| 24-25 | | | |
| 25-26 | | | |
| 26-27 | | | |
| 27-28 | Pb-210, Hg, TOC | Walupt11 | 354554 |
| 28-29 | | | |
| 29-30 | | | |
| 30-31 | | | |

Table A2. Loon Lake core sectioning, collected August 21, 2007.

| Section (cm intervals) | Dating Analysis | Sample ID | Lab ID | Analysis | Sample ID | Lab ID |
|---|---|---|---|---|---|---|
| 0-2 | Pb-210, T Pb | Ln1 | 354521 | Hg, TOC | Loon1 | 354532 |
| 2-3 | -- | -- | -- | -- | -- | -- |
| 3-4 | Pb-210, T Pb | Ln2 | 354522 | Hg, TOC | Loon2 | 354533 |
| 4-5 | | | | | | |
| 5-6 | -- | -- | -- | Hg, TOC | Loon3 | 354534 |
| 6-7 | Pb-210, T Pb | Ln3 | 354523 | -- | -- | -- |
| 7-8 | | | | | | |
| 8-9 | -- | -- | -- | Hg, TOC | Loon4 | 354535 |
| 9-10 | -- | -- | -- | -- | -- | -- |
| 10-11 | Pb-210, T Pb | Ln4 | 354524 | -- | -- | -- |
| 11-12 | | | | | | |
| 12-13 | -- | -- | -- | Hg, TOC | Loon5 | 354536 |
| 13-14 | -- | -- | -- | -- | -- | -- |
| 14-15 | Pb-210, T Pb | Ln5 | 354525 | -- | -- | -- |
| 15-16 | | | | | | |
| 16-17 | -- | -- | -- | Hg, TOC | Loon6 | 354537 |
| 17-18 | -- | -- | -- | -- | -- | -- |
| 18-19 | Pb-210, T Pb | Ln6 | 354526 | -- | -- | -- |
| 19-20 | | | | | | |
| 20-21 | -- | -- | -- | -- | -- | -- |
| 21-22 | -- | -- | -- | Hg, TOC | Loon7 | 354538 |
| 22-23 | Pb-210, T Pb | Ln7 | 354527 | -- | -- | -- |
| 23-24 | | | | | | |
| 24-25 | -- | -- | -- | -- | -- | -- |
| 25-26 | -- | -- | -- | -- | -- | -- |
| 26-27 | -- | -- | -- | Hg, TOC | Loon8 | 354539 |
| 27-28 | Pb-210, T Pb | Ln8 | 354528 | -- | -- | -- |
| 28-29 | | | | | | |
| 29-30 | -- | -- | -- | -- | -- | -- |
| 30-31 | -- | -- | -- | -- | -- | -- |
| 31-32 | -- | -- | -- | -- | -- | -- |
| 32-33 | Pb-210, T Pb | Ln9 | 354529 | -- | -- | -- |
| 33-34 | | | | | | |
| 34-35 | -- | -- | -- | -- | -- | -- |
| 35-36 | -- | -- | -- | -- | -- | -- |
| 36-37 | -- | -- | -- | Hg, TOC | Loon9 | 354540 |
| 37-38 | Pb-210, T Pb | Ln10 | 354530 | -- | -- | -- |
| 38-39 | | | | | | |
| 39-40 | -- | -- | -- | -- | -- | -- |
| 40-41 | -- | -- | -- | -- | -- | -- |
| 41-42 | -- | -- | -- | -- | -- | -- |
| 42-43 | Pb-210, T Pb | Ln11 | 354531 | Hg, TOC | Loon10 | 354541 |
| 43-44 | | | | | | |

Table A3. Wannacut Lake core sectioning, collected August 22, 2007.

| Section (cm intervals) | Dating Analysis | Sample ID | Lab ID | Analysis | Sample ID | Lab ID |
|---|---|---|---|---|---|---|
| 0-2 | Pb-210, T Pb | Wan1 | 354500 | Hg, TOC | wanacut1 | 354511 |
| 0-2 | | | | | | |
| 2-3 | -- | -- | -- | Hg, TOC | wanacut2 | 354512 |
| 3-4 | Pb-210, T Pb | Wan2 | 354501 | Hg, TOC | wanacut3 | 354513 |
| 4-5 | | | | | | |
| 5-6 | Pb-210, T Pb | Wan3 | 354502 | Hg, TOC | wanacut4 | 354514 |
| 6-7 | | | | | | |
| 7-8 | -- | -- | -- | -- | -- | -- |
| 8-9 | Pb-210, T Pb | Wan4 | 354503 | Hg, TOC | wanacut5 | 354515 |
| 9-10 | | | | | | |
| 10-11 | Pb-210, T Pb | Wan5 | 354504 | -- | -- | -- |
| 11-12 | | | | | | |
| 12-13 | -- | -- | -- | Hg, TOC | wanacut6 | 354516 |
| 13-14 | Pb-210, T Pb | Wan6 | 354505 | -- | -- | -- |
| 14-15 | | | | | | |
| 15-16 | -- | -- | -- | -- | -- | -- |
| 16-17 | -- | -- | -- | Hg, TOC | wanacut7 | 354517 |
| 17-18 | Pb-210, T Pb | Wan7 | 354506 | -- | -- | -- |
| 18-19 | | | | | | |
| 19-20 | -- | -- | -- | -- | -- | -- |
| 20-21 | Pb-210, T Pb | Wan8 | 354507 | -- | -- | -- |
| 21-22 | | | | | | |
| 22-23 | -- | -- | -- | Hg, TOC | wanacut8 | 354518 |
| 23-24 | Pb-210, T Pb | Wan9 | 354508 | -- | -- | -- |
| 24-25 | | | | | | |
| 25-26 | -- | -- | -- | -- | -- | -- |
| 26-27 | -- | -- | -- | Hg, TOC | wanacut9 | 354519 |
| 27-28 | -- | -- | -- | -- | -- | -- |
| 28-29 | Pb-210, T Pb | Wan10 | 354509 | -- | -- | -- |
| 29-30 | | | | | | |
| 30-31 | -- | -- | -- | -- | -- | -- |
| 31-32 | -- | -- | -- | -- | -- | -- |
| 32-33 | Pb-210, T Pb | Wan11 | 354510 | Hg, TOC | wanacut10 | 354520 |
| 33-34 | | | | | | |

# Appendix B. Quality Assurance Data

Table B1. Measurement Quality Objectives.

| Parameter | Accuracy (% of True value) | Precision (Duplicate RPD %) | Bias (% of True value) | Lowest Concentration |
|---|---|---|---|---|
| Total Mercury | ± 40% SRM | < 25% | ± 40% LCS | 0.005 mg/Kg, dry |
| Total Lead | ± 40% SRM | < 25% | ± 40% LCS | 2 mg/Kg, dry |
| $^{210}$Lead | - | < 25% | - | .45pCi/g |

Table B2. Mercury.

| Matrix Spike (% recovery) | | | |
|---|---|---|---|
| Sample # | LMX1 (%) | LMX2 (%) | RPD (%) |
| 7504084 | 78 | 112 | 35.8 |
| 7354517 | 88 | 90 | 2.3 |
| 7354543 | 95 | 94 | 1.1 |
| 7354553 | 86 | 89 | 3.4 |

| Lab Method Blank | | |
|---|---|---|
| Sample # | Field ID | Result (mg/Kg) |
| MB07353H1 | Lab BLNK | 0.005 U |
| MB07264H1 | Lab BLNK | 0.005 U |
| MB07254H1 | Lab BLNK | 0.005 U |
| MB07254H2 | Lab BLNK | 0.005 U |
| MB07248H2 | Lab BLNK | 0.005 U |

| Lab Control Sample (% recovery) | | |
|---|---|---|
| Sample # | Field ID | % Recovery |
| ML07353H1 | Lab LCS | 97 |
| ML07264H1 | Lab LCS | 103 |
| ML07254H1 | Lab LCS | 104 |
| ML07254H2 | Lab LCS | 104 |
| ML07248H2 | Lab LCS | 101 |

U - Not detected at detection limit shown

Table B3. Total Lead.

| Matrix Spike (% recovery) | | | |
|---|---|---|---|
| Sample # | LMX1 (%) | LMX2 (%) | RPD (%) |
| 7504089 | 98 | 98 | 0.0 |
| 7354506 | 93 | 92 | 1.1 |
| 7354531 | 102 | 101 | 1.0 |

| Lab Method Blank | | |
|---|---|---|
| Sample # | Field ID | Result (mg/Kg) |
| MB07354I1 | Lab BLNK | 0.10 U |
| MB07260I1 | Lab BLNK | 0.10 U |
| MB07260I2 | Lab BLNK | 0.10 U |

| Lab Control Sample | | |
|---|---|---|
| Sample # | Field ID | % Recovered |
| ML07354I1 | Lab LCS | 105 |
| ML07260I1 | Lab LCS | 106 |
| ML07260I2 | Lab LCS | 106 |

U - Not detected at detection limit shown

Table B4. $^{210}$Lead.

| Laboratory Duplicate (RPD) | | | |
|---|---|---|---|
| Sample # | LDP1 (pCi/g) | LDP2 (pCi/g) | RPD (%) |
| 354500 | 7.06 | 6.72 | 5.0 |
| 354525 | 2.59 | 2.38 | 8.5 |

| Lab Method Blank | | | |
|---|---|---|---|
| Sample # | Field ID | Result (pCi/g) | MDC (pCi/g) |
| 7257522 | Lab BLNK | -0.169 U | 0.312 |
| 7257523 | Lab BLNK | 0.018 U | 0.314 |

| Lab Control Sample (% recovery) | | |
|---|---|---|
| Sample # | Field ID | % Recovery |
| 7257522 | Lab LCS | 108 |
| 7257523 | Lab LCS | 109 |

MDC - method detection criteria
U - Not detected at detection limit shown

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# Appendix C. Mercury Flux Profiles for the 2006 Study Lakes

Figure C1. Lake St. Clair

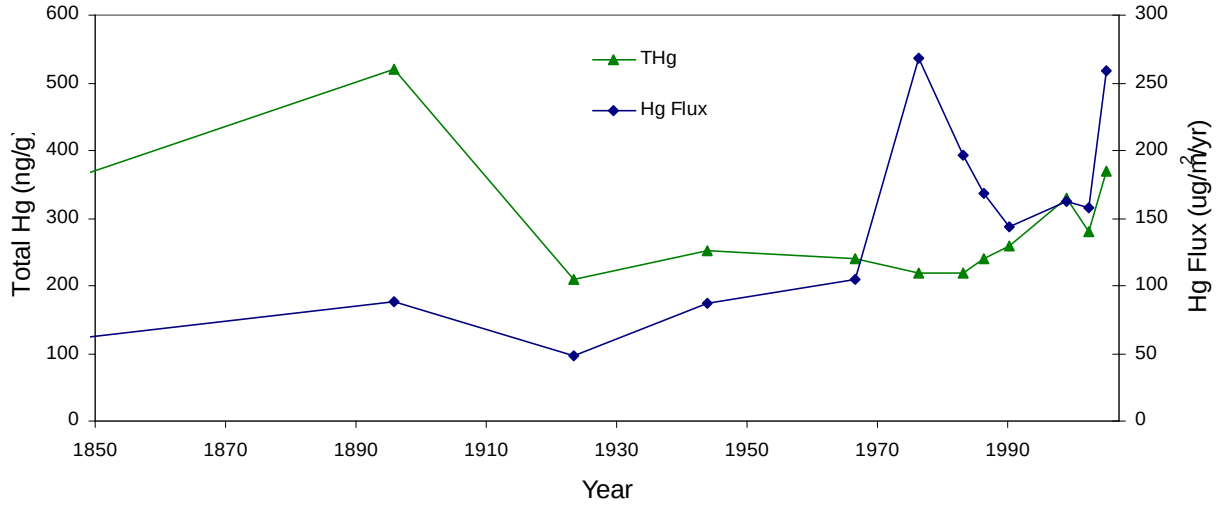



Figure C2. Lake Sammamish

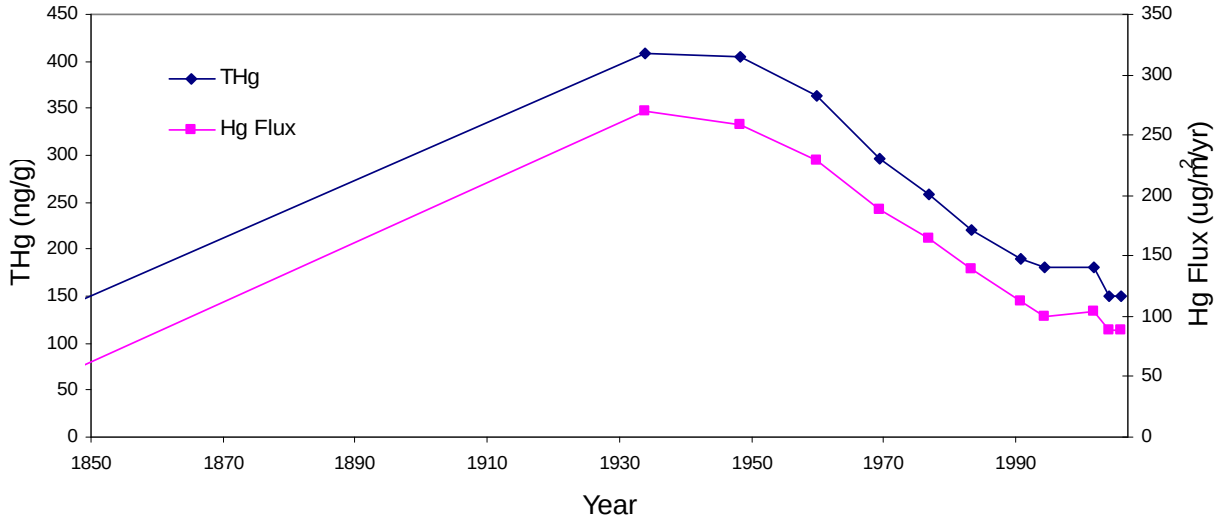
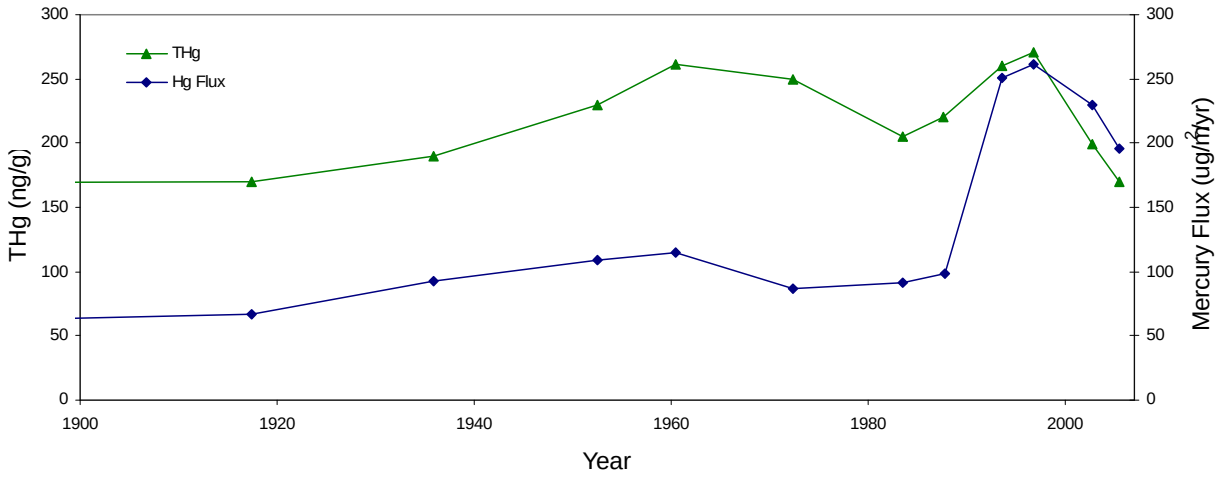



Figure C3. Lake Ozette



# Appendix D. Glossary and Acronyms

**Anthropogenic** – human-caused.

**Bathymetry** – measure of depth of a waterbody.

**Ephemeral stream** – a stream channel that carries water only during and immediately after rainfall or snowmelt.

**Horizons** –subsections of the sediment core (typically 1 cm).

**Morphology** – shape (e.g., channel morphology).

**Point source** – sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water.

| | |
|---|---|
| CRS | constant rate of supply |
| Ecology | Washington State Department of Ecology |
| Hg | mercury |
| LCS | laboratory control samples |
| MSH | Mount St. Helens |
| Pb | lead |
| PBTs | persistent, bioaccumulative, toxic chemicals |
| RPD | relative percent difference |
| SMAR | sediment mass accumulation rate |
| THg | total mercury |
| TOC | total organic carbon |