



DEPARTMENT OF
ECOLOGY
State of Washington

Determination of PBT Chemical Trends in Selected Washington Lakes Using Age-Dated Sediment Cores

2008 Sampling Results

June 2009

Publication No. 09-03-030

Publication and Contact Information

This report is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0903030.html

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search User Study ID, CFUR0004.

Ecology's Study Tracker Code for this study is 06-501-02-03.

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Determination of PBT Chemical Trends in Selected Washington Lakes Using Age-Dated Sediment Cores

2008 Sampling Results

by

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Waterbody Numbers:

Lake Washington	WA-08-9350
Lacamas Lake	WA-28-9050
Offutt Lake	WA-13-9110

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Abstract

This report presents results from the third year of a study to evaluate contaminant trends in lakes using age-dated sediment cores. During August 2008, the Washington State Department of Ecology (Ecology) collected deep sediment cores from Lake Washington (King County), Lacamas Lake (Clark County), and Offutt Lake (Thurston County). Ecology analyzed sediment horizons for mercury, lead, and polycyclic aromatic hydrocarbons (PAHs). Dates were applied to each sediment horizon based on ^{210}Pb measurements.

Lake Washington sediments received substantial contaminant loading over the first half of the 1900s. Concentrations of mercury and lead declined significantly after peaking in the 1950s and 1970s, respectively. PAH concentrations display an erratic pattern since the 1960s. The most recent sediment intervals show a declining trend in PAH concentrations. Organic carbon-normalized PAH concentrations were 10 – 45 times higher in Lake Washington than in Offutt and Lacamas Lakes since the 1970s.

Trends at Lacamas Lake displayed overall decreases for all three contaminants during the 1900s. The observed trend appears to be closely tied to increasing sedimentation rates in the lake. The uppermost sediment horizon had the lowest contaminant concentrations for all three analytes when compared to the other study lakes.

Offutt Lake sediments displayed an increasing trend in lead and mercury after the 1850s. Concentrations reached their maximum during the 1970s where they remain through recent sediments. PAH concentrations were low at the lake and had little variation when compared to the other two study lakes. The highest total PAH concentration was found near the top of the sediment core.

Acknowledgements

The authors of this report would like to thank the following Department of Ecology staff for their contribution to this study:

- Dale Norton, Keith Seiders, and Brandee Era-Miller for help with sample collection.
- Manchester Environmental Laboratory staff for help and dedication to analytical services: Leon Weiks, Nancy Rosenbower, Dean Momohara, Dickey Huntamer, John Weakland, Karin Feddersen, Stuart Magoon, and others.
- Dale Norton for guidance and review of the draft report.
- Art Johnson for reviewing the draft report.
- Joan LeTourneau and Cindy Cook for formatting and editing the final report.

Introduction

In 2000, a *Proposed Strategy to Continually Reduce Persistent, Bioaccumulative Toxins in Washington State* (Gallagher, 2000) was developed by the Washington State Department of Ecology (Ecology). The plan seeks to reduce, and where possible, eliminate persistent, bioaccumulative, and toxic (PBT) chemicals through phasing out use and production. 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, 2003). A chemical action plan (CAP) for polybrominated diphenyl ethers (PBDEs) was finalized in 2006 (Geller, 2006). Recently, a draft CAP was issued for lead (Davies, 2008), and a CAP examining polycyclic aromatic hydrocarbons (PAHs) is expected in 2010.

A portion of the PBT strategy is aimed at monitoring spatial and temporal trends of PBTs in Washington lake sediments (Gallagher, 2000). Paleolimnological studies have been a useful way of investigating historical rates of contaminant deposition to lake sediments (Yake, 2001; Gallagher et al., 2004; Kamman and Engstrom, 2002; and Engstrom et al., 2007). Coring studies allow for examination of trends and evaluation of current contaminant levels over pre-industrial levels.

This is the third year of a statewide study. The first two years were aimed at quantifying mercury concentrations only (Furl, 2007, 2008). The goal of the study is to evaluate historical trends in contaminant accumulation statewide through the use of age-dated sediment cores. A complete project plan for the sediment coring effort is described in detail by Coats (2006) and Meredith and Furl (2008). This report presents data from three single deep sediment cores collected from Lake Washington, Lacamas Lake, and Offutt Lake, in western Washington. Analytes included mercury, lead, and PAHs.

Contaminant Descriptions

Mercury

Mercury contamination is a widespread global phenomenon 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 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).

Natural sources of mercury include weathering of mercury-bearing rocks and soil, volcanic activity, forest fires, and degassing from water surfaces. Anthropogenic sources include combustion of fossil fuels, metal production, and industrial processes. Currently, the largest point source of anthropogenic mercury in Washington State is from the TransAlta coal-fired power plant in Centralia (EPA, 2006).

Lead

Lead is a naturally occurring element, but its anthropogenic distribution has greatly increased environmental exposure. Lead is considered a metal of concern because it is widespread and persistent in the environment, bioaccumulative, and is highly toxic to humans and wildlife. It is a powerful neurotoxin, and children are especially at risk from exposure. The use of alkyl-lead additives in gasoline since the 1920s resulted in widespread lead pollution in the environment. With U.S. restrictions on leaded gasoline, atmospheric lead concentrations have declined considerably (ATSDR, 2007).

Historically, lead was emitted from a large smelter located in Ruston (near Tacoma) from 1890 – 1985. Today, point sources of lead to the environment in Washington State include industrial releases such as mining, the Hanford nuclear reservation, military bases, large energy users, and sewage treatment plants. Nonpoint sources of lead to the environment occur through product use, ammunition, aviation fuel, and road dust (Davies, 2008). Low concentrations of lead naturally enter surface waters through weathering of bedrock and soils.

PAHs

PAHs are organic, lipophilic contaminants with widespread environmental prevalence. The compounds are formed primarily from the incomplete combustion of carbon-containing materials. PAHs also occur in natural deposits of oil, coal, and tar. Several PAHs are known carcinogens (ATSDR, 1995). Anthropogenic sources of PAHs such as vehicles, heating and power plants, industrial processes, and open burning are believed to be the principal sources to the environment (Van Metre and Callender, 2000).

Sediment Core Studies in Washington

Several freshwater sediment coring studies examining contaminant trends have been conducted in Washington lakes. During the first two years (2006-07) of the current study, Ecology examined cores from Sammamish, Ozette, St. Clair, Loon, Wannacut, and Walupt Lakes for mercury contamination (see map in Appendix A). From these six lakes, mercury fluxes between 5 – 200 $\mu\text{g}/\text{m}^2/\text{yr}$ were recorded. Mercury fluxes recorded in eastern Washington were lower than in western Washington (Furl, 2007, 2008).

In 2002, Ecology and 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.

In 2002, The 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. The additional study lakes included Terrell, Samish, Baker, Wiser, and Fazon Lakes.

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

From 1992-2001, the USGS (Van Metre et al., 2004) conducted a national sediment coring study of 56 lakes, including Lake Washington. Sediments were analyzed for a variety of organic and inorganic contaminants including mercury, lead, and PAHs. In Lake Washington, mercury and lead concentrations increased substantially above background in the early 20th century. Between 1940 and 1970, levels peaked and then began to fall. The PAH record displays a decrease in the most recent sediments from previous highs in the 1970s.

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

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Methods

Site Descriptions

Figure 1 displays the locations of the lakes and coring sites.

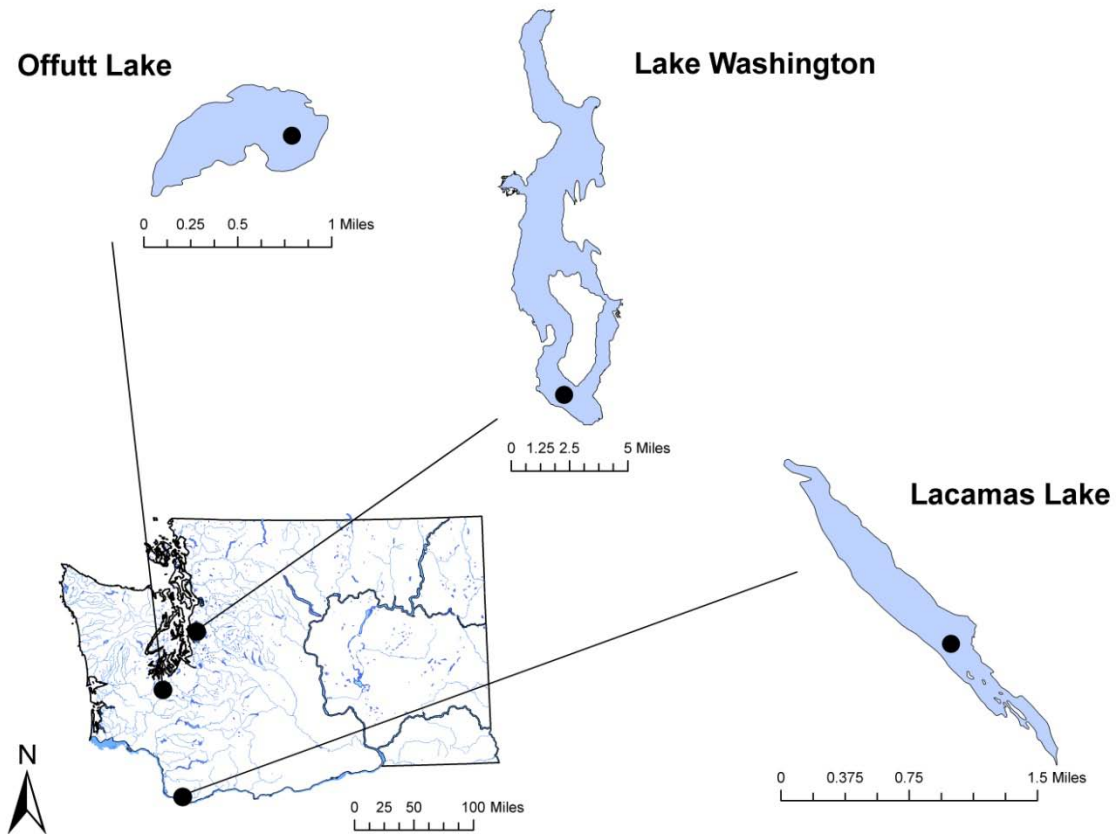


Figure 1. 2008 study lakes.

Table 1 contains information on the catchment area, lake morphology, and precipitation.

Table 1. 2008 study lakes site data.

Lake:	Washington	Lacamas	Offutt
Surface Area (acre)	21,500	320	200
Drainage Area (acre)	300,000	41,152	1728
Volume (acre-ft)	2,350,000	7500	2900
Coring Site Depth (ft)	119	20	20
Maximum Depth (ft)	214	65	25
Mean Depth (ft)	108	24	15
DA:SA Ratio ¹	14.0	128.6	8.6
Precipitation ²	923	1284	1274
Altitude (ft)	20.6	179	230
Coring Site Latitude/Longitude (dd ³)	47.5193 / -122.2543	45.6137 / -122.4220	46.9159 / -122.8225

¹Drainage-area to surface-area ratio.

²Precipitation data provided by PRISM www.prism.oregonstate.edu.

³Decimal degrees.

Lake Washington

Lake Washington (in King County) is located between Seattle and Bellevue, two miles east of Puget Sound. Soils in the area consist primarily of Vashon till deposits, but also include some advance outwash deposits, alluvial deposits, non-glacial floodplains, and bedrock. The lake is surrounded by houses and three large parks. There is an industrial section at the south end of the lake. Land use in the area is primarily urban residential, industrial, and commercial. Lake Washington drains through the Ballard Locks into Puget Sound (Ecology, 2008).

Lacamas Lake

Lacamas Lake (in Clark County) is located just east of Vancouver, WA. The lake was created by the glacially induced Missoula floods, and the water level was subsequently raised when two dams were built on Lacamas Creek (Clark County, 2008). Soils in the area are Quaternary-Miocene sediments, comprised mostly of clay, silt, sand, and some gravel. Water flows into the lake from Lacamas Creek at the northeast corner and drains into Lacamas Creek on the southeast corner, eventually draining into the Washougal River (Bortleson et al., 1976). Land use is primarily agricultural and undeveloped forest with some residential, commercial, and industrial development (Ecology, 2008).

Offutt Lake

Offutt Lake (in Thurston County) is located about four miles north of Tenino. Soils surrounding the lake are primarily Vashon morainal deposits with the exception of a section of alluvial deposits on the southeast corner of the lake. There is some suburban development in the area, and the remainder of land use is agricultural and undeveloped land (Ecology, 2008). There is a perennial inflow at the east side of the lake, and water drains out through a channel on the west side (Bortleson et al., 1976).

Field Methods

Sediment cores were collected from deep, flat areas of the lakes using a Wildco stainless steel box corer containing a 13cm x 13cm x 50cm acrylic liner. Collection efforts were guided by the Ecology Environmental Assessment Program (EAP) standard operating procedure for *Collection of Freshwater Sediment Core Samples using a Box or KB Corer* (Furl and Meredith, 2008). Cores were determined suitable for subsampling if the sediment-water interface was intact and the core deep enough to date sediments to pre-anthropogenic influence (approximately 35-45cm). Overlying water was siphoned off the top of the core, and 1cm sections were removed in the field using an extruding device.

Surface sediment grabs were collected using a 0.1m² stainless steel ponar grab sampler at the coring location (within 3m) for grain size analyses. Surface sediment sampling was conducted in accordance with the EAP standard operating procedure for *Freshwater Sediment Sampling* (Blakley, 2008). Sediment grab samples were kept if the sediment-water interface was preserved. Overlying water was siphoned out of the ponar grab, and the top 2cm of the sediments were removed using a stainless steel spoon.

The corer, ponar grab, and all equipment coming into contact with sediments were cleaned prior to sampling using the following procedure: Liquinox detergent and hot water wash, nitric acid rinse, de-ionized water rinse, and acetone rinse. The equipment was air dried and wrapped in foil until used in the field. The cleaning procedure was followed between lakes. Sampling equipment was washed with ambient lake water after coming in contact with sediments until a suitable sample was obtained.

Core sections and surface sediment grab samples were placed in 8oz. I-Chem jars with Teflon-lined lids, placed in plastic bags, and put on ice in coolers until transport to Ecology headquarters. Core samples remained in coolers for no more than 48 hours before being frozen at Ecology headquarters at -20° C. Grab samples were stored at 4° C until grain size analysis.

Field sampling was conducted in August 2008.

Sample Preparation and Analysis

Core sediment samples were processed at Ecology headquarters by homogenizing individual 1-cm horizons until the sediments were uniform in color and texture. Sub-samples were taken from the sediment homogenate and placed in the proper pre-cleaned jars for chemical analysis. All chemical analyses for the sediment core were performed on 1-cm intervals. The grab samples were analyzed for grain size only. Appendix B includes detailed information on the chemical analyses performed for each core.

Mercury

Samples were shipped frozen to Manchester Environmental Laboratory (MEL) in pre-cleaned 2oz I-Chem jars. Sediments were digested with 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 and measured with conventional cold vapor atomic absorption. Digestion and analysis was conducted according to EPA Method 245.5.

Lead

Samples were shipped frozen to MEL in pre-cleaned 2oz I-Chem jars. Sediments were digested with nitric acid and hydrogen peroxide (EPA Method 3050B) and analyzed by ICP-MS (EPA Method 200.8).

^{210}Pb

Forty-five samples were measured for ^{210}Pb radioactivity by Test America, Richland. Samples were shipped in nitric rinsed polystyrene jars provided by the laboratory. ^{210}Pb was determined by counting beta emissions from concentrated lead sulfate after allowing for ^{210}Bi ingrowth (decay product of ^{210}Pb). Samples near the top of the core were tested at a higher density where ^{210}Pb is at its greatest, and spread out further deeper in the core. The same intervals measured for ^{210}Pb were also analyzed for stable lead and total mercury.

PAHs

MEL measured 30 samples for 22 PAHs. Sediments were shipped frozen in pre-cleaned 4oz I-Chem jars. Samples were extracted on an accelerated solvent extractor with methylene chloride and analyzed with capillary GC/MS (MEL modification of EPA SW 846 8270). Extracts were cleaned using silica gel following EPA Method 3630C.

Total Organic Carbon

MEL measured 30 samples for TOC. Samples were shipped frozen and measured according to Puget Sound Estuary Protocol (PSEP) methodology (EPA, 1986). A sediment aliquot was acidified to remove inorganic carbon. The sample was then combusted at 900°C, and carbon dioxide was measured for TOC calculations.

Grain Size

Surface grabs were measured for grain size (gravel, sand, silt, clay) at each of the coring locations. Sediments were cooled to 4°C, remaining unfrozen until analysis. Analysis was completed using sieving and pipet techniques according to Puget Sound Estuary Program protocol (EPA, 1986).

Data Quality

MEL prepared case narratives describing the quality for all analytical data. The narratives include a description of results, laboratory quality assurance, and special issues encountered during analysis. Case narratives are available upon request. Laboratory measurement quality objectives, along with the results of laboratory quality assurance tests, can be found in Appendix C. Data quality over the entire project was generally good. Measurement quality objectives (MQOs) were met for each of the 6 constituents measured with the exception of PAHs. Results on quality control samples are summarized below.

Mercury and Lead

MEL measured 45 sediment samples for mercury and lead. Quality control consisted of laboratory control samples, matrix spikes, matrix spike duplicates, and method blanks.

For mercury, matrix spikes and laboratory control samples were recovered at an average of 97.8% and 101.5%, respectively. Matrix spike duplicates had an average relative percent difference (RPD) of 4.6%. All method blanks were non-detects at 0.005 mg/Kg.

For lead, matrix spikes and laboratory control samples were recovered at an average of 97.3% and 104% respectively. Matrix spike duplicates had an average RPD of 3.7%. All method blanks were non-detects at 0.1 mg/Kg.

²¹⁰Pb

Test America Richland measured 45 samples for ²¹⁰Pb activity. Sample counts were done in three 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 100%, method blanks were not detected above 0.200 pCi/g, and duplicates had an average RPD of 8.7%. Results were not used if uncertainty (± 2 standard deviations of the result) was greater than 45%. This resulted in 40 valid samples used in core dating.

PAHs

MEL measured 30 samples for PAHs. Quality control consisted of surrogate recoveries (2-Fluorobiphenyl, Pyrene-10, and Terphenyl-D14), matrix spikes, matrix spike duplicates, method blanks, laboratory control samples, and sample duplicates. Data from quality assurance tests were generally good with the exception of very low matrix spike recoveries on one of the

matrix spikes. Low recoveries were likely due to extraction losses in the matrix spike. The MEL case narrative for PAH analyses is included in Appendix D.

Total Organic Carbon

MEL measured 30 samples for TOC. Quality control consisted of blanks, control samples, and duplicates. Method blanks were non-detects above 0.1 mg/Kg. The relative percent difference between duplicates was < 1%, and control samples were recovered at an average of 91%.

Grain Size

Data quality was judged on the grain size measurements by comparing sample triplicates. Quality control tests were not run on sample material used in the project, but were conducted with different sediments tested in the same batch. Triplicate RPD averaged 6.9%.

Sedimentation Modeling and Data Calculations

Sedimentation Modeling

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 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 and Charles and Hites, 1987).

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

Mercury Flux Calculations

Mercury flux rates ($\mu\text{g}/\text{m}^2/\text{yr}$) were calculated as the product of sediment mass accumulation rates (SMARs) and dry weight mercury concentrations:

$$\text{Dry Weight Concentration (ng/g)} * \text{SMAR (g}/\text{cm}^2/\text{yr)} * 10 = \text{Mercury Flux Rate (}\mu\text{g}/\text{m}^2/\text{yr)}$$

Mercury flux rate results are used to estimate net deposition to the lake. Flux rates normalize the variance involved with interpreting dry weight concentrations under varying sedimentation rates.

PAH Data Processing

Measured PAH concentrations are reported as $\mu\text{g}/\text{Kg}$ dry weight (dw) and normalized to TOC for comparison purposes. TOC values ranged from 2.3 – 10.5% among the three sites. TOC-normalized concentrations were calculated by dividing the dry weight PAH concentration by the decimal fraction representing percent TOC. Summing procedures were conducted according to the Washington State Sediment Management Standards rule (Ecology, 1995). Only detected concentrations were included in total PAH sums. Results for lab duplicates were not averaged. A list of the PAHs analyzed is found in Appendix D.

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Results and Discussion

Core Dates and Sedimentation Rates

Lead-210 results are located in Appendix B. Estimated supported ^{210}Pb levels and unsupported ^{210}Pb yearly flux derived from core inventories are shown in Table 2. Atmospheric ^{210}Pb deposition measured over a 7-year period in Seattle found a mean annual deposition of 0.198 pCi/cm^2 with the standard error of the mean as ± 0.108 (Nevissi, 1985). While the estimated unsupported yearly flux at Lake Washington ($0.38 \text{ pCi/cm}^2/\text{yr}$) is slightly outside of the upper standard error of the mean, the values are within estimated ranges found at other Washington coring locations (Furl, 2007, 2008).

Table 2. Estimated supported ^{210}Pb and yearly unsupported ^{210}Pb flux.

Lake	Supported ^{210}Pb (pCi/g)	Unsupported ^{210}Pb Yearly Flux (pCi/cm ² /yr)
Washington	0.27	0.38
Lacamas	0.73	0.19
Offutt	0.52	0.18

Sedimentation rates along with their estimated dates are plotted in Figure 2.

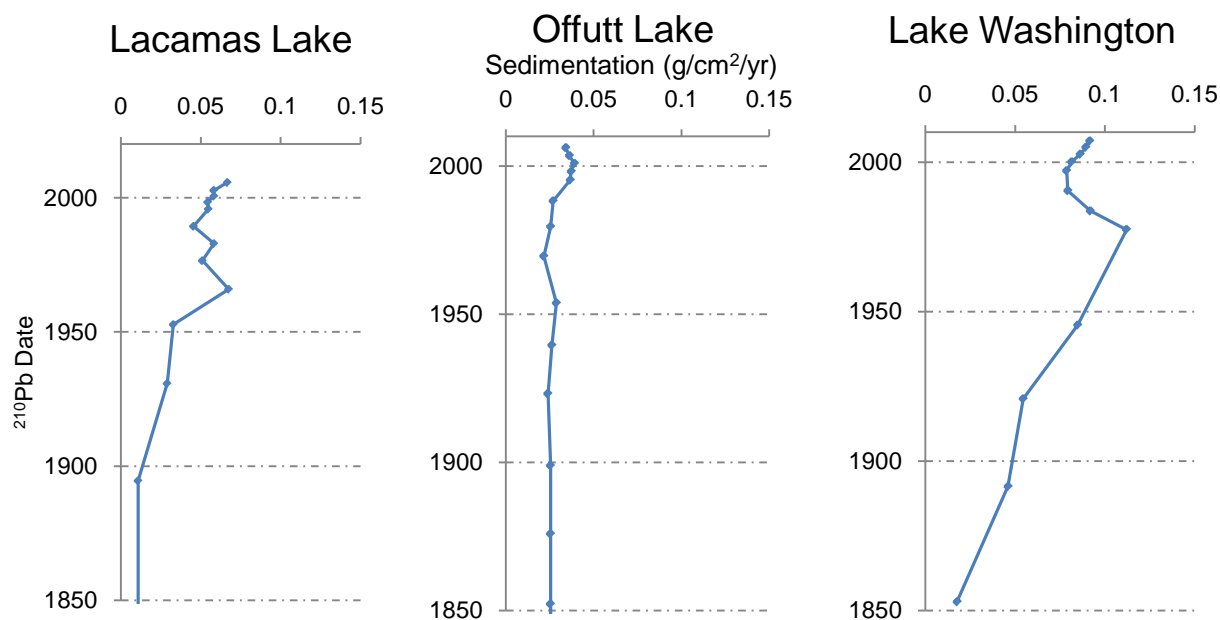


Figure 2. Sedimentation rates (g/cm²/yr) and estimated dates (^{210}Pb dates) for the 2008 study lakes.

Sedimentation rates among the study lakes ranged from 0.01 – 0.11 g/cm²/yr. As expected, higher sedimentation rates were found at Lake Washington compared to the less urbanized basins of Lacamas and Offutt. Pre-industrial (before 1850) rates at all three lakes were less than 0.03 g/cm²/yr. Sedimentation rates from previous coring reports are included in Table 3. Values from the current report are within typical ranges found at western Washington sites.

Table 3. Sedimentation rates from previous (2006-07) coring studies.

Lake	Sedimentation Range (g/cm ² /yr)	Peak Year
Loon Lake ¹	0.0090 - 0.0248	1993
Wannacut Lake ¹	0.0094 - 0.0229	1937
Lake Ozette ²	0.0223 - 0.1153	2004
Lake Sammamish ²	0.0188 - 0.0637	1950
Lake St. Clair ²	0.0170 - 0.0895	1983

¹ Furl 2008.

² Furl 2007 - ²¹⁰Pb values are included in report. Sedimentation rates and associated year are not included in 2007 report.

Total Organic Carbon and Grain Size

TOC concentrations varied between lakes ranging from 2.3 – 10.5%. Average percent TOC throughout the core was 3.0, 4.9, 10.1 for Lake Washington, Lacamas Lake, and Offutt Lake, respectively. Percent TOC varied little within each sediment core (< 2%).

Percent fines (% < 0.0625 mm) in sediment grab samples from the coring sites were 75, 49, and 35 at Washington, Lacamas, and Offutt, respectively.

Contaminant Profiles

Mercury

Mercury fluxes and dry weight concentrations are shown in Figure 3 with their corresponding dates.

Dry weight concentrations ranged from 57 – 411 ng/g throughout the cores with the uppermost horizons (0 - 2 cm) ranging from 100 – 182 ng/g. Flux values ranged from 12 – 386 µg/m²/yr over the entire length of the cores, with the upper values ranging from 62 – 147 µg/m²/yr.

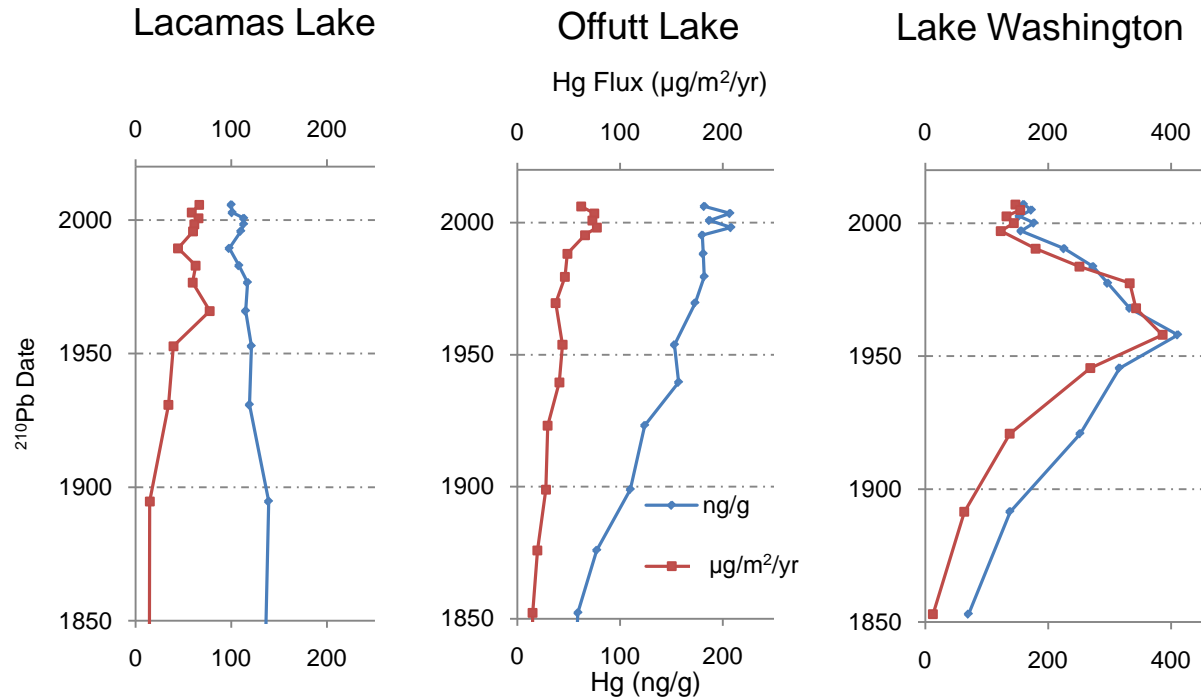


Figure 3. Mercury flux rates ($\mu\text{g}/\text{m}^2/\text{yr}$) and estimated dates (^{210}Pb dates) for the 2008 study lakes (note scale change).

Mercury concentration profiles were dissimilar between lakes. Concentrations at Lacamas Lake decline throughout the core reaching their minimum at the top of the core. The reduction in mercury concentrations coincides with increasing sedimentation rates. Offutt Lake concentrations reach their maximum near the top of the core where they are approximately 3 times higher than the deepest intervals. Lake Washington mercury concentrations peak during the 1950s and decline through the late 1990s. The shape of the Lake Washington mercury concentration profile was similar to a core taken by Van Metre et al. (2004) from the north end of the lake. However, Van Metre et al. (2004) recorded mercury concentrations nearly double levels found in the current 2008 study.

Mercury flux profiles at Lacamas and Offutt Lakes were similar, increasing slowly after 1900. Current flux rates at both lakes are approximately $65 \mu\text{g}/\text{m}^2/\text{yr}$. At Lake Washington, mercury flux and concentration had similar profiles. Current fluxes to Lake Washington are approximately $150 \mu\text{g}/\text{m}^2/\text{yr}$.

Flux rates recorded at the study lakes were within ranges found at other Washington State coring sites (Furl, 2007, 2008). Table 4 displays flux range, peak year, and average modern flux (2000 – present) for all lakes sampled as part of this long-term study. Lake Offutt and Lacamas Lake have the lowest average modern flux rates in western Washington. While average modern flux at Lake Washington is more than double Offutt and Lacamas, it is still within previously recorded values.

Table 4. Flux rate range, peak year, and recent averages from current (2008) and previous (2006-07) coring studies.

Lake	Flux Range ($\mu\text{g}/\text{cm}^2/\text{yr}$)	Peak Year	Average Flux 2000 - present ($\mu\text{g}/\text{cm}^2/\text{yr}$)	n
Washington	12 - 386	1940	144.4	4
Lacamas	14 - 77	1966	63.6	3
Offutt	14 - 77	1998	70.0	3
Wannacut ²	2 - 361	1932	10.5	1
Loon ²	2 - 22	1995	15.1	1
Sammamish ³	18 - 273	1934	94.0	3
St. Clair ³	17 - 271	1975	214.4	2
Ozette ³	37 - 261	1997	212.8	2

¹ n - Number of measurements used in 2000 - present flux average.

² Furl 2008.

³ Furl 2007, fluxes are not reported.

Lead

Lead profiles are displayed in Figure 4.

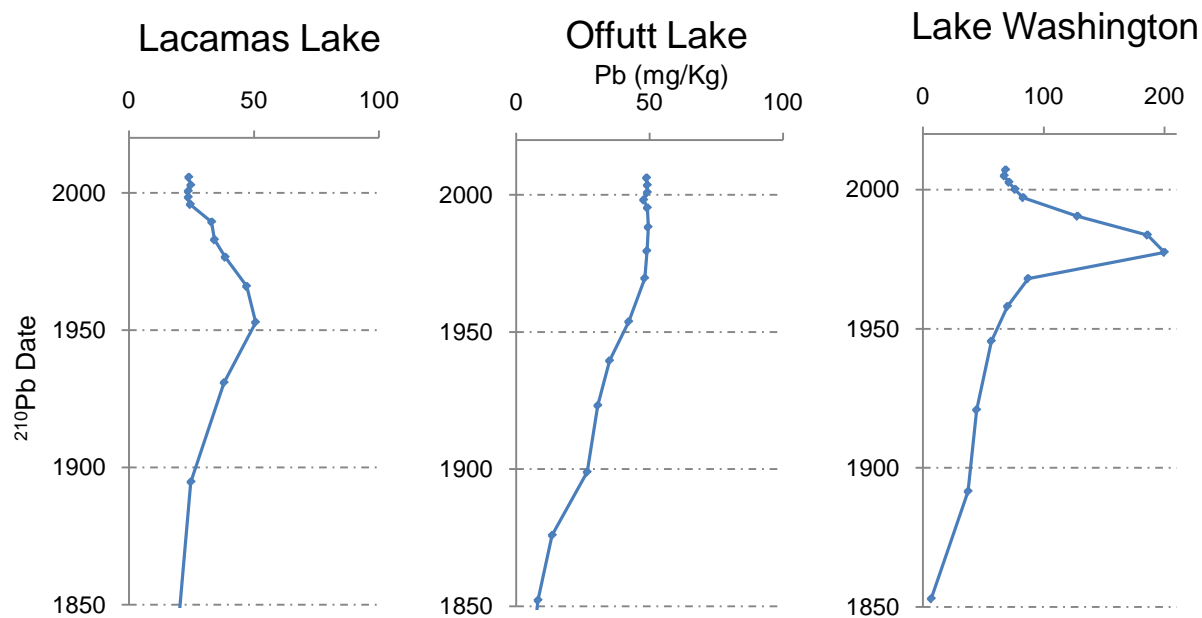


Figure 4. Lead concentrations (mg/Kg) and estimated dates (²¹⁰Pb dates) for the 2008 study lakes (note scale change).

Lead concentrations ranged from 6 – 200 mg/Kg for the entire length of the cores. The uppermost horizons (0 – 2 cm) ranged from 24 – 69 mg/Kg. Lead concentrations at Offutt and Washington Lakes were elevated by 1900. Increased concentrations at these two lakes reflect elevated atmospheric levels from the Asarco smelter in Tacoma which began refining lead in 1890. Lead concentrations at Lacamas Lake began increasing by 1930.

Lead concentration profiles at the three lakes were incongruent. Lead levels at Lacamas Lake peaked shortly after 1950 and began decreasing as sedimentation rates increased. Concentrations have remained constant since the mid 1990s. Offutt lake concentrations have been increasing since the 1850s and have remained stable near their maximum since the 1970s. Concentrations at Lake Washington displayed a typical lead signature, peaking in the mid-1970s followed by substantial decline. Concentrations have remained fairly constant during the 2000s at Lake Washington.

Lead concentrations were measured in the first two years of the study to corroborate dates calculated from the ^{210}Pb dating model. Lead concentrations from five lakes statewide ranged from 1 – 138 mg/Kg. Lead was also measured in the Lake Washington sediment core taken by Van Metre et al. (2004) in 1998. Concentrations ranged from 19 – 285 mg/Kg, peaking during the mid-1970s.

PAHs

Summed PAH concentrations for the cores are displayed in Figure 5.

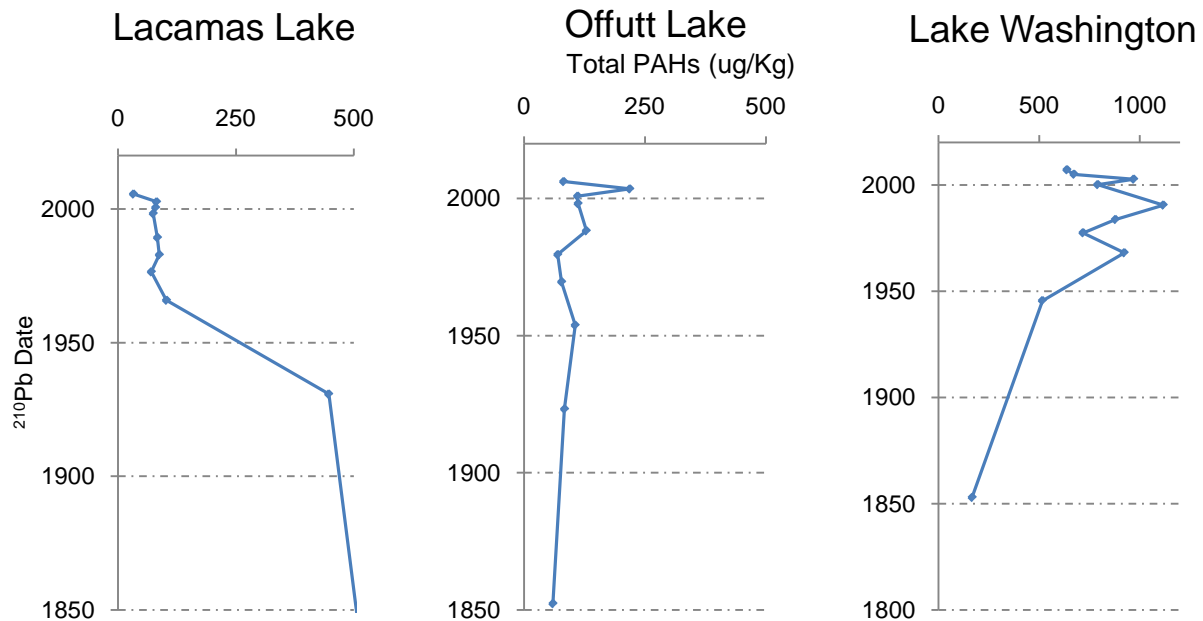


Figure 5. Total summed PAHs ($\mu\text{g}/\text{Kg}$) and estimated dates (^{210}Pb dates) for the 2008 study lakes (note scale change).

The sum of detected PAHs ranged from 33 – 1117 $\mu\text{g}/\text{Kg}$. Concentrations in the uppermost horizons (0 – 2 cm) ranged from 33 – 638 $\mu\text{g}/\text{Kg}$. Concentrations in the 2 – 3 cm horizon ranged from 82 – 673 $\mu\text{g}/\text{Kg}$ and were greater than the 0 – 2 cm horizon in all cases. The apparent declines are likely the result of elevated detection limits in the 0 – 2 horizon at all three lakes. PAH profiles among lakes were dissimilar in concentration and pattern. Levels at Lacamas Lake have declined steadily coinciding with increased sedimentation rates. Concentrations at Offutt Lake have remained fairly stable and low. However, the highest value in the Offutt Lake core was found at the 2 -3 cm horizon. Concentrations at Lake Washington increased from the 1850s until the late 1960s. Since the 1960s, the profile displays an erratic pattern with concentrations ranging from 638 – 1117 $\mu\text{g}/\text{Kg}$. The most recent intervals (0-2 cm and 2-3 cm) indicate declines in Lake Washington PAH concentrations over older sediment intervals.

PAH concentrations were also expressed as $\mu\text{g}/\text{Kg}$ organic carbon (Figure 6). The TOC normalized concentrations allow for comparisons between lakes while allowing for varying TOC concentrations. Based on this measurement ($\mu\text{g}/\text{Kg}$ organic carbon), concentrations at Lake Washington are approximately 10 – 45 times higher than Offutt and Lacamas Lakes since the 1970s. This is a reflection of the dense urban land use in Lake Washington’s drainage area.

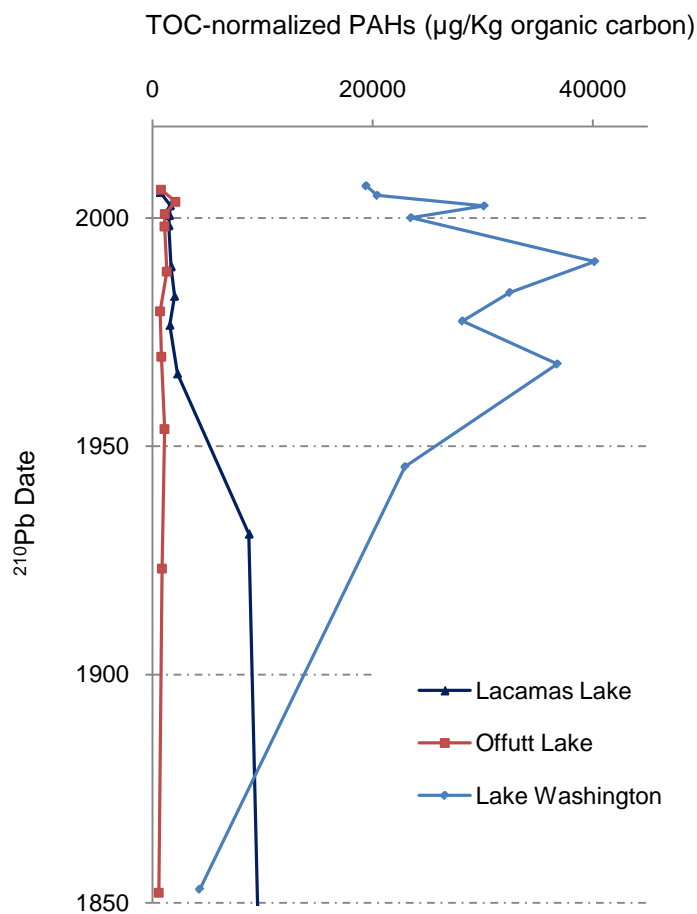


Figure 6. TOC-normalized PAH sums and estimated dates (^{210}Pb dates) for the three 2008 study lakes.

PAH concentrations in age-dated sediment cores from Lake Washington have been recently examined by other researchers. PAHs were analyzed by Van Metre et al. (2005) in the sediment core previously discussed. Wakeham et al. (2004) analyzed PAHs in a Lake Washington core taken in 2000. Concentrations recorded by Wakeham et al. (2004) were significantly elevated over values reported by Van Metre et al. (2005) and the current study. The location of the coring site was not reported. Additionally, both studies found a decline in summed PAHs during the 1990s not corroborated by the current study (Table 5).

Table 5. Average total PAH sums over three time periods for the current study, Wakeham et al. (2004), and Van Metre et al. (2005).

Study	Average Total PAHs ($\mu\text{g}/\text{Kg}$)		
	1965-1975	1990-2000	2000-2008
Furl et al. (2009)	821 (n=2)	954 (n=2)	760 (n=3)
Wakeham et al. (2004)	7333 (n=3)	2133 (n=2)	-
Van Metre et al. (2005)*	658	241	-

* Number of samples included in decadal averages was not specified. Core was recovered in 1998.

Parent PAH ratios have been widely used to discriminate between combustion and petroleum sources in environmental samples (Yunker et al., 1996; Budzinski et al., 1997). While several ratios have been proposed, the ratio using fluoranthene and pyrene was the only ratio examined since these two were the only PAHs detected in all samples. Yunker et al. (2002) proposes a fluoranthene/fluoranthene + pyrene (Fl/Fl + Py) ratio of 0.40 as the petroleum/combustion transition point. Additionally, Yunker et al. (2002) propose ratios between 0.40 – 0.50 to represent liquid fossil fuel combustion, whereas > 0.50 are characteristic of grass, wood, or coal combustion. Fl/Fl + Py ratios are displayed in Figure 7.

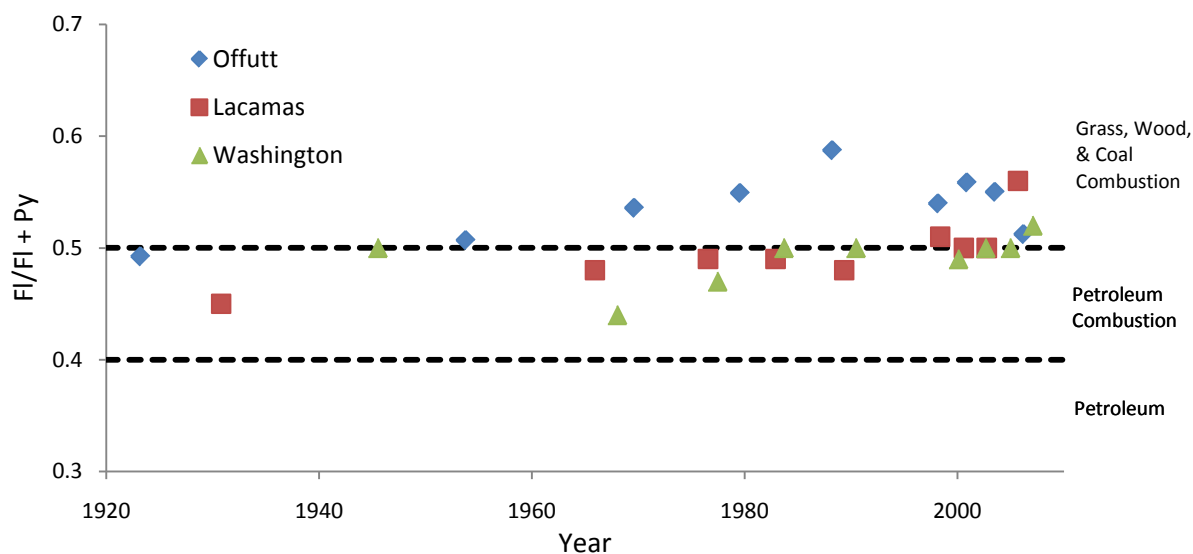


Figure 7. Fluoranthene/Fluoranthene + Pyrene ratios at the 2008 study lakes.

Average ratios during the 1900s were 0.54, 0.50, and 0.49 for Offutt, Lacamas, and Washington, respectively. Using the ratio interpretation proposed by Yunker et al. (2002), all three lakes are dominated by combustion-derived sources.

Conclusions

This study was the third year of a five-year study on present and historical contaminant trends in Washington State lake sediments. Deep sediment cores were collected from Lake Washington, Lacamas Lake, and Offutt Lake and analyzed for mercury, lead, and PAHs. Dates and sedimentation rates were assigned to the sediments using the constant rate of supply model.

Overlying contaminant trends for each core varied by lake and analyte. Lake Washington has received higher contaminant loads than Lacamas Lake or Offutt Lake. However, concentrations of mercury and lead at all three lakes were found within expected concentrations based on previous Washington State sediment core studies.

Lake Washington sediments received substantial contaminant loading over the first half of the 1900s. Concentrations of mercury and lead have declined significantly after peaking in the 1950s and 1970s respectively. PAH concentrations display an erratic pattern of increases and declines since the 1960s. Decreases in PAH concentrations during the 1990s recorded by other researchers were not corroborated. However, the most recent sediment intervals measured display a declining trend. TOC-normalized PAH concentrations were 10 – 45 times higher in Lake Washington compared to Offutt and Lacamas Lakes since the 1970s.

The Lacamas Lake sediment core displayed decreasing trends for all three contaminants in the 1990s. Decreases in contaminant concentrations coincide with increased sedimentation rates. This relationship suggests sediment sources to the lake contain lower contaminant concentrations than the preexisting sediment matrix. Concentrations of mercury, lead, and PAHs in the uppermost sediment horizon were lower than the other two lakes.

Offutt Lake sediment profiles displayed increasing trends in lead and mercury after the 1850s. Concentrations increased until the 1970s where they began leveling off. Current levels of both metals remain near their historical maximum. PAH concentrations were low and had little variation when compared to the other study lakes. The highest summed PAH concentration was found near the top of the core in the 2 – 3 cm horizon.

Recommendations

As a result of this 2008 study, the following recommendations are made for the next two years of this study:

1. Include at least one urban waterbody each year to further investigate PAH trends.
2. For more accurate sediment chronologies, measure ^{210}Pb in multiple horizons 35 cm and deeper to ensure accurate supported ^{210}Pb levels are calculated. If a core cannot be recovered deeper than 35 centimeters, consider measuring ^{226}Ra to estimate supported ^{210}Pb .
3. Continue to add additional PBT chemicals, such as PBDEs and perfluorinated compounds, as needed.
4. Evaluate additional indicators of petrogenic and pyrogenic sources of PAHs.
5. Continue to expand the geographic coverage of the sediment coring effort to include southeastern and central Washington.

References

ATSDR, Agency for Toxic Substances and Disease Registry, 1995. Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). U.S. Department of Health and Human Services.

ATSDR, Agency for Toxic Substances and Disease Registry, 2007. Toxicological Profile for Lead. U.S. Department of Health and Human Services.

Appleby, P.G. and F. Oldfield, 1978. The Calculation of Lead-210 Dates Assuming a Constant Rate of Supply of Unsupported ^{210}Pb to the Sediment. *Catena*, Vol. 5, 1-8.

Bortleson, G.C., N.P. Dion, J.B. McConnell, and L.M. Nelson, 1976. Reconnaissance Data on Lakes in Washington, Volume 4 Clark, Cowlitz, Grays Harbor, Lewis, Pacific, Skamania, and Thurston Counties. *Water Supply Bulletin 43*, Vol 4. United States Geological Survey in Cooperation with the Washington State Department of Ecology.

Blakley, N., 2008. Standard Operating Procedure for Obtaining Freshwater Sediment Samples. Washington State Department of Ecology, Olympia, WA. SOP Number EAP040.
www.ecy.wa.gov/programs/eap/quality.html.

Budzinski, H., I. Jones, J. Bellocq, and others, 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry*. Vol. 58: 85-97.

Charles, M.J. and R.A. Hites, 1987. Paper/Book Chapter: Sediments as Archives of Environmental Pollution Trends. Copyright 1987 American Chemical Society. Book Title: Sources and Fates of Aquatic Pollutants. Eds. Ronald A. Hites and S.J. Eisenreich.

Clark County Public Works - Clean Water Program, Focus: Lacamas Lake.
Retrieved 1/23/2009 from Clark County on the World Wide Web:
www.co.clark.wa.us/water-resources/documents/Monitoring/focus%20-%20lacamas.pdf

Coots, R., 2006. Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-113. www.ecy.wa.gov/biblio/0603113.html

Davies, H., 2008. Washington State Lead Chemical Action Plan (Public Review Draft). Washington State Department of Ecology, Olympia, WA. Publication No. 08-07-009.
www.ecy.wa.gov/biblio/0807009.html

Ecology, 1995. Sediment Management Standards, Chapter 173-204 WAC. Washington State Department of Ecology. Revised December, 1995.
<http://www.ecy.wa.gov/biblio/wac173204.html>

Ecology, 2008. GIS database, Land use by parcel layer, Hydrogeology layer. Washington State Department of Ecology. Accessed: September 2008.

- EPA, 2006. Toxics Release Inventory. United States Environmental Protection Agency. www.epa.gov/triexplorer. Accessed February 10, 2008.
- EPA, 1986. Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound. United States Environmental Protection Agency. 49 p.
- Engstrom, D.R. and E.B. Swain, 1997. Recent Declines in Atmospheric Mercury Deposition in the Upper Midwest. *Environmental Science and Technology*, 31 960-967.
- Engstrom, D.R., S.J. Balogh, and E.B. Swain, 2007. History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnology and Oceanography*, 52(6): 2467-2483.
- Furl, C., 2007. History of Mercury in Selected Washington Lakes Determined from Age-Dated Sediment Cores: 2006 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-019. www.ecy.wa.gov/biblio/0703019.html
- Furl, C., 2008. History of Mercury in Selected Washington Lakes Determined from Age-Dated Sediment Cores: 2007 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 08-03-012. www.ecy.wa.gov/biblio/0803012.html
- Furl, C. and C. Meredith, 2008. Standard Operating Procedure for Collection of Freshwater Sediment Core Samples Using a Box or KB Corer. Washington State Department of Ecology, Olympia, WA. SOP Number EAP038. www.ecy.wa.gov/programs/eap/quality.html
- Gallagher, M., 2000. Proposed Strategy to Continually Reduce Persistent, Bioaccumulative Toxins (PBTs) in Washington State. Washington State Department of Ecology, Olympia, WA. Publication No. 00-03-054. www.ecy.wa.gov/biblio/0003054.html
- Gallagher, L., R.W. MacDonald, and D.W. Paton, 2004. The Historical Record of Metals in Sediments from Six Lakes in the Fraser River Basin, British Columbia. *Water, Air, and Soil Pollution*, 152: 257-278.
- Geller, L., 2006. Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Final Report. Washington State Department of Ecology, Olympia, WA. Publication No. 05-07-048. www.ecy.wa.gov/biblio/0507048.html
- Kamman, N.C. and D.R. Engstrom, 2002. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ²¹⁰Pb dated sediment cores. *Atmospheric Environment* 36: 1599 – 1609.
- Meredith, C. and C. Furl, 2008. Addendum #1 to Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-113ADD1. www.ecy.wa.gov/biblio/0603113add1.html

Nevissi, A.E., 1985. Measurement of ^{210}Pb Atmospheric flux in the Pacific Northwest. *Health Physics*. 45(2): 169-174.

Norton, D., 2004. Mercury in Lake Whatcom Sediments, Spatial Distribution, Depositional History, and Tributary Inputs. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-019. www.ecy.wa.gov/biblio/0403019.html

Paulson, A. J., 2004. Sources of Mercury in Sediments, Water, and Fish of the Lakes of Whatcom County, Washington: U.S. Geological Survey Scientific Investigations Report 2004-5084, 98 pages. Prepared in Cooperation with the Whatcom County Health Department and the Washington State Department of Ecology.

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

Rudd, J.W.M., 1995. Sources of methylmercury to freshwater ecosystems: a review. *Water, Air, Soil Pollution*. 80: 697-713.

Van Metre, P. and E. Callender, 2000. Urban Sprawl Leaves its PAH Signature. *Environmental Science and Technology*. Vol. 34: 4064-4070.

Van Metre, P., J. Wilson, C. Fuller, E. Callender, and B. Mahler, 2004. Collection, Analysis and Age-Dating of Sediment Cores From 56 U.S. Lakes and Reservoirs Sampled by the U.S. Geological Survey, 1992-2001. United States Geological Survey. <http://pubs.usgs.gov/sir/2004/5184/>

Van Metre, P. and B. Mahler, 2005. Trends in Hydrophobic Organic Contaminants in Urban and Reference Lake Sediments across the United States, 1970-2001. *Environmental Science and Technology*. Vol. 39: 5567-5574.

Wakeham, S., J. Forrest, C. Masiello, and others, 2004. Hydrocarbons in Lake Washington Sediments, A 25-Year Retrospective in an Urban Lake. *Environmental Science and Technology*. Vol. 38: 431-439.

Yake, B., 2001. The Use of Sediment Cores to Track Persistent Pollutants in Washington State - A Review. Washington State Department of Ecology, Olympia, WA. Publication No. 01-03-001. www.ecy.wa.gov/biblio/0103001.html

Yunker, M.B., L.R. Snowdon, R.W. Macdonald, and others, 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environmental Science and Technology*. Vol. 30: 1310-1320.

Yunker, M.B., R.W. Macdonald, R. Vingarzan, and others, 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*. Vol. 33: 489-515.

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Appendices

Appendix A. PBT Trend Monitoring Coring Locations

Appendix B. Sediment Core and Surface Sediment Data

Appendix C. Quality Assurance Data

Appendix D. Case Narrative for PAHs

Appendix E. Glossary, Acronyms, and Abbreviations

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Appendix A. PBT Trend Monitoring Coring Locations

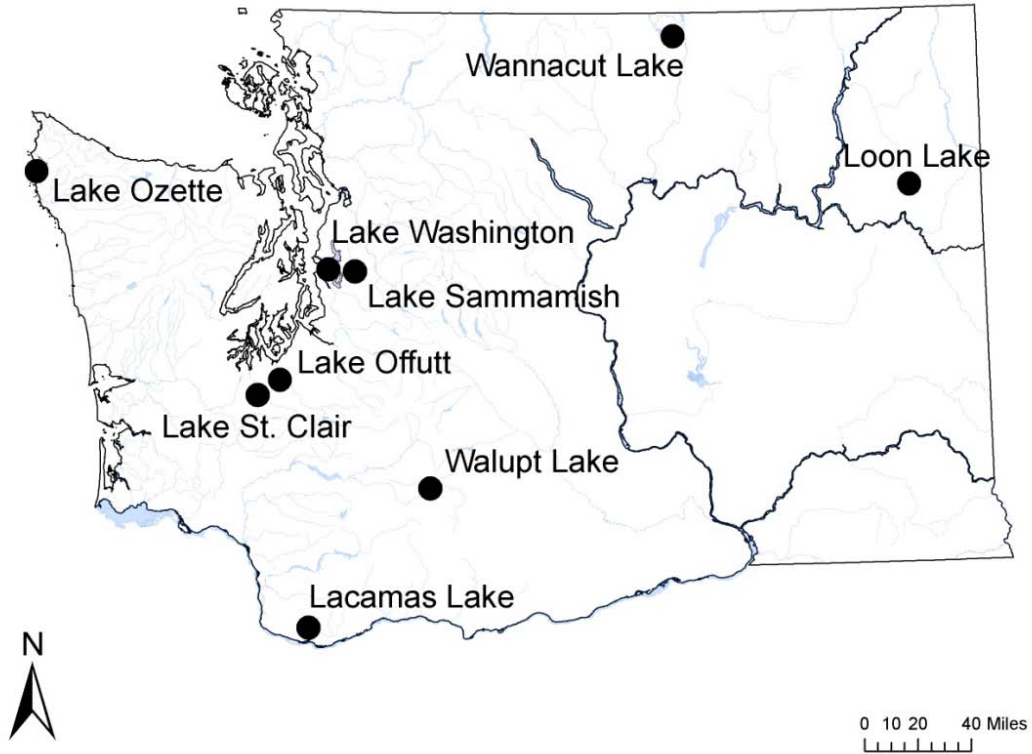


Figure A-1. Waterbodies Cored by Ecology for PBT Trend Monitoring 2006-2008.

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Appendix B. Sediment Core and Surface Sediment Data

Table B-1. Lake Washington core sectioning

Table B-2. Lacamas Lake core sectioning

Table B-3. Offutt Lake core sectioning

Table B-4. ²¹⁰Pb Results

Table B-1. Lake Washington core sectioning, collected August 13, 2008.

Section (cm intervals)	Analyte				Field ID	Sample #
	Mercury (ng/g)	Lead (mg/Kg)	Total PAHs (ug/Kg)	TOC (%)		
0-2	160	68.5	638J	3.29	Wa02	08334462
2-3	173	67.4	673J	3.3	Wa03	08334463
3-4	153	71.3	970J	3.22	Wa04	08334464
4-5	177	76.4	791J	3.37	Wa05	08334465
5-6	156	83	----	----	Wa06	08334466
6-7	----	----	----	----	----	----
<u>7-8</u>	226	128	1117J	2.78	Wa08	08334467
8-9	----	----	----	----	----	----
9-10	273	186	879J	2.71	Wa10	08334468
10-11	----	----	----	----	----	----
11-12	297	200	718J	2.55	Wa12	08334469
12-13	----	----	----	----	----	----
13-14	----	----	----	----	----	----
14-15	333	87.1	923J	2.51	Wa15	08334470
15-16	----	----	----	----	----	----
16-17	----	----	----	----	----	----
17-18	411	70.1	----	----	Wa18	08334471
18-19	----	----	----	----	----	----
19-20	----	----	----	----	----	----
20-21	316	56.7	516J	2.25	Wa21	08334472
21-22	----	----	----	----	----	----
22-23	----	----	----	----	----	----
23-24	----	----	----	----	----	----
24-25	252	44.5	----	----	Wa25	08334473
25-26	----	----	----	----	----	----
26-27	----	----	----	----	----	----
27-28	----	----	----	----	----	----
28-29	138	37.5	----	----	Wa29	08334474
29-30	----	----	----	----	----	----
30-31	----	----	----	----	----	----
31-32	----	----	----	----	----	----
32-33	70.4	7	167J	3.89	Wa33	08334475
33-34	----	----	----	----	----	----
34-35	----	----	----	----	----	----
35-36	----	----	----	----	----	----
36-37	66.6	5.7	----	----	Wa37	08334476

J – Analyte positively identified, approximate concentration

Table B-2. Lacamas Lake core sectioning, collected August 12, 2008.

Section (cm intervals)	Analyte				Field ID	Sample #
	Mercury (ng/g)	Lead (mg/Kg)	Total PAHs (ug/Kg)	TOC (%)		
0-2	100	23.9	33J	4.74	Lac02	08334446
2-3	101	24.7	82J	5.11	Lac03	08334447
3-4	113	23.7	80J	5.23	Lac04	08334448
4-5	113	23.7	75J	5.23	Lac05	08334449
5-6	110	24.5	----	----	Lac06	08334450
6-7	----	----	----	----	----	----
7-8	98	33.1	84J	4.95	Lac08	08334451
8-9	----	----	----	----	----	----
9-10	108	34.2	88J	4.43	Lac10	08334452
10-11	----	----	----	----	----	----
11-12	117	38.5	71J	4.51	Lac12	08334453
12-13	----	----	----	----	----	----
13-14	----	----	----	----	----	----
14-15	115	47.1	103J	4.56	Lac15	08334454
15-16	----	----	----	----	----	----
16-17	----	----	----	----	----	----
17-18	121	50.7	----	----	Lac18	08334455
18-19	----	----	----	----	----	----
19-20	----	----	----	----	----	----
20-21	119	38.1	447J	5.11	Lac21	08334456
21-22	----	----	----	----	----	----
22-23	----	----	----	----	----	----
23-24	139	24.8	----	----	Lac24	08334457
24-25	----	----	----	----	----	----
25-26	----	----	----	----	----	----
26-27	135	18.6	----	----	Lac27	08334458
27-28	----	----	----	----	----	----
28-29	----	----	----	----	----	----
29-30	----	----	----	----	----	----
30-31	129	16.2	577J	5.48	Lac31	08334459
31-32	----	----	----	----	----	----
32-33	----	----	----	----	----	----
33-34	124	13.5	----	----	Lac34	08334460

J – Analyte positively identified, approximate concentration

Table B-3. Offutt Lake core sectioning, collected August 11, 2008.

Section (cm intervals)	Analyte				Field ID	Sample #
	Mercury (ng/g)	Lead (mg/Kg)	Total PAHs (ug/Kg)	TOC (%)		
0-2	182	48.9	82J	10.8	Off02	08334430
2-3	207	49.2	219J	10.5	Off03	08334431
3-4	187	49.2	111J	9.93	Off04	08334432
4-5	208	47.8	112J	10.2	Off05	08334433
5-6	180	49.2	----	----	Off06	08334434
6-7	----	----	----	----	----	----
7-8	181	49.5	129J	9.99	Off08	08334435
8-9	----	----	----	----	----	----
9-10	182	49	70J	10.1	Off10	08334436
10-11	----	----	----	----	----	----
11-12	173	48.2	78J	9.64	Off12	08334437
12-13	----	----	----	----	----	----
13-14	----	----	----	----	----	----
14-15	153	42.2	106J	9.66	Off15	08334438
15-16	----	----	----	----	----	----
16-17	----	----	----	----	----	----
17-18	157	35	----	----	Off18	08334439
18-19	----	----	----	----	----	----
19-20	----	----	----	----	----	----
20-21	124	30.6	84J	9.86	Off21	08334440
21-22	----	----	----	----	----	----
22-23	----	----	----	----	----	----
23-24	----	----	----	----	----	----
24-25	110	26.6	----	----	Off25	08334441
25-26	----	----	----	----	----	----
26-27	----	----	----	----	----	----
27-28	----	----	----	----	----	----
28-29	77.3	13.5	----	----	Off29	08334442
29-30	----	----	----	----	----	----
30-31	----	----	----	----	----	----
31-32	----	----	----	----	----	----
32-33	59	8.15	60NJ	10.5	Off33	08334443
33-34	----	----	----	----	----	----
34-35	----	----	----	----	----	----
35-36	57	6.28	----	----	Off36	08334444

J – Analyte positively identified, approximate concentration

NJ – Analyte tentatively identified, approximate concentration

Table B-4. ²¹⁰Pb Results.

Site	Interval	Field ID	Sample #	Result (pCi/g)	Uncertainty (2sd)
Offutt Lake	0-2	OFF02	08334430	5.35	± 1.19
	2-3	OFF03	08334431	4.71	± 1.05
	3-4	OFF04	08334432	4.10	± 0.90
	4-5	OFF05	08334433	3.97	± 0.90
	5-6	OFF06	08334434	3.72	± 0.82
	7-8	OFF08	08334435	4.02	± 0.95
	9-10	OFF10	08334436	3.34	± 0.76
	11-12	OFF12	08334437	2.96	± 0.73
	14-15	OFF15	08334438	1.64	± 0.45
	17-18	OFF18	08334439	1.31	± 0.45
	20-21	OFF21	08334440	1.04	± 0.33
	24-25	OFF25	08334441	0.75	± 0.34
	28-29	OFF29	08334442	0.49	± 0.25
	32-33	OFF33	08334443	0.27U	± 0.34
	35-36	OFF36	08334444	0.52	± 0.23
Lacamas Lake	0-2	LAC02	08334446	3.29	± 0.76
	2-3	LAC03	08334447	3.41	± 0.79
	3-4	LAC04	08334448	3.23	± 0.72
	4-5	LAC05	08334449	3.17	± 0.74
	5-6	LAC06	08334450	3.02	± 0.71
	7-8	LAC08	08334451	2.99	± 0.68
	9-10	LAC10	08334452	2.17	± 0.55
	11-12	LAC12	08334453	2.08	± 0.50
	14-15	LAC15	08334454	1.46	± 0.41
	17-18	LAC18	08334455	1.73	± 0.43
	20-21	LAC21	08334456	1.30	± 0.40
	23-24	LAC24	08334457	1.23	± 0.34
	26-27	LAC27	08334458	0.72	± 0.32
	30-31	LAC31	08334459	0.73	± 0.25
	33-34	LAC34	08334460	2.05	± 0.54
Lake Washington	0-2	WA02	08334462	4.24	± 0.91
	2-3	WA03	08334463	4.08	± 0.89
	3-4	WA04	08334464	3.97	± 0.89
	4-5	WA05	08334465	3.86	± 0.85
	5-6	WA06	08334466	3.66	± 0.83
	7-8	WA08	08334467	3.00	± 0.70
	9-10	WA10	08334468	2.18	± 0.57
	11-12	WA12	08334469	1.56	± 0.40
	14-15	WA15	08334470	0.75	± 0.34
	17-18	WA18	08334471	0.70	± 0.33
	20-21	WA21	08334472	0.90	± 0.26
	24-25	WA25	08334473	0.73	± 0.23
	28-29	WA29	08334474	0.49	± 0.20
	32-33	WA33	08334475	0.439J	± 0.17
	36-37	WA37	08334476	0.271U	± 0.22

sd - Standard deviation.

U - Not detected above the reported limit

J - Estimate

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Appendix C. Quality Assurance Data

- Table C-1. Measurement Quality Objectives
- Table C-2. Total Organic Carbon
- Table C-3. Mercury
- Table C-4. Total Lead
- Table C-5. ²¹⁰Pb
- Table C-6. PAHs

Table C-1. Measurement Quality Objectives.

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
PAHs	±65% SRM	25	±20% LCS	40 µg/Kg, dry
Lead ²¹⁰	----	25	----	1 dpm/g

LCS – Laboratory Control Sample
 RPD – Relative Percent Difference
 SRM – Standard Reference Material

All samples were received by MEL in proper condition. MEL conducted analyses of TOC, mercury, total lead, and PAHs. Grain size was analyzed by Columbia Analytical Services Inc., and TestAmerica Inc. performed the ²¹⁰Pb analyses. Quality control consisted of laboratory duplicates, matrix spikes, matrix spike duplicates, laboratory control samples, method blanks, standard reference material, and surrogate recoveries.

Data quality for the entire project was generally good. Several matrix spikes for mercury and total lead were not calculated due to insufficient spike. The laboratory did not encounter any other problems in the analyses of lead or mercury. Matrix spike recoveries were poor for one PAH sample. The poor recoveries were likely due to extraction losses rather than non-homogeneity in the native sample. The case narrative for PAHs is included in Appendix D. All other case narratives are available upon request.

Table C-2. Total Organic Carbon

Lab Duplicate

Sample #	LDP1	LDP2	RPD (%)
08334456	4.59	4.57	0.4

Lab Method Blanks

Sample #	Field ID	Result (mg/Kg)
GB08232T1	Lab BLNK	0.1 U
GB08234T1	Lab BLNK	0.1 U

Lab Control Samples (% Recovery)

Sample #	Field ID	% Recovery
GL08232T1	Lab LCS	94
GL08234T1	Lab LCS	87

RPD - Relative Percent Difference

U - Not detected at detection limit shown

Table C-3. Mercury

Matrix Spikes (% Recovery)

Sample #	LMX1 (%)	LMX2 (%)	RPD (%)
08334450	86	91	5.5
08334476	109	105	3.7

Lab Method Blanks

Sample #	Field ID	Result (mg/Kg)
MB08234H1	Lab BLNK	0.005 U
MB08246H1	Lab BLNK	0.005 U
MB08246H2	Lab BLNK	0.005 U
MB08248H1	Lab BLNK	0.005 U

Lab Control Samples (% Recovery)

Sample #	Field ID	% Recovery
ML08234H1	Lab LCS	107
ML08246H1	Lab LCS	103
ML08246H2	Lab LCS	92
ML08248H1	Lab LCS	104

RPD - Relative Percent Difference

U - Not detected at detection limit shown

Table C-4. Total Lead

Matrix Spikes (% Recovery)

Sample #	LMX1 (%)	LMX2 (%)	RPD (%)
08334440	89	93	4.4
08334458	105	102	2.9

Lab Method Blanks

Sample #	Field ID	Result (mg/Kg)
MB08232I2	Lab BLNK	0.1 U
MB08238I3	Lab BLNK	0.1 U
MB08238I4	Lab BLNK	0.1 U

Lab Control Samples (% Recovery)

Sample #	Field ID	% Recovery
ML08232I2	Lab LCS	104
ML08238I3	Lab LCS	103
ML08238I4	Lab LCS	105
ML08248H1	Lab LCS	104

RPD - Relative Percent Difference

U - Not detected at detection limit shown

Table C-5. ²¹⁰Pb

Lab Duplicates

Sample #	Sample Result (pCi/g)	Duplicate Result (pCi/g)	RPD (%)
08334430	5.35	4.84	10.5
08334446	3.29	3.08	6.8
08334462	4.24	4.64	8.6

Lab Method Blanks

Sample #	Field ID	Result (mg/Kg)
8242363	Lab BLNK	.125U
8242365	Lab BLNK	.142U
8242366	Lab BLNK	.193U

Lab Control Samples

Sample #	Field ID	% Recovery
8242363 LCS	Lab LCS	102
8242365 LCS	Lab LCS	107
8242366 LCS	Lab LCS	90

RPD - Relative Percent Difference

U - Not detected at detection limit shown

Table C-6. PAHs

Lab Duplicates

Analyte	Sample # 08334440			Sample # 08334468		
	Sample (µg/kg)	LDP1 (µg/kg)	RPD (%)	Sample (µg/kg)	LDP1 (µg/kg)	RPD (%)
Naphthalene	95 U	97 U	----	50 U	99 U	----
2-Methylnaphthalene	95 U	97 U	----	51 U	99 U	----
1-Methylnaphthalene	95 U	97 U	----	52 U	99 U	----
2-Chloronaphthalene	95 U	97 U	----	53 U	99 U	----
Acenaphthylene	95 U	97 U	----	54 U	99 U	----
Acenaphthene	95 U	97 U	----	55 U	99 U	----
Dibenzofuran	95 U	97 U	----	5.1 J	99 U	180.4
Fluorene	95 U	97 U	----	50 U	99 U	----
Phenanthrene	19 J	35 J	59.3	72	74 J	2.7
Anthracene	95 U	6.2 J	175.5	12 J	15 J	22.2
Carbazole	190 UJ	194 UJ	----	101 UJ	198 UJ	----
Fluoranthene	32 J	76 J	81.5	123	101	19.6
Pyrene	33 J	76 J	78.9	124	113	9.3
Retene	95 U	87 J	8.8	50 U	99 U	----
Benzo(a)anthracene	95 U	97 U	----	52	52 J	0.0
Chrysene	95 U	98 U	----	84	83 J	1.2
Benzo(b)fluoranthene	95 U	99 U	----	81 J	43 J	61.3
Benzo(k)fluoranthene	95 U	100 U	----	35 J	31 J	12.1
Benzo(a)pyrene	95 U	101 U	----	60	52 J	14.3
Indeno(1,2,3-cd)pyrene	95 U	102 U	----	173 J	282 J	47.9
Dibenzo(a,h)anthracene	95 U	103 U	----	50 U	99 U	----
Benzo(ghi)perylene	95 U	33 J	96.9	58	43 J	29.7

Matrix Spikes (% Recovery)

Analyte	Sample # 08334430			Sample # 08334454		
	LMX1 (%)	LMX2 (%)	RPD (%)	LMX1 (%)	LMX2 (%)	RPD (%)
Naphthalene	66	48	31.6	42	17	84.7
2-Methylnaphthalene	75	54	32.6	44	14	103.4
1-Methylnaphthalene	70	50	33.3	40	13	101.9
2-Chloronaphthalene	59	34	53.8	34	14	83.3
Acenaphthylene	88	83	5.8	75	19	119.1
Acenaphthene	84	68	21.1	54	16	108.6
Dibenzofuran	95	90	5.4	81	21	117.6
Fluorene	106	103	2.9	96	18	136.8
Phenanthrene	100	98	2.0	94	23	121.4
Anthracene	105	103	1.9	99	25	119.4
Carbazole	121	117	3.4	113	112	0.9
Fluoranthene	94	93	1.1	90	22	121.4
Pyrene	99	96	3.1	93	23	120.7
Retene	95	93	2.1	88	18	132.1
Benzo(a)anthracene	95	94	1.1	93	22	123.5
Chrysene	94	92	2.2	88	20	125.9
Benzo(b)fluoranthene	85	84	1.2	82	20	121.6
Benzo(k)fluoranthene	90	89	1.1	86	23	115.6
Benzo(a)pyrene	90	91	1.1	88	23	117.1
Indeno(1,2,3-cd)pyrene	82	83	1.2	82	26	103.7
Dibenzo(a,h)anthracene	91	90	1.1	90	20	127.3
Benzo(ghi)perylene	90	90	0.0	90	24	115.8
Total PAHs	1974	1843	6.9	1742	533	106.3

Lab Method Blanks

Analyte	Sample # OB08338S1		Sample # OB08343S1	
	Result (µg/Kg)	Qualifier	Result (µg/Kg)	Qualifier
Naphthalene	34	U	34	U
2-Methylnaphthalene	34	U	34	U
1-Methylnaphthalene	34	U	34	U
2-Chloronaphthalene	34	U	34	U
Acenaphthylene	34	U	34	U
Acenaphthene	34	U	34	U
Dibenzofuran	34	U	34	U
Fluorene	34	U	34	U
Phenanthrene	34	U	34	U
Anthracene	34	U	34	U
Carbazole	69	UJ	69	U
Fluoranthene	34	U	34	U
Pyrene	34	U	34	U

Analyte	Sample # OB08338S1		Sample # OB08343S1	
	Result (µg/Kg)	Qualifier	Result (µg/Kg)	Qualifier
Retene	34	U	34	U
Benzo(a)anthracene	34	U	2.8	J
Chrysene	34	U	34	U
Benzo(b)fluoranthene	34	U	34	U
Benzo(k)fluoranthene	34	U	34	U
Benzo(a)pyrene	34	U	34	U
Indeno(1,2,3-cd)pyrene	34	U	34	U
Dibenzo(a,h)anthracene	34	U	34	U
Benzo(ghi)perylene	34	U	34	U

Lab Control Samples

Analyte	Sample # OL08338S1	Sample # OL08338S2	Sample # OL08343S1	Sample # OL08343S2
	% Recovery			
Naphthalene	75	60	81	85
2-Methylnaphthalene	83	63	89	95
1-Methylnaphthalene	78	59	85	92
2-Chloronaphthalene	72	52	85	93
Acenaphthylene	86	81	86	92
Acenaphthene	92	73	96	102
Dibenzofuran	95	88	94	101
Fluorene	106	101	104	111
Phenanthrene	98	94	94	99
Anthracene	105	101	101	105
Carbazole	120	115	107	111
Fluoranthene	95	93	90	92
Pyrene	98	93	93	98
Retene	93	89	90	96
Benzo(a)anthracene	95	92	92	95
Chrysene	94	93	91	93
Benzo(b)fluoranthene	84	80	82	85
Benzo(k)fluoranthene	92	89	87	90
Benzo(a)pyrene	92	89	89	91
Indeno(1,2,3-cd)pyrene	79	78	80	82
Dibenzo(a,h)anthracene	88	88	88	89
Benzo(ghi)perylene	87	87	88	89

Appendix D. Case Narrative for PAHs

Manchester Environmental Laboratory
7411 Beach Dr E, Port Orchard, Washington 98366

Case Narrative **January 8, 2009**

Subject: Hg in Sediment Cores - 2008

Sample(s): 08-334430 to -334433, -334435 to -334438, -334440, -334443, -334446 to -334449, -334451 to -334454, -334456, -334460, -334462 to -334465, -334467 to -334470, -334472 and -334475.

Project ID 1600-08

Officer(s): Chad Furl

By: Dickey Huntamer

Semivolatiles PAH

Analytical Method(s)

The semivolatile sediment samples were extracted on the Accelerated Solvent Extractor (ASE) with methylene chloride following the Manchester modification of the EPA SW 846 8270 with capillary GC/MS analysis of the sample extracts. The extracts were cleaned up using silica gel, EPA Method 3630C.

Holding Times

Samples were stored frozen until extraction. All samples were prepared and analyzed within the method holding times.

Instrument Tuning

Calibration against DFTPP is acceptable for the initial calibration, continuing calibration and all associated sample analyses.

Calibration

Instrument calibrations and calibration checks were performed in accordance with the appropriate method. The December 23rd initial calibration correlation coefficients were within the acceptance range of 1.000 - 0.995 for linear curve, 0.99 for quadratic fit or an average response of $\leq 15\%$. Carbazole had only 4 points in the curve so all results were qualified, J

The Initial Calibration Verification (ICV) was within the acceptable limits of +/- 30% for the December 23rd initial calibration.

Back calculations for the initial calibration were all within acceptance limits.

QC Limits for the Continuing Calibration (CC) are +/- 20%.

All target analytes were within the maximum of 20% in the continuing calibrations for December 24th, and December 25th. Carbazole was low in both continuing calibrations so all carbazole results were qualified, J.

Blanks

No target compounds were detected in laboratory blank OB08339S1 and a low level of benzo(a)anthracene in OB08343S1. The amount in the second blank was less than 1/5 the amount detected in the samples.

Compounds that were found in the sample and blank were considered native to the sample if the area counts in the sample are greater than or equal to 5 times the area counts in the associated method blank.

Surrogates

All surrogate recoveries were within the limits of 18%-137% for d14-terphenyl, 50%-150% for d10-pyrene and 30%- 115% for 2-fluorobiphenyl except for 2-fluorobiphenyl in samples-334433 (23%), -334446 (9.4%) and -334449 (25%). Since the other two surrogates were acceptable no qualifiers were added.

Matrix Spikes

Matrix spike recoveries for sample -334430 were within the limits of 50% to 150% except for 2-chloronaphthalene, (59%, 33%). No qualifiers were added since one recovery was acceptable.

The Relative Percent Differences (RPD) were less than 40% for all compounds except 2-chloronaphthalene (56%). 2-Chloronaphthalene was not qualified, J as this analyte was not detected in the native sample..

Matrix spike recoveries for sample -334454 were within the limits of 50% to 150% except for Naphthalene (42%, 17%), 2-methylnaphthalene (44%, 14%), 1-methylnaphthalene (40%, 13%) and 2-chloronaphthalene, (34%, 14%). Recoveries of all the compounds were low in -334454

LMX2 but only the compounds listed above were low in both matrix spikes. Results for the native sample were qualified, J for these compounds.

The Relative Percent Differences (RPD) was greater than 40% for all compounds due to the low recoveries of all the compounds in LMX2 compared to the acceptable recoveries in LMX1. No further qualifiers were added to the native sample -334454 other than those mentioned above since the difference is likely due to extraction losses in the matrix spike rather than non-homogeneity in the native sample..

Duplicates

A duplicate was run on sample -334440. The Relative Percent Differences (RPD) for those compounds detected was within the acceptable limit of 40% except for phenanthrene (58%), fluoranthene (81%), and pyrene (79%). All were detected below the reporting limit and are qualified, J.

A duplicate was run on sample -334468. The Relative Percent Differences (RPD) for those compounds detected was within the acceptable limit of 40% except for benzo(b)fluoranthene (61%) and indeno(1,2,3-cd)pyrene (48%). Both compounds were qualified, J in sample -334468 and -334468 LDP1. Dibenzofuran was detected below the reporting limit in only one sample so no RPD could be calculated.

Laboratory Control Samples

The laboratory control samples were spiked at a level of 10 ug, equivalent to 20 ug/Kg.

Two laboratory control samples (LCS) were analyzed with each sample batch. These are identified as OL08338S1 and OL08338S2 in batch one and OL08343S1 and OL08343S2 in batch 2. All recoveries were within acceptable limits 50% to 150%.

The Relative Percent Differences (RPD) was less than 40% for all compounds.

One NIST 1944 Certified Reference Material (CRM) was analyzed with each sample batch. These are identified as OL08338S3 and OL08343S3. It appears that the lighter PAH compounds were lost in the silica gel. Results are summarized in the attached table.

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Appendix E. Glossary, Acronyms, and Abbreviations

Analyte: Parameter measured in sediment.

Anthropogenic: Human-caused.

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

Flux rate: Sediment accumulation rate times analyte concentration. Estimates net deposition to the coring site.

Horizon: Sediment interval measured in centimeters along a vertical gradient.

Nonpoint source: Unconfined and diffuse sources of contamination. Pollution that enters water from dispersed land-based or water-based activities. This includes, but is 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 National Pollutant Discharge Elimination System program.

Petrogenic PAHs: Derived from petroleum inputs.

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.

Pyrogenic PAHs: Derived from combustion sources.

Sediment: Solid fragmented material, that is transported and deposited by water, ice, or wind, that forms layers on the earth's surface.

Acronyms and Abbreviations

Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
Hg	Mercury
MEL	Manchester Environmental Laboratory
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PBT	Persistent Bioaccumulative and Toxic
Ra	Radium
Rn	Radon
RPD	Relative Percent Difference
TOC	Total Organic Carbon