PBT Chemical Trends Determined from Age-Dated Lake Sediment Cores, 2012 Results

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2012 Highlighted Findings

- Lead and mercury levels are decreasing in Stevens and West Medical Lakes
- PFCs are increasing in Stevens and West Medical Lakes
- Contaminant trends in Deer Lake were inconsistent

Why Does it Matter?

PBTs are a concern because they remain in the environment for a long time, they increase up the food chain, and they have toxic effects on fish, wildlife, and humans. PBTs are considered the "worst of the worst" chemicals. Ecology monitors PBTs in the environment to gather information on whether these toxic chemicals are increas-ing, decreasing, or staying the same.

Overview

The Washington State Department of Ecology's (Ecology's) Persistent, Bioaccumulative, and Toxic chemical (PBT) Monitoring Program began collecting sediment cores from freshwater lakes in 2006 to help characterize the occurrence and temporal trends of PBTs in Washington State. A single, deep sediment core is collected from three lakes per year and age-dated in order to construct historical contaminant deposition profiles.

In 2012, Ecology analyzed PBTs (lead, mercury, and perfluorinated compounds [PFCs]) in sediment cores collected from Deer Lake, Lake Stevens, and West Medical Lake (Figure 1).

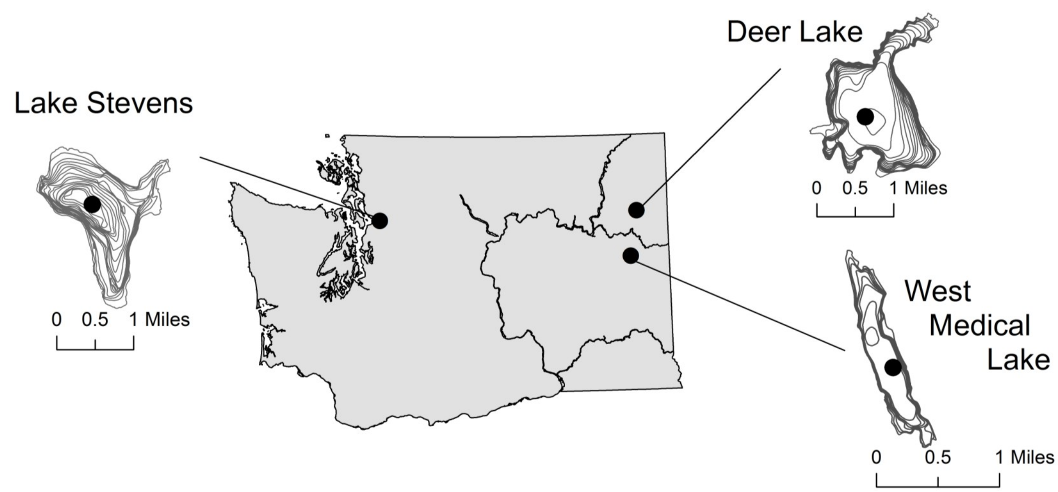

Figure 1. Freshwater Sediment Coring Locations in 2012.

The information collected will help guide development of future chemical action plans (CAPs) as well as track progress on existing actions to reduce PBT levels in the environment. Ecology develops CAPs to evaluate uses and releases of PBTs in Washington State and make recommendations on actions to protect human health and the environment.

For More Information

PBT Monitoring Program website: www.ecy.wa.gov/programs/eap/toxics/pbt.html

Chemical Action Plan website: www.ecy.wa.gov/programs/swfa/pbt/caps.html

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Methods

This study followed a Quality Assurance Project Plan and related addendums (Coots, 2006; Meredith and Furl, 2008; and Mathieu, 2012). Sediment cores measuring 35-45 cm deep were collected using a Wildco© box corer according to Ecology's standard operating procedures for sediment core collection (Furl and Meredith, 2008b). Decontamination of equipment coming into contact with samples consisted of the following protocol: Liquinox detergent and hot water wash, 10% nitric acid rinse, and 100% methanol rinse.

Table 1 provides laboratory preparation and analysis methods for the parameters analyzed. A list of the 13 PFCs analyzed is included in Mathieu (2012). Ecology's Manchester Environmental Laboratory (MEL) carried out all analyses except for PFCs and grain size. Axys Analytical Services Ltd. performed the PFC analysis and Analytical Resources Inc. analyzed grain size.

All data met measurement quality objectives (MQOs), with the exception of total lead. Two matrix spikes for total lead were outside of MQOs due to sample inhomogeneity. The associated samples were qualified as estimates.

Table 1. Sample Preparation and Analysis.

Analyte	No. of Samples	Method Description	Analytical Method
^{210}Pb	45	Alpha Spectroscopy	Lab-specific
T-Pb	45	ICP-MS	EPA 200.8
Hg	45	CVAA	EPA 245.5
PFCs	24	HPLC-MS/MS	AXYS Method MLA-041
TOC	30	Acidification and CO_2 measurement	PSEP-EPA, 1986
Grain Size	3	Sieve and pipet	PSEP-EPA, 1987

ICP: inductively coupled plasma, MS = mass spectrometry, CVAA: cold vapor atomic absorption, HPLC = high performance liquid chromatography, TOC: total organic carbon

Study Locations

Deer Lake lies in Stevens County, 35 miles north of Spokane. Lakeshore development includes several resorts and homes, with the majority of the watershed forested. Surface water enters the lake through several ephemeral streams and flows out through a channel at the southwest corner. The basin geology consists of metamorphic rock, with continental glacial outwash and sedimentary deposits at the surface (Dion et al., 1976).

Located in Snohomish County, Lake Stevens has seen a sharp increase in commercial and residential development since the 1970s. The lake shoreline is densely populated and the lake itself receives heavy recreational usage. Surface water inflow is through three perennial streams, with an outflow stream that empties into the Pilchuck River. Basin geology consists of glacial drift with local alluvium, with gravelly and sandy loam soils (Bortleson et al., 1976).

West Medical Lake is located 15 miles southwest of Spokane in a largely agricultural area. The shoreline does not contain any near shore development, but a former dump is located along the shoreline, with debris such as old car parts reaching the near shore. Wastewater treatment plant (WWTP) effluent from the City of Medical Lake has been discharged into the lake since the 1960s, though currently the effluent receives advanced treatment and is considered reclaimed water. No natural sources of inflow or outflow exist, resulting in very long water residence times. Geology in the area is dominated by basalt and metamorphic rocks and area soils consist of silt and stony silt loam (McConnell et al., 1976).

Table 2. Physical Descriptions of 2012 Study Lakes.

Waterbody	Max Depth (ft)	Mean Depth (ft)	Surface Area (ac)	Drainage Area (ac)	DA:SA	Volume (ac ft)	Elevation (ft)
Deer Lake	75	52	1,100	11,650	10.6	57,000	2,474
Lake Stevens	155	63	1,040	4,370	4.2	65,000	210
West Medical Lake	35	22	220	1,180	5.4	4,900	2,423

Core Dating

Dates were calculated for the three cores using ^{210}Pb values and the constant rate of supply (CRS) model (Appleby and Oldfield, 1978). Supported ^{210}Pb was estimated as the average activity present at deep intervals where it appeared to no longer decline. Average supported ^{210}Pb levels were 1.8, 0.18, and 0.57 pCi/g for Deer, Stevens, and West Medical Lakes, respectively, shown as dashed lines in Figure 2.

Yearly unsupported ^{210}Pb fluxes in Deer, Stevens, and West Medical Lakes were 0.19, 0.23, and 0.17 pCi/cm^2/yr, which is within the range of values estimated for other sediment cores in Washington State. These values are also close to estimated fluxes calculated using atmospheric ^{210}Pb deposition measured in Washington State (Nevissi, 1985).

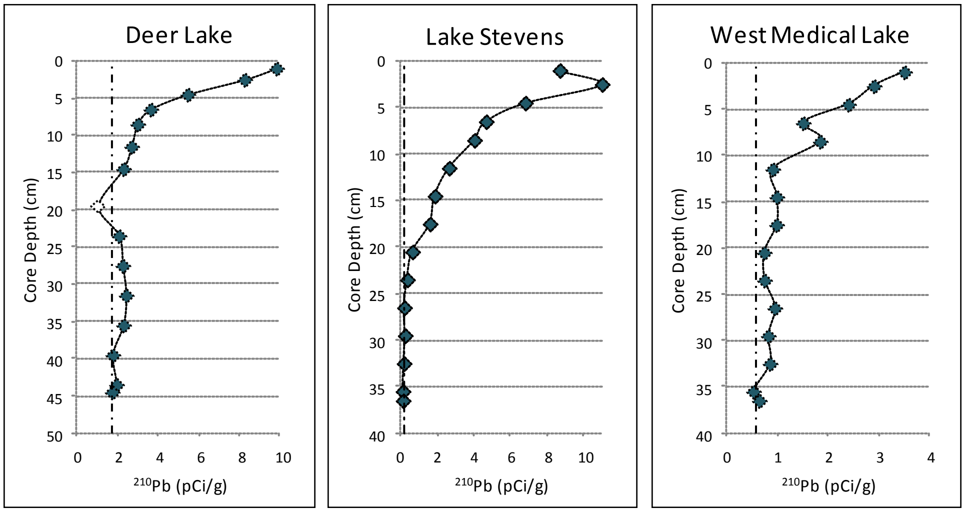


Figure 2. ^{210}Pb Activity Plotted Against Sediment Core Depth.
Dashed lines represent supported ^{210}Pb. The unfilled marker indicates an ash layer (Deer Lake); this data point was excluded.

Sedimentation Rates

Deer Lake sedimentation rates were within the 0.005-0.122 g/cm^2/yr range found at other Washington State lakes with comparable watershed sizes (Mathieu and Friese, 2012). Sedimentation started increasing in the 1920s and was highest between 1950 and 1967. Since the late 1960s, sedimentation rates have steadily decreased to a present-day rate of 0.02 g/cm^2/yr.

Sedimentation rates in Lake Stevens were fairly low but similar to other urban Western Washington lakes (e.g., Angle and American Lakes, which ranged 0.003-0.034 g/cm^2/yr). Lake Stevens sedimentation rates exhibited a typical profile, with values increasing steadily over the 20th century. Current sedimentation rates are 0.02 g/cm^2/yr.

West Medical Lake contained two higher than expected sedimentation rate peaks, in the 1960s and 1980s. Increased in-lake productivity during those times likely caused the higher sedimentation rates. Highly eutrophic lakes accumulate sediment rapidly (Binford and Brenner, 1986). Current sedimentation rates are closer to the average statewide level of 0.05 g/cm^2/yr.

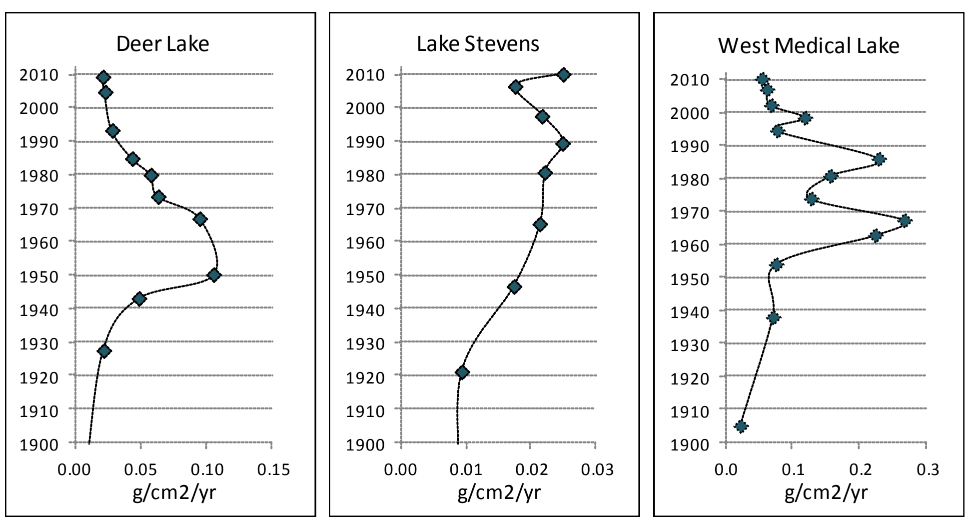


Figure 3. Estimated Sedimentation Rates (g/cm^2/yr).

Lead

Profiles

The Deer Lake sediment core contained baseline lead levels until the 1970s and then started to rise. Lead peaked in 2005 at 78.5 mg/kg and then decreased to 40.6 mg/kg in the most current layer, similar to background levels found in other Northeastern Washington lakes (Johnson et al., 2011). This profile reflects inputs other than leaded gasoline as the main contamination source of lead. Johnson et al. (2013) points to lead smelting in British Columbia as a main driver of historical and current metals deposition in the vicinity. Similar to Deer, a core from nearby Black Lake showed rapidly increasing lead in the 1970s, and Johnson et al. (2013) attributed it to a delayed response to lead smelting emissions.

Lead concentrations in the Lake Stevens core were elevated by 1920. Fairly high levels were found throughout most of the 20th century, until a decrease from 1990 to the present. Lead peaked in 1981 at 262 mg/kg.

West Medical Lake contained the lowest lead concentrations of the three lakes. Levels were elevated by 1900 until the 1960s. Levels decreased consistently over the second half of 20th century.

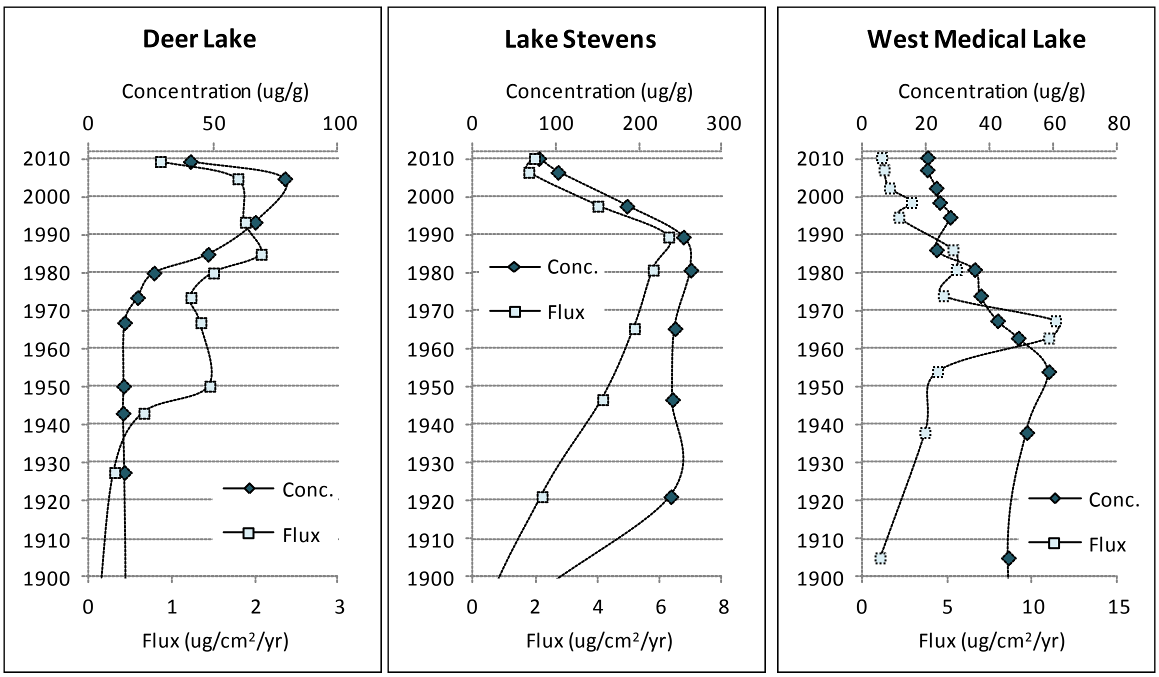


Figure 4. Lead Concentration (ug/g) and Flux (ug/cm^2/yr) Profiles in Sediment Cores.

Enrichment

Enrichment factors (EFs) were calculated as individual lead concentrations divided by the average of stable pre-industrial lead concentrations at the bottom of the core. This average is referred to as a "baseline" level in this report.

Deer Lake lead enrichment was low throughout the core, with modern concentrations only three times greater than baseline levels. Lake Stevens had much higher EFs, particularly between 1920 and 1990, with a peak of 60. Being an urban lake, Stevens has been exposed to a number of different sources, most notably automobile emissions.

The West Medical Lake core did not reach baseline conditions and, therefore no enrichment factors were calculated.

Table 3. Lead Concentrations and Enrichment Results.

Lake	Range (ug/g)	Baseline (ug/g)	Peak Enrichment	Modern Enrichment
Deer	12.5 - 78.5	13.7	5.7 (2005)	3.0 (2009)
Stevens	2.8 - 262	4.4	60 (1981)	18 (2010)
West Medical	20.2 - 58.4	not reached	n/a	n/a

Mercury

Profiles

Mercury concentrations at Deer Lake were modest relative to the other two lakes, with levels typical of non-urban and non-point source lakes. Concentrations started inclining around 1970 and increased steadily until the mid-2000s. The most recent sediment layer contained 143 ng/g of mercury, similar to that of other surface sediments recently analyzed in lakes in the Northeast corner of the state (Johnson et al., 2011).

Lake Stevens, a more urbanized lake, contained much higher levels. Mercury concentrations peaked in the mid 20th century at Lake Stevens, and have consistently declined since the 1960s. Modern levels are at 261 ng/g.

Mercury levels in West Medical Lake were substantially elevated in the first half of the 20th century. Levels were around 600 ng/g between 1900 and 1960, and then decreased steadily to the current concentration of 112 ng/g. Several facilities, including a hospital, discharged waste directly to the lake until the WWTP was built in the 1960s. The steady decrease from that point likely reflects removal from the treatment processes.

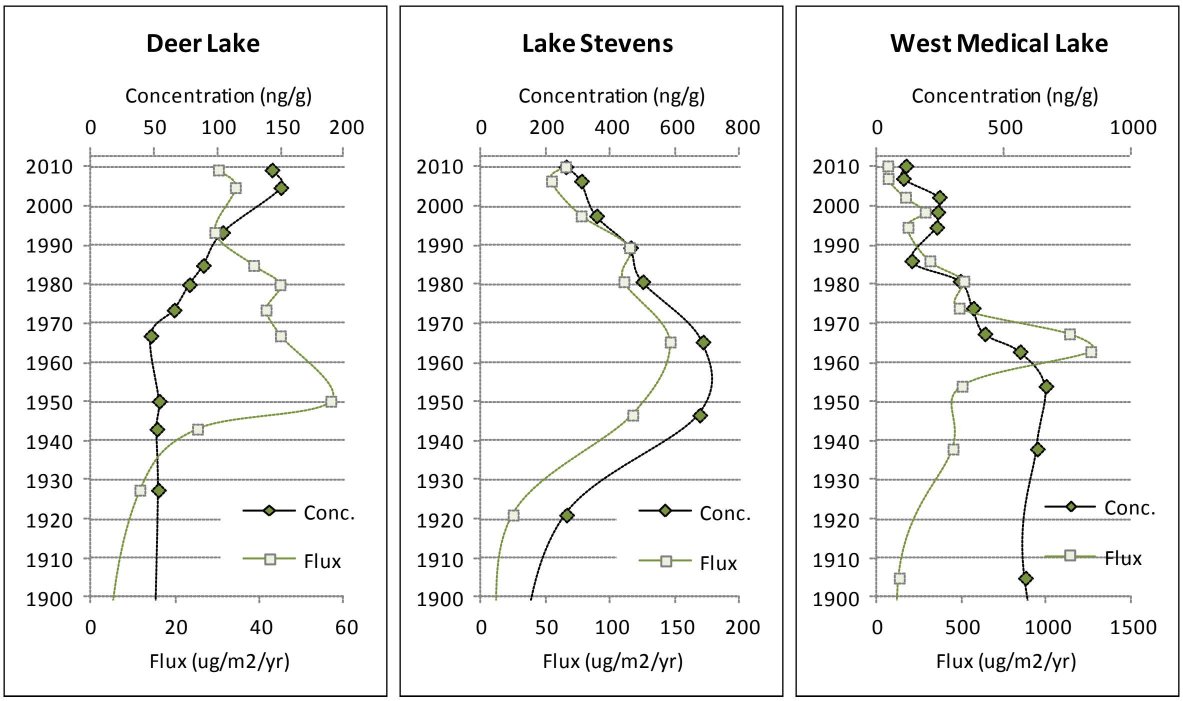


Figure 5. Mercury Concentration (ng/g) and Flux (ug/m^2/yr) Profiles in Sediment Cores.

Enrichment

Mercury enrichment was low throughout the Deer Lake core. Modern sediments were enriched at a factor of 3.7 times higher than baseline levels. Lake Stevens mercury EFs peaked in the 1960s at 8.4. Concentrations and EFs are comparable to sediments analyzed from Angle Lake, also an urban lake (Mathieu and Friese, 2012). However, mercury levels in Lake Stevens declined earlier than in Angle Lake and current concentrations are much lower.

West Medical Lake EFs could not be calculated, as core samples did not reach baseline levels.

Table 4. Mercury Concentration and Enrichment Results.

Lake	Range (ug/g)	Baseline (ug/g)	Peak Enrichment	Modern Enrichment
Deer	38.3 - 150	38.3	3.9 (2005)	3.7 (2009)
Stevens	77.5 - 685	81.3	8.4 (1965)	3.2 (2010)
West Medical	102 - 967	not reached	n/a	n/a

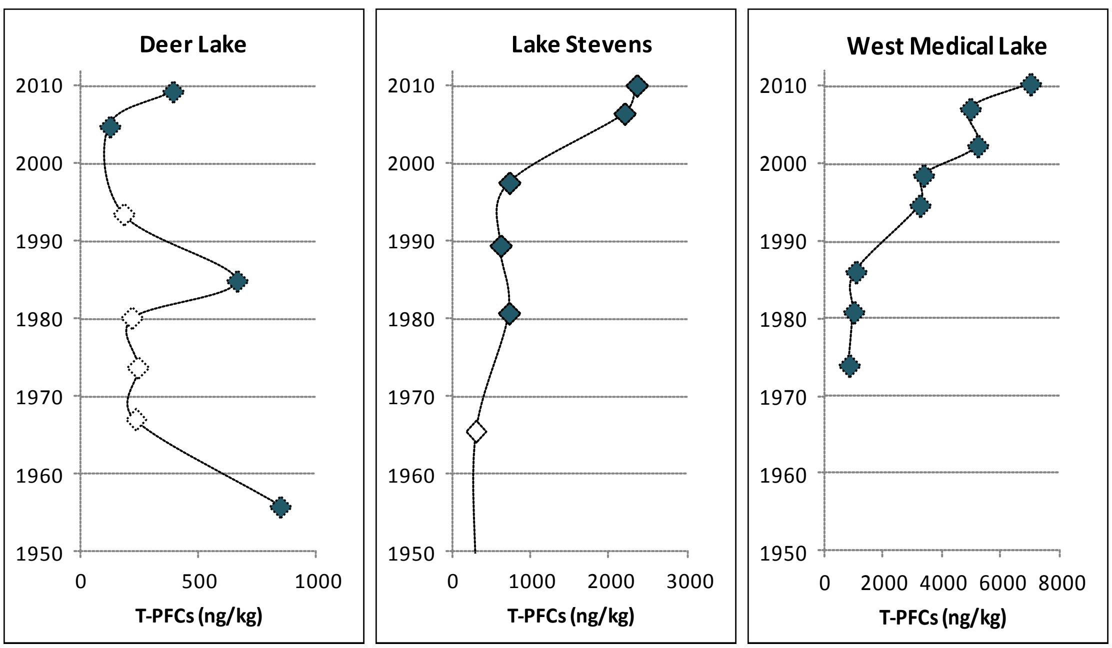
Perfluorinated Compounds (PFCs)

PFCs are a group of man-made chemicals that exhibit surfactant properties as well as oil and water repellency and fire resistance. They are used to make stain resistant and waterproof coatings for textiles, carpets, and paper; they are also used in fire fighting foams and as leveling agents in paints and lubricants. Because PFCs contain strong carbon-fluorine bonds, they do not break down. Consequently, PFCs are globally distributed in the environment, having been measured in remote locations, such as the Arctic (Giesy and Kannan, 2001). PFCs also bioaccumulate and have shown toxic effects in animal studies (Lau, 2012).

Manufacturers first started producing PFCs in the 1950s. Due to concern over environmental persistence, perfluorooctane sulfonate (PFOS) was voluntarily phased out in 2000-2002 and a stewardship program with eight major chemical makers laid out a plan for eliminating perfluorooctanoic acid (PFOA) and other long-chained PFC emissions and production by 2015.

Total PFCs

Sediment core profiles of total PFCs (the sum of all detected PFCs in a sample) are presented in Figure 7.



Enrichment factors were not calculated because no natural source of PFCs exists and no ambient background level has been established.

Figure 7. Total PFC Concentration (ng/kg) Profiles in Sediment Cores.
Unfilled markers indicate PFCs were not detected at the level shown.

At least one PFC was detected in 50% of the Deer Lake samples. Total concentrations in Deer Lake were lower than the other two lakes. Concentrations were erratic but appear to have generally declined from the 1950s. The most recent Deer Lake sediment layer contained 392 ng/kg of total PFCs.

PFCs were detected in five out of eight samples in the Lake Stevens core. The profile shows a fairly constant level of PFCs between 1980 and 2000, with a large increase in the late 2000s. Total PFCs in the top-most sediment sample were 2,350 ng/kg. PFCs were not detected in two sediment samples dated before 1950 (data not shown in graph).

All West Medical Lake samples contained at least one PFC and total concentrations were the highest out of the three cores. Total PFCs increased from the 1980s through the top of the core, with levels peaking in the most recent layer, at 7,000 ng/kg.

PFCs

Individual Compounds

PFOS was the most commonly detected compound (58% of samples), and was measured at the highest concentrations in two of the cores. Perfluorooctane sulfonamide (PFOSA) was the second most frequently detected compound, followed by Perfluorododecanoic acid (PFDoA) and Perfluoroundecanoic acid (PFUnA). In general, PFCs with a carbon chain length of eight or greater were detected, while the shorter chain compounds were not. Partitioning studies have found that higher chain length PFCs (i.e., C8 and above) have a greater affinity for sediment adsorption than the lower chained compounds (Higgins and Luthy, 2006).

Five PFC compounds were detected in the Deer Lake samples. Concentrations measured in this core were lower than the other two lakes and no general pattern of individual PFCs emerged. The highest concentrations were measured in the oldest sample (1956), which was unexpected given the history of PFC production.

Four compounds were detected in the Lake Stevens core, with PFOS being the most dominant. The higher chained compounds, PFUnA and PFDoA, were detected in the most recent samples (dated 2007 and 2010). PFOS remained fairly stable in the 1980s and 1990s, and then increased substantially to maximum levels in the late 2000s.

West Medical Lake had the greatest number of detected compounds of the three sediment cores. PFOS dominated the sample make-up, but 4-8 compounds were found in each sample.

The higher chained PFCs—perfluorononanoic acid (PFNA), PFUnA, and PFDoA—first appeared in the mid 1990s and linearly increased through the top of the core. Whereas, PFOS, PFOA, PFOSA and Perfluorodecanoic acid (PFDA) were present in every sample analyzed and also increased linearly from the 1970s to the most recent layer.

PFCs were detected in West Medical Lake surface water and fish tissue in a 2008 statewide PFC survey (Furl and Meredith, 2010). PFC levels in surface waters analyzed from West Medical Lake were the highest out of 14 water-bodies sampled and levels in fish tissues from the lake were the third highest out of seven waterbodies. The authors concluded that WWTP discharges to the lake and a long water residence time make it a “worst case” scenario for PFC contamination.

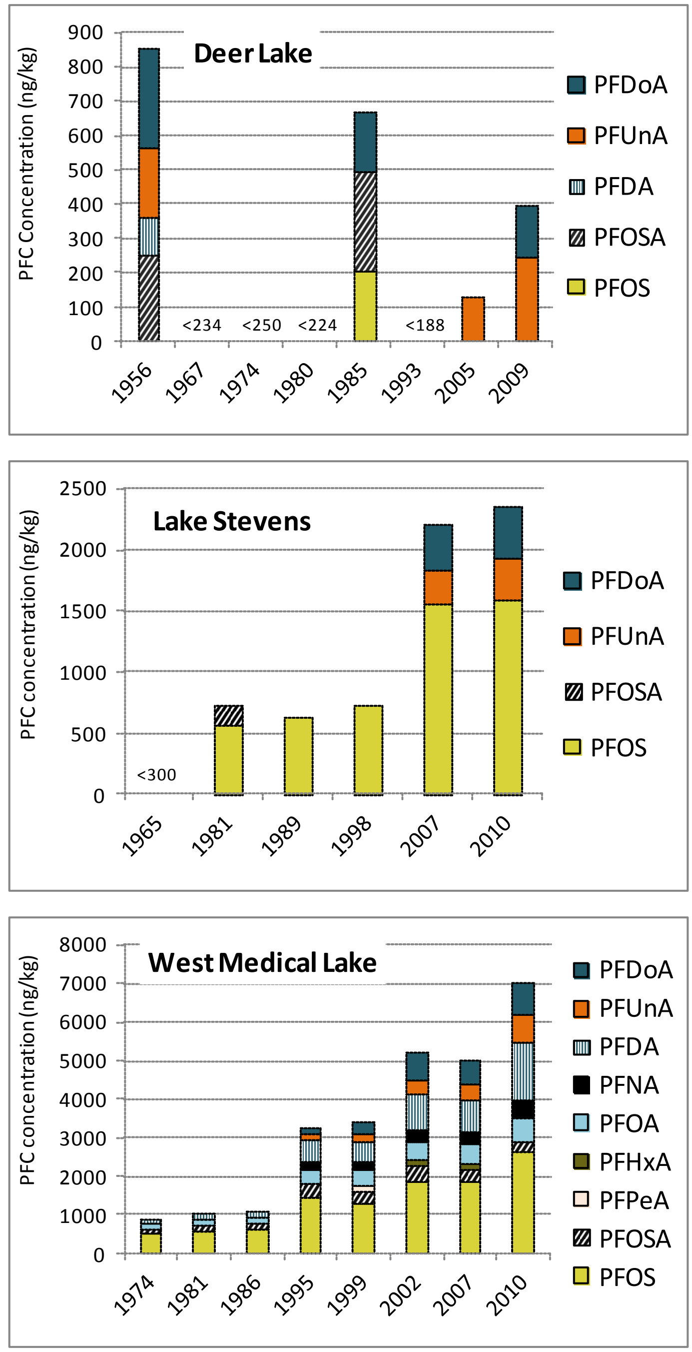


Figure 8. Concentrations of individual PFCs (ng/kg) in Sediment Cores.
A less-than sign indicates sample was not detected at level reported.

Conclusions

Lead, mercury, and PFCs were analyzed in sediment cores from Deer Lake, Lake Stevens, and West Medical Lake in 2012. Historical deposition profiles of the contaminants revealed the following trends:

- Sedimentation rates of Deer and Stevens Lakes exhibited typical profiles, with a current rate of 0.02 $g/cm^2/yr$. West Medical Lake contained two very high sedimentation rate peaks, in the 1960s and 1980s, likely caused by increased productivity in the lake. Current rates were closer to average statewide levels (0.05 $g/cm^2/yr$).
- Lead concentrations in Deer Lake remained close to baseline conditions until the 1970s, when concentrations started increasing. Levels peaked in 2005 and then decreased in the top-most core sample. Lead levels in the Lake Stevens core were elevated by 1920 and remained high until 1990, when levels started decreasing. West Medical Lake contained the lowest lead levels, which have consistently decreased since the 1960s.
- Mercury levels in Deer Lake were relatively low, but showed an increasing trend between 1970-2005. Mercury concentrations at Lake Stevens and West Medical Lake peaked in the mid 20th century and have declined since then.
- PFCs were detected in half of the Deer Lake samples. Concentrations were erratic, but lower than the other two lakes and generally decreased after the 1950s.
- PFCs were detected in the Lake Stevens core samples from 1980-2012. Total PFCs were low and consistent between 1980 and 2000, but increased substantially in the late 2000s.
- PFCs were detected in all West Medical Lake samples, beginning in the 1970s. Concentrations increased throughout the core, until a maximum of 7,000 ng/kg (total PFCs) in the top-most layer.

Recommendations

The findings of this 2012 study support the following recommendations:

- The increasing trends in PFCs warrant further investigation into environmental levels of these contaminants in Washington State. A follow-up study to Ecology's 2008 PFC survey (Furl and Meredith, 2010) would be helpful in determining whether PFCs are increasing in biota and/or wastewater treatment plant (WWTP) effluent.
- The author recommends analyzing alternative flame retardants in sediment cores collected in 2013. An Ecology study (Johnson and Friese, 2012) reported measurable levels of hexabromocyclododecane in fish tissue from Washington lakes and recommended including this contaminant in future monitoring studies. Trend data for alternative flame retardants are lacking in Washington State; more data would help Ecology prioritize these chemicals.

References

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.

Binford, M.W. and M. Brenner. 1986. Dilution of ^{210}Pb by organic sedimentation in lakes of different trophic states, and application to the studies of sediment-water interactions. Limnology and Oceanography, 31: 584-595.

Bortleson, G.C., G.T. Higgins, J.B. McConnell, and J.K. Innes. 1976. Data on Selected Lakes in Washington, Part 3. Water Supply Bulletin 342.

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 Number 06-03-113. https://fortress.wa.gov/ecy/publications/summarypages/0603113.html

Dion, N.P., G.C. Bortleson, J.B. McConnell, and L.M. Nelson. 1976. Reconnaissance Data on Lake in Washington: Pend Oreille, Spokane, and Steven Counties. Water-Supply Bulletin 43.

Furl, C. and C. Meredith, 2010. Perfluorinated Compounds in Washington Rivers and Lakes. Washington State Department of Ecology, Olympia, WA. Publication Number 10-03-034. https://fortress.wa.gov/ecy/publications/summarypages/1003034.html

Giesy, J.P. and K. Kannan, 2001. Global Distribution of Perfluorooctane Sulfonate in Wildlife. Environmental Science and Technology, Vol. 35: 1339-1342.

Higgins, C.P. and R.G. Luthy, 2006. Sorption of Perfluorinated Surfactants on Sediments. Environmental Science and Technology, Vol. 40: 7251-7256.

Johnson, A. , M. Friese, J. Roland, A. Fernandez, C. Gruenfelder, B. Dowling, and T. Hamlin, 2011. Background Characterization for Metals and Organic Compounds in Northeast Washington Lakes, Part 1: Bottom Sediments. Washington State Department of Ecology, Olympia, WA. Publication Number 11-03-035. https://fortress.wa.gov/ecy/publications/summarypages/1103035.html

Johnson, A. and M. Friese, 2012. PBTs Analyzed in Bottom Fish from Four Washington Rivers and Lakes. Washington State Department of Ecology, Olympia, WA. Publication Number 12-03-042. https://fortress.wa.gov/ecy/publications/summarypages/1203042.html

Johnson, A., M. Friese, R. Coots, J. Roland, B. Dowling, and C. Gruenenfelder, 2013. Metals Concentrations in Sediments of Lakes and Wetlands in the Upper Columbia River Watershed: Lead, Zinc, Arsenic, Cadmium, Antimony, and Mercury. Washington State Department of Ecology, Olympia, WA. Publication Number 13-03-012. https://fortress.wa.gov/ecy/publications/SummaryPages/1303012.html

Lau, C., 2012. Perfluorinated Compounds. Molecular, Clinical, and Environmental Toxicology, Vol. 101: 47-86.

Mathieu, C., 2012. Addendum 2 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 Number 12-03-119. https://fortress.wa.gov/ecy/publications/summarypages/1203119.html

Mathieu, C. and M. Friese, 2012. PBT Chemical Trends in Washington State Determined from Age-Dated Lake Sediment Cores. Washington State Department of Ecology, Olympia, WA. Publication Number 12-03-045. https://fortress.wa.gov/ecy/publications/summarypages/1203045.html

McConnell, J.B., G.C. Bortleson, and J.K. Innes, 1976. Data on Selected Lakes in Washington, Part 4. Water Supply Bulletin 42.

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 Number 06-103-113ADD1. https://fortress.wa.gov/ecy/publications/SummaryPages/0603113ADD1.html

Nevissi, A.E., 1985. Measurement of ^{210}Pb Atmospheric Flux in the Pacific Northwest. Health Physics, Vol. 45: 169-174.

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