

Lake Whatcom Total Phosphorus Accumulation in Sediments



William Hobbs, Environmental Assessment Program

Key Findings

- Rates of total organic carbon and total phosphorus accumulation increased from 1900-1950, likely due to inputs from the surrounding watershed.
- Rates of total organic carbon and total phosphorus accumulation decreased from the 1950s to the 1980s.
- Rates of total organic carbon and total phosphorus accumulation have increased since the 1980s, likely due to greater inputs of algal or in-lake material.
- During 1950-2000, total phosphorus sediment accumulation averaged 0.024 ± 0.003 mg/cm²/yr.

Overview

The Washington State Department of Ecology (Ecology) has been assessing Persistent, Bioaccumulative, and Toxic Chemicals (PBTs) deposition trends to lakes through dated sediment cores for the last ten years. In 2015, Ecology collected a sediment core from the northern basin (basin 1) of Lake Whatcom in Bellingham, Whatcom County (Mathieu and McCall, 2016). Sediments were analyzed for lead radioisotopes (dating), elemental lead (Pb), mercury (Hg), total organic carbon (TOC), and brominated flame retardants (BFRs).

Lake Whatcom has been under study by Ecology since the 1990s. Issues of low dissolved oxygen in the lake, linked to inputs of phosphorus, led to a total maximum daily load (TMDL) study (Pickett and Hood, 2008). An extensive period of modelling took place concurrent with and following the initial investigation (Berger and Wells, 2005; Cadmus Group and CDM, 2007; Butcher, 2008).

The goal of this project is to provide Ecology's partner organizations working on the TMDL with an understanding of the total phosphorus (TP) that has accumulated in the recent (upper 10 cm = ~post-1950) sediments of Lake Whatcom. To meet this goal, Ecology analyzed archived sediment core samples collected in 2015 for TP and summarized the potential mass and accumulation of TP within discrete sediment layers.

Methods and data quality

This study followed a quality assurance project plan (QAPP; Hobbs, 2017) which was written as an addendum to a previous QAPP for PBT monitoring (Mathieu, 2015). The parameters of interest are TP, TOC, and total nitrogen (TN) content of the sediments. Ecology's Manchester Environmental Laboratory carried out all analyses. Archived sediments were analyzed within the holding period for TP (two years) using EPA method 6020. Carbon and nitrogen were analyzed using EPA method 440 by combustion. Sediments were also analyzed for the percent composition of organic, carbonate, and mineral fractions (Dean, 1974; Heiri et al., 2001).

A total of 13 sediment intervals dated between pre-1900 and 2000 were analyzed. For TP accumulation, results were summarized (mean and median) into three time periods: 1950-2000, 1900-1950, and pre-1900. TP accumulation was aggregated over time periods to reduce the influence of phosphorus mobility in the sediment and to provide a

For More Information

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

Lake Whatcom TMDL: <http://www.ecy.wa.gov/programs/wq/tmdl/LkWhatcom/LkWhatcomTMDL.html>

Methods and Data Quality (cont'd)

more robust estimate with the small number of samples. Sediment from the post-2000 period had been used up in the previous study (Mathieu and McCall, 2016).

The methods and data quality for the sediment age-dating using radioisotopes have been previously described by Mathieu and McCall (2016). Dating of the sediment core provided a reliable age-depth model to estimate specific years associated with each sediment layer. Relative percent differences between sample duplicates were <5% for TP, TOC, and TN, with the exception of one TOC sample which was 14%. All quality control samples met the QAPP measurement quality objectives.

Results – sediment dating and accumulation rates

Sediments were dated using ^{210}Po and ^{210}Pb by alpha spectroscopy (Figure 1). The constant-rate-of-supply (CRS) model was used to establish rates of sediment deposition from the ^{210}Pb activity (Appleby and Oldfield, 1978). Dating by ^{210}Pb methods has a limit of approximately 150 years based on the radioisotope half-life of 22.3 years. In the Lake Whatcom sediment core, the last 150 years represents approximately 20 cm of sediment accumulation.

The sediment accumulation rate (SAR) at the location of the sample core has varied over time (Figure 1). The SAR increased from the late 1800s until 1950, decreased from 1950 to the late 1980s, and increased since the late 1980s. Rates estimated for this sediment core are similar to those published from a previous sediment core from the same basin ($\sim 0.045 \text{ g/cm}^2/\text{yr}$; Paulson and Norton, 2008).

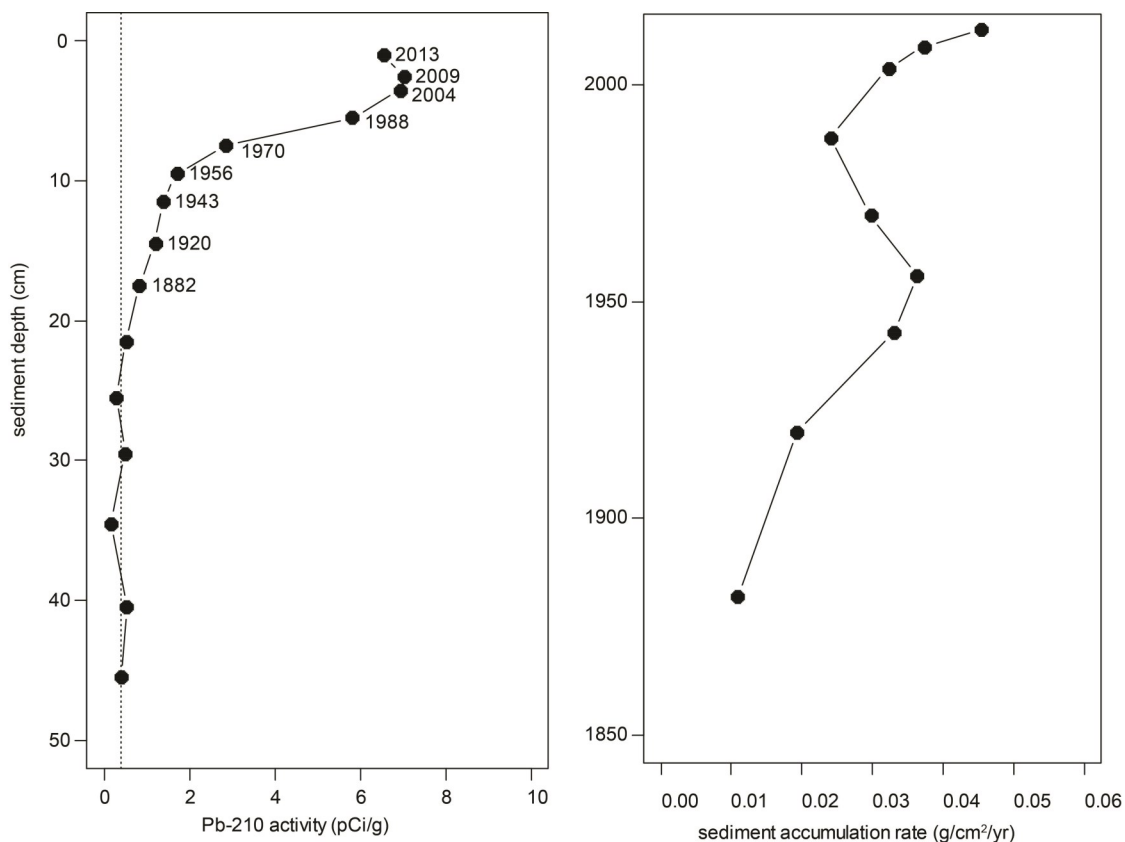


Figure 1. ^{210}Pb activity plotted against sediment core depth (left) and sediment accumulation rate over time (right).

Results – sediment composition and origin

Sediments were analyzed for the relative percent composition of organic, carbonate, and mineral material (Figure 2). Lake Whatcom sediment at the core location is composed mostly of organic and mineral material. In the early 1800s, the sediments were largely organic but changed to being mostly mineral through the 1800s and 1900s.

The trends of mineral and organic flux¹ show the greater inputs of material to the lake post-1900 (Figure 2). The flux of organic material peaked at ~1950 and decreased until the 1980s, while mineral flux remained fairly stable after peaking at ~1950.

Similar to the trend in organic matter content, the TOC concentration and flux in the sediment core shows a large increase in organic carbon post-1900 up to a peak at ~1950 (Figure 3). After 1950 the inputs of organic carbon to the lake sediment decreased dramatically but increased again in the 1990s.

The ratio of C:N in lake sediments is often used to decipher between a terrestrial C and aquatic C source, based on the knowledge that terrestrial C is more refractory (Kaushal and Binford, 1999). Generally a higher ratio (>15) suggests that the organic matter is likely of terrestrial origin. The increase in organic matter post-1900 to 1950 seems related to inputs from terrestrial ecosystems (surrounding watershed), while the more recent increase in TOC (post-1990) has a lower C:N, suggesting more of an in-lake or algal source (Figure 3).

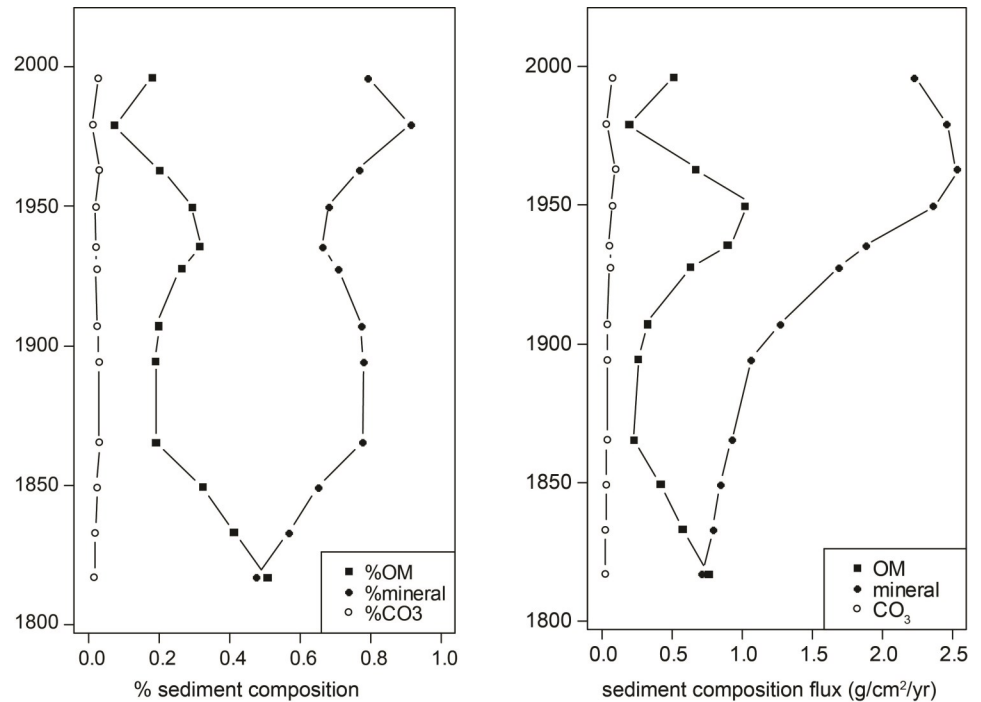


Figure 2. Sediment composition and flux.

OM = organic matter; mineral = mineral matter; CO₃ = carbonate

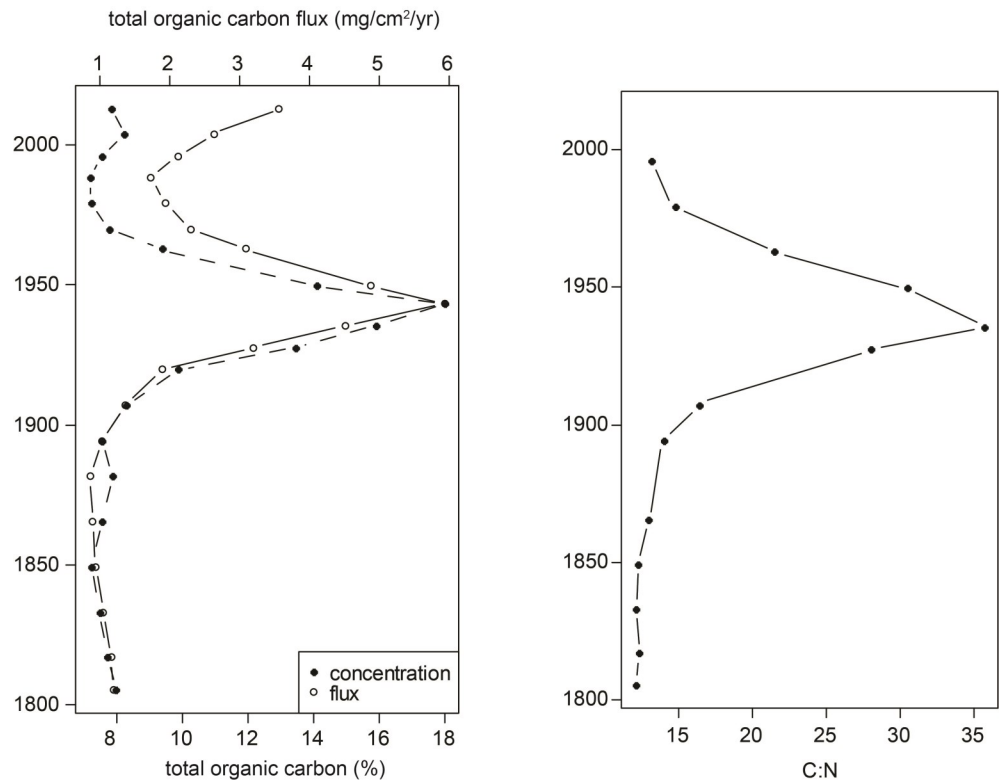


Figure 3. Trends in total organic carbon (TOC) concentration and flux, and carbon:nitrogen (C:N)

¹ Flux is the sediment accumulation rate (SAR) multiplied by the percent composition or concentration.

Results – total phosphorus accumulation

The trend of TP concentrations in the sediment core increases dramatically in the late 1800s (Figure 4). The trend of TP accumulation in the sediments (flux) also increases in the late 1800s and then again in the early 1900s. This later increase continues until ~1950, similar to the trend in TOC. The highest accumulation of TP in the location of the core occurs at ~1950 and the late 1990s, acknowledging that the post-2000 sediments were not analyzed for TP and could be higher.

Summarizing the accumulation of TP into an average for three periods, and correcting the accumulation rates for sediment focusing², shows greater accumulation in the modern (1950-2000) period than the historical period (pre-1900) (Figure 4). Modern TP accumulation rates are 0.024 ± 0.003 mg/cm²/yr (mean \pm sd), compared with a pre-1900 accumulation rate of 0.0097 ± 0.0093 (Table 1).

Based on the modern (1950-2000) TP accumulation rate and the area of the lake bottom which is below 1 meter water depth³ (assumed to be the depositional environment), the mass of TP being deposited in basin 1 of Lake Whatcom is 454 kg/yr (1067 lbs/yr). This calculation assumes that the measured TP accumulation rate presented here represents a basin-wide rate.

Table 1. Summary of total phosphorus accumulation.

period	n	mean	sd	median	median absolute deviation
1950 - 2000	3	0.0244	0.0030	0.0238	0.0031
1900 - 1950	4	0.0211	0.0062	0.0219	0.0052
pre-1900	6	0.0097	0.0014	0.0093	0.0007

n: number; *sd*: standard deviation

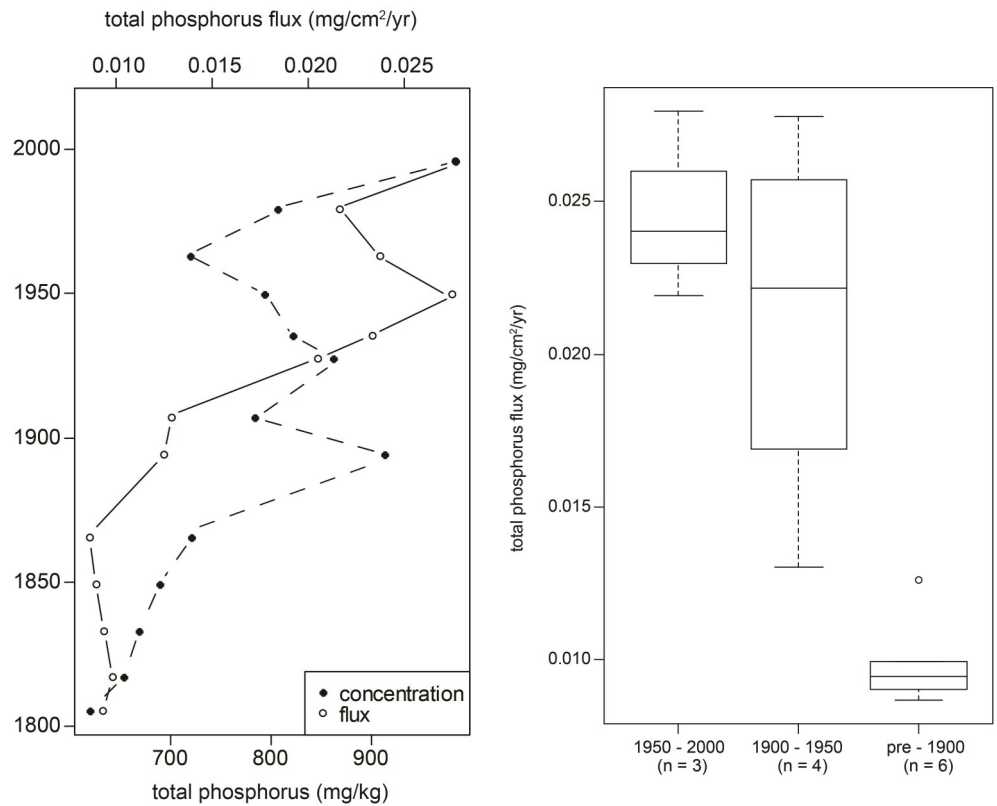


Figure 4. Profile of total phosphorus concentration and accumulation (left) and focus-corrected total phosphorus accumulations over 3 time periods (right).

² Sediment deposition in lakes can be influenced by the shape of the basin, where focusing of the sediments occurs towards the deepest locations of the basin. A correction factor can be applied to the sediment accumulation rates using the 210-Pb results; this focus-correction allows for an estimate of basin-wide SAR.

³ 1,986,878 m² from Mitchell et al., 2010.

Discussion

The goal of this project was to provide an estimate of the TP accumulation in sediments of the northern basin (basin 1) of Lake Whatcom. The trend of TP accumulation in the sediment core shows a large increase from the early 1900s to 1950. The deposition of phosphorus to lake bottom sediments reflects TP inputs and internal cycling of TP within the lake. Sediment TP in cores has therefore been used in the past as an indicator of historical changes in the nutrient enrichment of lakes that may lead to excessive algal growth or issues of low dissolved oxygen (Anderson et al., 1993; Engstrom, 2005; Engstrom et al., 2009). However, sediment TP is often used as part of a multi-proxy or multiple lines-of-evidence approach. The reason is that phosphorus in lake sediments is not stable and can migrate to upper sediment layers under changes in the redox or oxygen content of the sediments (Mortimer, 1942; Søndergaard et al., 1993; Rydin, 2000). Phosphorus is generally bound in large part to oxo-hydroxides of iron and manganese which are redox-sensitive metals; therefore, as the oxidation state of the metals changes, phosphorus can be released. The historical trend of TP in a sediment core therefore has limitations.

In the Lake Whatcom core, the trend of TOC and sediment accumulation broadly mimic the TP accumulation trend. While it is possible that post-depositional processes can also alter TOC concentrations, the broadly similar trends provide some evidence that the post-1900 increase in TP reflects an increase in TP inputs to the lake. Furthermore, it appears likely that the source of organic inputs to the lake sediment may have changed over time, from terrestrial to aquatic, possibly with the enrichment of TP in the lake during 1900-1950.

The estimates of TP accumulation provided in this report have caveats and are not intended to be used as a precise measure of TP flux throughout the northern basin of Lake Whatcom. These estimates should be limited to broad or back-of-the-envelope comparisons of TP flux in the basin. For example, the previous modeling study by Cadmus Group and CDM (2007) suggested a total TP load of $0.0028 \text{ mg/cm}^2/\text{yr}$ (0.25 lbs/ac/yr) to the entire lake, which is an order of magnitude less than the TP sediment accumulation measured in basin 1 ($0.024 \text{ mg/cm}^2/\text{yr}$). A more precise assessment of TP accumulation and loading in the sediments of Lake Whatcom would require multiple core locations within the basin (e.g. Engstrom, 2005) and an additional proxy of nutrient loading that is not mobile (e.g. fossil algal pigments).

Conclusions

Ecology analyzed archived sediment core material from Lake Whatcom to estimate total phosphorus (TP) trends and rates of accumulation. The following conclusions can be drawn:

- Sediments in the location of the core site are composed mainly of mineral material but were largely organic in the early-1800s.
- Rates of TOC and TP accumulation increased during 1900-1950. The ratio of sediment C:N suggests this increase was due to inputs from the surrounding watershed.
- Rates of TOC and TP accumulation decreased from the 1950s to the 1980s.
- Rates of TOC and TP accumulation have increased since the 1980s. Limited sediment C:N data suggest this increase is due to greater inputs of algal or in-lake material.
- During 1950-2000, TP sediment accumulation averaged $0.024 \pm 0.003 \text{ mg/cm}^2/\text{yr}$.
- A more precise estimate of TP accumulation and loading could be undertaken using multiple sediment cores and an additional proxy of nutrient loading that is not mobile in sediments.

References

- Anderson, N.J., Rippey, B., and Gibson, C.E., 1993. A comparison of sedimentary and diatom-inferred phosphorus profiles: implications for defining pre-disturbance nutrient conditions. *Hydrobiologia*. 253: 357-366.
- 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* 5:1-8.
- Berger, C.J. and S.A. Wells, 2005. Lake Whatcom Water Quality Model. Prepared by Portland State University for Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-007. <https://fortress.wa.gov/ecy/publications/summarypages/0910007.html>
- Butcher, J., 2008. Lake Whatcom Models Review. Prepared by Tetra Tech for Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-013. <https://fortress.wa.gov/ecy/publications/summarypages/0910013.html>
- Cadmus Group Inc. and CDM, 2007. Final Model Report for the Lake Whatcom Watershed TMDL Model Project. Prepared for U.S. Environmental Protection Agency Region 10 and Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-010. <https://fortress.wa.gov/ecy/publications/summarypages/0910010.html>
- Dean, W.E. Jr., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. *J. Sed. Petrol.* 44: 242-248.
- Engstrom, D.R., 2005. Long-term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration. *Lake and Reservoir Management* 21:95-106.
- Engstrom, D.R., J.E. Almendinger, and J.A. Wolin, 2009. Historical changes in sediment and phosphorus loading to the upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin. *Journal of Paleolimnology* 41:563-588.
- Heiri, O., A. Lotter, and G. Lemcke, 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments. *Journal of Paleolimnology* 25:101-110.
- Hobbs, W.O., 2017. Addendum 6 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 17-03-105. <https://fortress.wa.gov/ecy/publications/SummaryPages/1703105.html>
- Kaushal, S. and M.W. Binford, 1999. Relationship between C: N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. *Journal of Paleolimnology* 22:439-442.
- Mathieu, C., 2015. Addendum 5 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 15-03-113. <https://fortress.wa.gov/ecy/publications/SummaryPages/1503113.html>
- Mathieu, C. and M. McCall, 2016. PBT Chemical Trends Determined from Age-Dated Lake Sediment Cores, 2015 Results. Washington State Department of Ecology, Olympia, WA. Publication Number 16-03-046. <https://fortress.wa.gov/ecy/publications/SummaryPages/1603046.html>
- Mortimer, C.H., 1942. The exchange of dissolved substances between mud and water in lakes. *The Journal of Ecology*, 147-201.
- Paulson, A.J. and D. Norton, 2008. Mercury Sedimentation in Lakes in Western Whatcom County, Washington, USA and its Relation to Local Industrial and Municipal Atmospheric Sources. *Water, Air, and Soil Pollution* 189: 5-19.
- Pickett, P. and S. Hood, 2008. Lake Whatcom Watershed Total Phosphorus and Bacteria Total Maximum Daily Loads: Volume 1. Water Quality Study Findings. Washington State Department of Ecology, Olympia, WA. Publication Number 08-03-024. <https://fortress.wa.gov/ecy/publications/summarypages/0803024.html>
- Rydin, E., 2000. Potentially mobile phosphorus in Lake Erken sediment. *Water Research*, 34, 2037-2042.
- Søndergaard, M., Kristensen, P., and Jeppesen, E., 1993. Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Søbygaard, Denmark. *Hydrobiologia*, 253(1-3), 345-356.

Glossary of terms

CRS Model: A model developed by Appleby and Oldfield (1978) applied to ^{210}Pb measurements in a sediment core to estimate dates and varying sedimentation rates. The model works by measuring the difference in supported and unsupported ^{210}Pb in sediment horizons, and the relation of that difference to the inventory of unsupported ^{210}Pb of the whole core. 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.

Flux: An estimated rate of net deposition of a chemical or particle to the lake. Flux rates normalize the variance involved with interpreting dry weight concentrations under varying sedimentation rates. Contaminant flux rates were calculated as the product of the sediment mass accumulation rate and dry weight contaminant concentration.

Focus Factor: A focus factor corrects for the focusing of fine-grained sediments to the coring location or the transport of sediments away from coring sites. Sediment cores for this study are often collected in the deepest part of the lake, and fine-grained sediments preferentially deposit in these areas.

Sediment Accumulation Rate: The modeled rate of sediment accumulation to the lake bottom at the location of the sediment core. Units in mass per sediment area per year.

Supported ^{210}Pb : Supported ^{210}Pb is represented by the small amount of the precursor gas ^{222}Rn (radon) that is captured in soils. Supported ^{210}Pb in this study was estimated as the average ^{210}Pb value at deep intervals where it appeared to no longer decline.

Unsupported ^{210}Pb : Unsupported ^{210}Pb represents the atmospherically deposited ^{210}Pb resulting from the decay of ^{222}Rn that escapes into the atmosphere. Unsupported ^{210}Pb in this study was estimated by subtracting supported ^{210}Pb from total ^{210}Pb at a given depth.

Department of Ecology contacts

Author: William Hobbs
Environmental Assessment Program
P.O. Box 47600
Olympia, WA 98504-7600

Communications Consultant
Phone: 360-407-6764

This report is available on the Department of Ecology's website at
<https://fortress.wa.gov/ecy/publications/SummaryPages/1703014.html>

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search Study ID, WHOB006.

If you need this document in a format for the visually impaired, call 360-407-6764.

Persons with hearing loss can call 711 for Washington Relay Service.

Persons with a speech disability can call 877-833-6341.