DEPARTMENT OF
ECOLOGY
State of Washington

PBT Trends in Lake Sediment Cores:

2019 and 2020 Results

July 2024

Publication 24-03-018

Publication Information

This report is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/SummaryPages/2403018.html.

Data for this project are available in Ecology's EIM Database.
Study ID: SEDCORE19 and SEDCORE20.

The Activity Tracker Code for this study is 06-513.

Suggested Citation
Mathieu, C. 2024. PBT Trends in Lake Sediment Cores: 2019 and 2020 Results. Publication 24-03-018. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2403018.html.

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area:

- WRIAs: 7, 10, 13, 15, 17, 18
- HUC Numbers: 17110011, 17110014, 17110018, 17110019, 17110020

Contact Information

Publications Team
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 564-669-3028

Washington State Department of Ecology – https://ecology.wa.gov

Headquarters, Olympia	360-407-6000
Northwest Regional Office, Shoreline	206-594-0000
Southwest Regional Office, Olympia	360-407-6300
Central Regional Office, Union Gap	509-575-2490
Eastern Regional Office, Spokane	509-329-3400

PBT Trends in Lake Sediment Cores:

2019 and 2020 Results

by

Callie Mathieu

Table of Contents

List of Figures

List of Tables

Abstract

The Washington State Department of Ecology has monitored persistent, bioaccumulative, and toxic (PBT) chemicals in freshwater sediment cores since 2006. This report presents results from the 2019 and 2020 sampling years of the long-term monitoring study. In 2019 we collected sediment cores from Blackmans, Sutherland, and Wildcat Lakes to reconstruct profiles of per- and polyfluoroalkyl substances (PFAS), and in 2020 from Hicks and Spanaway Lakes for analysis of hexabromocyclododecane (HBCD).

PFAS in Blackmans Lake sediments rose between the mid-1950s through the 1990s, where concentrations peaked and then remained stable. PFAS fluxes continued to rise in Blackmans Lake through 2014, and then declined slightly in the years following. PFAS concentrations and fluxes in Wildcat Lake were low but increased from the late 1940s through the late 1980s and then plateaued. No PFAS were detected in Sutherland Lake sediments in any year analyzed; PFAS accumulation in this lake is predominantly via atmospheric deposition.

HBCD increased sharply beginning in the 1980s until peaking in the most recent sediment layer at Hicks Lake and in 2009/2014 at Spanaway Lake, following the pattern of commercial use of HBCD. The temporal trends and concentrations of HBCD observed in Hicks and Spanaway Lakes were similar to those observed in other parts of the world without industrial or textile manufacturing inputs. Hicks Lake had slightly higher concentrations than typically seen in urban residential waterbodies, which may be attributed to the combination of its dense residential watershed and high organic carbon content in sediments.

We recommend continued monitoring of PFAS and HBCD as part of this long-term study, as potential reductions in lake sediments may be observed in future sampling events following major commercial phase outs over the last ten years.

Introduction

The Washington State Department of Ecology's (Ecology's) Persistent, Bioaccumulative, and Toxic (PBT) Monitoring Program began a study in 2006 to assess environmental trends through age-dated lake sediment cores. This study carries out environmental monitoring of PBTs in Washington State's environment, as recommended in Ecology's PBT Strategy (Gallagher 2000). The state's PBT Rule (WAC 173-333) listed 24 chemicals or chemical groups, and two metals of concern, that met the criteria and laid out a plan to address them through chemical action plans. The goal of the rule was to reduce and phase out uses, releases, and exposures of PBTs in Washington state through recommendations of multi-media and cross-program measures.

The PBT Monitoring Program collects sediment cores from three lakes throughout the state each year to construct historical deposition profiles of PBTs in the environment to see whether levels in the environment are increasing or decreasing. Selected sediment core layers are analyzed for a target analyte from the PBT Rule, as well as a suite of parameters to age-date the sediment layers. On a rotating basis, target PBTs include polycyclic aromatic hydrocarbons (PAHs), per- and polyfluoroalkyl substances (PFAS), hexabromocyclododecane (HBCD), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs), and mercury.

This report presents results from the 2019 and 2020 sampling years of the long-term monitoring study. In 2019, the target analyte group was PFAS, and sediment cores were collected from Blackmans, Sutherland, and Wildcat Lakes. In 2020, sediment cores were collected from Hicks and Spanaway Lakes for analysis of HBCD.

Per- and Polyfluoroalkyl Substances (PFAS)

PFAS are a large group of chemicals containing carbon-fluorine bonds. They are used in many applications for their hydrophobic and lipophobic properties and because they are highly stable. Found in both industrial and consumer products, they are primarily used as water-, stain-, and oil- repellent coatings, as well as in aqueous film-forming foams (AFFFs) and other applications like metal plating suppressants. PFAS are a concern because they are widespread in the environment, and some compounds are highly persistent, bioaccumulative, and toxic.

This study analyzed 15 PFAS (listed in Appendix A): perfluoroalkyl acids (PFAAs) containing carbon chains length of 4-14 and two perfluoroalkane sulfonamides. While the entire class of PFAS includes thousands of individual compounds, the PFAA subgroup are terminal degradation products that are resistant to further breakdown under normal conditions and typically are the substances found in sediments. PFAAs can be described as "long-chain" or "short-chain." The long-chain group includes perfluoroalkyl carboxylates (PFCAs) with eight or more carbons and perfluoroalkyl sulfonates (PFSAs) with six or more carbons. The short-chain group includes PFCAs with seven carbons or less and PFSAs with five carbons or less.

Evidence has suggested carcinogenic potential from exposure to PFAAs, as well as high cholesterol and reproductive, developmental, and immunological effects (US EPA 2016a). Other human health concerns include increased liver enzymes, decreased vaccination response, thyroid disorders, and pregnancy-induced hypertension and preeclampsia (US EPA 2016b). Human health concerns are primarily associated with the long-chain PFAAs, but short-chain PFAAs have shown similar effects, typically occurring at higher doses (ITRC 2023).

PFAS have been known as ubiquitous contaminants in the environment with a worldwide distribution since the early 2000s (Giesy and Kannan 2001). In Washington State, PFAS have been detected in surface water, sediments, and fish of freshwater systems (Furl and Meredith 2010; Johnson and Friese 2012; Mathieu 2013; Mathieu and McCall 2017), stormwater (Medlen 2018), and marine sediments (Long et al. 2013; Dutch et al. 2021). PFAS are released to the environment as emissions during manufacturing and the use and disposal of products containing PFAS (OECD 2013). PFAS can be transported into and through the environment via stormwater, discrete releases (such as AFFF release), wastewater treatment plant (WWTP) effluent, biosolids applications, landfill leachate, and atmospheric deposition (ITRC 2023).

PFAS have been used since the 1950s, but U.S. manufacturers largely phased out the most highly bioaccumulative substances in the 2000s (perfluorooctane sulfonate [PFOS]) and 2010s (perfluorooctanoate [PFOA] and long-chain PFAAs). In 2022, Ecology and the Washington State Department of Health (DOH) drafted a chemical action plan to address PFAS in the state (Ecology and DOH 2022). Washington state has moved to restrict PFAS in food packaging, AFFFs, cosmetics, carpets, and after-market stain and water-proofing treatments. Ecology is currently considering action on other priority products such as textiles, ski wax, non-stick cookware, cleaning products, and fire-fighter protective gear by 2025.

Hexabromocyclododecane (HBCD)

HBCD refers to a technical mixture of brominated flame retardants, composed primarily of three isomers: alpha-, beta-, and gamma-. The largest use of HBCD was in extruded and expanded polystyrene (XPS and EPS) foam to provide thermal insulation in buildings. It has also been used as a flame retardant in furniture upholstery and other textiles, and in latex binders, adhesives, and paints (Environment Canada 2011), as well as in solder used in automobile replacement parts (US EPA 2022).

HBCD exhibits high aquatic toxicity and is a human health concern for reproductive, developmental, and neurological effects (US EPA 2010). While HBCD has been manufactured since the 1960s, concern over the persistence, bioaccumulation, and toxicity of HBCD grew in the 2000s and it was listed as a persistent organic pollutant under the Stockholm Convention in 2013. Commercial users of it in the United States began to phase it out during the 2010s. Manufacturing of HBCD in the U.S. fell from 10-50 million pounds over 2007-2011, to 1-10 million pounds per year between 2012-2015 (US EPA 2020). By 2017, it was no longer manufactured or imported domestically in the United States (US EPA 2020).

HBCD has been widely detected throughout the environment, including in air, sediment, water, and aquatic biota (Covaci et al. 2006), and freshwater fish and sediments in Washington State (Johnson and Friese 2012; Mathieu and McCall 2014; Mathieu and Wong 2016). HBCD can enter the environment through the use and disposal of products containing HBCD (US EPA

2010) and can be transported long distances through the atmosphere (Covaci et al. 2006). Diffuse particulate releases to soil can occur during construction and demolition of XPS- or EPS-insulated buildings, and particulates containing HBCD can be transferred to air or stormwater runoff and through WWTP effluent or landfill emissions (US EPA 2010).

Methods

This study was carried out following the Quality Assurance Project Plan (QAPP) (Mathieu 2016), QAPP addendums (Mathieu 2019; Mathieu and Bednarek 2020), and standard operating procedure EAP038 *Collection of Freshwater Sediment Core Samples Using a Box or KB Corer* (Mathieu 2023). Brief descriptions of the project methods are given below.

Study Locations

Study locations were selected using criteria outlined in the QAPP and described in the QAPP addendums. Figure 1 displays their locations and Table 1 gives relevant physical characteristics. More detailed descriptions of the lakes and their watersheds are provided in Appendix B.

In 2019, sediment cores were collected from our target locations: Blackmans Lake, Lake Sutherland, and Wildcat Lake. Blackmans Lake was selected to capture PFAS concentrations and fluxes in a lake with urban and residential development. Wildcat Lake was chosen based on its proximity to potential AFFF release sites at a nearby military base and a small private airport, although the lake is not hydrologically connected to known AFFF releases. Other potential sources at Wildcat Lake include residential septic systems. Lake Sutherland served as a reference lake for the 2019 sampling year, as it lies in a primarily forested, undeveloped watershed near the edge of Olympic National Forest. Aside from residential sources along the shoreline (such as septic systems) and a state highway near the northern shore, PFAS sources are likely dominated by atmospheric deposition at Sutherland Lake.

In 2020, sediment cores were collected from Hicks Lake and Spanaway Lake. Field staff were unsuccessful in retrieving cores from two out of three target study locations in 2020. Lake Kapowsin was a target listed in the QAPP but contained too much woody debris within the sediments for a proper core and boat launch construction at Leland Lake prevented access to the lake. Spanaway Lake was used as an alternate study location in 2020, as we had permits for the site and it met criteria outlined in the QAPP. We did not collect a core from a third location, due to permit limitations and field conditions. Hicks Lake reflects HBCD inputs in a densely residential watershed and Spanaway Lake represents a mixed-use urban and residential watershed.

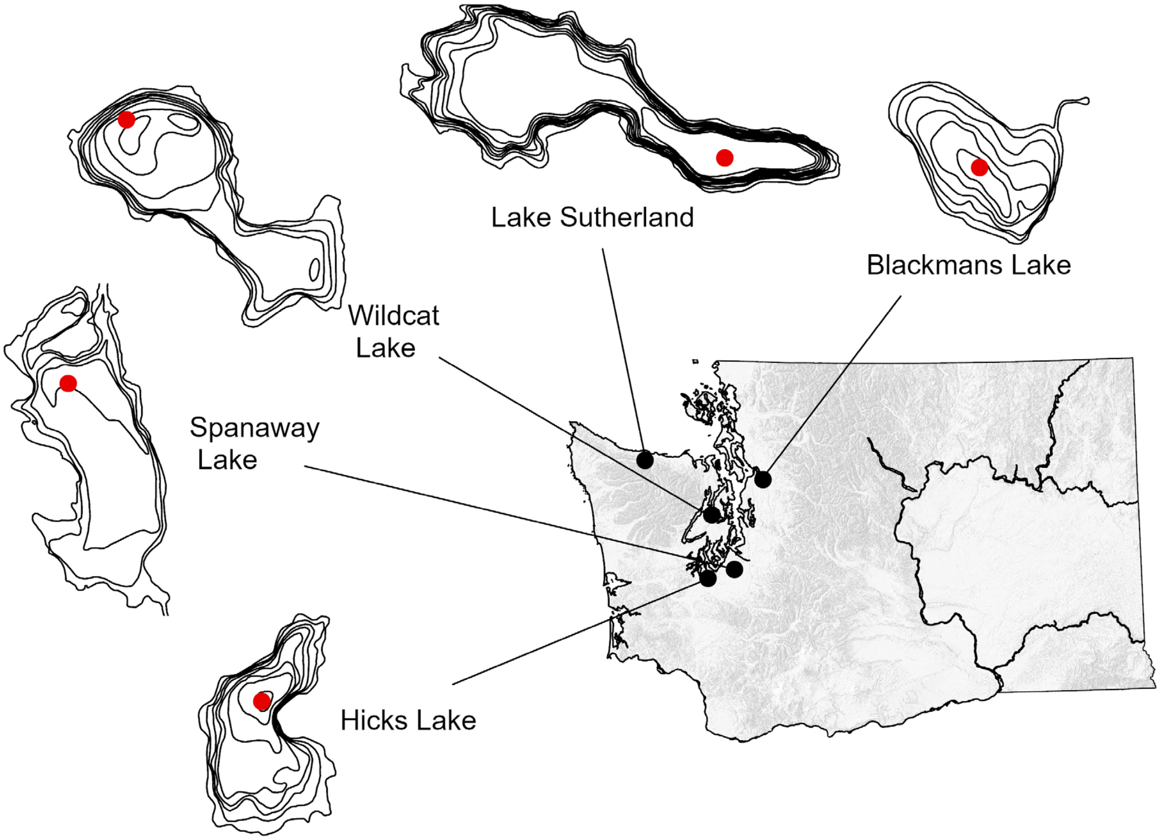

Figure 1. Map of 2019 and 2020 study locations.

Table 1. Physical descriptions of the study locations.

Collection Year	Waterbody	County	Elevation (ft)	Max Depth (ft)	Mean Depth (ft)	Lake Area (ac)	Watershed Area (ac)	WA: LA
2019	Blackmans Lake	Snohomish	140	29	14	57	518	9
2019	Lake Sutherland	Clallam	525	86	57	370	5,107	14
2019	Wildcat Lake	Kitsap	377	33	18	120	1,600	13
2020	Hicks Lake	Thurston	162	35	18	160	1,152	7
2020	Spanaway Lake	Pierce	320	28	16	280	10,880	39

ac = acre; WA:LA = watershed area to lake area ratio

Field Methods

Sediment cores were collected from deep, flat areas of the study lakes—as estimated from lake bathymetric maps and confirmed in the field with a depth sounder. Field staff used a Wildco stainless steel box corer fitted with a 13 cm x 13 cm x 50 cm acrylic liner to collect the core. Sediment cores were retained for subsampling if the desired depth was reached (approximately 35-45 cm) and the sediment-water interface was intact. Field staff siphoned overlying water off the top of the core and then used an extruding device and table to section the core into 1 cm intervals. The top 2 cm of the core were sectioned together to provide enough material for analysis where the water content is greatest, resulting in limited dry weight of sediment.

The box corer and all equipment in contact with the sediments were decontaminated prior to use following the procedures outlined in the QAPP. Field staff wore clean nitrile gloves for sample handling. Samples were kept in coolers in the field and chain of custody was kept throughout the study.

Sample Preparation and Analysis

Staff processed the sediment core samples by homogenizing 1 cm intervals (2 cm for the top of the core) in stainless steel bowls with stainless steel spoons until the sediments were uniform in color and texture. Subsections of the sediment interval were then placed into jars, stored frozen, and submitted to the laboratory for analyses. Sediment samples for PFAS and HBCD were centrifuged, and overlying water was decanted prior to freezing.

Samples were analyzed for the parameters and by the methods outlined in Table 2. Manchester Environmental Laboratory (MEL) conducted analyses of PFAS, total lead, and total organic carbon. Contract laboratories analyzed HBCD (SGS AXYS Analytical Services Ltd.) and radiochemistry (Eurofins TestAmerica). Sample results were reported as dry weight.

Table 2. Analytical Methods.

Parameter	Sampling Year	Sample Prep Method	Analytical Method	Instrument	Laboratory
PFAS	2019	AOAC2007.01 modified	EPA SW8321B modified	LC-MS/MS isotopic dilution	MEL
HBCD	2020	Laboratory-specific method	MLA-070 Rev 02	LC-MS/MS isotopic dilution	SGS AXYS Analytical, Sydney BC
T-Pb	2019, 2020	EPA 6020	EPA 6020	ICP-MS	MEL
TOC	2019, 2020	SM5310B (preacidified)	SM5310B (preacidified)	TOC-V_{CSH} analyzer	MEL
^{210}Po	2019, 2020	Alpha spectroscopy	HASL-300 A-01-R	Alpha spectroscopy	Eurofins TestAmerica, St. Louis
^{226}Ra	2019, 2020	Gamma spectroscopy	HASL-300 A-01-R	Alpha spectroscopy	Eurofins TestAmerica, St. Louis

T-Pb = total lead; TOC = total organic carbon; ^{210}Po = 210 polonium isotope; ^{226}Ra = 226 radium isotope

Data Quality

All data for this project were accepted and deemed usable as qualified. For the 2019 samples, all measurement quality objectives (MQOs) were met with the following exceptions:

- **Polonium isotope (^{210}Po) analysis:** One out of three lab duplicate pairs had a relative percent difference (RPD) greater than 20%. The RPD was 22% for this pair and the associated field sample was qualified "J"—indicating an estimated value. The source sample was used for age-dating analysis as qualified, and this exceedance is unlikely to affect the results.
- **PFAS analysis**: Several analytes had matrix spike and surrogate recoveries higher than MQOs. This did not affect results because the analytes were undetected in the associated samples and no qualifications were made. Likewise, perfluorotridecanoate (PFTrDA) had a laboratory control sample (LCS) recovery greater than MQOs but was not detected in the samples and no qualifiers were added. It was determined, high recoveries were due to a combination of matrix effects and the low solubility of the analytes in the solvent mix.

MQOs for the 2020 samples were met except for a high LCS recovery for ^{226}Ra. Affected results were qualified "J" as estimates. The ^{226}Ra results are ancillary data used to support interpretation of the sediment cores and this exceedance is not likely to affect the results of this study.

Data Processing

All cores were age-dated using ^{210}Pb activities and the constant rate of supply (CRS) model (Appleby and Oldfield 1978). ^{210}Po was measured in our samples via alpha spectroscopy and assumed to be in equilibrium with ^{210}Pb and is referred to as ^{210}Pb from here on out. Supported ^{210}Pb values were calculated as an average activity at deep intervals where there was no further apparent decline. Three intervals throughout the core were analyzed for ^{226}Ra activities by alpha spectroscopy, and those values helped confirm the supported ^{210}Pb values. Percent solids were used to calculate dry mass and an assumed sediment density of 2.7 g/cm^3 was used based on other Washington State coring studies (Paulson 2004).

Results and Discussion

Core Dating

Figure 2 displays the estimated dates and associated dating uncertainties for the sediment cores. Average supported ^{210}Pb activities used in the cores ranged from 0.11-0.23 pCi/g. Average ^{226}Ra activities from three intervals selected throughout the cores (upper, middle, and lower) agreed well with the supported ^{210}Pb values: 0.18-0.26 pCi/g.

Yearly unsupported ^{210}Pb fluxes estimated from the core dating models were in the range of 0.10-0.24 pCi/cm^2/yr. These values were used to calculate a "focus factor" by dividing the core estimates by fluxes calculated from lake-specific precipitation values and atmospheric ^{210}Pb deposition measured in Washington State (Lamborg et al. 2013). Focus factors are applied to contaminant fluxes throughout this report to correct for the focusing of fine-grained sediments to coring sites or the transport of sediments away from the coring sites. The use of focus-corrected contaminant fluxes allows us to directly compare results among lakes. Focus factors were 0.78, 0.81, 0.67, 0.38, and 1.1 for Blackmans, Sutherland, Wildcat, Hicks, and Spanaway Lakes, respectively.

A decrease in ^{210}Pb activities occurring at sediment depths of 7-12 cm in the Wildcat Lake core is likely a result of post-depositional mixing. This can occur from bioturbation, water movement, or a slumping of older sediment on top of newer sediment. The model used to date the core is fairly robust for mixing of this magnitude, with estimates of errors of 2 years occurring with a mixing zone spanning 10 years (Appleby 2001).

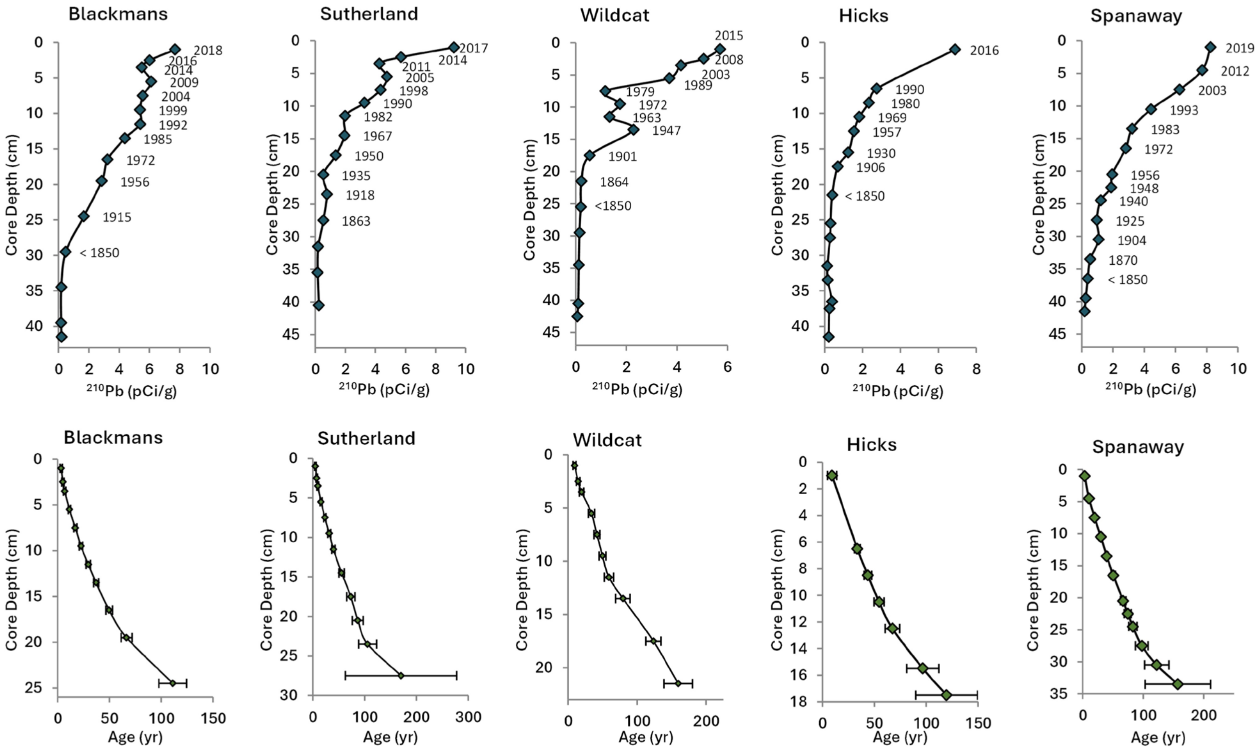

Figure 2. ^{210}Pb Activities plotted against sediment core depth (upper row) and modeled age of sediment core depth with associated uncertainties (bottom row).

Sediment Accumulation Rates and TOC

Figure 3 presents the sediment mass accumulation rates (MARs) estimated for the 2019 and 2020 lake sediment cores. Rates were calculated using the CRS model for all cores. Sediment MARs were generally low across the lakes, with average MARs ranging from 0.10-0.03 g/cm^2/yr.

Sediment accumulation rates began increasing slightly between the early 1900s and 1920s for most sites. The rate of sediment accumulation increased between the 1960s and the top of the core for Blackmans, Hicks, and Spanaway Lakes, likely due to increased watershed development during those years. Sutherland and Wildcat Lakes saw periods of increased sediment accumulation at different points in time: 1930s for Sutherland and 1970s in the Wildcat Lake core. However, the sudden increase in sediment MAR at Wildcat Lake in the 1970s is likely due to the post-depositional mixing discussed in the previous section and should be interpreted with caution.

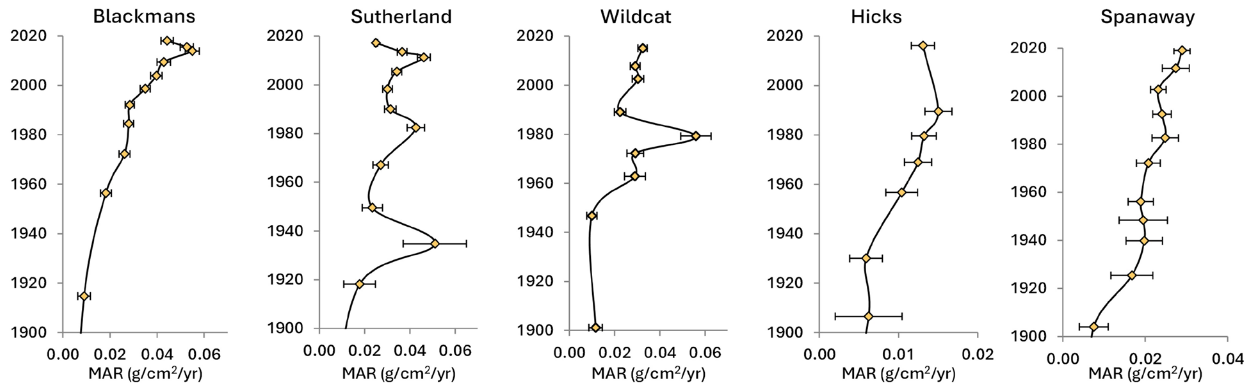

Figure 3. 2019 and 2020 profiles of estimated sediment mass accumulation rates (MAR).

Total organic carbon (TOC) profiles in the 2019 and 2020 sediment cores are shown in Figure 4. Concentrations of TOC changed little over the length of the core at Blackmans, Hicks, and Spanaway Lakes, ranging from 13-20%. Wildcat Lake also had stable TOC, though concentrations declined between 1960 and the top of the core (range = 7.5-11%). Lake Sutherland TOC remained within a range of 4.0-6.5%, with an uptick in organic carbon occurring around 2014.

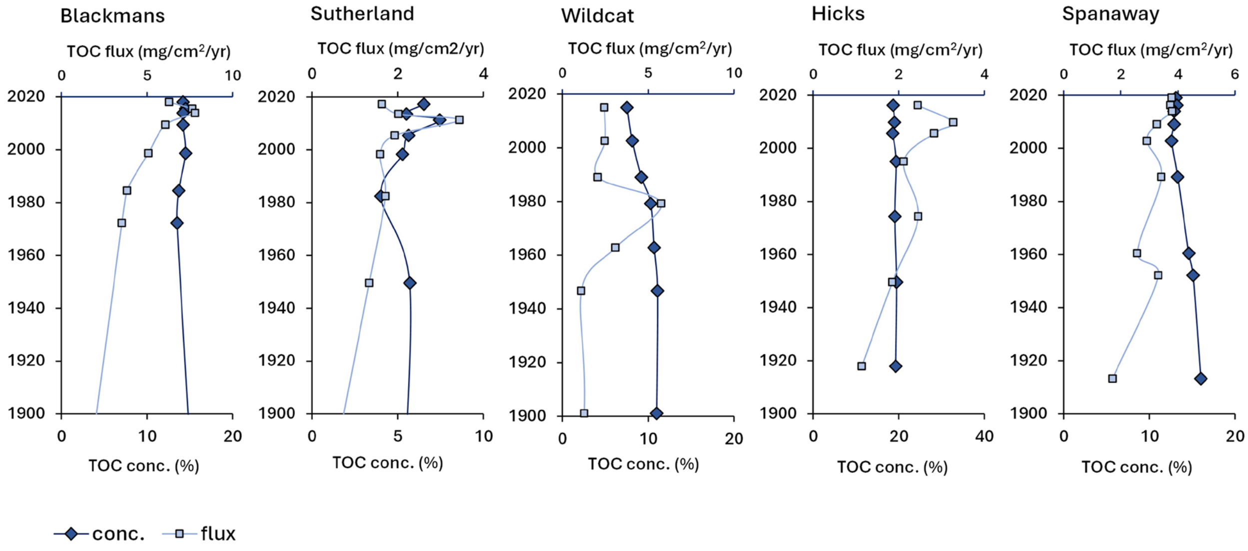

Figure 4. 2019 and 2020 Profiles of TOC concentrations (dark blue diamonds) and fluxes (light blue squares).

Lead Profiles

Total lead was measured in ten intervals of each sediment core. Figure 5 displays profiles of total lead concentrations and fluxes for the 2019 and 2020 cores.

Sediment lead accumulation began increasing in the first half of the 20th century at all lakes. Lead concentrations and fluxes peaked around the 1980s at Sutherland, Wildcat, and Spanaway Lakes and then declined over the next several decades. Lead concentrations peaked in 1972 at Blackmans Lake and then declined steadily between the 1980s and 2019, but fluxes remained relatively unchanged after the 1970s apart from a spike of increased lead fluxes around 2014. Hicks Lake sediments showed increasing lead concentrations and fluxes throughout the 1900s, with peaks in the 2000s (2006 and 2010, respectively) and a slight decrease in the top-most sediment layer.

Background concentrations of lead were captured in the pre-1850 sediments of all cores (1.6-4.6 mg/kg). Lead concentrations and fluxes remained low in Sutherland and Wildcat Lake sediments throughout the core. Modern lead concentrations in Sutherland and Wildcat averaged 15 and 43 mg/kg, after peaks of 43 and 50 mg/kg, respectively. In contrast, Blackmans, Hicks, and Spanaway Lakes contained sediments with somewhat elevated lead levels, reflective of their locations in developed watersheds. Modern (post-2000) lead concentrations in these lakes ranged from 97-115 mg/kg. Peak concentrations in Hicks, Spanaway, and Blackman Lakes were 149, 154, and 204 mg/kg, respectively.

Lead fluxes were generally low in the Sutherland, Wildcat, and Hicks cores, with modern flux ranges of 0.4-0.9 µg/cm^2/yr and peak fluxes of 0.9-1.8 µg/cm^2/yr. Fluxes in Blackmans and Spanaway Lakes were higher, with modern fluxes of 3.0-4.4 µg/cm^2/yr and peaks of 4.5-5.0 µg/cm^2/yr.

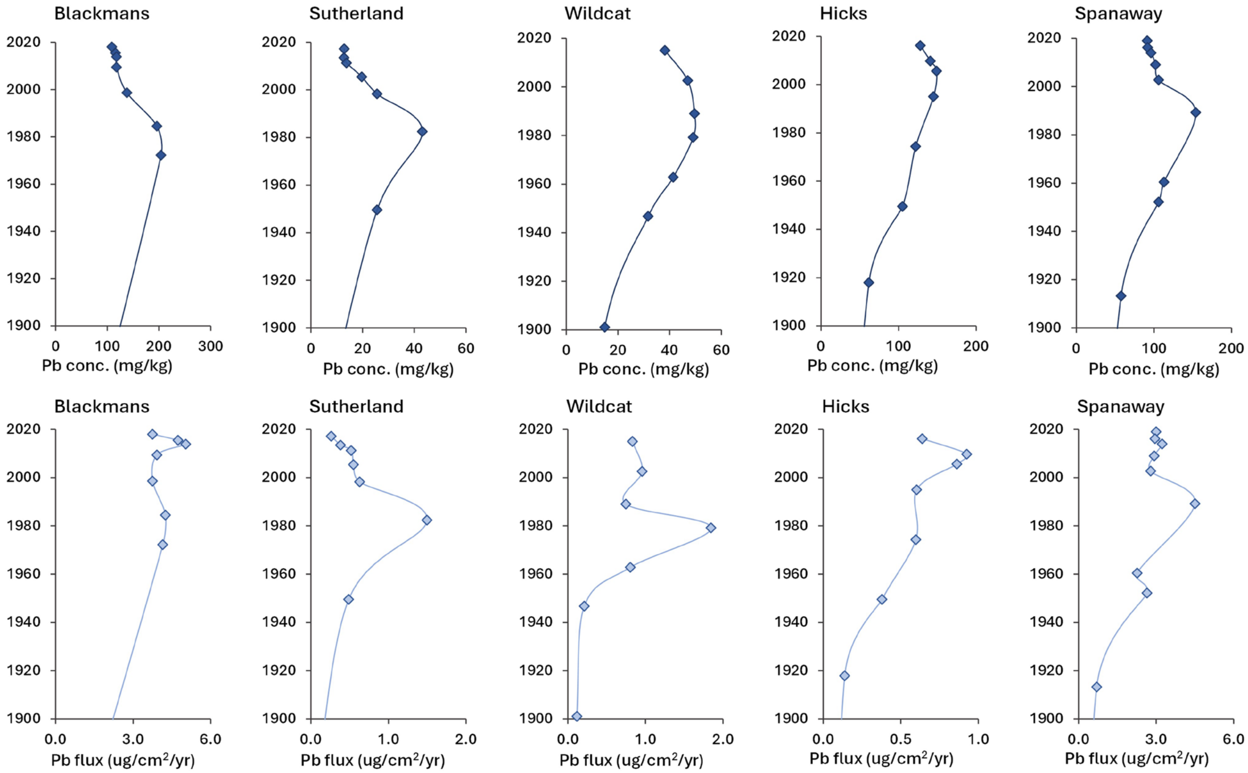

Figure 5. 2019 and 2020 profiles of total lead concentrations (top row) and total lead fluxes (bottom row).

Per- and Polyfluoroalkyl Substances (PFAS)

Sediment cores collected from Blackmans, Sutherland, and Wildcat Lakes were analyzed for PFAS in 2019. Fifteen PFAS were measured in 12 sediment intervals of each core. Appendix A gives a complete list of PFAS analyzed and their reporting limits. Total PFAS (T-PFAS) concentrations were calculated as the sum of all detected PFAS, including "J" qualified values.

T-PFAS profiles

At least one PFAS was detected in all sediments from Blackmans and Wildcat Lakes deposited after the mid-1940s. No PFAS were detected in sediments dated prior to that in the Wildcat Lake core, and we did not test any sediments older than that at Blackmans Lake. Lake Sutherland sediments did not contain PFAS at or above the method detection limits of 0.1-0.5 ng/g for any interval analyzed.

Figure 6 displays the dated profiles of sediment T-PFAS for Blackmans and Wildcat Lakes. Blackmans Lake PFAS concentrations and fluxes rose between the mid-1950s through the 1990s, where concentrations peaked and then varied but remained within a stable range of 9-13 ng/g (modern average = 12 ng/g). T-PFAS fluxes continued to rise between the 1990s and 2014, and then declined slightly in the years following. Modern T-PFAS fluxes to Blackmans Lake ranged from 0.40-0.56 ng/cm^2/yr, with an average of 0.44 ng/cm^2/yr. Sediments in Blackmans Lake were high in total organic carbon compared to other sites (14-15%), which may explain the higher than expected PFAS concentrations. The PFAS detected tend to sorb onto organic carbon (Higgins and Luthy 2006; Ahrens et al. 2009) and positive correlations have been reported between PFAS and organic carbon in sediments (Mussabek et al. 2019).

Wildcat Lake sediments contained low levels of PFAS. T-PFAS concentrations generally increased from the late 1940s through the late 1980s and then remained within a narrow range of 0.7-0.9 ng/g through 2019. The modern T-PFAS concentration was 0.83 ng/g. T-PFAS fluxes followed a similar pattern. An influx of PFAS occurring in the 1970s can be seen in the graph, though this is likely due to mixing in the core and may not represent an actual flux increase. Fluxes appeared to continue to increase slightly between the 1990s and 2019, though values remained low throughout the core. Modern fluxes ranged from 0.014-0.019 ng/cm^2/yr (average of 0.18 ng/cm^2/yr).

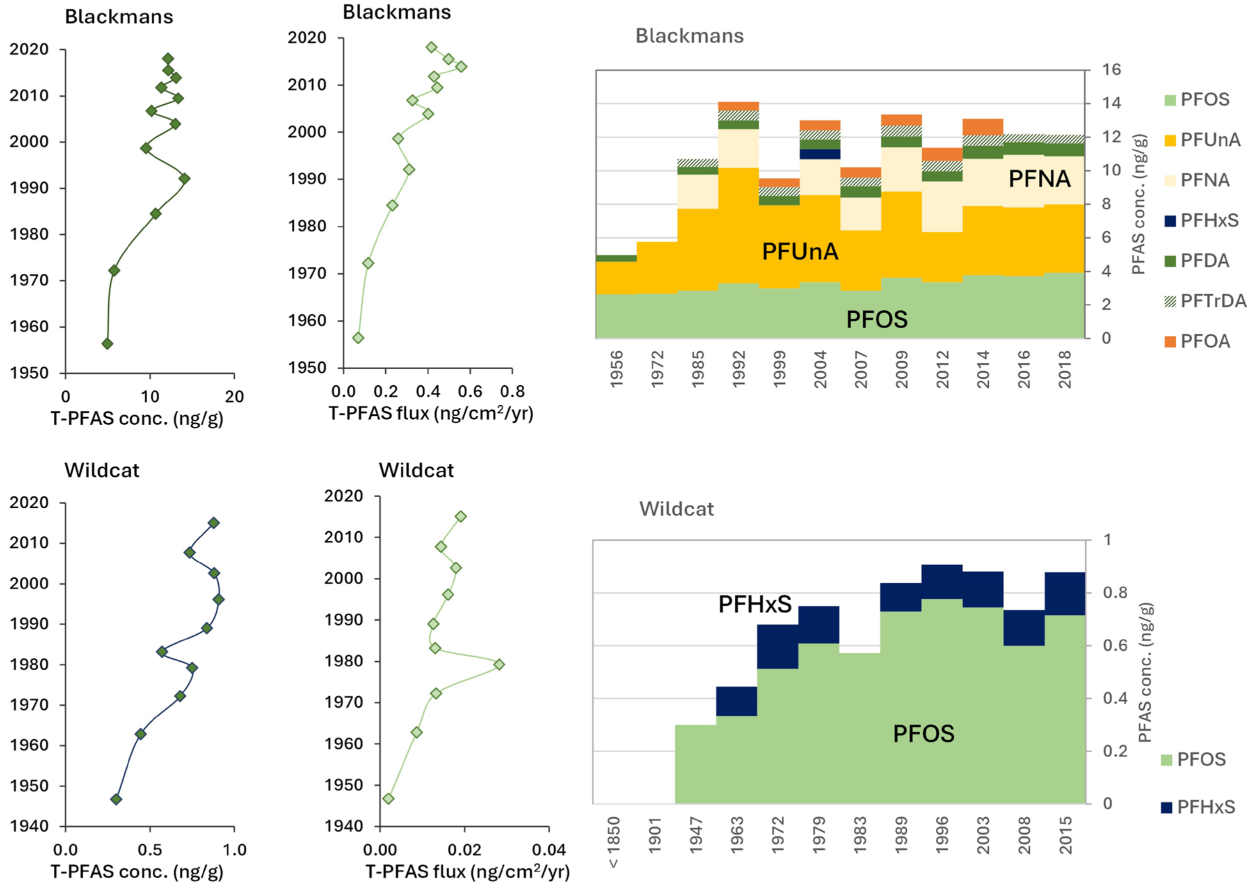

Figure 6. T-PFAS concentrations, T-PFAS fluxes, and individual PFAS profiles in Blackmans Lake (top row) and Wildcat Lake (bottom row) sediment cores.

Individual PFAS profiles

In Blackmans Lake, PFOS, perfluoroundecanoate (PFUnA), and perfluorononanoate (PFNA) were the dominant PFAS in sediments. PFOS and PFUnA were present since the 1950s, with PFUnA peaking in concentration in the early 1990s at 6.9 ng/g and ranging from 2.0-5.2 ng/g throughout the other intervals. PFOS remained steady throughout the core at concentrations of 2.6-3.9 ng/g, making up between 25-50% of the total. The relative abundance of PFUnA compared to PFOS is higher than typically observed in sediments. PFUnA is found as a breakdown product from carpets, stain-proofing for textiles, some AFFFs, and food packaging (Ogunsuyi et al. 2023). The source of PFUnA to Blackmans Lake is unclear.

PFNA first appeared in the 1980s in the Blackmans Lake core and was generally present around 3.0 ng/g from then until the present and contributed around 20% of the total PFAS concentration. Perfluorodecanoate (PFDA) and PFTrDA were also detected frequently in the core samples beginning in the 1980s, at relatively low concentrations (less than 1 ng/g). PFOA was detected at low levels (less than 1 ng/g), and only between 1992-2014.

The total PFAS burden in Wildcat Lake sediments was almost completely made up of PFOS. PFOS accounted for 70-100% of the total PFAS concentration between the 1950s through the top of the core. However, concentrations of PFOS were still low, at less than 1.0 ng/g. Perfluorohexane sulfonate (PFHxS) was the only other compound detected and first appeared in the 1960s. Concentrations of PFHxS were below 0.2 ng/g. The presence of PFHxS co-ocurring with PFOS in sediments has been suggested as an indicator of AFFF sources (D'Agostino and Mabury 2017; MacInnis et al. 2019).

Out of the 15 PFAS analyzed in the sediment core samples, only the seven discussed above were detected. Perfluoroalkyl carboxylates (PFCAs) with carbon chain lengths of 9 or more and PFSAs tend to sorb to sediments and are well preserved in sediments, making them appropriate for tracking temporal trends through sediment cores (Codling et al. 2018). The other PFAS analyzed, such as short chain PFCAs, PFOA, and precursor compounds are more water-soluble and generally are not detected in sediments in non-point source areas. This limitation was recognized in the QAPP for this study, with the awareness that environmental trends of short chain compounds would likely not be captured in sediment cores.

Comparison to other studies

Trends

The Blackmans and Wildcat Lake cores show similar temporal trends seen in other areas of North America. PFAS levels also increased from the 1950s-1970s through the early to mid-2000s in sediment cores collected from the Great Lakes (Yeung et al. 2013; Codling et al. 2014; Guo et al. 2016; Codling et al. 2018), Canadian Arctic lakes (MacInnis et al. 2019), and the Puget Sound (Strivens et al. 2021). Previous Washington lake sediment cores have also showed consistent increases over this period, with maximum concentrations occurring in the top layer (2010) (Mathieu 2013). Whereas, in sediment cores collected in Europe, PFAS concentrations peaked earlier, in the late 20th century (Langberg et al. 2021; Mourier et al. 2019).

Concentrations and fluxes

PFAS concentrations in Sutherland and Wildcat Lakes (non-detects and less than 1 ng/g, respectively) were low and comparable to levels observed in remote or background areas. Balgooyen et al. (2022) reported a background value of 0.21 ng/g for PFAS in bed sediment of tributaries in Wisconsin. Sediment cores collected from remote lakes in the Great Lakes area contained similar peak T-PFAS (sum of PFAAs) concentrations (1.7-3.7 ng/g) and fluxes (0.017-0.021 ng/cm^2/yr) to Wildcat Lake (0.9 ng/g and 0.028 ng/cm^2/yr) (Guo et al. 2016). Codling et al. (2018) reported a range of T-PFAS in surface sediments collected from the Great Lakes of 1.5-4.6 ng/g (Codling et al. 2018). Compared to previous sediment cores in Washington, Wildcat Lake had very similar concentrations and fluxes to Lake Stevens in Snohomish County, which is surprising given the higher urban density surrounding Lake Stevens compared to the more forested Wildcat Lake (Mathieu 2013).

Blackmans Lake PFAS levels were comparable to those recorded in West Medical Lake in Spokane County (especially fluxes). West Medical Lake receives WWTP discharges and has a long water residence time, which is likely why PFAS levels are so high in the lake. Both lakes are eutrophic, though sediment accumulation rates were much higher for West Medical Lake. The Blackmans Lake surface sediment PFAS concentration and flux of 12 ng/g and 0.42 ng/cm^2/yr were also comparable to a Lake Ontario core profile, which reached a peak of 13 ng/g and 0.41 ng/cm^2/yr in the top sediment layer (Guo et al. 2016). The authors noted that sources to Lake Ontario include diffuse inputs from a large population and commercial/industrial base, similar to residential and commercial land uses surrounding Blackmans Lake.

While Blackmans Lake contained high PFAS concentrations, they were not as high as levels seen in areas of point-source PFAS contamination—like fire training areas and manufacturing releases. Mussabek et al. (2019) collected a sediment core near an AFFF-impacted site and found max concentrations of 76 ng/g. In France, a sediment core collected downstream of a fluoropolymer plant reached a peak T-PFAS concentration of 51 ng/g in the 1990s (Mourier et al. 2019), four times higher than peak levels found in Blackmans Lake.

Hexabromocyclododecane (HBCD) Profiles

Three HBCD isomers (alpha-, beta-, and gamma-) were measured in nine sediment intervals from each core collected at Hicks Lake and Spanaway Lake. Total HBCD concentrations given below are sums of all three isomers. Total values include only detected results and include "J" qualified values.

T-HBCD profiles

Figure 7 displays the HBCD profiles for Hicks and Spanaway Lakes. HBCDs were consistently detected in both lake sediment cores. Profiles from the two lakes showed sediment T-HBCD concentrations and fluxes were low until increasing in the 1980s. This is consistent with the beginning of the use of HBCD in insulation boards (UNEP 2010) which led to dramatic increases in the environment.

Hicks Lake T-HBCD concentrations and fluxes continued to increase through the top of the core, with the maximum occurring in the most-recent sediments, at 69 ng/g and 0.34 ng/cm^2/yr. HBCD was detected at a very low concentration in a sediment layer dated 1918, which may be due to pore-water migration from the upper sediments since HBCD wasn't used commercially until the 1960s (UNEP 2010).

In Spanaway Lake, T-HBCD peaked between 2009 and 2014, at around 8 ng/g in concentration and 0.2 ng/cm^2/yr in fluxes, and then declined between 2014 and the top of the core (2019). This reduction in sediment HBCD concentrations and fluxes is consistent with U.S. manufacturers phasing out use of it during the 2010s. The top sediment layer had a T-HBCD concentration of 4.8 ng/g and a flux of 0.14 ng/cm^2/yr.

Individual HBCD profiles

The gamma- isomer was the dominant HBCD in all sediments analyzed, making up 86-90% of the total HBCD burden, on average across both cores. Alpha-HBCD contributed around 7-9% of the total in the Hicks Lake samples and between 10-28% in most Spanaway Lake samples. Beta-HBCD contributed the least in both cores, averaging 2-3% of the T-HBCD concentration. This isomeric make-up is close to that of commercial mixtures which are comprised of gamma- (75-89%), alpha- (10-13%), and beta- (1-12%) (Covaci et al. 2006; Marvin et al. 2011).

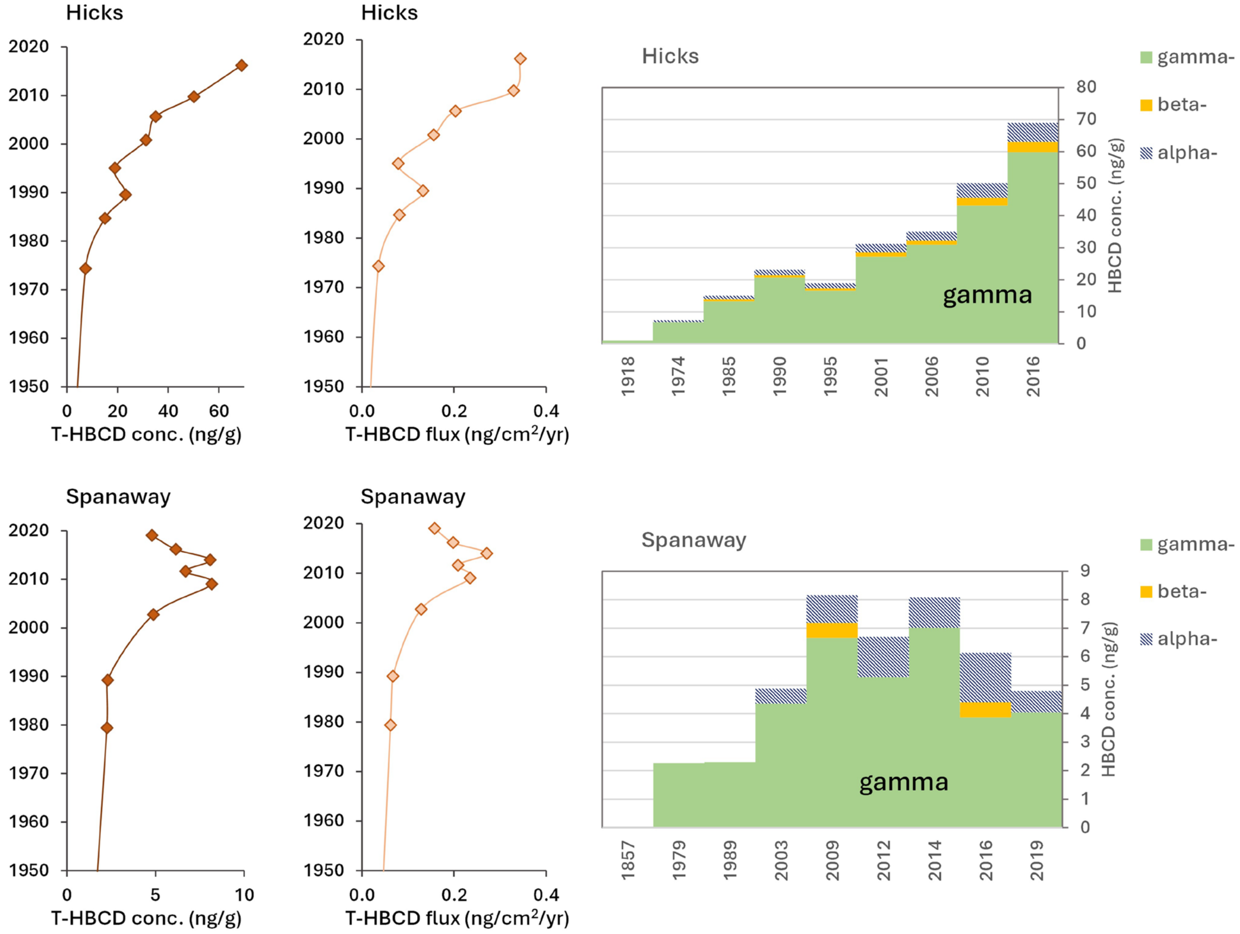

Figure 7. T-HBCD concentrations, T-HBCD fluxes, and individual HBCD profiles in Hicks Lake (top row) and Spanaway Lake (bottom row) sediment cores.

Comparison to other studies

Trends

Increases in HBCD levels starting in the 1980s-1990s and rising consistently through the top of the core has also been demonstrated with sediment cores collected in Australia, Europe, and Asia (Drage et al. 2015; Kohler et al. 2008; Al-Odaini et al. 2015). This reflects the growing commercial use of it beginning in the 1980s and 1990s and increases in market share following the phase out of other brominated flame retardants. Two studies in Europe reported only detecting HBCD in the top sediments of a core, suggesting recent use of it in the watershed (Poma et al. 2014; Evenset et al. 2007). Previous Washington State sediment cores also showed this pattern of HBCD appearing in the 1980s and increasing through the top of the core (Mathieu and McCall 2014).

Sediment cores collected in several lakes of England showed peak HBCD inputs occurring at various points in the 1980s, 1990s, and 2000s, with declines from peak levels at all cores except for the most urban site (Yang et al. 2016).

Concentrations and fluxes

Peak T-HBCD concentrations observed in this study are comparable to freshwater sediments reported from other areas with diffuse or mixed (non-industrial) sources (Figure 8). Hicks Lake was on the high end of the range of maximum non-industrial HBCD values reported in the literature, but 1-2 orders of magnitude below values reported from areas with known inputs from textile manufacturing (La Guardia et al. 2012; Oh et al. 2014). The high levels in Hicks Lake sediments are likely due to dense residential development in the watershed and high organic carbon content of the sediments. Organic carbon-normalized HBCD concentrations in Hicks Lake were similar to or lower than organic carbon-normalized values reported in lakes from Europe (Yang et al. 2016; Poma et al. 2014; Evenset et al. 2007).

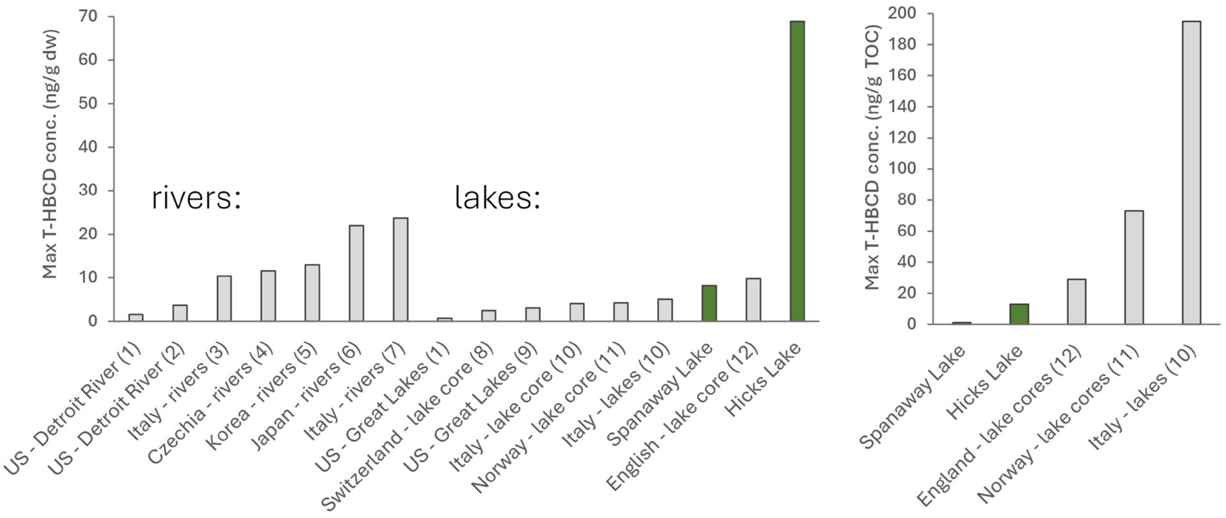

Figure 8. Maximum T-HBCD concentrations reported in freshwater sediments from diffuse or mixed sources on a ng/g dry weight basis (left pane) and organic carbon basis (right pane).

References: (1) Letcher et al. 2015; (2) Marvin et al. 2006; (3) Luigi et al. 2015; (4) Stiborova et al. 2017; (5) Jeong et al. 2014; (6) Oh et al. 2015; (7) Poma et al. 2014; (8) Kohler et al. 2008; (9) Yang et al. 2012; (10) Poma et al. 2014; (11) Evenset et al. 2007; (12) Yang et al. 2016.

In comparison to previous Washington sediment cores, Spanaway Lake HBCD concentrations were similar to those observed in Cavanaugh Lake (Skagit County) and Kitsap Lake (Kitsap County) (Mathieu and McCall 2014). Both Cavanaugh and Kitsap are Puget Sound lowland lakes with similar potential sources to Spanaway. Hicks Lake contained higher concentrations than any other Washington sediment core, but fluxes were similar to or lower than other lakes.

Conclusions

This report presents results from the 2019 and 2020 sampling years of a long-term monitoring study to evaluate PBT trends in lake sediments of Washington State. The following conclusions were made:

Per- and polyfluoroalkyl substances

- PFAS concentrations and fluxes in Blackmans Lake sediments rose between the mid-1950s through the 1990s, where post-1990 concentrations had a stable trend, despite some variability. PFAS fluxes continued to rise in Blackmans Lake between the 1990s and 2014, and then declined slightly in the years following.
- PFAS concentrations in Wildcat Lake were low, but generally increased from the late 1940s through the late 1980s and then remained stable through 2019. PFAS fluxes followed a similar pattern.
- No PFAS were detected in Sutherland Lake sediments in any year analyzed. This is a mostly remote and undeveloped waterbody where the major sources expected were atmospheric deposition.
- Sutherland and Wildcat Lake PFAS concentrations (non-detects and less than 1 ng/g, respectively) would be considered low compared to other areas. Blackmans Lake contained higher PFAS concentrations, but not at levels typical of highly contaminated waterbodies, like near fire training areas and manufacturing facilities.

Hexabromocyclododecane

- Sediment core profiles showed HBCD concentrations and fluxes increased sharply in the 1980s at both Hicks and Spanaway Lakes, until peaking in the most recent sediment layer at Hicks and in 2009/2014 at Spanaway Lake. This pattern follows trends in commercial use of HBCD.
- Sediments from both lakes had an isomeric pattern similar to commercial mixtures, with abundance in the order of -gamma > -alpha > -beta.
- The temporal trends and concentrations of HBCD observed in Hicks and Spanaway Lakes were similar to those observed in other parts of the world lacking industrial or textile manufacturing inputs. Hicks Lake had higher concentrations than typically seen in urban residential waterbodies, which may be attributed to the combination of its dense residential watershed and high organic carbon content in sediments.

Recommendations

Results of this 2019 and 2020 study support the following recommendations.

- Continue monitoring trends of PFAS and HBCD in the environment as part of the long-term sediment core program. With major phase outs of both chemical groups occurring over the last ten years, potential reductions in lake sediments might be observed in future sampling events.
- Future PFAS analyses should use U.S. Environmental Protection Agency (US EPA) Method 1633 to achieve lower detection limits. Reporting limits for this study were too high to capture low-level signals from the background lake site. Greater sensitivity will allow for detections in lakes where atmospheric deposition is likely the only or primary source.

References

Ahrens, L., N. Yamahita, L.W.Y. Yeung, S. Taniyasu, Y. Horii, P.K.S. Lam, and R. Ebinghaus. 2009. Partitioning Behavior of Per- and Polyfluoroalkyl Compounds between Pore Water and Sediment in Two Sediment Cores from Tokyo Bay, Japan. Environmental Science and Technology, Vol. 43: 6969–6975.

Al-Odaini, N.A., W.J. Shim, G.M. Han, M. Jang, and S.H. Hong. 2015. Enrichment of hexabromocyclododecanes in coastal sediments near aquaculture areas and a wastewater treatment plant in a semi-enclosed bay in South Korea. Science of the Total Environment, Vol. 505: 290–298.

Appleby, P.G. 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M. and J.P. Smol (eds) Tracking environmental change using lake sediments volume 1: basin analysis, coring, and chronological techniques. Kluwer Academic Publishers, Dordrecht, pp 171–203.

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

Balgooyen, S. and C.K. Remucal. 2022. Tributary Loading and Sediment Desorption as Sources of PFAS to Receiving Waters. American Chemical Society Environmental Science and Technology Water, Vol. 2: 436–445.

Codling, G., A. Vogt, P.D. Jones, T. Wang, P. Wang, Y.-L. Lu, M. Corcoran, S. Bonina, A. Li, N.C. Sturchio, K.J. Rockne, K. Ji, J.-S. Khim, J.E. Naile, and J.P. Giesy. 2014. Historical trends of inorganic and organic fluorine in sediments of Lake Michigan. Chemosphere, Vol. 114: 203–209.

Codling, G., S. Hosseini, M.B. Corcoran, S. Bonina, T. Lin, A. Li, N.C. Sturchio, K.J. Rockne, K. Ji, H. Peng, and J.P. Giesy. 2018. Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan. Environmental Pollution, Vol. 236: 373–381.

Covaci, A., A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.V. Heeb, H. Leslie, C.R. Allchin, and J. De Boer. 2006. Hexabromocyclododecanes (HBCDs) in the Environment and Humans: A Review. Environmental Science and Technology, Vol. 40: 3679–3688.

D'Agostino, L.A. and S.A. Mabury. 2017. Certain Perfluoroalkyl and Polyfluoroalkyl Substances Associated with Aqueous Film Forming Foam are Widespread in Canadian Surface Waters. Environmental Science and Technology, Vol. 51: 13603–13613.

Drage, D., J.F. Mueller, G. Birch, G. Eaglesham, L.K. Hearn, and S. Harrad. 2015. Historical trends of PBDEs and HBCDs in sediment cores from Sydney estuary, Australia. Science of the Total Environment, Vol. 512–513: 177–184.

Dutch, M., V. Partridge, S. Weakland, and D. Burgess. 2021. Pharmaceuticals, Personal Care Products, and Per- and Polyfluoroalkyl Substances in Puget Sound Sediments: 2010–2019 Date Summary. Washington State Department of Ecology, Olympia. Publication 21-03-015. https://apps.ecology.wa.gov/publications/SummaryPages/2103015.html

Ecology [Washington Department of Ecology] and DOH [Washington State Department of Health]. 2022. Per- and Polyfluoroalkyl Substances Chemical Action Plan. Washington State Department of Ecology, Olympia. Publication 21-04-048. https://apps.ecology.wa.gov/publications/documents/2104048.pdf

Environment Canada. 2011. Screening Assessment Report on Hexabromocyclododecane, Chemical Abstracts Service Registry Number 3194-55-6. Environment Canada, Health Canada.

Evenset, A., G.N. Christensen, J. Carroll, A. Zaborska, U. Berger, D. Herzke, and D. Gregor. 2007. Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjøen, Bjørnøya, Norwegian Arctic. Environmental Pollution, Vol. 146: 196-205.

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

Gallagher, 2000. Proposed Strategy to Continually Reduce Persistent Bioaccumulative Toxics (PBTs) in Washington State. Washington State Department of Ecology, Olympia. Publication 00-03-054. https://apps.ecology.wa.gov/publications/UIPages/SummaryPages/0003054.html

Giesy, J.P. and K. Kannan. 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environmental Science and Technology, Vol. 35: 1339–1342.

Guo, R., D. Megson, A.L. Myers, P.A. Helm, C. Marvin, P. Crozier, S. Mabury, S.P. Bhavsar, G. Tomy, M. Simcik, B. McCarry, and E.J. Reiner. 2016. Application of a comprehensive extraction technique for the determination of poly- and perfluoroalkyl substances (PFASs) in Great Lakes Region sediments. Chemosphere, Vol. 164: 535–546.

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

ITRC. 2023. PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1. Interstate Technology Regulatory Council, Washington DC. https://pfas-1.itrcweb.org/fact-sheets/

Jeong, G.H., N.R. Hwang, E.-H. Hwang, B.-C. Lee, and J. Yoon. 2014. Hexabromocyclododecanes in crucian carp and sediment from the major rivers in Korea. Science of the Total Environment, Vol. 470–470: 1471–1478.

Johnson, A. and M. Friese. 2012. PBTs Analyzed in Bottom Fish from Four Washington Rivers and Lakes: Hexabromocyclododecane, Tetrabromobisphenol A, Chlorinated Paraffins, Polybrominated Diphenylethers, Polychlorinated Naphthalenes, Perfluorinated Organic Compounds, Lead, and Cadmium. Washington Department of Ecology, Olympia. Publication 12-03-042. https://apps.ecology.wa.gov/publications/summarypages/1203042.html

Kohler, M., M. Zennegg, C. Bogdal, A.C. Gerecke, P. Schmid, N.V. Heeb, M. Sturm, H. Vonmont, H.-P.E. Kohler, and W. Giger. 2008. Temporal Trends, Congener Patterns, and Sources of Octa-, Nona-, and Decabromodiphenyl Ethers (PBDE) and

Hexabromocyclododecanes (HBCD) in Swiss Lake Sediments. Environmental Science and Technology, Vol. 42: 6378–6384.

La Guardia, M.J., R.C. Hale, E. Harvey, T. Matteson Mainor, and S. Ciparis. 2012. In Situ Accumulation of HBCD, PBDEs, and Several Alternative Flame-Retardants in the Bivalve (*Corbicula fluminea*) and Gastropod (*Elimia proxima*). Environmental Science and Technology, Vol. 46: 5798–5805.

Lamborg, C.H., D.R. Engstrom, W.F. Fitzgerald, and P.H. Balcom. 2013. Apportioning global and non-global components of mercury deposition through 210Pb indexing. Science of the Total Environment, Vol. 448: 132-140.

Langberg, H.A., H.P.H. Arp, G.D. Breedveld, G.A. Slinde, A. Hoiseter, H.M. Gronning, M. Jartun, T. Rundberget, B.M. Jenssen, and S.E. Hale. 2021. Paper product production identified as the main source of per- and polyfluoroalkyl substances (PFAS) in a Norwegian lake: Source and historic emission tracking. Environmental Pollution, Vol. 273: 116259.

Letcher, R.J., Z. Lu, S. Chu, G.D. Haffner, K. Drouillard, C.H. Marvin, and J.J.H. Ciborowski. 2015. Hexabromocyclododecane Flame Retardant Isomers in Sediments from Detroit River and Lake Erie of the Laurentian Great Lakes of North America. Bulletin of Environmental Contamination and Toxicology, Vol. 95: 31–36.

Long, E.R., M. Dutch, S. Weakland, B. Chandramouli, and J.P. Benskin. 2013. Quantification of pharmaceuticals, personal care products, and perfluoroalkyl substances in the marine sediments of Puget Sound, Washington, USA. Environmental Toxicology and Chemistry 32: 1701–1710.

Luigi, V., M. Giuseppe, and R. Claudio. 2015. Emerging and priority contaminants with endocrine active potentials in sediments and fish from the River Po (Italy). Environmental Science and Pollution Research, Vol. 22: 14050–14066.

MacInnis, J.J., I. Lehnherr, D.C.G. Muir, R. Quinlan, and A.O. De Silva. 2019. Characterization of perfluoroalkyl substances in sediment cores from High and Low Arctic lakes in Canada. Science of the Total Environment, Vol. 666: 414–422.

Marvin, C.H., G.T. Tomy, J.M. Armitage, J.A. Arnot, L. McCarty, A. Covaci, and V. Palace. 2011. Hexabromocyclododecane: Current Understanding of Chemistry, Environmental Fate and Toxicology and Implications for Global Management. Environmental Science and Technology, Vol. 45: 8613–8623.

Marvin, C.H., G.T. Tomy, M. Alaee, and G. MacInnis. 2006. Distribution of hexabromocyclododecane in Detroit River suspended sediments. Chemosphere, Vol. 64: 268–275.

Mathieu, C. 2013. PBT Chemical Trends in Washington State Determined from Age-Dated Lake Sediment Cores, 2012 Sampling Results. Washington State Department of Ecology, Olympia. Publication 13-03-036. https://apps.ecology.wa.gov/publications/SummaryPages/1303036.html

Mathieu, C. 2016. Quality Assurance Project Plan: Long-Term Monitoring of Persistent, Bioaccumulative, and Toxic Chemicals Using Age-Dated Lake Sediment Cores. Washington State Department of Ecology, Olympia. Publication 16-03-118. https://apps.ecology.wa.gov/publications/SummaryPages/1603118.html

Mathieu, C. 2019. Addendum 2 to Quality Assurance Project Plan: Long-Term Monitoring of Persistent, Bioaccumulative, and Toxic Chemicals Using Age-Dated Lake Sediment Cores. Washington State Department of Ecology, Olympia. Publication 19-03-116. https://apps.ecology.wa.gov/publications/SummaryPages/1903116.html

Mathieu, C. 2023. Standard Operating Procedure EAP038, Version 1.4, Collection of Freshwater Sediment Core Samples Using a Box or KB Corer. Washington State Department of Ecology, Olympia. Publication 23-03-208. https://apps.ecology.wa.gov/publications/SummaryPages/2303208.html

Mathieu, C. and J. Bednarek. 2020. Addendum 3 to Quality Assurance Project Plan: Long-Term Monitoring of Persistent, Bioaccumulative, and Toxic Chemicals Using Age-Dated Lake Sediment Cores. Washington State Department of Ecology, Olympia. Publication 20-03-113. https://apps.ecology.wa.gov/publications/SummaryPages/2003113.html

Mathieu, C. and M. McCall. 2014. PBT Chemical Trends Determined from Age-Dated Lake Sediment Cores, 2013 Results. Washington State Department of Ecology, Olympia. Publication 14-03-036. https://apps.ecology.wa.gov/publications/SummaryPages/1403036.html

Mathieu C. and M. McCall. 2017. Survey of Per- and Poly-fluoroalkyl Substances (PFASs) in Rivers and Lakes, 2016. Washington State Department of Ecology, Olympia, WA. Publication 17-03-021. https://apps.ecology.wa.gov/publications/SummaryPages/1703021.html

Mathieu, C. and S. Wong. 2016. Brominated Flame Retardants, Alkylphenolic Compounds, and Hexabromocyclododecane in Freshwater Fish of Washington State Rivers and Lakes. Washington State Department of Ecology, Olympia. Publication 16-03-012.

Medlen, J. 2018. Clark County Local Source Control Partnership Monitoring, Findings and Recommendations, 2017. Washington State Department of Ecology, Olympia. Publication 18-03-018. https://apps.ecology.wa.gov/publications/SummaryPages/1803018.html

Mourier, B., P. Labadie, M. Desmet, C. Grosbois, J. Raux, M. Debret, Y. Copard, P. Pardon, H. Budzinski, and M. Babut. 2019. Combined spatial and retrospective analysis of fluoroalkyl chemicals in fluvial sediments reveal changes in levels and patterns over the last 40 years. Environmental Pollution, Vol. 253: 1117–1125.

Mussabek, D., L. Ahrens, K.M. Persson, and R. Berndtsson. 2019. Temporal trends and sediment-water partitioning of per- and polyfluoroalkyl substances (PFAS) in lake sediment. Chemosphere, Vol. 227: 624–629.

OECD, 2013. OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.

Ogunsuyi, O.M., P.T. Fasakin, O.P. Ajibiye, O.I. Ogunsuyi, and K.O. Adekoya. 2023. Perfluoroundecanoic acid induces DNA damage, reproductive and pathophysiological dysfunctions via oxidative stress in male Swiss mice. Chemosphere, Vol. 338: 139491.

Oh, J.K., K. Kotani, S. Managaki, and S. Masunaga. 2014. Levels and distribution of -hexabromocyclododecane and its lower brominated derivative in Japanese riverine environment. Chemosphere, Vol. 109: 157–163.

Paulson, A. 2004. Sources of Mercury in Sediments, Water, and Fish of the Lakes of Whatcom County, Washington. USGS Scientific Investigations Report 2004-5084. Prepared in cooperation with the Whatcom County Health Department and the Washington State Department of Ecology.

Poma, G., C. Roscioli, and L. Guzzella. 2014. PBDE, HBCD, and novel brominated flame retardant contamination in sediments from Lake Maggiore (Northern Italy). Environmental Monitoring and Assessment, Vol. 186: 7683–7692.

Stiborova, H., M. Kolar, J. Vrkoslavova, J. Pulkrabova, J. Hajslova, K. Demnerova, and O. Uhlik. 2017. Linking toxicity profiles to pollutants in sludge and sediments. Journal of Hazardous Materials, Vol. 321: 672–680.

Strivens, J.E., L.-J. Kuo, Y. Liu, and K.L. Noor. 2021. Spatial and temporal baseline of perfluorooctanesulfonic acid retained in sediment core samples from Puget Sound, Washington, USA. Marine Pollution Bulletin, Vol. 167: 112381.

UNEP. 2010. Hexabromocyclododecane Risk Profile. United Nations Environment Programme, POPs Review Committee of the Stockholm Convention.

US EPA [United State Environmental Protection Agency]. 2010. Hexabromocyclododecane (HBCD) Action Plan. U.S. Environmental Protection Agency. United States Environmental Protection Agency.

US EPA [United State Environmental Protection Agency]. 2016a. Health Effects Support Document for Perfluorooctane Sulfonate (PFOS). United States Environmental Protection Agency, Office of Water. Publication number EPA 822-R-16-002.

US EPA [United State Environmental Protection Agency]. 2016b. Health Effects Support Document for Perfluorooctanoic Acid (PFOA).
United States Environmental Protection Agency, Office of Water. Publication number EPA 822-R-16-003.

US EPA [United State Environmental Protection Agency]. 2020. Risk Evaluation for Cyclic Aliphatic Bromide Cluster (HBCD). United State Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention. EPA Document #740-R1-8006.

US EPA [United State Environmental Protection Agency]. 2022. Final Revised Unreasonable Risk Determination for HBCD, June 2022.
https://www.epa.gov/system/files/documents/2022-06/HBCD_Final%20Revised%20URD_June%202022.pdf

Yang, R., H. Wei, J. Guo, and A. Li. 2012. Emerging Brominated Flame Retardants in the Sediment of the Great Lakes. Environmental Science and Technology, Vol. 46: 3119–3126.

Yang, C., N.L. Rose, S.D. Turner, H. Yang, B. Goldsmith, S. Losada, J.L. Barber, and S. Harrad. 2016. Hexabromocyclododecanes, polybrominated diphenyl ethers, and polychlorinated biphenyls in radiometrically dated sediment cores from English lakes, ~1950–present. Science of the Total Environment, Vol. 541: 721–728.

Yeung, L.W.Y., A.O. De Silva, E.I.H. Loi, C.H. Marvin, S. Taniyasu, N. Yamashita, S.A. Mabury, D.C.G. Muir, and P.K.S. Lam. 2013. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. Environment International, Vol. 59: 389–397.

Glossary, Acronyms, and Abbreviations

Glossary

CRS Model: The Constant Rate of Supply (CRS) Model is applied to ^{210}Pb measurements in sediment core samples to estimate dates and varying sedimentation rates (Appleby and Oldfield 1978). 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: Flux is an estimated rate of net deposition of a contaminant 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 because fine-grained sediments preferentially deposit in these areas.

Supported ^{210}Pb: Supported ^{210}Pb is represented by the small amount of 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.

Acronyms and Abbreviations

AFFF	aqueous film-forming foam
CRS	constant rate of supply
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
EPS	expanded polystyrene
HBCD	hexabromocyclododecane
LCS	laboratory control sample
MARs	mass accumulation rates
MDL	method detection limit
MEL	Manchester Environmental Laboratory
MQO	measurement quality objective
MS	matrix spike
MSD	matrix spike duplicate
N-EtFOSAA	N-ethyl perfluorooctane sulfonamide acetate N-MeFOSAA N-methyl perfluorooctane sulfonamide acetate
PAHs	polycyclic aromatic hydrocarbons

Pb	lead
PBDEs	polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic
PCBs	polychlorinated biphenyls
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substance
PFBS	perfluorobutane sulfonate
PFCA	perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoate
PFDoDA	perfluorododecanoate
PFHpA	perfluoroheptanoate
PFHxA	perfluorohexanoate
PFHxS	Perfluorohexane sulfonate
PFNA	perfluorononanoate
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPeA	perfluoropentanoate
PFSA	perfluoroalkyl sulfonate
PFTeDA	perfluorotetradecanoate
PFTrDA	perflurotridecanoate
PFUnA	perfluoroundecanoate
Po	polonium
Ra	radium
RL	reporting limit
Rn	radon
RPD	Relative percent difference
T-	total-
TOC	Total organic carbon
US EPA	U.S. Environmental Protection Agency
WWTP	Wastewater treatment plant
XPS	extruded polystyrene

Units of Measurement

ac	acre
°C	degrees centigrade
cm	centimeter
dw	dry weight
ft	feet
g	gram, a unit of mass
g/cm^3	grams per centimeter cubed
mg/kg	milligram per kilogram
ng/g	nanograms per gram (parts per billion)
$ng/cm^2/yr$	nanograms per centimeter squared per year
pCi/g	picocuries per gram
$pCi/cm^2/yr$	picocuries per centimeter squared per year
$\mu g/cm^2/yr$	microgram per centimeter squared per year

Appendices

Appendix A. PFAS Analytes and Reporting Limits

Table A-1. PFAS measured and median reporting limits for this study.

Analyte name	CAS Number	Acronym	Median RL (ng/g dw)	Median MDL (ng/g dw)
Perfluorobutane sulfonate	45187-15-3	PFBS	1.8	0.1
Perfluorodecanoate	73829-36-4	PFDA	1.8	0.1
Perfluorododecanoate	171978-95-3	PFDoDA	3.6	0.1
Perfluoroheptanoate	120885-29-2	PFHpA	1.8	0.3
Perfluorohexane sulfonate	108427-53-8	PFHxS	1.8	0.6
Perfluorohexanoate	92612-52-7	PFHxA	1.8	0.3
Perfluorononanoate	72007-68-2	PFNA	1.8	0.2
Perfluorooctane sulfonate	45298-90-6	PFOS	1.8	0.2
Perfluorooctanoate	45285-51-6	PFOA	1.8	0.2
Perfluoropentanoate	45167-47-3	PFPeA	1.8	0.5
Perfluorotetradecanoate	365971-87-5	PFTeDA	7.3	0.1
Perfluorotridecanoate	862374-87-6	PFTrDA	7.3	0.1
Perfluoroundecanoate	196859-54-8	PFUnA	1.8	0.1
N-ethyl perfluorooctane sulfonamide acetate	2991-50-6	N-EtFOSAA	1.8	0.2
N-methyl perfluorooctane sulfonamide acetate	2355-31-9	NMeFOSAA	1.8	0.2

RL = reporting limit
MDL = method detection limit

Appendix B. Study Location Descriptions

Blackmans Lake

Blackmans Lake is a small lake within the city of Snohomish in Snohomish County. The watershed surrounding the lake is largely made up of residences and commercial development, which replaced logging and agriculture during the 1970s-1990s (ESA 2017). Water enters the lake through Grass Bottom Creek and two small inlets and flows out of the lake through Swifty Creek to the South. Precipitation in the area averages around 44” a year. The underlying basin geology is made up of Vashon till and recessional outwash (WGS 2022).

Lake Sutherland

Lake Sutherland is a remote lake on the Olympic Peninsula (Clallam County) near the edge of Olympic National Forest. Its watershed is largely undeveloped forestland, though there are several residences along the shoreline and a state highway near the northern shore. The lake is fed via several perennial streams around the lake and flows out to Indian Creek on the Eastern shore. An average of 58” of rain falls on the lake and watershed annually. The lake is surrounded by underlying volcanic rocks and landslide deposits (WGS 2022). Lake Sutherland was formed sometime after an ice sheet retreated about 13,000 years ago by landslides that separated a large waterbody into present-day Lake Crescent and Lake Sutherland (Logan and Schuster 1991).

Wildcat Lake

Wildcat Lake is located on the Kitsap Peninsula in a mostly forested watershed of Kitsap County. Ten percent of the watershed is impervious, with most development being residential (Kitsap County 2010). This lake was chosen based on its proximity to potential AFFF releases sites at a nearby military base and a small private airport. Neither of which are hydrologically connected via surface water, but regional re-deposition of PFAS has been found to be relevant to PFAS loading to waterbodies. The average yearly precipitation for Wildcat Lake is about 60”. Soils surrounding the lake include till along the south shore and advanced outwash near the outlet of Wildcat Creek (Kitsap County 2010).

Hicks Lake

Hicks Lake is a 160-acre lake in the city of Lacey, Thurston County. It is the first of four lakes interconnected by Woodland creek, which eventually discharges into Henderson Inlet. The downstream lakes are Pattison Lake, Long Lake, and Lake Lois. The shoreline consists of residential waterfront lots. Land use in the watershed is primarily dense residential, but also includes small undeveloped forest lots and some commercial properties. There is a public access point on the west side of the lake via the Washington Fish and Wildlife boat launch and Wanschers Community Park. The lake is primarily used for recreational boating, fishing, and swimming. The watershed geology consists mostly of glacial till and some alluvial sediments (WGS 2022).

Spanaway Lake

Spanaway Lake is in Pierce County within a watershed dominated by residential, commercial, and military land. Many residences in the area use on-site septic systems, including along the lake shoreline (Hobbs et al. 2022) and as many as 4,000 are on septic systems in the watershed (Pierce County 2016). Major hydrological inputs to the lake include groundwater discharge and inflow from Coffee Creek on the southern shoreline (Pierce County 2017). Surface water drains from the lake to the north through Spanaway Creek. Average annual precipitation to the lake is 41”. Spanaway Lake’s watershed is composed of highly permeable glacial till and outwash soils overlying bedrock deposits, resulting in very little surface water runoff (Pierce County 2017; Johnson et al. 2011).

Appendix B References

ESA. 2017. City of Snohomish Shoreline Master Program Shoreline Inventory and Characterization. Prepared for City of Snohomish.

Hobbs, W., E. Frame, F. Sweeney, I. Struewing, N. Sienkiewicz, J. Lu, E. Villegas, and R. Labiosa. The Historical Prevalence of Cyanobacteria in Spanaway Lake, Pierce County, Washington. Washington State Department of Ecology, Olympia, WA. Publication 22-03-009. https://apps.ecology.wa.gov/publications/SummaryPages/2203009.html

Johnson, K.K., M.E. Savoca, & B. Clothier, 2011. Numerical simulation of the groundwater-flow system in the Chambers-Clover Creek watershed and vicinity, Pierce County, Washington: U.S. Geological Survey Scientific Investigations Report 2011-5086, 108 p.

Kitsap County. 2010. Final Draft Shoreline Inventory and Characterization. Kitsap county Department of Community Development, Environmental Programs, Port Orchard, WA.

Logan, R.L. and R.L. Schuster. 1991. Lake Divided: The Origin of Lake Crescent and Lake Sutherland, Clallam County, Washington. Washington Geology, Vol. 19: 38–42.

Pierce County, 2016. Spanaway Lake Management Plan. Pierce County Public Works and Utilities, Surface Water Management. https://www.piercecountywa.gov/DocumentCenter/View/78545/Spanaway-Lake-Management-Plan

Pierce County, 2017. Final Spanaway Lake watershed-scale stormwater management plan. Prepared in compliance with NPDES Phase I Municipal Stormwater Permit, S5C5c Watershed-scale Stormwater Planning Requirements by Pierce County, Washington, with assistance from Brown and Caldwell.

WGS [Washington Geological Survey]. 2022. Surface geology, 1:500,000 scale-GIS data, February 2022: Washington Geological Survey Digital Data Series 25, version 5.0, previously released June 2010. https://fortress.wa.gov/dnr/geologydata/publications/data_download/ger_portal_surface_geology_500k.zip

Appendix C. Supporting data

Table C-1. Total organic carbon and radiochemistry results for the Blackmans Lake core.

Lake	Sediment interval (cm depth)	TOC (%)	^{210}Pb (pCi/g)	^{226}Ra (pCi/g)
Blackmans	0–2	14	7.69 J	---
Blackmans	2–3	14	6.02	---
Blackmans	3–4	14	5.50	---
Blackmans	5–6	14	6.12	---
Blackmans	7–8	---	5.57	---
Blackmans	9–10	15	5.38	---
Blackmans	11–12	---	5.40	0.30
Blackmans	13–14	14	4.38	---
Blackmans	16–17	13	3.24	---
Blackmans	19–20	---	2.86	---
Blackmans	24–25	---	1.67	0.25
Blackmans	29–30	16	0.48	---
Blackmans	34–35	---	0.18	---
Blackmans	39–40	18	0.18	---
Blackmans	41–42	18	0.20	0.19

--- = not analyzed in that interval; J = estimated value.

Table C-2. Total organic carbon and radiochemistry results for the Sutherland Lake core.

Lake	Sediment interval (cm depth)	TOC (%)	^{210}Pb (pCi/g)	^{226}Ra (pCi/g)
Sutherland	0–2	6.5	9.23	---
Sutherland	2–3	5.5	5.7	---
Sutherland	3–4	7.5	4.26	---
Sutherland	5–6	5.6	4.77	---
Sutherland	7–8	5.3	4.35	---
Sutherland	9–10	---	3.28	0.171
Sutherland	11–12	4.0	1.99	---
Sutherland	14–15	---	1.95	---
Sutherland	17–18	5.7	1.37	---
Sutherland	20–21	---	0.537	---
Sutherland	23–24	---	0.778	0.26
Sutherland	27–28	5.3	0.54	---
Sutherland	31–32	---	0.20	---
Sutherland	35–36	7.0	0.16	---
Sutherland	40–41	8.5	0.24	0.21

--- = not analyzed in that interval; J = estimated value.

Table C-3. Total organic carbon and radiochemistry results for the Wildcat Lake core.

Lake	Sediment interval (cm depth)	TOC (%)	^{210}Pb (pCi/g)	^{226}Ra (pCi/g)
Wildcat	0–2	7.5	5.71 J	---
Wildcat	2–3	---	5.06	---
Wildcat	3–4	8.2	4.16	---
Wildcat	5–6	9.2	3.70	---
Wildcat	7–8	10	1.17	---
Wildcat	9–10	---	1.75	0.26
Wildcat	11–12	11	1.34	---
Wildcat	13–14	11	2.29	---
Wildcat	17–18	11	0.56	---
Wildcat	21–22	---	0.23	0.16
Wildcat	25–26	11	0.20	---
Wildcat	29–30	---	0.15	---
Wildcat	34–35	9.9	0.13	---
Wildcat	40–41	---	0.11	---
Wildcat	42–43	10	0.07	0.16 J

--- = not analyzed in that interval; J = estimated value.

Table C-4. Total organic carbon results for the Hicks Lake core.

Lake	Sediment interval (cm depth)	TOC (%)
Hicks	0–2	19
Hicks	2–3	19
Hicks	3–4	19
Hicks	5–6	19
Hicks	9–10	19
Hicks	13–14	20
Hicks	16–17	19
Hicks	29–30	18
Hicks	39–40	17
Hicks	42–43	16

Table C-5. Radiochemistry results for the Hicks Lake core.

Lake	Sediment interval (cm depth)	^{210}Pb (pCi/g)	^{226}Ra (pCi/g)
Hicks	0–2	6.88	---
Hicks	6–7	2.75	---
Hicks	8–9	2.33	---
Hicks	10–11	1.83	---
Hicks	12–13	1.54	---
Hicks	14–15	---	0.27 J
Hicks	15–16	1.24	---
Hicks	17–18	0.69	---
Hicks	21–22	0.396	---
Hicks	23–24	---	0.25 J
Hicks	25–26	0.31	---
Hicks	27–28	0.28 U	---
Hicks	31–32	0.14 U	---
Hicks	33–34	0.16 U	---
Hicks	36–37	0.39	---
Hicks	37–38	0.248	---
Hicks	38–39	---	0.32 J
Hicks	39–40	---	---
Hicks	41–42	0.21 U	---

--- = not analyzed in that interval; J = estimated value.

Table C-6. Total organic carbon results for the Spanaway Lake core.

Lake	Sediment interval (cm depth)	TOC (%)
Spanaway	0–2	13
Spanaway	2–3	13
Spanaway	3–4	13
Spanaway	5–6	13
Spanaway	7–8	13
Spanaway	11–12	13
Spanaway	19–20	15
Spanaway	21–22	15
Spanaway	29–30	16
Spanaway	40–41	17

Table C-7. Radiochemistry results for the Spanaway Lake core.

Lake	Sediment interval (cm depth)	^{210}Pb (pCi/g)	^{226}Ra (pCi/g)
Spanaway	0–2	8.24	---
Spanaway	4–5	7.71	---
Spanaway	7–8	6.26	---
Spanaway	8–9	---	0.22 J
Spanaway	10–11	4.44	---
Spanaway	13–14	3.23	---
Spanaway	16–17	2.82	---
Spanaway	17–18	---	0.21 J
Spanaway	20–21	1.95	---
Spanaway	22–23	1.89	---
Spanaway	24–25	1.22	---
Spanaway	27–28	0.98	---
Spanaway	30–31	1.09	---
Spanaway	33–34	0.55	---
Spanaway	36–37	0.39	---
Spanaway	38–39	---	0.10 J
Spanaway	39–40	0.27	---
Spanaway	41–42	0.20	---

--- = not analyzed in that interval; J = estimated value.