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Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan[☆]

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ABSTRACT

Current and historical concentrations of 22 poly- and perfluorinated compounds (PFASs) in sediment collected from Lake Superior and northern Lake Michigan in 2011 and Lake Huron in 2012 are reported. The sampling was performed in two ways, Ponar grabs of surface sediments for current spatial distribution across the lake and dated cores for multi-decadal temporal trends. Mean concentrations of the sum of PFASs ($\sum$PFASs) were 1.5, 4.6 and 3.1 ng g^{-1} dry mas (dm) in surface sediments for Lakes Superior, Michigan and Huron, respectively. Of the five Laurentian Lakes, the watersheds of Superior and Huron are the less densely populated by humans, and concentrations observed were typically less and from more diffuse sources, due to lesser urbanization and industrialization. However, some regions of greater concentrations were observed and might indicate more local, point sources. In core samples concentrations ranged from <LOQ to 46.6 ng g^{-1} dm among the three lakes with concentrations typically increasing with time. Distributions of PFASs within dated cores largely corresponded with increase in use of PFASs, but with physiochemical characteristics also affecting distribution. Perfluoroalkyl sulfonates (PFSAs) with chain lengths >7 that include perfluoro-n-octane sulfonate (PFOS) bind more strongly to sediment, which resulted in more accurate analyses of temporal trends. Shorter-chain PFASs, such as perfluoro-n-butanoic acid which is the primary replacement for C8 PFASs that have been phased out, are more soluble and were identified in some core layers at depths corresponding to pre-production periods. Thus, analyses of temporal trends of these more soluble compounds in cores of sediments were less accurate. Total elemental fluorine (TF) and extractable organic fluorine (EOF) indicated that identified PFASs were not a significant fraction of fluorine containing compounds in sediment (<0.01% in EOF).

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1. Introduction

Distributions of perfluorochemicals (PFASs) have been characterized previously in a range of environmental matrices including sediment (Higgins and Luthy, 2006), snow (Codling et al., 2014a) and the atmosphere (Ahrens et al., 2011). Some PFASs are persistent in the environment and can cause toxicities (Surma and Zieliński, 2015). However, production volumes and historical distributions of PFASs are still not fully understood (Paul et al., 2009). If available archived material of the matrix of interest (e.g. water or sediment) can be used for monitoring or retrospective assessments, but such archives are either unavailable or only intermittent. In addition, some archived materials are not suitable for the assessment of some compounds of interest, or were not appropriately stored or are potentially contaminated during collection or storage. Due to widespread use of perfluorinated materials in seals, tubing and packing of samples, these effects are particularly an issue for PFASs. Therefore, to measure historical trends it is necessary to investigate materials where deposition occurs such as snow on glaciers (Wang et al., 2014) or sediment (Codling et al., 2014b). Sediments provide a matrix that preserves an historical record of releases to the environment.

High production volume compounds such as PFASs have their waste streams and atmospheric emissions monitored at source or bulk industrial use such that they are within agreed limits of discharge to the environment. However, when a compound is used it can enter the environment over the lifetime of the products containing it, so complete prevention of contamination is impossible (Prevedouros et al., 2006; Paul et al., 2009). Concern over potential effects of PFASs grew rapidly when they were found to be widespread in the environment, persistent and toxic during both *in-vitro* and *in-vivo* studies (Renner, 2001). In a comprehensive assessment of piscivorous animals from across the globe it was found that perfluorochemical surfactants were ubiquitous in biota and that aquatic systems were primary repositories (Giesy and Kannan, 2002). Further concerns about exposure of humans and potential for adverse effects on health have also been investigated for several PFASs, including perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS). A study of >600 pregnant women showed a statistically significant correlation was observed between exposure and immune system efficiency in offspring between 1 and 4 years (Dalsager et al., 2016).

The Laurentian Great Lakes of North America have been used for transport and waste disposal for hundreds of years; but it was not until the urbanization and industrialization of the region that activities of human affected more than local areas. Similar to other contaminants, PFASs may have ubiquitously contaminated the Great Lakes (Giesy et al., 2006). PFAS have been detected in the waters of these lakes (Furdui et al., 2008). The food chain in the lakes, from *Diporeia* to trout, was also contaminated (Stahl et al., 2014; Furdui et al., 2008, 2007; Kannan et al., 2005). However, information on the accumulation of PFASs in the sediment of the Great Lakes is scarce (Codling et al., 2014b). Knowing current as well as historical status and trends of concentrations in sediment cores is useful for showing current and past exposure as well as elucidating potential sources and efficacies of controls on production, changes in patterns of use and mitigation of releases.

Partitioning behaviors of PFASs in sediments have been investigated for PFOA, PFNA, PFDA, perfluoro-n-undecanoate (PFUnA), PFOS, perfluoro-n-decanesulfonate (PFDS), 2-N-methylperfluoro-n-octanesulfonamido acetic acid (N-MeFOSAA), and 2-N-ethylperfluoro-n-octanesulfonamido acetic acid (N-EtFOSAA). Results of those studies have shown sediment- and solution-specific characteristics influence sorption with organic carbon in sediment and electrostatic interactions being key factors (Higgins and Luthy, 2006). A study of partitioning behaviors between PFASs and pore water or particulates in sediment indicated that PFASs of chain length <7 carbons are more likely to remain in pore-water than to be associated with particles in sediments, and therefore could be subject to distribution to deeper sediment layers (Ahrens et al., 2010). These findings are of importance in interpreting concentrations in sediments collected from cores, because uptake might change both spatially and temporally with environmental changes and the greater use of short chain PFASs in the last decade may be more difficult to measure accurately in sediment.

Lake Superior is the most northern of the North American (Laurentian) Great Lakes, and its dominant outflow is through the St. Mary's River into Lake Huron. Lake Superior is relatively remote with low population density in its watersheds and has relatively lesser concentrations of persistent organic pollutants (POPs) in sediments, compared to the other Great Lakes (Li et al., 2006, 2009). The long residence time (171 y) of the water in Lake Superior is of concern in contaminant accumulation. Lakes Huron and Michigan share some common features, with similar elevation, latitudes, and water surface area. The southern parts of both lakes are more industrialized and densely populated than the northern parts. In the more remote regions, PFAS contamination may be primarily from atmospheric deposition.

The objective of this study was to investigate historical trends in concentrations of PFASs in the northern region of the Laurentian Great Lakes at 20 locations (9 Lake Superior, 2 Lake Michigan, 9 Lake Huron) as well as the current surface sediment (upper 40 mm; n = 82) as part of the Great Lakes Sediment Surveillance Program.

2. Methods

2.1. Chemicals and reagents

Distilled HPLC grade or equivalent acetonitrile (ACN; Fisher Scientific, Ottawa, ON Canada) and methanol (EMD Chemicals, Gibbstown, NJ, USA) were used during extraction. Acetic acid (99% pure) was from Sigma Aldrich. Water used during extraction and for LCMS-MS milli-rho was further purified by use of a Millipore system (18 Ω) and cleaned using Waters OASIS WAX cartridge (60 mg 6 cc) to remove PFAS contaminants. Extraction of samples used Waters HLB cartridges (60 mg 6 cc). Perfluorinated standards were purchased from Wellington Laboratories (Guelph, ON, Canada), and included 9 mass labelled recovery standards, 29 compounds were initially screened for but based upon previous investigations (Codling et al., 2014a,b) only 22 are discussed in this report (see SI Table S1). All samples were extracted in polypropylene Falcon tubes (Fisher Scientific, later referred to as tubes).

2.2. Collection and characterization of sediments

Sample collection took place on Lakes Superior and Michigan in 2011 and on Lake Huron in 2012, onboard of Research Vessel *Lake Guardian*. Two types of sediment samples were collected; Ponar-grab samples and core samplessee Fig. 1. The Ponar grab sampler collected ‘surface’ sediment with a scoop area of 152 × 152 mm. The grabbed sediment was homogenized using an electric drill fitted with a 127 mm diameter paddle. Given that the depth of penetration of the Ponar is dependent on compaction of sediments and that sedimentation rate varies, the sample therefore represents the region where water/sediment interaction occurs but can include several decades of sedimentation in any sample. Core samples were taken using the Model MC-400 Multi-corer (Ocean Instruments, San Diego, California), with samples collected concurrently into 4 polycarbonate tubes. Each tube was 58 cm in length with a maximum penetration depth into sediment of 34.5 cm. Cores were sectioned into 0.5–2 cm layers and the sections from the 4 tubes combined and homogenized to form a single sample for a particular depth.

All collected samples were characterized for bulk and dry density, particle density, water and solids contents, and organic carbon content. For cores, the rates of sedimentation were obtained from profiles of ^{210}Pb and validated with the ^{137}Cs activity from nuclear weapons fallout that peaked in 1964. The sediment focusing factor (FF) at each coring site was determined based on the accumulation of ^{210}Pb. Measurements were calibrated to certified standards. Details of the sampling and laboratory measurements have been described elsewhere (Guo, 2015; Guo et al., 2016). While it is theoretically possible that there might be differences between the two-year sample periods, given sedimentation rates it is unlikely to be significant.

2.3. Extraction

Samples were lyophilized and homogenized by hand in a solvent cleaned pestle and mortar. Large material (stones, mussel shells, etc.) was removed using tweezers and samples were passed through a 2 mm copper filter. A 2.5 g sample (±0.1 g) was placed into a tared, 50 mL polypropylene (pp) tube, and 200 μL of a 10 ng/mL surrogate mass labelled PFASs introduced. PFASs were extracted by use of previously described methods (Naile et al., 2010) with modifications for greater sample mass. In brief the extraction consisted of, in sequence, a 10 mL 1% acetic acid solution, 2 x 5 mL 90:10 methanol (MeOH)/1% acetic acid water extractions and a 10 mL 1% acetic acid solution. After each solvent was added the sample was vortexed for 30 s and sonicated for 15 min. Each tube was centrifuged at 1300 G for 5 min and the supernatant transferred and combined in a clean 50 mL tube. Cleanup was performed by passing extracts through a pre conditioned HLB cartridge with a 75 mL reservoir under gravity using 3 × 5 mL nanopure water rinses of the tube. Conditioning was with 5 mL of MeOH and water added in sequence.

After samples had been passed through under gravity, 5 mL of 0.1% acetic acid was added to rinse the cartridge and it was left under vacuum for ~20 min to dry. Elution consisted of 10 mL of MeOH and 6 mL of toluene collected in individual PP-15 mL tubes. Tubes were concentrated under ultrapure N_2 (4.5 grade) in a water bath at 25 °C; once the toluene fraction was reduced to <0.5 mL it was combined with the MeOH washings, taken to dryness and reconstituted in 200 μL of MeOH with 20% 1% acetic acid. Samples were transferred to PP-GC vials with inbuilt 250 μL inserts and non-Teflon based seals (Canadian Laboratories). Quantification followed the method described by previously described methods (Codling et al., 2014a,b) by use of LC-MS/MS and multiple paired, parent and transition ions for qualification of individual compounds and external calibration.

To assess the fraction of PFASs that make up the total fluorine loading in sediment, total fluorine (TF) and extractable organic fluorine (EOF) was extracted by use of previously described methods (Codling et al., 2014a,b). Thirteen additional characteristics were measured in this study, 6 bulk characteristics, (wet density, dry density, % solids, % water, particle density and porosity) and 6 chemical characteristics organic matter (OM), total carbon (TC), inorganic carbon (IC), black carbon (BC), total nitrogen (TN) and organic carbon minus black carbon (NBOC).

2.4. QA/QC

Prior to extraction all solvents were tested for PFASs. Since contamination from PFOA was observed, MeOH and acetonitrile

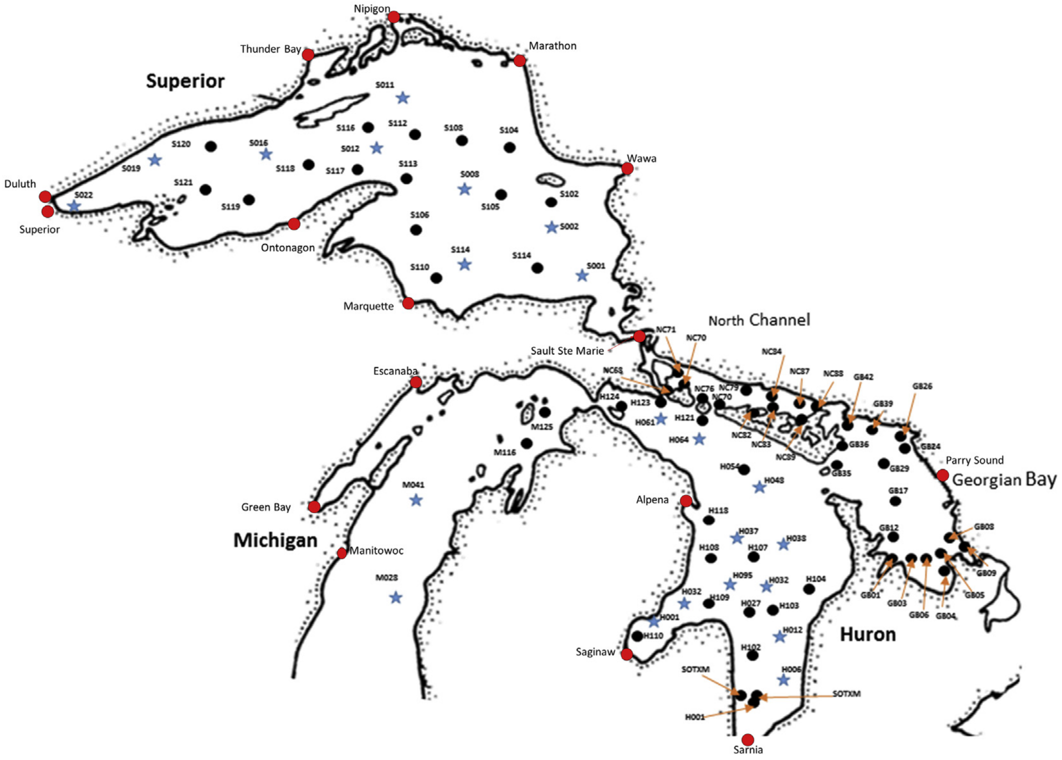

Fig. 1. Sampling locations, stars represent sites where core and Ponar samples were collected while circles are for Ponar samples only, coordinates for sites are located in SI. Red Circles are the major cities around the lakes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

were further distilled and Millipore-water ran through OASIS wax extraction (2 L per 6 cc 60 mg cartridge). These extraction solvents were retested, and no PFAS was observed above the limit of detection (LOD), which was set as 3 times the baseline. The cleaned solvents were used throughout. The use of glassware was minimized during the extraction to avoid loss of PFASs.

During sampling on each lake, 3 field and 3 travel blanks consisting of sodium sulfate were created, with field blanks exposed at intervals during sediment collection and onboard processing. During extraction, a solvent blank was performed for every 10 samples. The criterion for detection was set as 3 times the baseline set at 30s either side of the sample peak. Drift was validated against internal standard and samples adjusted for identification if required. Positive identification was through duplicate paired parent to daughter ions with a calculated variability criterion of less than 10%. Where field blanks had positive identification, method detection limit (MDL) consisting of the mean of the blank plus 3 times the standard deviation of the blanks was used, and measured concentrations less than MDL are omitted from the discussion, (see SI Table 1 for LOD and MDL values). During statistical analysis 2/3 the MDL is used where compounds were below the MDL.

Median recovery of mass labelled surrogates was from 73 to 81% for Lake Huron (LH) with the exception of perfluoro-n-[1,2–$^{13}C_2$] undecanoic acid (PFuDA[m+2]) that was 50.3%; while for Lake Superior (LS) and Michigan (LM), the median recoveries were 57–76% with PFuDA[m+2] at 35%. Lesser recoveries for LS and LM indicated need for an additional cleanup using Envi-Carb to remove matrix interferences. Samples for which recovery was poor (<30%) were omitted from the discussion.

Cores collected at sites H037 in Lake Huron, M028 in Lake Michigan, and S001 and S114 in Lake Superior could not be dated. Core dating required that Pb210 and Cs137 show similar profiles, along with this other markers such as atomic testing peaks were used. Where profiles differ or inconsistencies occur then the core could not be dated. Results from these cores are used but the depth (cm) is presented rather than the actual date. Because rates of sedimentation ranged from a high of >1 cm/year (H001) to much lower values resulting in dates >100 years (S002) in some cores at depth, the non-datable core samples will be treated with caution in interpretation of trends. Comparisons of sedimentation rates in this study were similar to those reported previously for Lake Superior (Song et al., 2004) and Lake Huron (Kemp et al., 1974; Kemp and Harper, 1977).

Data analysis was performed using Excel 2016 (Microsoft), and Sigma Plot 13 (Systat Software), statistical analysis for nearest neighbor used SPSS (IBM Analytics), and SIMCA 14 for PCA and PLS analysis (Umetrics). Mapping visualization for Ponar used online software (mapsdata).

3. Results and discussion

Of the 22 PFASs characterized in this study, 6 were not detected > LOD in core samples from Lake Michigan (n = 30) including perfluoro-n-octadecanoic acid (PFDoDA), perfluoro-n-hexadecanoic acid (PFHxDA), perfluoro-1-octanesulfonamidoacetic acid (FOSAA), perfluoro-1-octanesulfonamide (FOSA), 2-N-methylperfluoro-1-octanesulfonamido–ethanol (N-MeFOSE), 2-N-ethylperfluoro-1-octanesulfonamido-ethanol (N-EtFOSE). Of the samples from Lake Superior (n = 132), N-MeFOSE and N-EtFOSE were not detected in core sample; while 4 compounds were not detected in cores from Lake Huron samples (n = 136) including N-EtFOSAA, N-MeFOSAA, N-MeFOSE, and N-EtFOSE.

Ponar samples had a greater number of non-detected compounds compared to core samples, with 14 compounds not detected in any Lake Michigan Ponar sample > LOD, these being PFOA, PFHxA, PFNA, PFDA, perfluoro-n-dodecanoic acid (PFDoDA), PFDS, perfluoro-n-tridecanoic acid (PFTrDA), perfluoro-n-tetradecanoic acid (PFTeDA), PFHxDA, FOSAA, N-MeFOSAA, N-EtFOSAA, FOSA, N-MeFOSE and N-EtFOSE, however this consisted of only 4 samples. For Lake Superior (n = 24), 13 compounds were not detected, these being PFNA, PFDA, PFuDA, PFDoDA, perfluoro-n-butanoic acid (PFBA), PFTrDA, PFTeDA, FOSAA, N-MeFOSAA, N-EtFOSAA, FOSA, N-MeFOSE, and N-EtFOSE, and 5 compounds were not detected for Lake Huron (n = 49; PFDA, N-MeFOSAA, N-EtFOSAA, N-MeFOSE, and N-EtFOSE).

Concentrations of the sum of PFASs ($\sum_{22}$PFASs) in Ponar samples are illustrated and compared in Fig. 2, while in the Fig. S1 presents PFOA and PFOS concentrations separately. The means were 4.6, 3.1 and 1.5 ng g^{-1} dm for Lakes Michigan, Huron, and Superior, respectively (Table 1). The greatest concentration of $\sum_{22}$PFASs observed in core samples was 68.3 ng g^{-1} dm in Lake Michigan, which was due primarily to a maximum of 46.7 ng g^{-1} dm of perfluro-n-heptanoic acid (PFHpA) in the 1–2 cm layer (dated 2003) of core M041. A number of other PFASs also had greater concentration and accumulation at this site than at other sites in the lake. Site M041 was in the north basin near the deepest spot of the lake and has strong sediment focusing (FF > 2). A previous study reported the maximum concentration of PFHpA of 3.4 ng g^{-1} dm (Codling et al., 2014a,b). Concentrations of PFHpA in core M041 were as much as ten-fold greater than those in other cores from the same region as M041. Therefore, the greater concentrations of PFHpA in M041 might represent a point source (Codling et al., 2014a,b). Another factor may be circulation patterns of water, M041 is at the point where the north and south basin gyres meet, so there might be greater sediment deposition at that location. However, when compared to concentrations of PFHpA in Ponar grabs, M041 concentrations of PFHpA were not greater. Ponar and core samples though taken at approximate the same location the research vessel could not hold perfect station due to jets or anchor causing sediment disturbance therefore Ponar and core may experience variation, though for M041 this is the greatest variance observed. Sample S008 from Lake Superior exhibited the greatest concentration of $\sum_{22}$PFASs in the 2006 (0–1 cm) core layer, and this was caused by PFDS. However, this result was not observed in samples at greater depth in the core or in Ponar grabs. Therefore, this might represent an isolated source or be due to a site-specific factor. The $\sum_{22}$PFASs observed in this study are similar to those observed in Resolute Lake (2003) and Meretta Lake (2005) in Canada where sediment was exposed to localized contamination (Stock et al., 2007), and in general is greater than those observed in other locations (Table S3).

Though no PFASs study for sediment has to date been published on the Great Lakes in a study of organic contaminants in tissues of fishes including 9 PFASs in samples collected in the period 2008–2012, PFASs were determined to constitute approximately 1–20% (by mass) of the total loading of contaminants (McGoldrick and Murphy, 2016). However, of the 5 Great Lakes, Superior exhibited the least concentration of PFASs in fishes with PFOS 3.7 ng g^{-1} dm compared to 27.4 ng g^{-1} dm in Huron and 11.6 ng g^{-1} dm in Michigan. These results were similar to those observed by Williams and Schrank (2016) in fishes from Lakes Superior and Michigan, with fishes from Lake Michigan containing a greater body burdens. Variation among concentrations in sediments among Lakes Huron, Michigan and Superior was similar to that observed for fish.

Frequencies of detection of major classes of ionic PFASs are presented in Fig. S2 for core samples and S3 for Ponar. PFDA was the most frequently detected compound among sediment cores and Ponar samples. In cores of sediment from Lake Michigan, seven

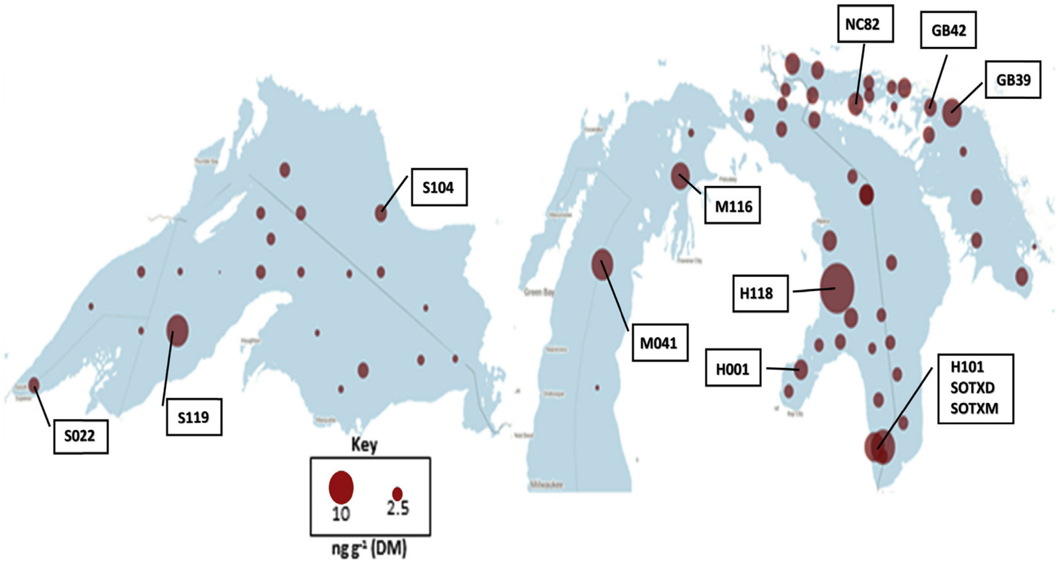

Fig. 2. Concentrations of ∑22 PFAS sediments collected by use of Ponar grab sampler from the Northern Great Lakes. Size of the circle corresponds to relative intensities of ∑22 PFAS measured at each location.

Table 1
Mean and range of concentrations (ng g^{-1} dm) of PFAS in Ponar grab samples and cores from Lakes Michigan, Superior and Huron. The LOQ is defined as 3 times baseline.

PFAS	Sediment Cores			Ponar Grabs		
	Superior	Michigan	Huron	Superior	Michigan	Huron
PFOS	1.1	1.8	1.3	0.1	0.9	0.9
	(0.1, 2.7)	(0.1, 8.2)	(0.0, 11.2)	(0.1, 0.2)	(0.2, 1.6)	(0.1, 2.5)
PFOA	0.8	0.8	0.6	0.1	ND	0.5
	(0.1, 2.4)	(0.1, 3.3)	(0.1, 5.3)	(0.0, 0.3)		(0.1, 3.0)
PFPeA	1	0.4	2.1	0.4	1.3	2.2
	(0.1, 2.8)	(0.2, 0.7)	(0.0, 22.1)	(0.2, 0.6)	(0.3, 2.2)	ND
PFHxA	1	0.6	0.6	0.3	ND	0.6
	(0.1, 2.1)	(0.2, 1.7)	(0.0, 4.8)	(0.1, 0.9)		(0.1, 0.9)
PFHpA	1.5	7	0.4	1.4	0.1	0.7
	(0.2, 6.7)	(0.0, 46.7)	(0.0, 2.1)	(0.0, 8.5)	ND	(0.0, 1.9)
PFNA	1.2	0.9	0.4	ND	ND	0.7
	(0.0, 2.6)	(0.1, 3.0)	(0.0, 3.1)			(0.0, 0.8)
PFDA	4.2	2.1	0.1	ND	ND	ND
	(0.1, 21.3)	(0.4, 11.0)	(0.0, 0.5)			
PFUDA	0.7	0.7	0.6	ND	0.7	1.8
	(0.3, 1.6)	(0.7, 0.9)	(0.0, 3.0)		ND	(0.0, 14.7)
PFDODA	0.1	ND	0.4	ND	ND	0.8
	(0.1, 0.1)		(0.1, 2.3)			(0.2, 1.3)
PFBS	1.5	2.4	1.4	0.6	3.6	0.6
	(0.0, 5.6)	(0.3, 7.3)	(0.0, 6.3)	(0.2, 1.1)	(0.4, 9.0)	(0.5, 0.6)
PFHxS	1.2	1.2	0.5	0.9	1	0.9
	(0.1, 3.1)	(0.3, 2.9)	(0.0, 3.4)	(0.5, 1.0)	ND	(0.0, 1.8)
PFBA	2.3	4.6	5.6	ND	1.6	3.5
	(1.4, 11.6)	ND	(0.1, 31.1)		ND	ND
PFDS	3.8	0.8	0.1	0.2	ND	1.2
	(0.1, 29.9)	(0.1, 1.9)	(0.0, 0.5)	ND		(0.1, 3.9)
PFTrDA	1.5	0.1	1.5	ND	ND	1.4
	(0.7, 1.8)	ND	(0.1, 9.9)			(1.1, 1.6)
PFTeDA	1.3	0.6	0.4	ND	ND	1.5
	(0.5, 1.7)	(0.0, 1.7)	(0.0, 2.7)			(0.1, 2.3)
PFHxDA	1	ND	1.8	2	ND	5.4
	(0.0, 2.0)		(0.0, 7.5)	ND		(3.0, 9.3)
FOSAA	1	ND	1	ND	ND	1.4
	(0.1, 1.8)		(0.0, 6.0)			ND
FOSA	1.2	ND	0.6	ND	ND	0.2
	(1.2, 1.2)		(0.1, 5.3)			(0.2, 0.4)
∑PFAS	8.7	10.9	4.7	1.5	4.6	3.1
	(<LOQ, 46.6)	(1.1, 68.3)	(<LOQ, 46.5)	(0.0, 10.5)	(0.2, 10.1)	(0.0, 26.0)

PFAS including PFOS, PFDA, PFDS, PFHpA, PFNA, PFHxA and PFHxS, were identified in more than 50% of samples, with PFOS occurring at the greatest concentration. In Lake Superior three PFAS including PFuDA, PFOA and PFHxS and in Lake Huron 4 PFASs including PFBS, PFHpA, PFNA and PFDA, were detected in more than 50% of core samples. Ponar samples exhibited a lesser frequency of detection with most PFASs detected in <50% of samples. For Lake Michigan PFPeA, PFOA and PFDA were the most frequently detected PFAS with PFPeA the most frequently detected and also the most abundant. In Lake Huron PFDA, PFNA and PFHxA were the most frequently detected while no PFAS was observed in >50% of samples from Lake Superior.

Lesser frequencies of detection observed for most PFASs in this study might be due to their lesser affinities for sediment, which is a function of their lesser K_{OC} values (Bečanová et al., 2016; Higgins and Luthy, 2006). Values of log *Koc* of approximately 2.8 for PFOA and 3.0 for PFOS have been predicted (Zareitalabad et al., 2013). PFASs might therefore be classified into 3 groups; those that bind more tightly to sediment, such as PFOS, and PFDA; those that exhibit moderate sorption like PFOA and PFHxS and those that are not readily bound to sediment, such as PFBA and PFHxA (Zhao et al., 2012). The frequency of detection observed in this study largely supports this hypothesis.

3.1. Spatial pattern suggests potential local sources

The greatest concentrations are identified in samples from Lake Huron at location H118 which is within 30 km of the Wurtsmith Air Force base (Fig. 2). The core from site H037 (50 km from the air base) also contained relatively great concentrations of PFASs compared to other locations (Fig. 3) in Lake Huron. The Ponar grab sample at H118 had concentrations of 2.5 ng g^{-1} dm for PFOA and 3.0 ng g^{-1} dm for PFOS, which are comparable to those in the upper 2 layers in core H037 (3.8 ng g^{-1} dm for PFOA and 1.4 ng g^{-1} dm for PFOS). Other locations in Lake Huron, where concentrations of PFASs were greater, were in the southern end of the lake near the city of Sarnia. This region has multiple small townships surrounding it and Sarnia itself has a population of approximately 72,000 inhabitants. A complex of chemical companies in the vicinity of Sarnia is called "Chemical Valley" and in 2011 the city had the greatest level of particulate air pollution in Canada. However, concentrations of PFASs observed in sediment are not significantly greater than the main body of the lake. Measurements of flame-retardants (FRs) and polychlorinated biphenyls (PCBs) in surface sediments of the Northern Great Lakes have also been undertaken. For FRs, the greatest concentrations were observed in sediments from Saginaw Bay where samples H001 and H110 were collected (Guo et al., 2016). For PCBs, the northern region of Lake Huron near H048 exhibited the greatest concentrations of most contaminants (Marvin et al., 2004), however a more recent study of PCBs indicates that the upper sediment profile is more akin to PBDEs with H001 at a greater concentration (Li et al., personal communication). Neither PCB nor PBDE exhibited similar profiles to those of PFASs observed in this study for Lake Huron. Given the sources of PCBs, FRs and PFASs might be mostly released directly during production, municipal waste, and use, it may be that point sources such as industry vary or the transport process in the lake causes differences in deposition. However, both surveys of sediment showed consistently that of all the northern Great Lakes, Lake Superior is the least affected by anthropogenic contaminants.

The Ponar samples collected from the North Channel (NC; n = 12) and Georgian Bay (GB; n = 11) regions of Lake Huron had mean concentrations of 2.4 ng g^{-1} dm and 2.2 ng g^{-1} dm, and ranged from <LOQ to 5.2 ng g^{-1} dm and from <LOQ to 8.2 ng g^{-1} dm, respectively, for $\sum_{22}$PFASs. These concentrations are similar to those in the lake proper, where the total mean was 3.0 ng g^{-1} dm. The greatest concentrations of total PFASs in sediments from NC were in sediments from the mouth of a small bay 30 km from the Manitoulin Airport and some small townships. In the GB region, the greatest concentration was located at GB39, 23 km from the Killarny Airport but in a region largely covered by provincial parks. Site GB42 was closer to the airport (10 km); though the concentration was greater than the mean, it was not as great as that at GB39 nor did the two sites exhibit similar profiles. There have been numerous studies that have indicated airports may be local sources of perfluorinated compounds (e.g. de Solla et al., 2012; Stock et al., 2007).

On Lake Superior, the greatest concentration of PFASs in Ponar sediment was observed at site S119 located near the Town of Ontonagon, Michigan where the Smurfit-Stone Container (38 km) paper mill was located until 2010. Concentrations of PFASs in Ponar grab samples were greater near Duluth, MN and in coastal regions where rates of sedimentation might be greater (Paul et al., 2009). A survey of concentrations of PFASs in fishes from Lakes Superior and Michigan also observed that these were less in Lake Superior than the other lakes, but also that fish near Ontonagon were the most contaminated (Williams and Schrank, 2016).

Concentrations of PFASs in Ponar samples M125 and M028 from Lake Michigan (n = 4) were relatively small, probably due to the fact that these two locations were relatively remote from any potential sources of PFASs such as urban areas or industries. Concentrations of PFASs at M041 and M118 were similar to the greatest concentrations observed in Lake Superior. Similar concentrations to those observed at locations M041 and M118 were observed in Ponar grabs taken during a previous study of Lake Michigan (Codling et al., 2014a,b).

Principle component analysis was performed to further assess the variance between individual Ponar samples within each lake and among the three lakes for all identified PFASs (Fig. S5). There was no distinctive grouping of each lake, though as noted in Superior, S119 and S011 are very different from the mean, as is H108 in Lake Huron. Concentrations in surface Ponar samples from Lake Superior and Northern Lake Michigan were similar, while those from the three regions of Lake Huron, Lake Huron proper, Georgian Bay and North Channel are all similar such that no distinction could be made.

3.2. Core profiles reflect production history and downward transport

Global production of PSOF has been estimated to have been <500 t $year^{-1}$ during the 1970s and as much as 4500 t $year^{-1}$ in 2005 before reduction of C8 PFASs and greater use of shorter chain C4 and alternative PFAS (Paul et al., 2009). At most coring sites of this study, variation in concentrations with sediment depth reflects the production history of PFASs, with a peak observed at a depth corresponding to calendar year 2005 followed by a slight decrease thereafter (Fig. 3).

Some PFASs were observed in sediments deposited prior to 1940 and are indicative of complexities of using a natural medium such as sediments for monitoring. For example, pore water is a transport vector for PFASs, particularly shorter chain compounds such as PFBA and PFBS (Ahrens et al., 2009). Other PFAS such as PFOA bind to sediment relatively weakly and might reenter pore water under the right conditions (Higgins and Luthy, 2006). Measured concentrations of this study were the sums of PFs both sorbed on sediment particles and in pore water. Transport to deeper sediment may have occurred and could explain some of the PFASs observed at deeper layers than would have been expected based on when they were manufactured. The occurrence of downward diffusion was reported

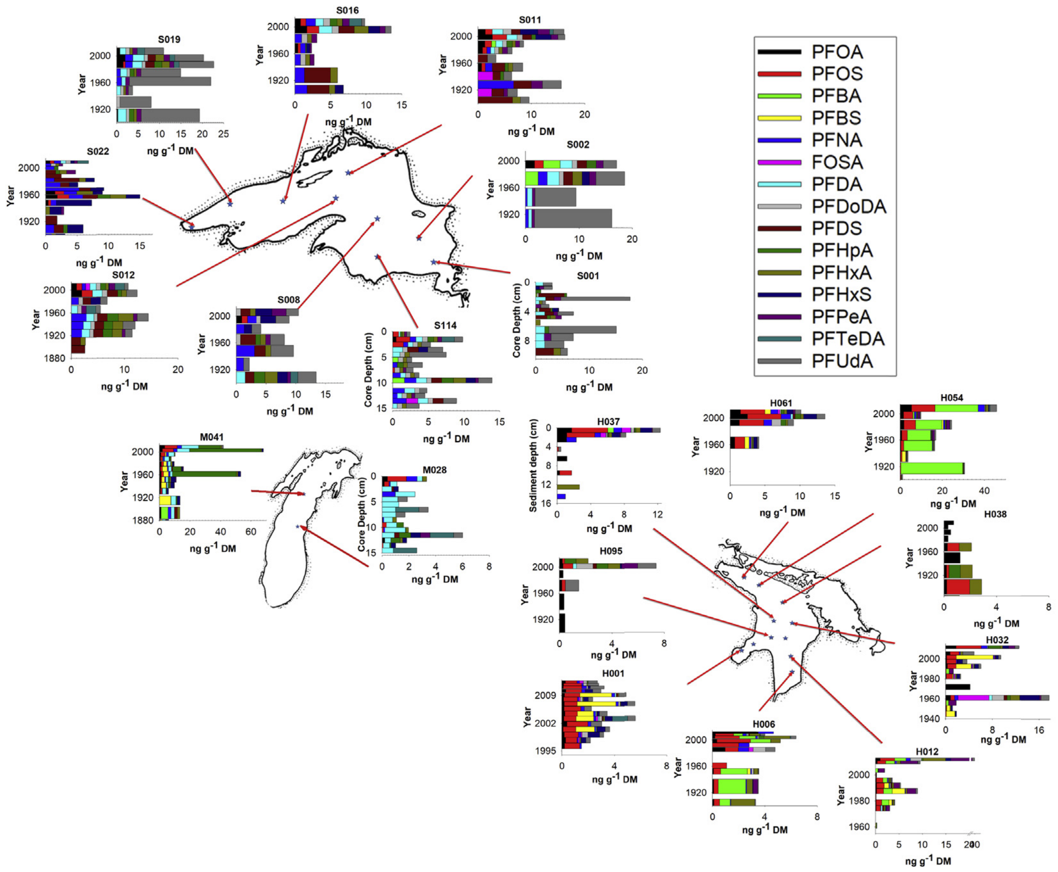

Fig. 3. Core samples for all 3 lakes, all cores are date corrected and show only those samples from 1890 to the present, H037, M028, S114, and S001are not dated due to inconsistency so the upper 15 layers are presented. H001 had the greatest rate of sedimentation with the 15 layers extracted corresponding to that from 1995 to 2011.

for some herbicides in the same sediment cores used in this work (Guo et al., 2016). Two other factors must also be considered. First, disturbance of sediment by bioturbation or storms will also cause post-deposition sediment mixing and allow pore water infiltration to deeper sediment. Second, in deeper water, such as in Lake Superior, depositions of PFASs bound to material in the lake surface water may take a significant period of time to reach the sediment, and be subject to photolysis and microbial degradation as seen on marine snow deposition (Alldredge and Silver, 1988).

Among targeted PFASs that sorb more tightly to sediments, such as PFOS and PFDA and that have intermediate affinities to sediments, such as PFOA and PFHxS (Zhao et al., 2012), differences in deposition were observed, with an average onset of increases from 1940 to 2011 (Fig. S4). PFASs with lesser affinities to particulates, such as PFOS also exhibited increases but the trend was less clear.

Sediments cores taken from sites M041, S012, S022, H032 and H095 exhibited greater concentrations of PFASs at depths corresponding to ~1960. A similar trend was observed in sediment cores from Lake Michigan (Codling et al., 2014a,b). It was hypothesized in that study that this result might be due to changes in discharges of compounds to the lakes after the increase in industry during the Second World War and the following prosperity of the 1950–70s. The implementation of the Clean Water Act of 1972 resulted in the subsequent decreases observed in cores of sediments (Ludsin et al., 2001). However, as the mass of PFASs produced increased and greater uses were identified for some compounds environmental discharge during use and disposal may become a significant secondary source. For locations such as H032, S012 and S022 where ~1960s were the greatest observable concentration it may be that industrial discharge was a significant source.

Trends in concentrations of PFASs in sediment cores from Lake Superior were less well defined at some locations such as S001, S012, and S114, which are located in deeper water with depths of 98, 245 and 409 m, respectively. Sample S008 also exhibited a similar profile of relative concentrations of PFASs with the exception of PFDS being greater in the upper 1 cm. Given the depth of water and the long water residence time of 171 years in the lake (Minor et al., 2012), it might be that deeper sediments are less influenced by concentrations of PFASs in surface waters. In oceanic water during particle sinking of marine snow, many factors including thermocline layers, bacteria, and fish affect the breakdown and recycling of material (Lampitt et al., 1993). In lakes, this is less of an issue as essential elements such as iron (Fe) are more abundant and depth is less so particle scavenging is not as efficient. In Lake Superior, the greater depth of water than the other lakes may create less effective deposition of contaminants due to recycling.

Site H001 is of interest since the rate of sedimentation at that location was greater than those at any other coring sites with the 15 layers corresponding to being deposited from 1995 to 2012. This site was near the mouth of the Saginaw River. Historically the DOW Chemical manufacturing facility in Midland, Michigan, General Motors and other industries have discharged chemical pollutants to the river (Echols et al., 2014). Both PFOS and PFOA were commonly observed in these sediments but the concentration remained relatively stable over the period represented by the cores and at concentrations similar to the rest of Lake Huron.

3.3. *Total fluorine, extractable fluorine, physical factors and PFASs*

It has been shown during monitoring of tissues of humans and wildlife that the commonly measured ionic PFASs can represent a significant fraction of total fluorine (Yeung et al., 2009; Miyake et al., 2007). In Lake Michigan, PFASs were quantified to represent <0.01% of the TF (Codling et al., 2014a,b). In this work, concentrations of TF and EOF were measured at 19 locations in Lake Huron, 19 in Lake Superior, and 2 Lake Michigan, and for 2 core samples from Lake Huron, 2 core samples in Lake Michigan, and 6 core samples Lake Superior (S19 and S22 for TF only). Concentrations of TF ranged from 2.3 to 9706 mg kg^{-1} dm, with a mean of 331 mg kg^{-1}, dm (SI Fig. 6). The greatest concentration of TF was observed in Lake Michigan where concentrations were similar to those measured during previous studies (Codling et al., 2014a,b). When principal component analysis (PCA) of the surface Ponar TF and EOF for the lakes was performed (SI Figure S7 A), analysis of the primary loading component indicated that TF and EOF have near equal weightings. The greater variance observed in Lake Superior was at S022 where the St Louis River enters the lake. In Lake Huron, H054, H038, H109, H048, H110 and H104 all show greater variance from the mean observation for Huron sediment, and these were all located in the North West portion of the main lake; no clear cause was identified for these variances observed, though these samples were all from the deeper region of the Lake where the maximum lake depth was located. Michigan samples were both at far greater TF than that observed in either of the other lakes. The USGS report on the Great Lakes highlights that around Lakes Huron and Superior the surficial geology is silt and clay from glacial lake deposition while Lake Michigan has large regions of till and bedrock that may be the cause of variance (Neff et al., 2005). Comparison of PFASs concentrations to TF and EOF indicated no discernible pattern; this is similar to that observed in Lake Michigan (Codling et al., 2014a,b), however novel techniques in PFAS determination indicates many compounds not typically screened for (Fakouri Baygi et al., 2016).

PCA analysis of surface Ponar characteristics (Log10 adjusted) were compared to identify major variance within sample groups and which features were predominant (SI Fig. S7B). The major variance observed in the study was for OM and OC. Some of these chemical properties are linked; for example, OM is normally approximately double that of OC so we would anticipate that if OM is driving variance OC would be also showing comparable variance. Organic carbon has previously been identified in controlled laboratory studies as a major factor contributing to sorption of PFASs, however it has been shown that in real-world studies this correlation often does not occur (Zareitalabad et al., 2013). In this study, no direct correlation was found between concentrations of OC and concentrations of individual PFASs or $\sum_{22}$PFAS in either Ponar or core samples. Similarly, by use of multivariate analyses of all characteristics, no components individually or in combinations were associated with concentrations of PFASs. One reason for this might be that concentrations of PFASs in the northern Great Lakes are relatively small, compared to those measured in Lakes Erie and Ontario (McGoldrick and Murphy, 2016). The variance of physiochemical properties in Lake Michigan is discussed in greater detail by Bonina et al. (2017).

4. Conclusions

The three northern Great Lakes (Michigan, Superior and Huron) have been influenced by use of fluorinated materials. Most locations have concentrations that indicate non-point source contamination. However, concentrations of PFASs in sediments at a few sites in this study were greater, which might indicate influences from more local sources. PFASs most commonly observed in sediments during this study are those that typically sorb more tightly to sediments, such as PFOS, which might limit the value of sediment as a long term monitoring medium. In Lake Superior, the deeper sediment typically contained lesser concentrations of PFASs. Given the longer residence time of water in Lake Superior, there might be some breakdown or uptake of these compounds before reaching the sediment layer. Uses of PFBA and PFBS as replacement PFASs in products will likely result in greater releases to the environment, so the status and trends of concentrations of these persistent PFASs in various matrices should be monitored. Based upon their physical-chemical properties, however, sediment might not be the best medium for such monitoring.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.01.065.

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Supplementary Information

Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan

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Table S1: PFCs and mass labelled compounds used in this study

Name	Carbon Number	Abbreviation	Molecular Formula	Molecular Weight
Perfluoroalkyl compounds				
Perfluoro-n-butanoic acid	C4	PFBA	$C_4HF_7O_2$	214.0396
Perfluoro-n-pentanoic acid	C5	PFPeA	$C_5HF_9O_2$	264.0474
Perfluoro-n-hexanoic acid	C6	PFHxA	$C_6HF_{11}O_2$	314.0552
Perfluoro-n-heptanoic acid	C7	PFHpA	$C_7HF_{13}O_2$	364.0630
Perfluoro-n-octanoic acid	C8	PFOA	C8HF15O2	414.0708
Perfluoro-n-nonanoic acid	C9	PFNA	$C_9HF_{17}O_2$	464.0786
Perfluoro-n-decanoic acid	C10	PFDA	$C_{10}HF_{19}O_2$	514.0864
Perfluoro-n-undecanoic acid	C11	PFUDA	$C_{11}HF_{21}O_2$	564.0942
Perfluoro-n-tridecanoic acid	C13	PFTrDA	$C_{13}HF_{25}O_2$	664.1098
Perfluoro-n-tetradecanoic acid	C14	PFTeDA	$C_{14}HF_{27}O_2$	714.1176
Perfluoro-n-hexadecanoic acid	C16	PFHxDA	$C_{16}HF_{31}O_2$	814.1332
Potassium Perfluoro-1-butanesulfonate	C4	PFBS	$C_4HF_9O_3S$	300.100
Sodium Perfluoro-1-hexanesulfonate	C6	PFHxS	C6HF13O3S	400.115
Sodium Perfluoro-1-octanesulfonate	C8	PFOS	$C_8HF_{17}O_3S$	500.13
Sodium Perfluoro-1-decanesulfonate	C10	PFDS	$C_{10}F_{21}O_3S$	600.145
Perfluorododecanoic Acid	C12	PFDODA	C12HF2302	614.0980
Perfluorinated precursors				
Perfluoro-1-octanesulfonamide	C8	FOSA	$C_8H_2F_{17}NO_2S$	499.15
2-N-ethylperfluoro-1-octanesulfonamido-ethanol	C12	EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	571.25
2-N-methylperfluoro-1-octanesulfonamido –ethanol	C11	MeFOSE	$C_{11}H_8F_{17}NO_3S$	557.23
Perfluoro-1-octanesulfonamidoacetic acid	C10	FOSAA	$C_{10}H_4F_{17}NO_4S$	557.18
N-methylperfluoro-1-octanesulfonamidoacetic acid	C11	MeFOSAA	$C_{11}H_8F_{17}NO_4S$	571.21
N-ethylperfluoro-1-octanesulfonamidoacetic acid	C12	EtFOSAA	$C_{12}H_8F_{17}NO_4S$	585.24
Mass Labelled Recovery Standards				
sodium perfluoro-1-hexane [$^{18}O_2$]sulfonate	C6	NaPFHxS [M+4]	$C_6F_{13}S^{18}O_2{}^{16}ONa$	426.0968
sodium perfluoro-1- [1,2,3,4-$^{13}C_4$]octanesulfonate	C8	NaPFOS [M+4]	$^{13}C_4{}^{12}C_4F_{17}SO_3Na$	526.0823
perfluoro-n-[1,2,3,4-$^{13}C_4$] butanoic acid	C4	PFBA [M+4]	$^{13}C_4HF_7O_2$	218.0090
perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid	C6	PFHxA [M+2]	$^{13}C2^{12}C_4HF_{11}O_2$	316.0399
perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid	C8	PFOA [M+4]	$^{13}C_4{}^{12}C_4HF_{15}O_2$	418.0402
perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid	C9	PFNA [M+5]	$^{13}C_5{}^{12}C_4HF_{17}O_2$	469.0404
perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	C10	PFDA [M+2]	$^{13}C_2{}^{12}C_8HF_{19}O_2$	516.0711
perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid	C11	PFUdA [M+2]	$^{13}C_2{}^{12}C_9HF_{21}O_2$	566.0789
perfluoro-n-[1,2-$^{13}C_2$] dodecanoic acid	C12	PFDoA [M+2]	$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	616.0867

Table S2: Recoveries of mass labeled compounds from sediments from 3 Great Lakes.

Mass Labeled Compounds	**Lake Superior**		**Lake Michigan**		**Lake Huron**	
	Average	**% dev**	**Average**	**% dev**	**Average**	**% dev**
^{13}C PFOA	60.6	32.3	57.7	34.8	88.8	57.9
^{13}C PFOS	34.8	39.8	34.5	40.6	86.0	31.5
^{13}C PFDOA	63.0	34.5	62.5	35.5	70.9	16.8
^{13}C PFNA	69.9	38.5	69.3	39.3	85.0	34.7
^{13}C PFDA	68.2	32.0	67.6	33.1	79.3	65.6
^{13}C PFUDA	65.6	31.7	65.0	32.8	69.0	39.9
^{13}C PFBA	77.4	34.3	76.8	35.3	87.2	62.8

Table S3. Concentration of PFCs in sediment from this study and the literature (ng g^{-1} dm)

Location number of samples and year of sample collection		PFOS	PFOA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	PFUdA	PFDoA	PFBS	PFHxS	PFBA	PFDS	PFTeDA	FOSA	∑PFCs	Ref.
Northern Great Lakes (Lake Superior, Huron and Michigan), 2010-2012	Mean Range	1.1 LOQ - 11.2	0.6 LOQ - 5.3	1.3 LOQ - 22.1	0.6 LOQ - 4.8	1.8 LOQ - 8.5	0.8 LOQ - 3.1	3.2 LOQ - 11.0	0.9 LOQ - 14.7	0.4 LOQ - 2.3	1.8 LOQ - 9.0	1.0 LOQ - 3.4	3.2 LOQ - 31.1	1.2 LOQ - 29.9	1.0 LOQ - 2.7	0.7 LOQ - 5.3	6.4 LOQ - 68.3	This Study
Lake Michigan USA Ponar-surface samples (*n* = 27), 2010	Mean Range	0.45 ND – 1.2	0.21 ND – 0.42	0.17 ND – 1.30							0.2 ND – 0.5		0.57 ND – 1.0		0.05 ND – 0.2	0.05 ND – 0.1	2.33 0.9 – 4.9	Codling et al., 2014
Lake Michigan USA Sediment cores (*n* = 48), 2010	Mean Range	2.7 ND – 12.8	0.75 ND – 3.7	0.15 ND – 0.82							0.5 ND – 7.9		0.4 ND – 1.32		0.1 ND – 0.3	0.48 ND – 0.8	4.4 0.4 – 24.1	Codling et al., 2014
Nansi Lake, China (n=20), 2013	Mean Range	0.42 0.2 - 0.8	0.25 0.1 - 0.4			<LOD	0.08 0.03 - 0.15	0.15 0.03 - 0.3	0.2 0.1 - 0.4		<LOD						1.09 0.5 - 1.8	Cao et al., 2015
Morava River, Czech Republic (n=15), 2007	Range	LOQ - 0.8										LOQ-3.81					6.8	Bečanová et al., 2016
Llobregat basin, Spain (n=14), 2010	Mean Range	11.4 0.2 - 11.4	1.52 0.4 – 1.5	0.33 0.3-1.1	ND	0.4	3.87	0.15 0.1 – 0.6	0.1 0.1 - 0.4	0.17 0.1 - 0.2		0.12 0.03 – 0.29	3.67 0.6 - 12.9	ND	ND	1.27	16.1 8.4 – 37.5	Campo et al., 2015*
Coastal Korea (n=12) 2009	Mean Range	1.5 <0.2 – 5.8	1 <0.2 – 2.4	ND	ND	ND	ND	ND	ND	ND	ND	ND					2.1 0.6 – 8.2	Naile et al., 2012
L'Albufera Natural Park, Spain (n=12), 2009	Mean Range	1.8 0.1 – 4.8	3.2 0.03 – 10.9		0.03 0.02 – 0.1	0.1 0.02 - 0.1	0.25 ND – 1.24	0.4 ND – 1.3			0.02 ND – 0.02			0.38 ND – 2.0			6.2 0.3 - 17.4	Pico et al., 2011
Orge River, France (n=3) 2010	Mean	4.3 ± 0.3	< 0.07		0.1 ± 0.01	0.03 ± 0.01	0.05 ± 0.01	0.3 ± 0.02	0.3 ± 0.01	1.7	<0.05	0.1 ± 0.02		0.12 ± 0.01	0.9 ± 0.03		8.4 ± 1.5	Labadie and Chevreuil, 2011
L'Albufera Natural Park Valencia, Spain (n=14) 2010	Mean Range	1.79 0.1-4.8	3.19 0.03-10.9		0.03 <0.02 - 0.1	0.1 <0.02 – 1.0	0.25 ND - 1.2	0.21 ND - 1.3			0.02 ND - 0.02			0.38 <ND - 2			6.2 0.3 - 17.4	Pico et al., 2012
Tangxun Lake, China	Mean Range	74.4 10.9 – 623	2.4 0.5 – 6.4	<0.54	< 0.31	0.45 0.2-1.4	<0.28 0.3 – 0.4	0.14 n.d. – 0.3	0.8 0.4 – 3.3	1.5 0.8 - 18.4	50.8 21.1 - 114	3.5 0.9 - 13.2	16.3 5.3 – 61.2				151 10.9 - 800	Zhao et al., 2013
Western Scheldt, The Netherlands (n=8), 2009	Range	0.1- 48																Esparza et al., 2011
^{A}Cantabria, Spain (n=3) 2009	Max	ND – 0.1	ND – 0.02				ND					ND					0.02 – 0.13	Gomez et al., 2011
Rota River, Germany (n=11), 2006	Mean Range	0.04 0.02 - 0.1	0.21 0.1 - 0.3															Becker et al., 2009
^{B}Tokyo Bay, Japan (n=2) 2010	Mean Range	ND	0.1				0.6 ND – 2.5	4.1 0.2 - 14	5.5 0.2 - 15.6	1.7 0.1 – 4.8		3.7 0.5 - 9				ND	120.7 39-221	Zushi et.al 2010
Haihe River and Dagu Drainage, China (n=8) 2010	Mean Range	1.8 - 7.3 0.1 -2.3	0.9 -3.7 0.3 – 1.7															Li et.al 2011
Taihu Lake, China (n=30) 2010	Mean Range	0.92 0.1-6.7	0.13 ND-0.85		0.06 ND-0.34		0.2 ND-0.37	0.23 0.13-0.35	0.43 0.18-1.52	0.18 <0.04-0.23		0.08 ND-0.34	0.03 ND-0.09					Guo et al., 2015
Dianchi Lake (n=26) 2010	Median Range	0.25 0.07-0.83	0.12 ND-0.71														0.95 0.21-2.45	Zhang et al 2012
Daliao River System, China (n=11) 2008	Mean Range	31.2 5.2 - 203	0.21 0.1 - 0.4															Bao et al. 2009
Rivers, lakes, and canals, The Netherlands (n=19) 2007	Range	0.5 - 8.7	0.3 - 6.3															Kwadijk et al., 2010
San Francisco Bay USA (n=15) 2004	Mean Range	1.05 0.4 - 1.7	0.24 0.2 – 0.4				0.21 ND – 0.2	0.5 ND – 1.1	0.4 ND – 0.4	0.4 ND – 0.6		0.07		0.44 0.2 – 1.0			3.0 0.1 - 16	Higgins et.al 2005
Amituk Lake Canada (n=3) 2003	Range	0.9 - 1.5	1.9 - 8.4			ND - 1.0	0.2 - 0.4		1.4-3.4	0.5-0.6		<LOQ						Stock et al., 2007
Char Lake Canada (n=6) 2003	Range	1.1 - 25	0.4 - 3.4			0.3 - 1.6	ND - 1.4		2.7-5.9	<LOQ		<LOQ						
Resolutie Lake Canada (n=12) 2003	Range	23 - 90	6 - 16			3.1 - 49	0.2-6.1		1-5.8	ND - 15.1		1.6 -2 4.0						
Meretta Lake 2005 (n=3)	Range	55 - 57	13 - 15			22 - 29	3.8 - 4.4		0.2 - 0.5	ND - 3.8		12.0 - 17.0						
Taizi River, China (n-4) 2008	Mean	0.21	0.14				<0.1	0.1			0.19	<0.13					1.31	Bao et al., 2009
Hun River China (n-4) 2008	Mean	0.27	0.11				<0.1	<0.1			<0.1	<0.13					1.25	
Daliao River China (n=3) 2008	Mean	0.21	0.11				<0.1	<0.1			<0.1	<0.13					1.06	

ND are non-detects and LOQ the limits of quantification as proposed by the study in question. Data from Campo et al. (2015) includes compounds detected only once in a sample so no range is given for these compounds. ^{A}Samples from Gomez et al., only includes those samples from river sediment. ^{B}Marine sediment.

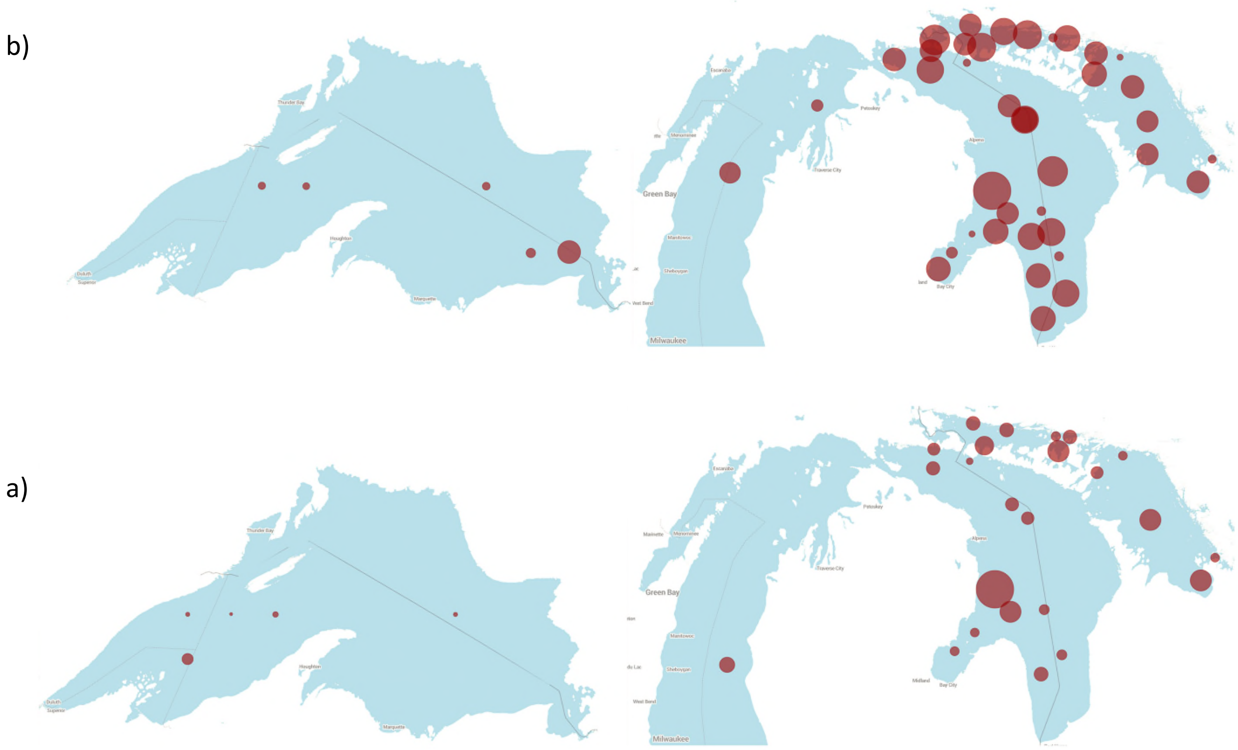

Figure S1: Relative intensities of PFOA[a] and PFOS[b] in surface sediments collected by use of a Ponar grab sampler from Lakes Huron, Superior and Michigan.

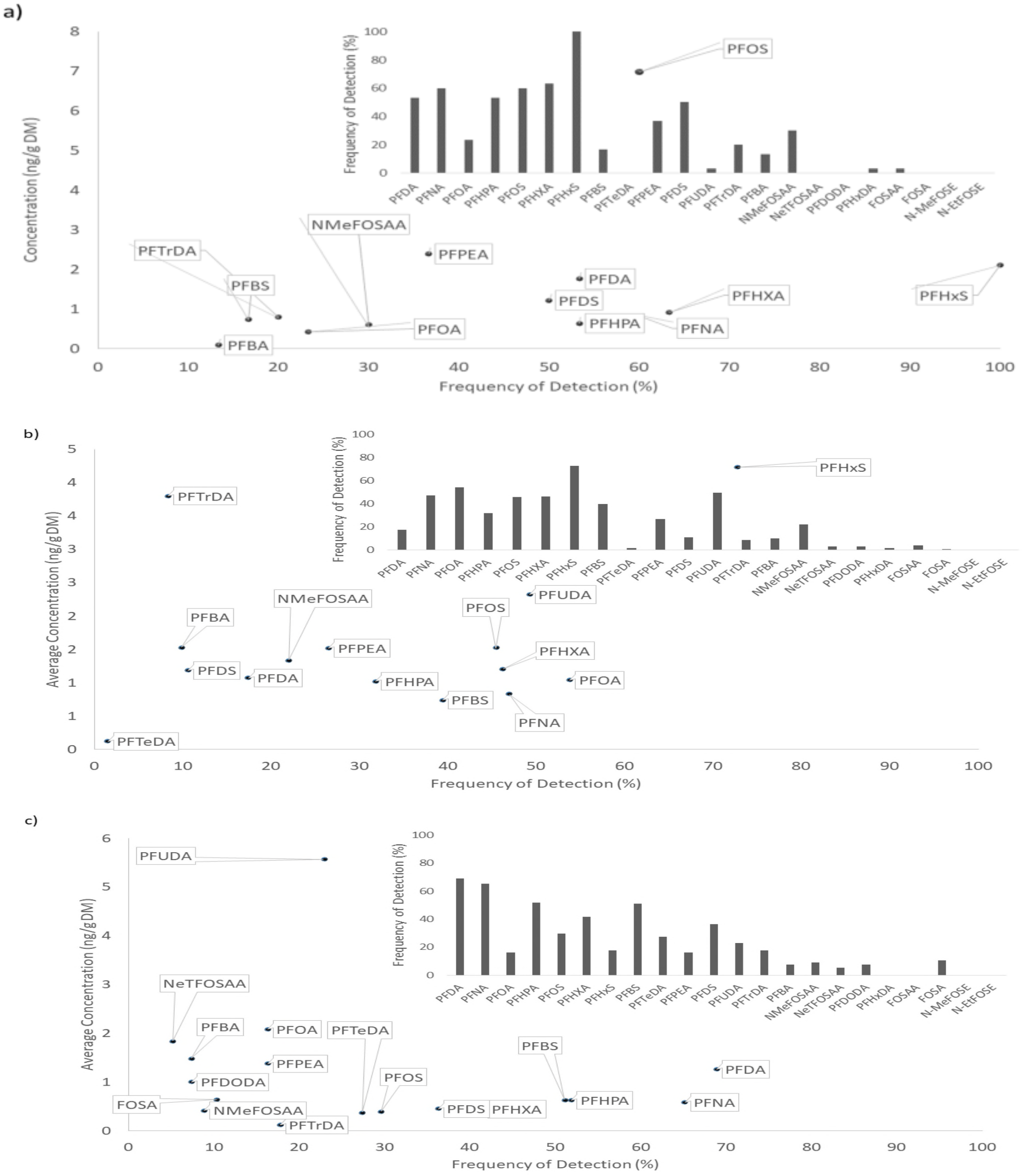

Figure S2: Profile of concentrations of PFCs in cores of sediments from Northern Great Lakes; a) Lake Michigan, b) Lake Superior and c) Lake Huron. The main graph is the frequency of detection and mean concentration at each Lake. Graph in upper corner are frequencies of detection for specific compounds.

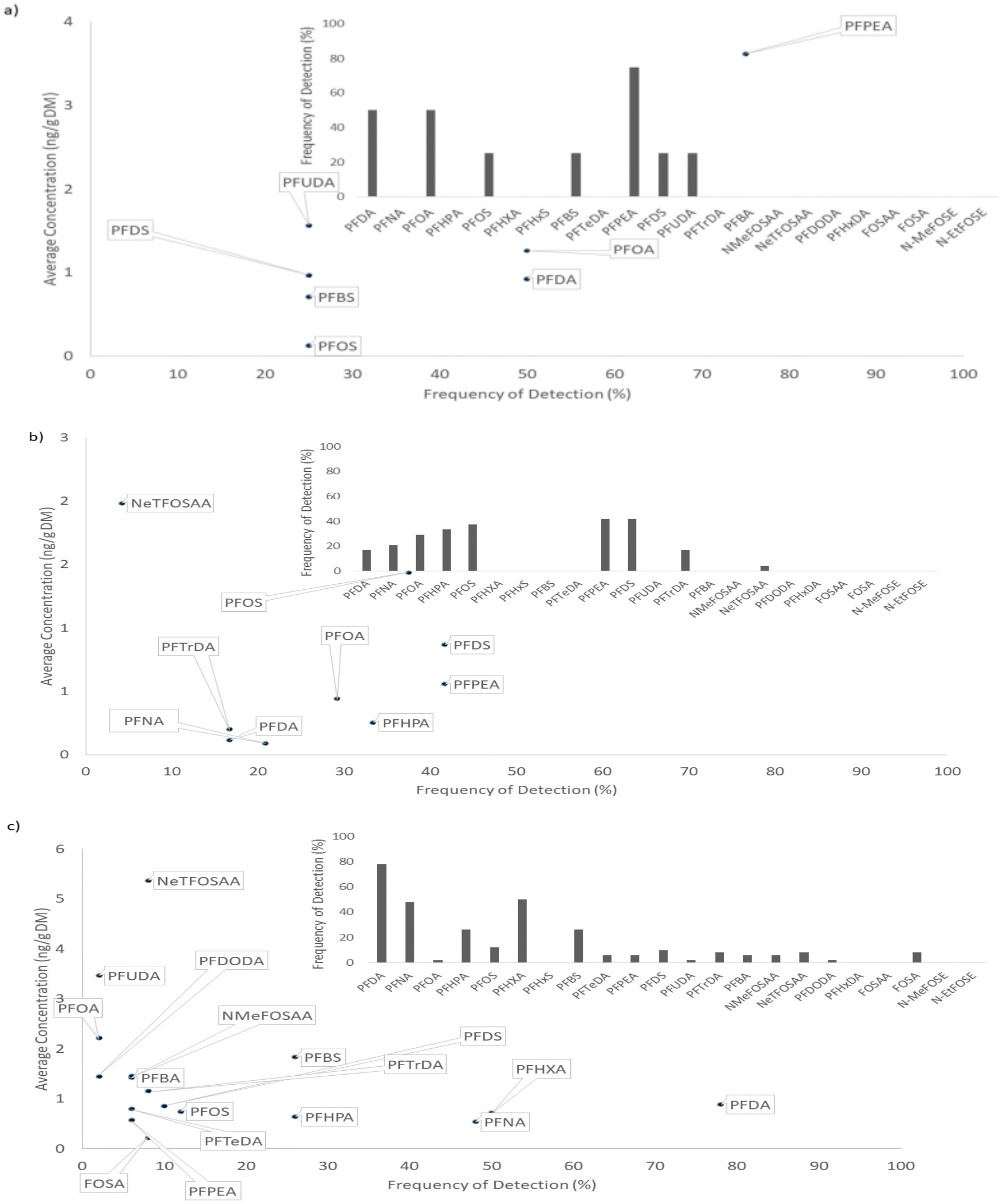

Figure S3: Profile of concentrations of PFCs in sediment collected by Ponar grabs from Northern Great Lake; a) Lake Michigan, b) Lake Superior and c) Lake Huron. The main graph is the frequency of detection and mean concentration at each Lake. Graph in upper corner is the frequency of detection for specific compounds.

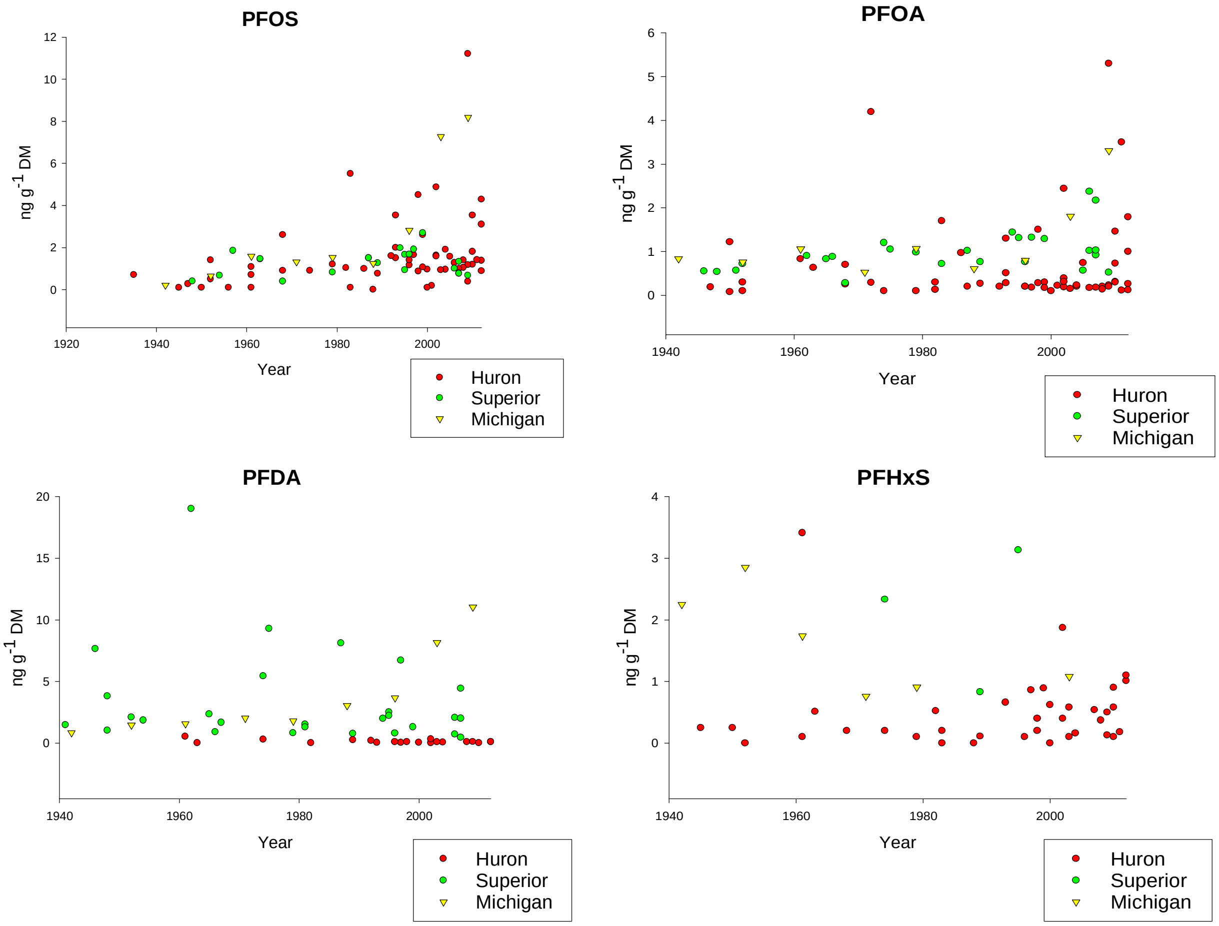

Figure S4: Concentrations of 4 PFCs in cores of sediments since 1940, from Lakes Huron, Superior and Michigan.

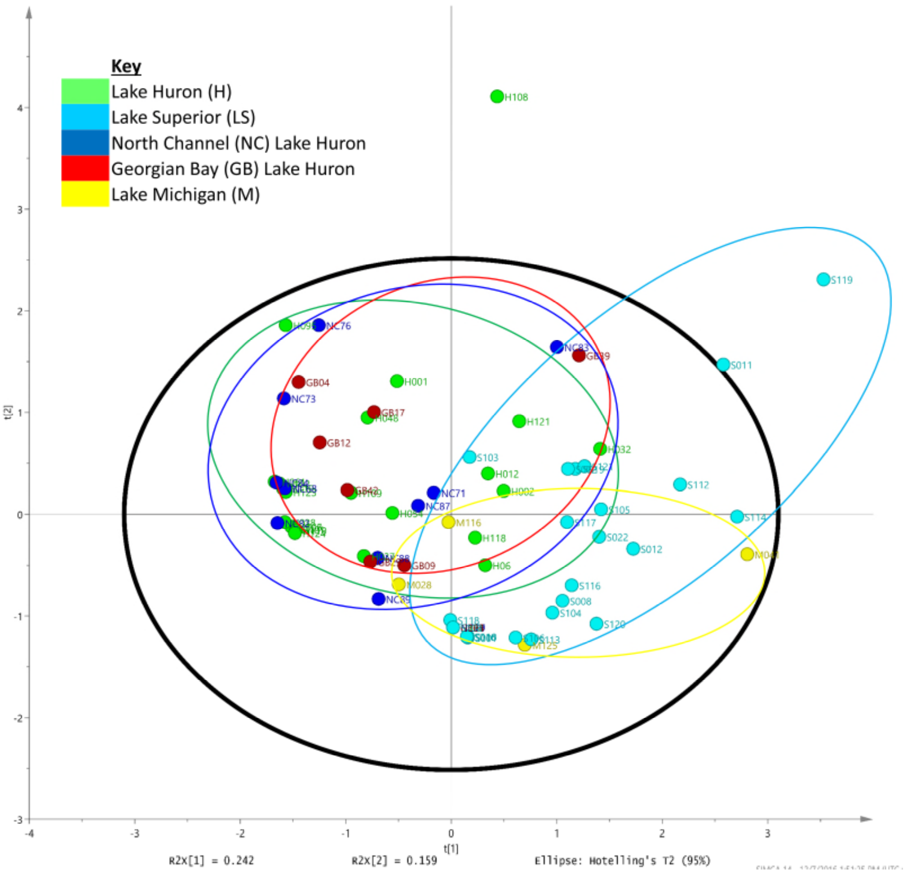

Figure S5. Principle component analysis of the $\sum_{22}$PFCs in surface Ponar samples of the northern Great Lakes.

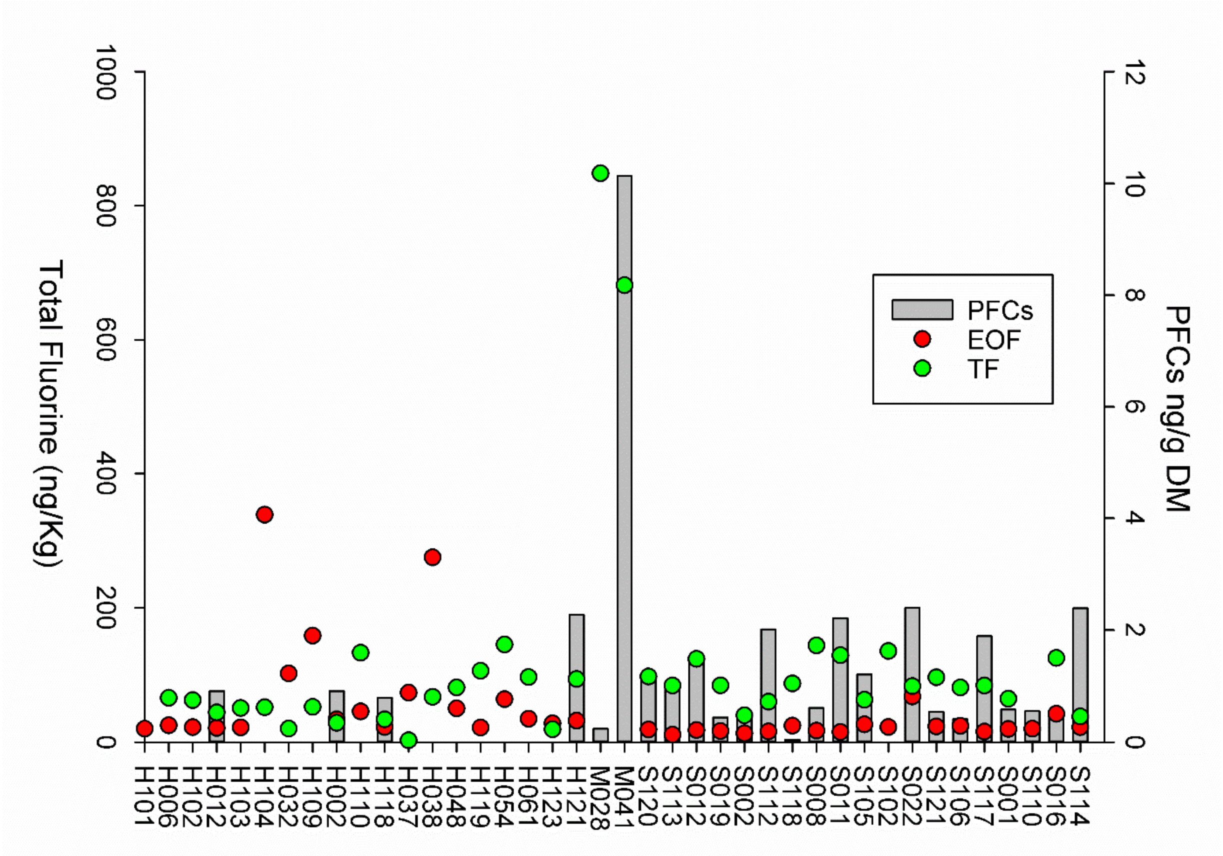

Figure S6: Concentrations of TF and EOF in sediments collected by use of Ponar sampler from Lakes Superior, Huron and Michigan. Concentration of ∑PFCs also identified.

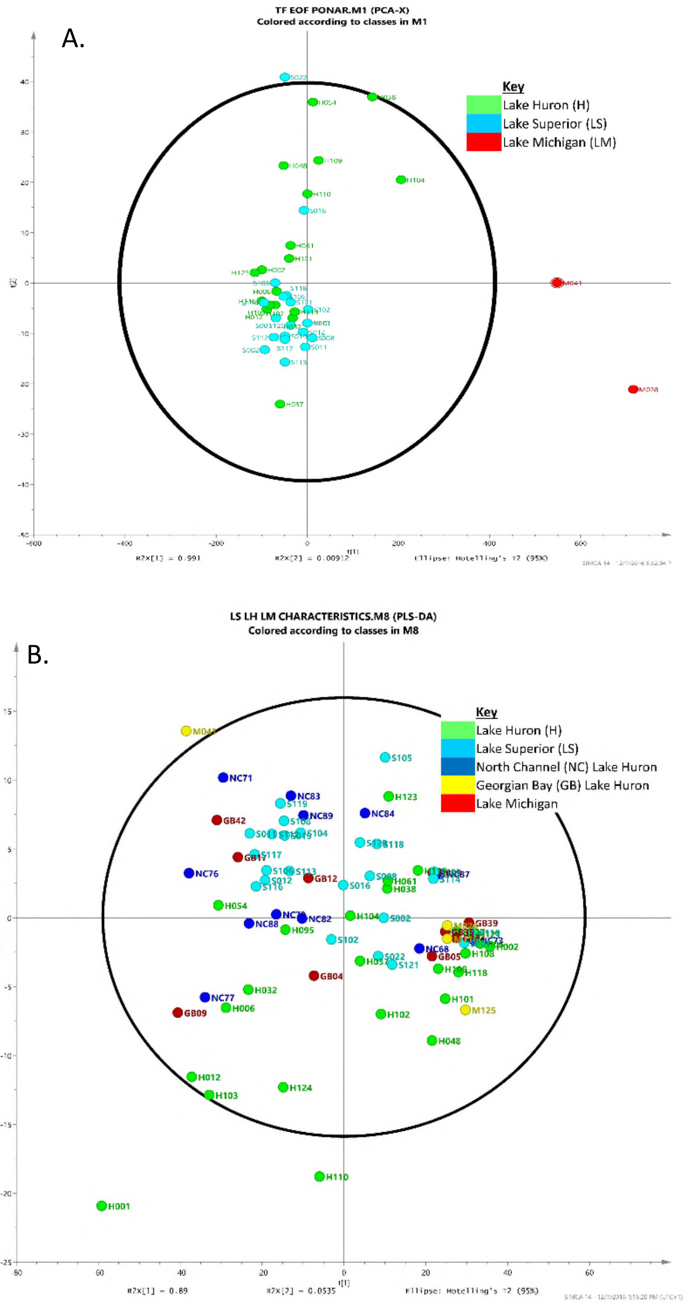

Figure S7: Principle component analysis of total fluorine (TF) and extracted organic fluorine (EOF) A. of surface sediment in Lakes Huron, and Superior. The physical bulk characteristics and carbon in the Great lakes B.

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