Spatial and temporal trends in poly- and per-fluorinated compounds in the Laurentian Great Lakes Erie, Ontario and St. Clair[☆]

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ABSTRACT

The temporal and spatial trends in sediment of 22 poly- and perfluorinated (PFAS) compounds were investigated in the southern Great Lakes Erie and Ontario as well as Lake St. Clair. Surface concentrations measured by Ponar grab samples indicated a trend for greater concentrations near to urban sites. Mean concentrations $\sum_{22}$PFAS were 15.6, 18.2 and 19 ng g^{-1} dm for Lakes St. Clair, Erie and Ontario, respectively. Perfluoro-n-butanoic acid (PFBA) and Perfluoro-n-hexanoic acid (PFHxA) were frequently determined in surface sediment and upper core samples indicating a shift in use patterns. Where PFBA was identified it was at relatively great concentrations typically >10 ng g^{-1} dm. However as PFBA and PFHxA are less likely to bind to sediment they may be indicative of pore water concentrations Sedimentation rates between Lake Erie and Lake Ontario differ greatly with greater rates observed in Lake Erie. In Lake Ontario, in general concentrations of PFAS observed in core samples closely follow the increase in use along with an observable change due to regulation implementation in the 1970s for water protection. However some of the more water soluble PFAS were observed in deeper core layers than the time of production could account for, indicating potential diffusion within the sediment. Given the greater sedimentation rates in Lake Erie, it was hoped to observe in greater resolution changes since the mid-1990s. However, though some decrease was observed at some locations the results are not clear. Many cores in Lake Erie had clearly observable gas voids, indicative of gas ebullition activity due to biogenic production, there were also observable mussel beds that could indicate mixing by bioturbation of core layers.

1. Introduction

In 2001, perfluoro-n-octane sulfonate (PFOS) was found to be ubiquitous in piscivorous animals, which alerted scientists and managers to the widespread and bioaccumulative behaviour of this perfluorosulfonate (Giesy and Kannan, 2001, 2002). Further studies into per- and poly-fluorinated compounds (PFASs) identified accumulation in abiotic matrices such as sediment (Codling et al., 2014) and glacial snow (Wang et al., 2014). The vector of transport for PFASs was not completely understood, because forms have been observed in the atmosphere of remote arctic locations (Ahrens et al., 2011) and in ocean water (Cai et al., 2012).

Between 1970 and 2002, an estimated 122,500 t of

perfluorosulfonates were produced with ~37% entering the environment (Paul et al., 2009). Uses of PFASs have been varied and included, among others, carpet stain protection, clothing, firefighting foams, paper, aviation fluids and packaging materials (Prevedouros et al., 2006). Releases to the environment have been and continue to be via multiple routes, including air and water during manufacture, loss during consumer use and disposal via landfill and incineration (Lang et al., 2016). In humans and wildlife, concentrations in blood in industrialized regions are as great as 30,000 ng mL^{-1}, while in Arctic sites more remote from industrialization and urbanization, including open ocean, concentrations in blood have been as great as 3000 ng mL^{-1} (Houde et al., 2006).

Concerns over the ubiquitous contamination of PFASs and the toxic potencies of longer chain (C8) chemicals have resulted in PFOS, its salts and perfluoro-n-octane sulfonyl fluoride (PFOS-F) being introduced to the Stockholm Convention on Persistent Organic Pollutants after its 4th meeting in 2009 (UNEP, 2009). In the United States, under the Toxic Substances Control Act (TSCA), two sub-categories of concern were created that include longer-chain alkyl carboxylic compounds (>C8) including perfluoro-n-octanoic carboxylic acid (PFOA) and those of >6 sulfonate carbons including PFOS and perfluoro-n-hexane sulfonic acid (PFHxS). The goals of TSCA listing include the removal of longer chain PFASs from products and emissions by 2015 (USEPA, 2016). In Canada, on January 13, 2009, PFOS and its salts were added to the virtual elimination list Part II compiled under subsection 65 (2) of CEPA 1999. The regulations demonstrate Canada is continuing in a commitment to virtually eliminate PFOS and to meet the requirements of the Perfluorooctane Sulfonate Virtual Elimination Act, that received Royal Assent on April 17, 2008 (Canada, 2016). This resulted in 87 compounds that could degrade to PFOS being banned from manufacture, use, transport or importation to Canada. To assess trends in environmental media and effectiveness of implementation of these regulations, it is important to know the environmental occurrence of these compounds at present and in the past.

There has been a large body of evidence demonstrating the accumulation of persistent compounds in sediments of the Great Lakes. Intensive surveys of sediment, have identified organochlorine pesticides (OCPs) (Kannan et al., 2006), and polychlorinated biphenyls (PCBs) (Hornbuckle et al., 2006; Li et al., 2009), along with mercury and other metals (Marvin et al., 2004). Among all five of the Laurentian Great Lakes (Superior, Huron, Ontario, Michigan and Erie) it was found that Lakes Erie and Ontario contained the greatest concentration of contaminants. In 2012, the US-Canada Great Lakes Water Quality Agreement listed 31 areas of concern (AOCs); 15 of them are within the drainage areas of Lakes Erie, Ontario, and St. Clair (USEPA, 2016). These AOCs were identified based on levels of legacy municipal and industrial contamination in the sediment and water. In Lake Erie, the Western Basin had the greatest mean concentrations of OCPs with the Detroit River having the greatest observed concentrations (Marvin et al., 2002). In Lake Ontario, sites in the southern region had the greatest concentration of contaminants for OCPs and PCBs than other sites (Marvin et al., 2004).

PFASs represent a significant fraction of total measured contaminants in fishes of the Great Lakes, and were more abundant in Lakes Erie and Ontario than in the other three lakes (McGoldrick and Murphy, 2016; Stahl et al., 2014). This pattern of contamination is mirrored in Herring gull eggs with Erie and Ontario eggs having significantly greater concentrations of PFAS than other lakes (Gebbink et al., 2009; Letcher et al., 2015). In a study of fish by Environment Canada and the US EPA, PFOS occurred at the 6th and 10th greatest concentrations of contaminants monitored in Lake Erie (70 ± 33 ng g^{-1} wm for Walleye) and Lake Ontario

(54 ± 30 ng g^{-1} wm for Lake Trout), respectively. These are greater than the PFOS concentrations of 27.4 ± 22, 3.7 ± 2.4, and 11.6 ± 4.3 ng g^{-1} wm measured in the fish of Lakes Huron, Superior and Michigan, respectively (McGoldrick and Murphy, 2016). Concentrations of perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorobutyric acid (PFBA), perfluorotridecanoic acid (PFTrDA), perfluorodecanoic acid (PFDoA), perfluoro nonanoic acid (PFNA) and PFOS were all within the top 40 contaminants measured in Erie and Ontario based upon concentration and frequency of determination (McGoldrick and Murphy, 2016).

Sediments of lakes can provide a historical record of chemicals loaded to surface waters. Concentrations of PFAS have been observed to increase in sediment with time (Codling et al., 2018; Codling et al., 2014; Stock et al., 2007). In Tokyo Bay, Japan, since the change from commercial use of longer chain PFAS to those with shorter chains, compounds detected in sediments have changed rapidly (Zushi et al., 2010). The question remains whether these changes in commercial formulations have resulted in observed changes in PFAS in the lower Great Lakes such as observed previously in the upper Great Lakes (Codling et al., 2018; Codling et al., 2014). Lakes Erie and Ontario are by far the most contaminated of the Great Lakes and Lake Erie has a greater sedimentation rate. Both of these factors make the lower Great Lakes potentially ideal for identification of current and historical trends in PFAS concentrations. In this study concentrations of 22 PFAS, total fluorine (TF) and extractable organically-bound fluorine (EOF) were measured in surface sediments and cores collected during 2013—2014 in Lakes Ontario, St. Clair and Erie.

2. Materials and methods

2.1. Collection of sediments

Samples of sediments were collected on board the *R/V Lake Guardian* in Lake Ontario (ON) in 2013 and Lake Erie (ER) in 2014, and by a small boat on Lake St. Clair (C) in 2014 (Fig. 1, and Supporting Information (SI) Table S1). Cores of sediments were collected simultaneously into four polycarbonate tubes (10 cm o. d. 9.5 cm i. d. and 59.6 cm long), by use of a model MC-400 Multi-Corer (Ocean Instruments, San Diego, California). In total, six cores were collected from Lake Erie, seven from Lake Ontario, and one from Lake St. Clair. Sectioning of the cores occurred immediately after collection, and the sections at the same sediment segment depth from four sub-cores were combined and homogenized in glass bowls. Cores from Lake Erie were sectioned into 2 cm segments throughout the length of the cores. Each core from Lake Ontario was sectioned into 1 cm segments for the first 10 cm, followed by 2-cm layers thereafter. The core from Lake St. Clair was sectioned into 1 cm segments for the first 15 cm and 2-cm layers thereafter.

Surface grab samples (later referred to as Ponar) were collected using a Ponar sampler at 45 locations in Lake Erie, 11 in Lake St. Clair and 59 in Lake Ontario (Fig. 1, SI Table S1). The sampler scoop area was 152 × 152 mm. Ponar samples were homogenized using a stainless steel mixing blade attached to a power drill.

Field blanks (n = 3 per lake) were sodium sulfate in glass jars which were exposed during extraction of cores; while travel blanks (n = 3 per lake) were remained closed, during collection. Depths of overlying water at sampling locations ranged from 1.4-6.4 m, 6-65 m and 25-230 m in Lake St. Clair, Erie and Ontario, respectively (SI Table S1).

2.2. Sample preparation and analysis

Detailed analytical methods used to identify and quantify PFAS
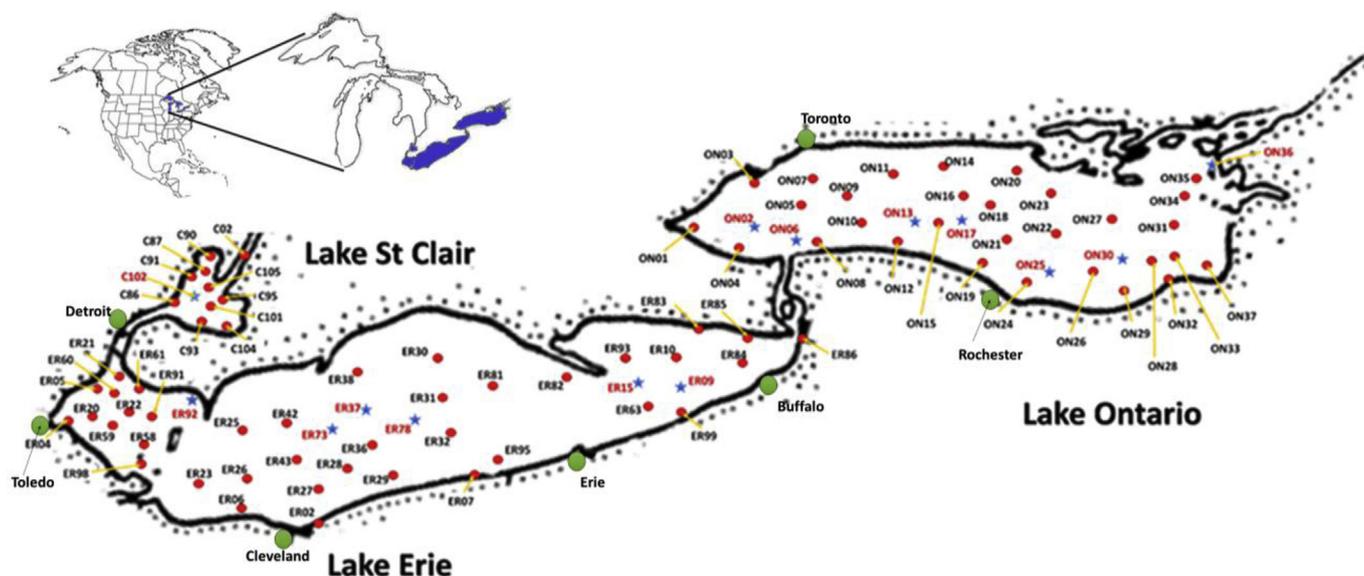
Fig. 1. Sampling locations for Ponar grab (red circles) and core (stars and red annotation) sediment samples in Lakes Erie (ER), St. Clair (C) and Ontario (ON). Green circles are the major conurbations of the lakes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

have been published previously (Codling et al., 2018). Standards used in this study are listed in SI Table S2 and include recovery compounds. HPLC grade or better methanol (MeOH; Gibbstown, USA), and acetonitrile (ACN; Fisher Scientific, Pittsburgh USA), were further purified by distillation. Acetic acid (AA: 98% Suprapure) and Envicarb were from Sigma-Aldrich (St. Louis USA). Sediment extraction for PFAS was by sonication followed by cleanup using SPE using the method described elsewhere (Codling et al., 2018; Naile et al., 2010). Prior to extraction, each 2.5 ± 0.1 g sample in a 50 mL polypropylene tube (PP: Fisher Scientific) was amended with 50 μL of a 0.1 μg mL^{-1} solution containing mass-labelled internal standards (SI Table S2). Samples were extracted with 10 mL 1% AA H$_2$O solution followed by two 5 mL extractions of 90:10 MeOH/1% AA solutions and 10 mL 1% AA H$_2$O solution. Each sample was vortexed, sonicated and centrifuged, and the supernatant collected in a clean 50-mL-PP tube. Cleanup was through Oasis HLB cartridges (6 cc 300 mg; Millford, USA) conditioned with 5 mL H$_2$O and MeOH in sequence. After loading onto the column, the sample was eluted by 10 mL of MeOH and 6 mL of toluene. The eluent was collected 2 15-mL-PP tubes, concentrated under N$_2$ and combined before taking to dryness and reconstituting in 200 μL of 5:1 MeOH/H$_2$O with 1% AA. Samples were transferred to PP-GC vials (VWR, Mont-Royal Canada). Additional cleanup was performed on Lake Erie samples using 0.5 g EnviCarb and triplicate extractions using MTBE.

An Agilent 1100 high performance liquid chromatograph (HPLC) was used for separation of analytes on a Betasil C18 column at 30 °C (Thermo Scientific, 100×2.1 mm, 5 μm particle size). Milli-pore water (A) and acetonitrile (B) with 10 mM ammonium acetate and 1% acetic acid was used as the mobile phase. Use of acetonitrile instead of MeOH as solvent was to improve peak shape of the shorter chain PFAS. Solvent gradient was 60% A held for 2 min then ramped to 100% B over 26 min and held for 8 min before returning to 60% A for 10 min. Detection and quantification of PFAS was by API 3500 triple quadruple mass spectrometer (Applied Biosystems/MSD SCIEX; Foster City, Canada). The MS was operated in multiple reaction monitoring (MRM) with a dwell time of 15s and ion spray voltage of -3500V and a source temperature of 450 °C. Desolvation gas, curtain gas and nebulizer gas were set at 12, 6, and 5 AU (arbitrary units). Details of the precursor and product ions are those

described previously and given in SI Table S2. Quantification was performed using a 7-point calibration (1, 2.5, 5, 10, 50, 100 and 250 ng mL^{-1}) with MeOH blanks every 6 samples. For each batch of 12 samples, an external standard was introduced to ensure signal intensity and drift did not occur. Quantification was performed using Analysist 1.4.1 software, (AB SCIEX, Darmstadt Germany). Multiple product ions were used for each compound to confirm detection. All compound concentrations are given in ng g^{-1} dry mass (dm).

TF and EOF were quantified by use of combustion ion chromatography as described by Codling et al. (2014) using sodium fluoride for external calibration. TF was measured using a 0.1 g of homogenized sediment and for EOF a 10 μL aliquot of the final PFAS extract was used. The F$^-$ measured in the EOF fraction was adjusted to account for the additional fluorine in the mass labelled standard added to the sample.

Sedimentation rates were determined from radionuclide profiles measured by gamma spectroscopy using previously described methods (Guo, 2015; Guo et al., 2016). In brief, mass accumulation rates and calendar date profiles were derived from regressions of unsupported ^{210}Pb activity vs. mass depth, with ^{137}Cs used for validation where its 1963 peak of deposition was identifiable in the profile. Dating results were consistent with previous studies of Lakes Erie and Ontario (Johnson, 1984; Robbins et al., 1978) and previous dating in other Great Lakes using the same method (Codling et al., 2018; Codling et al., 2014; Hermanson et al., 1991; Zhang and Wania 2012).

2.3. Quality control and assurance

Analytes of interest were not detected in instrumental blanks consisting of MeOH, after distillation, even though PFOA had been identified in solvent prior to distilling. All method blanks for Lakes Erie and Ontario were less than the limit of quantification (LOQ), set at 10 times the signal to noise (S/N) ratio. The instrument detection limit (LOD) was defined as S/N of 3. The average limit of detection (LOD) was 0.05 ng g^{-1} in samples from Lake Ontario and 0.11 ng g^{-1} in samples from Lake Erie. The greater mean LOD in Lake Erie was due to PFBA LOD of 0.72 ng g^{-1}, (detailed LODs are presented in Table S3).

Recoveries of the six mass-labelled PFAS were used to correct for losses during sample preparation. Where no appropriate internal standard (IS) was available, compounds with ± 1 carbon chain length were used. Thus, for these compounds, concentrations should be considered as approximations rather than absolute values. Mean recoveries of IS ranged from 67% for $^{13}C_2$PFDoA to 76% for $^{13}C_4$PFNA, with a mean of 73% for samples from Lake Erie, and 67% for $^{13}C_2$PFBA to 90% for $^{13}C_4$PFOA and a mean of 80%. In samples from Lake St. Clair, recovery ranged from 57% for $^{13}C_2$PFDA to $^{13}C_4$PFOA 84% with a mean of 69%.

3. Results and discussion

Overall, 20 of the 22 compounds targeted in this study were detected in sediments of Lakes St. Clair, Erie and Ontario core and Ponar sediment samples. N-MeFOSE and N-EtFOSE were not detected at concentrations greater than the LOQ in any sample (Table 1).

3.1. Surface sediments

Concentrations of $\sum$PFAS in sediments collected by use of Ponar sampler ranged from 1.0 (C90) to 88.7 (ON14) ng g^{-1} dm (Fig. 2, SI Table S3). Mean concentrations were 15.6, 18.2 and 19 ng g^{-1} dm for Lakes St. Clair, Erie and Ontario, respectively. The most prevalent PFAS observed were PFHxA and PFOS. PFBA, though less frequently observed, occurred at the greatest mean concentrations (14.2, 15.6 and 26.2 ng g^{-1} dm in Lakes Ontario, St. Clair and Erie, respectively). Comparison of latitudinal trends of relative concentrations among individual PFASs indicated regional similarities (Fig. 2). Patterns of concentrations of PFAS in the Great Lakes closely match densities of human population, where both Lakes Erie and Ontario have large populations compared to the other Great Lakes (Gewurtz et al., 2013; Houde et al., 2006).

PFBA and PHFxA are more water soluble than other PFASs and thus less likely to bind to sediment (Higgins and Luthy, 2006). Thus, these compounds might be present mostly in pore water, rather than bound to the particles of the sediment (Ahrens et al., 2009; Zhao et al., 2012). Frequent detection of these compounds in this study might reflect the now widespread use of these compounds as replacements for the longer-chain PFAS. Ponar samples in this study represent a homogeneous mixture of the upper 10 cm of sediments. Actual penetration depth **of** the Ponar varies with density of sediments. Based on dating of cores done on lake sediments in this study, Ponar samples represent many years of deposition, however Lake Erie has a greater rate of sedimentation than the other Great Lakes so a sample of sediment from Erie is likely to represent more recent sedimentation. Furthermore, the shape of the Ponar results in more sediment mass at the top and less at depth, thus the applicability of Ponar for comparison with deposition date is inexact. However, this upper sediment layer is where benthic organisms will be most in contact with sediments and associated contaminants. Thus, the current aquatic exposure from sediment and pore water occurs within these Ponar layers.

Lake St. Clair is relatively shallow AOC that is the primary route of travel for waters from the other great lakes (Michigan, Superior and Huron). The retention time for water in the lake is relatively short ~9 days and it is thought that due to the flow rate that the sediment scour and mixing might be significant. In Lake St. Clair, concentrations of $\sum$PFAS in samples collected by Ponar, ranged from 1.0 to 63.7 with a mean of 15.6 ng g^{-1} dm. Greater concentrations of $\sum$PFAS were observed in sediments from several locations: Anchor Bay, which is in the north of the lake; the mouth of the St. Clair River and along the western coast, which is almost entirely urbanized. This area is designated as an AOC (Custer et al.,

2016). Diffuse input from domestic and industrial uses are likely sources of PFAS, since land use on the east side of the lake is mainly farmland it is unlikely to be a major source (Prevedouros et al., 2006). Previous studies have found that upstream industry and municipal waste were likely sources of Hg and chlorinated hydrocarbons to the lake (Oliver and Bourbonniere, 1985). However, greatest concentrations of Hg in sediment were not consistent with those of organic contaminants, indicating potentially different sources of these two types of contaminants (Marvin et al., 2004). Site C02, which is ~25 km upstream of Lake St. Clair on the St. Clair River was significantly contaminated by PFASs compared to the mean for the lake. The river has long been identified as a source of contaminants to Lake St Clair (Hughes et al., 2014).

Greater concentrations of PFASs in sediments from Lake Erie were observed in coastal regions near to urban areas and the Detroit and Maumee Rivers, both of which are AOCs. Sediments from other AOCs around the Great Lakes have also been reported to contain concentrations of PFASs that were greater than the means for those lakes, respectively (Custer et al., 2016; USEPA, 2016). Spatial distributions of concentrations of PFASs in Lake St. Clair are similar to those for PCBs and Hg, with greater concentrations along the southern coast (Marvin et al. 2002, 2004). Least concentrations were in sediments from the central basin, where the circulation pattern might not be as affected by coastal waters (Marvin et al., 2002). In Lake Erie, PFOS was the dominant fluorinated contaminant in lake trout and walleye, followed by PFDA, PFUdA, PFBA, PFDoA and PFOA, while in sediments collected in this study, PFHxA was the most frequently detected PFAS, followed by PFOS, PFHxS and PFOA (McGoldrick and Murphy, 2016).

Lake Ontario is composed of three basins; the Niagara to the west, the Mississauga in the centre and the Rochester Basin. Lesser concentrations of $\sum$PFASs were observed in the central portion of the Mississauga and Rochester Basins, with the exception of ON34 that sits on a raised area of less depth than the deeper surrounding sites. Greater concentrations observed in Lake Ontario are consistent with an urban/industrial source such as Rochester, NY (ON24). Toronto, ON could be a major source of PFASs to Lake Ontario, although site ON03 near Toronto had relatively lesser concentrations of PFAS, similar to the trend previously observed for PCBs and dioxins (Marvin et al., 2002). This could be because ON03 is located near shore in the non-depositional zone, with less fine-grained sediment. Greatest concentrations of PFASs were observed at site ON14 in the northern portion of Lake Ontario, which is a wide, shallow region compared to the rest of the lake. Thus, that area might be influenced more by input from urban regions. The city of Oshawa, where a large-scale car manufacturing plant is located, is near site ON14, but closer still to ON11, yet concentrations of PFS were not greater ON11. Based on concentrations of other contaminants, such as Hg and other metals, the centre of Lake Ontario is considered to be a sink for contaminants (Marvin et al., 2002), however that appears not to be the case for PFAS. However, the fact that these surface samples were dominated by two of the most highly soluble PFAS compounds might indicate that greater concentrations of more mobile compounds might be found in the benthic interface than at depth (Ahrens et al., 2009; Cao et al., 2015).

Further statistical analysis of spatial trends using hierarchical cluster analyses, with data displayed graphically as heat maps and histograms was performed for Ponar samples from each lake. However given the frequency of identification of most PFAS <50% of samples most compounds could not be included in analysis so the value of this analysis was limited. Hierarchical clustering did indicate that PFBA and to a lesser extent PFBS are more dissimilar than the other PFASs in each lake. Locations closer to the coast tend to have greater concentrations than samples from the central lake, indicating local sources are still predominant.

Table 1
Mean concentrations (ng g^{-1} dm) of per- and polyfluorinated compounds (PFASs) in surficial sediments collected by Ponar grab sampler or in cores in Lakes Erie, Ontario and St. Clair. Values in brackets are the range of rate of detection and the superscripted are the detection frequency.

Compounds	Ponar			Cores		
	Ontario (n = 42)	St. Clair (n = 16)	Erie (n = 49)	Erie (n = 100)	St. Clair (n = 21)	Ontario (n = 143)
Concentration (ng g^{-1} dw)						
PFOS	1.8[38]	0.5[14]	1.7[44]	1.2[91]	ND	5.1[132]
	(0.1, 13.2)	(0.1, 1.0)	(0.2, 4.0)	(0.18, 7.09)		(0.0, 63.2)
PFOA	0.4[23]	0.4[6]	0.6[37]	1.76[38]	0.4[2]	3.0[90]
	(0.0, 1.4)	(0.3, 0.6)	(0.3, 1.7)	(0.16, 5.66)	(0.3, 0.5)	(0.0, 13.2)
PFPEA	1.1[6]	1.0[3]	2.5[7]	4.2[27]	7.8[1]	1.3[23]
	(0.1, 5.2)	(0.8, 1.5)	(1.0, 3.4)	(1.0, 18.2)		(0.0, 7.0)
PFHXA	0.9[41]	0.3[16]	0.3[48]	1.1[98]	0.4[20]	3.5[129]
	(0.2, 4.2)	(0.1, 1.2)	(0.1, 1.3)	(0.1, 1.8)	(0.2, 0.9)	(0.1, 62.5)
PFHPA	0.6[13]	0.1[3]	0.2[7]	0.79[23]	0.2[1]	0.3[75]
	(0.1, 6.8)	(0.0, 0.1)	(0.0, 0.4)	(0.78, 0.81)		(0.0, 1.8)
PFNA	0.3[7]	0.2[7]	0.3[29]	2.96[23]	0.7[4]	6.2[95]
	(0.2, 0.4)	(0.1, 0.2)	(0.2, 1.0)	(0.2, 20.4)	(0.3, 1.5)	(0.0, 395.1)
PFDA	1.2[19]	1.6[10]	0.9[32]	7.2[53]	1.5[5]	2.3[101]
	(0.2, 10.4)	(0.2, 3.6)	(0.1, 8.2)	(0.3, 45.7)	(1.0, 2.2)	(0.0, 35.2)
PFUdA	2.4[26]	4.9[5]	0.7[20]	18.3[50]	2.1[9]	4.7[115]
	(0.0, 21.2)	(0.3, 10.7)	(0.0, 5.2)	(0.1, 63)	(0.7, 5.1)	(0.0, 52.4)
PFDoA	2.8[5]	0.1[3]	0.1[16]	0.09[5]	ND	0.3[44]
	(0.3, 11.8)	(0.0, 0.1)	(0.0, 0.3)	(0.09, 0.1)		(0.0, 3.0)
PFBS	7.6[16]	19.3[1]	11.2[5]	9.64[43]	10.9[17]	16.7[90]
	(0.3, 42.2)		(4.9, 20.0)	(1.5, 63.8)	(2.1, 27.2)	(1.6, 77.8)
PFHxS	1.4[19]	0.8[13]	0.5[52]	1.79[52]	0.8[20]	2.0[86]
	(0.1, 5.2)	(0.1, 2.2)	(0.1, 2.7)	(0.18, 5.92)	(0.2, 1.6)	(0.1, 13.6)
PFBA	14.2[22]	25.0[6]	26.2[22]	8.1[27]	10.8[18]	19.8[43]
	(0.4, 41.0)	(3.1, 48.9)	(8.3, 56.3)	(1.8, 21.5)	(4.1, 35.9)	(0.3, 90.0)
PFDS	4.2[15]	0.6[3]	0.8[29]	6.43[48]	2.8[17]	4.7[52]
	(0.4, 15.4)	(0.3, 1.0)	(0.2, 1.7)	(0.6, 61.8)	(1.3, 3.7)	(0.2, 18.3)
PFTrDA	0.3[11]	0.3[11]	0.3[34]	0.54[19]	ND	3.0[84]
	(0.1, 0.4)	(0.2, 0.3)	(0.2, 0.4)	(0.25, 0.86)		(0.1, 57.0)
PFTeDA	0.2[6]	0.3[9]	0.3[23]	0.54[9]	ND	4.5[41]
	(0.1, 0.2)	(0.2, 0.4)	(0.2, 0.4)	(0.33, 0.80)		(0.1, 40.6)
PFHxDA	0.6[5]	0.1[3]	0.2[14]	0.70[5]	0.6[3]	1.3[44]
	(0.3, 1.7)	(0.0, 0.3)	(0.0, 0.3)	(0.60, 0.83)	(0.6, 0.6)	(0.0, 6.3)
FOSAA	0.9[13]	0.2[4]	0.1[18]	0.22[10]	0.2[5]	0.3[62]
	(0.0, 4.3)	(0.1, 0.3)	(0.0, 0.3)	(0.04, 0.35)	(0.2, 0.3)	(0.0, 2.6)
N-MeFOSAA	2.1[2]	ND	0.2[4]	0.82	ND	0.2[5]
	(0.3, 3.9)		(0.0, 0.3)	(0.82, 0.83)		(0.1, 0.3)
NeTFOSAA	3.2[6]	0.0[1]	0.1[5]	0.27[8]	ND	1.9[50]
	(0.1, 9.3)		(0.0, 0.3)	(0.09, 0.83)		(0.0, 29.7)
FOSA	0.3[11]	0.2[6]	0.3[34]	0.51[44]	0.2[1]	0.3[2]
	(0.2, 0.7)	(0.2, 0.3)	(0.2, 0.4)	(0.3, 0.9)		(0.2, 0.5)
∑PFASs	19.0[42]	15.6[16]	18.2[49]	28.69,[100]	23.5[21]	43.4[143]
	(1.7, 88.7)	(1.0, 63.7)	(2.4, 64.8)	(0.1, 197.3)	(0.0, 51.8)	(0.5, 210.0)
Recovery (%)						
13C PFOA	74.5	83.6	89.7	89.8	84.0	85.1
	(23.7, 130.5)	(73.7, 99.7)	(73.7, 139.9)	(73.7, 152.6)	(52.8, 146.7)	(73.7, 130.5)
13C PFOS	72.2	75.4	86.5	69.8	86.7	71.9
	(62.8, 106.6)	(42.5, 106.6)	(62.3, 128.0)	(62.8, 89.9)	(52.7, 135.8)	(61.7, 128.4)
13C PFDoA	67.3	67.2	73.8	58.7	75.5	68.9
	(47.3, 77.5)	(22.8, 77.5)	(53.8, 118.6)	(48.2, 115.6)	(67.5, 119.0)	(56.5, 77.5)
13C PFNA	76.3	62.5	71.8	70.6	77.8	65.7
	(66.3, 121.7)	(25.6, 84.8)	(65.6, 73.2)	(25.6, 121.7)	(55.7, 103.2)	(56.2, 121.7)
13C PFDA	71.2	57.0	81.9	87.3	83.9	70.3
	(51.6, 124.6)	(42.6, 64.1)	(61.6, 144.4)	(62.6, 124.6)	(46.6, 124.6)	(52.6, 124.6)
13C PFUdA	74.2	68.8	86.6	66.4	78.6	83.4
	(44.6, 122.9)	(38.6, 80.5)	(56.5, 118.7)	(60.6, 122.9)	(45.0, 122.9)	(43.4, 122.9)
13C PFBA	74.1	70.3	67.6	77.5	82.8	75.2
	(44.7, 98.1)	(44.7, 106.1)	(62.1, 105.1)	(44.7, 114.4)	(51.6, 127.5)	(62.0, 86.4)

3.2. Temporal trends

Mean concentrations of ∑PFAS observed in this study (Table 1) were greater than means of 2.3, 8.7, and 4.7 ng g^{-1} dm for Lakes Michigan, Superior and Huron, respectively (Codling et al., 2018; Codling et al., 2014) but similar to those observed in a Spanish river basin, and in the Morava River where concentrations were 16.1 and 6.8 ng g^{-1} dm, respectively (Bečanová et al., 2016; Campo et al., 2015). This elevated concentration is further substantiated by water collected during 2003, from Lakes Erie and Ontario (n = 16) that contained mean concentrations of PFOS and PFOA of 43 ± 18 and 39 ng L^{-1}, respectively (Marvin et al., 2004). In fish tissue, concentrations of PFASs were greatet in Lakes Erie and Ontario than in other Lakes. The mean concentration of PFOS in fishes from Lake Ontario was 70 ng g^{-1}, compared to 27 in Huron, 12 in Michigan and 4 ng g^{-1} in Lake Superior (McGoldrick and Murphy, 2016).

Lake Erie has a greater rate of sedimentation than does Lake Ontario and the other Great Lakes with the exception of specific
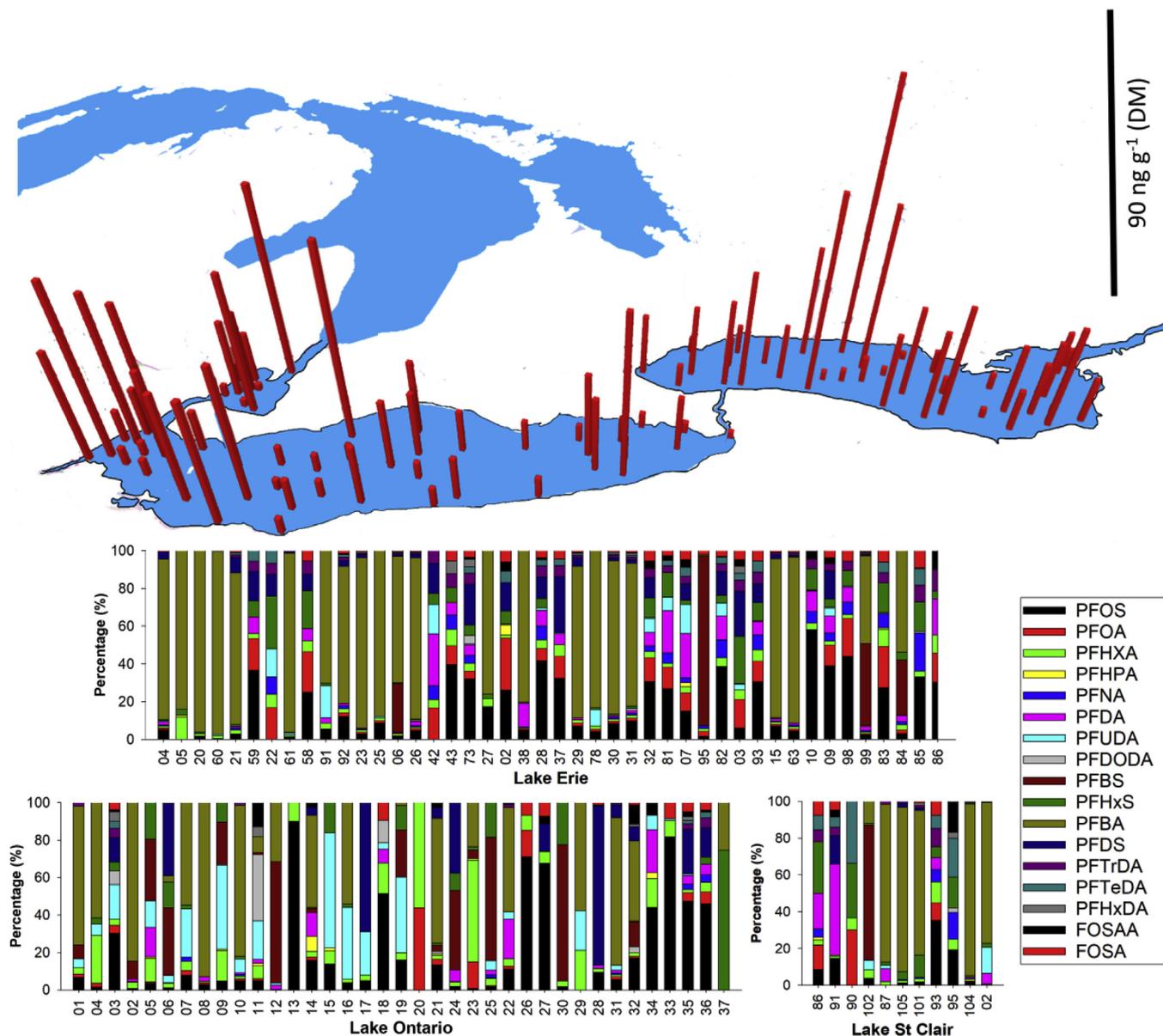
Fig. 2. Concentrations of $\sum$PFASs (ng g^{-1} dm) in surficial sediments collected by use of Ponar sampler from Lakes St. Clair and Erie, and Lake Ontario. Excel 3D map was used to illustrate the spatial distribution of Σ_{17}PFASs. Relative compositions (%) of predominant PFASs contributing to $\sum_{17}$PFASs in sediments, organized by latitude of the sampling sites is presented below.

sites such as Green Bay in Lake Michigan. The core length of 40—50 cm represents up to 100 years of sediment accumulation in Lake Erie, while sectioned cores from Lake Ontario might represent up to 400 years of sedimentation. Previous investigations of rates of sedimentation in other Laurentian Great Lakes indicated that on average most regions have lesser rates than did Lake Erie (Codling et al., 2018; Codling et al., 2014; Johnson 1984).

Temporal trends for individual cores are presented in Fig. 3, while individual compounds are shown in Fig. S1 and $\sum$PFASs are presented Fig. S2. In general, there was a trend of increasing concentrations of PFASs that closely matches historical production and is likely related to production and use of PFASs in the region. This trend is also supported by greater amounts of organic matter (OM) that might be linked to cultural eutrophication over the past century since increasing nutrient loading led to increased primary production and subsequent increased net OM deposition to the sediments (Fig. S3). However, given different rates of sedimentation

and thus dates assigned to layers in sediments, it might be that the observed trend reflects the greater number of samples related to 1995-2014.

Attempts to normalize data to sediment features such as organic matter that is seen as a vector for uptake to sediment proved inconclusive. However, since some OM is more labile it might be degraded, which would make correlations difficult or impossible. Uptake is based upon a range of factors and the compound has to be present at a stable concentration in the aquatic environment to cause uniform uptake. Interestingly, depositions of PFAS were not correlated with black carbon (BC), an indicator of combustion activity. A decreasing BC loading has been observed in all of the Great Lakes due to a combination of decreasing heavy industrial output in the post-WWII period, more efficient industrial operations and increasing air pollution regulations in the latter half of the 20th century. As regulations on emissions of for BC and PFAS might have occurred concurrently, some trend might have been anticipated,

but was not seen in this study.

In Lake Ontario (Fig. 3) temporal trends for deposition of $\sum$PFAS generally followed the trend observed previously for Lake Michigan, with patterns of relative concentrations closely resembling the profile of production of PFAS over the last 100 years (Codling et al., 2014; Paul et al., 2009; Prevedouros et al., 2006). At most locations, an increase was observed between the 1950s and 1960s with a decrease in the 70s. This is most easily observed for ON06, 13, 25 and 17 but is also notable to a lesser extent for ON02 and 30. These trends might be attributed to the 1972 Great Lakes Water Quality Agreement and subsequent work to mitigate input of contaminants from point sources. The greatest concentrations of PFAS for most cores in Lake Ontario occur within the last 15 years. The exception to this is seen at site ON36. At that location there appears to be no strong trend in concentrations of PFASs as a function of depth in the core. However, that site is also near the mouth of the St. Lawrence River and is a major shipping route, which would be expected to result in greater loading to the water phase, compared to open basin sites in the lake where atmospheric deposition is expected to be the dominant source pathway. In other locations such as ON13 (a site with greater sedimentation), greater concentrations of PFBS were measured in sediments deposited during the period 1985 to 1990. The cause of that result is probably not due to contamination at the time but diffusion of pore water with these more soluble PFASs (Higgins and Luthy, 2006). This trend has been observed for other locations where compounds observed in deeper sediment layers tend to be the more soluble. *n situl* downward diffusion of relatively polar compounds in sediment has been reported for atrazine and similar herbicides (Guo et al., 2016) as well as organophosphate ester flame retardants and plasticizers (Cao et al., 2017).

Cores used to assess temporal trends for Lake Erie are divided into two groups based on rates of sedimentation observed. ER15 and ER09 have sedimentation rates of approximately $0.5–0.6 \, g \, cm^{-2} \, year^{-1}$, while cores ER37, ER92, and ER73 sedimentation rates were $0.09–0.21 \, g \, cm^{-2} \, year^{-1}$. Of all the cores, ER37 in the central part of the lake has a PFAS uptake pattern similar to that observed in Lake Ontario. PFUdA was identified in most cores of sediments from Lake Erie compared to the other two lakes, where detection of PFUdA was restricted to after the mid-80s. In a study of Chinese sturgeon, concentrations of PFUdA, as well as other, longer-chain PFASs were found to be increasing in fish tissue, possibly due to a shift in use as restricted C8 PFASs are removed from products (Peng et al., 2010). ER15 was most frequently contaminated with PFUdA. That location is at the central area of the Eastern Basin with high sedimentation. However, elucidation of relative proportions of this PFAS associated with sediments vs. pore water will be needed to better understand if this compound becomes permanently bound. PFUdA as a longer-chain PFAS that is more likely to be sorbed to particles, but as a carboxylic acid its affinity for sediment might be weaker than some other molecules of similar size (Ahrens et al., 2009). In sediments from Tokyo Bay, Japan, concentrations of longer-chain PFASs (PFUdA, PFDoA, and PFTrDA) were greater than those of PFOS and PFOA and were increasing with time (Zushi et al., 2010). ER15 was also of interest because organic matter (OM) and total nitrogen (TN) in sediments from that location were both significantly decreasing from past to present, while at all other locations concentrations of OM and TN were increasing with towards the present (Fig. S3). This core also had abundant mussel beds which would indicate sediment mixing in the benthic zone due to bioturbation (Mittal and Rockne, 2010). Furthermore, these sites had clearly observable gas voids throughout much of the core, indicative of gas ebullition activity due to biogenic production of N_2 (from denitrification) and CH_4 and CO_2 (primarily from methanogenesis). Oxidation-reduction potential measurements on cores during sampling were consistent with reducing sediments under sulfate reducing or methanogenic conditions. Gas ebullition is known to facilitate upward mobilization of organic-rich sediment particles and hydrophobic organic pollution (Viana et al., 2012). For cores in Lake Erie, PFOS and PFHxA were ubiquitous in core layers.

In sediment from ER92 with layers in the core corresponding to 1959 to 2013, concentrations of both PFOS and PFHxA increased from earlier to more recently deposited sediments. ER92 is also of interest as for many other PFAS (excluding PFBA and NMeFOSE that appear throughout the core) concentrations peak around the late 1960s but do not show the increase in later years observed at other sites. In sediments from locations ER73 and ER37 there were no clear temporal trends for PFOS, PFHxA or any PFAS. In Tokyo Bay, Japan changes in concentrations of PFOS, N-EtFOSAA and N-MeFOSAA were detectable in layers of the core corresponding to years of deposition from 2000 to 2005, which could be attributed to changes in uses of these PFASs (Zushi et al., 2010). A similar trend was also observed in glacial snow (Young et al., 2007). In the current study, no trend of these PFASs, either increasing or decreasing, was observed from 1995-2014 in Lake Erie cores.

Total concentrations of PFASs in a single core of sediment from Lake St. Clair were mostly comprised of three compounds; PFBS, PFBA and PFDS. In fact, these three PFASs were present throughout the entire core. Given the shallow depth of the water column (5.2 m) from where that core was collected, it was anticipated that sedimentation would be influenced by surface water dynamics (such as storms and seiches) to a greater extent than might occur in sediments from deeper locations. Such disturbances prevented accurate dating of cores. PFOS was not detected in any layer and PFOA was detected in only two core layers. Although concentrations of PFUdA did increase within the core, it was not possible to determine if this was consistent for other locations in this region because only one core was obtained from the lake. However, compared to Lakes Erie and Ontario legacy PFASs like PFOA and PFOS were not accumulated in Lake St. Clair. When concentrations in cores are compared to those in Ponar samples from Lake St Clair concentrations are not as great as locations in Lake Erie. Possibly greater water flow through the lake and sediment movement prevents deposition.

3.3. Total fluorine and extractable fluorine

In biomonitoring studies of humans and animals it has been shown that extractable organic fluorine (EOF) represents a significant proportion of the total fluorine in the body. Because the method of extraction employed for sediments studied here was developed and validated for targeted PFAS, EOF represents only those compounds extracted by this method. However, in studies of tissues from humans a significant proportion of EOF is generally accounted for by $\sum$PFASs, with PFOA and PFOS representing significant proportions of the total (Yeung et al., 2006, 2009). In a previous study of cores of sediments from Lake Michigan, total concentrations of fluorine (TF) were several orders of magnitude greater than concentrations of EOF and concentrations of EOF were significantly greater than those of $\sum_{25}$PFAS (Codling et al., 2014).

EOF was measured in cores from two locations (ON17 and ON30) in Lake Ontario and two in Lake Erie (ER09 and ER15; Fig. S5). In biological samples, PFASs represent a significant portion of the total EOF, in this study it was found that EOF was 2-3 orders of magnitude greater than were concentrations of PFAS. In cores of sediments from Lake Ontario, concentrations of EOF decreased from 1900 until 1970s, with the greatest rate of loss in the 1970s followed by some increase to today. For samples in which TF and EOF were both quantified they exhibit similarity of trend but with
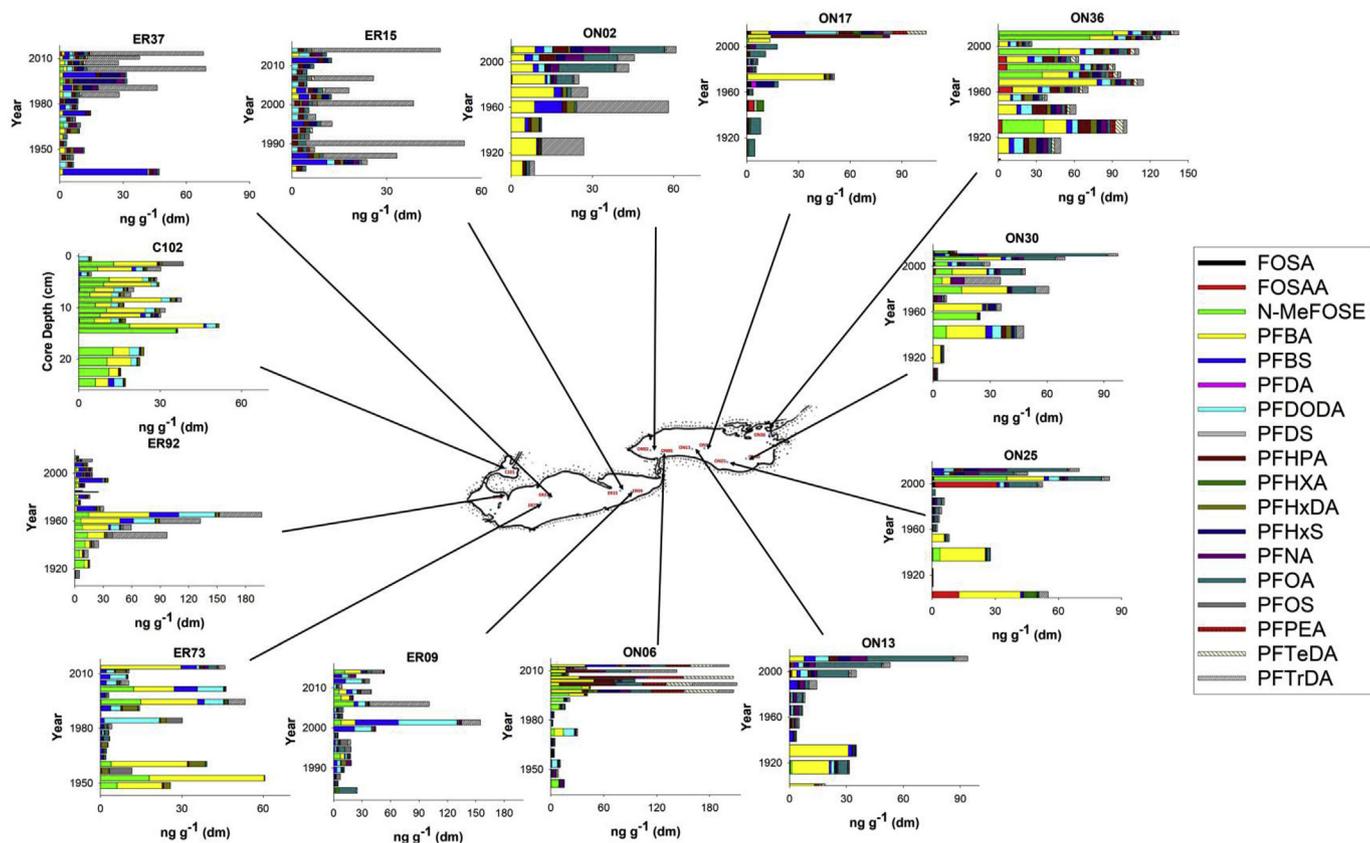
Fig. 3. Concentrations of $\sum$PFASs (ng g^{-1} dm) in cores of sediments from Lakes Erie and Ontario. Samples shown are those from the 1900s or all sample layers where dating was not available (C101). In addition to the total concentration of $\sum$PFASs, relative proportions of individual PFASs are given by colours.

absolute concentrations of EOF approximately half those of TF. For cores from Lake Ontario, where EOF was also measured conflicting results for TF were observed. Location ON25 had a peak of F- in the most recent sediment and ON13 had a significant peak around 1960. Given the short temporal trend represented by cores from Lake Erie, and the amount of natural variation among cores, the significance of that result is difficult to interpret. It is not clear if PFASs and use of fluorine, such as the fluoridation of drinking water, is associated with the increase in TF. Furthermore, EOF might be degraded to TF prior to sampling. However, this trend was not observed in Lake Michigan (Codling et al., 2014).

Concentrations of TF and EOF in surficial sediments collected by Ponar dredge varied among locations (Fig. S6). Although concentrations of EOF were orders of magnitude greater than those of individual PFAS (PFASs in ng g^{-1} dm, while EOF and TF at mg kg^{-1} dm level), the greatest concentration of EOF was observed in sediment from a location in Lake Erie near the city of Cleveland, OH (the largest municipality directly on Lake Erie); and this is consistent with greater concentrations of PFASs measured in that region. Correlations between concentrations of $\sum$PFASs and TF and EOF were not statistically significant for Lakes Erie or Ontario. When TF and EOF in surficial samples from each location are compared, there was no statistically significant correlation between concentrations of TF and EOF (R^2 = 0.4 for both lakes).

Differences in concentrations observed between EOF and $\sum$PFASs and the previous focus on a few legacy PFASs might indicate that other poly- and per-fluorinated compounds should be included in future studies. This is supported by a previous non-target screening study of fishes from the North American Great Lakes, where ~3570 possible C4-C10 fluorinated compounds were

tentitively identifed along with 30 compounds that had not been previously reported (Fakouri et al., 2016).

4. Conclusions

Concentrations of PFASs in sediment of Lakes Erie and Ontario have increased over the last 50 years. This observation is consistent with findings of previous studies. When concentrations of PFASs in Lake St. Clair were compared with concentrations of PFASs in sediments (Marvin et al., 2004) and fishes (McGoldrick and Murphy, 2016) in other Laurentian Great Lakes, it is clear that concentrations of PFASs in Lakes Ontario and Erie were greater than those in the other Great Lakes. Concentrations of surface sediment were dominated by PFBA and PFHxA, indicating that these compounds might not be bound to the solid phase of sediments, but rather represent PFASs associated with the interstitial water. This hypothesis is further substantiated by the finding that concentrations of PFBA in core samples were greater in deeper sediment than would have been predicted based on how much PFBA was being manufactured and used. That said the finding of PFBA and the choice to not exclude pore water from the study gives an interpretation of the conditions in the sediment water interphase and thus the compounds that benthic organisms will be exposed to. Thus, the concentrations observed are those that might enter the Great Lakes food chain.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.02.013.

References

Ahrens, L., Shoeib, M., Del Vento, S., Codling, G., Halsall, C., 2011. Polyfluoroalkyl Compounds in the Canadian Arctic Atmosphere Environmental Chemistry, vol. 8, pp. 399–406. https://doi.org/10.1071/EN10131.

Ahrens, L., Yamashita, N., Yeung, L.W.Y., Taniyasu, S., Horii, Y., Lam, P.K.S., Ebinghaus, R., 2009. Partitioning behavior of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay. Japan Environmental Science & Technology 43, 6969–6975. https://doi.org/10.1021/es901213s.

Bečanová, J., Komprdová, K., Vrana, B., Klánová, J., 2016. Annual dynamics of perfluorinated compounds in sediment: a case study in the Morava River in Zlín district. Czech Republic Chemosphere 151, 225–233. https://doi.org/10.1016/j.chemosphere.2016.02.081.

Cai, M., et al., 2012. Occurrence of Perfluoroalkyl Compounds in Surface Waters from the North Pacific to the Arctic Ocean Environmental Science & Technology, vol. 46, pp. 661–668. https://doi.org/10.1021/es2026278.

Campo, J., Pérez, F., Masiá, A., Picó, Y., Farré, M., Barceló, D., 2015. Perfluoroalkyl Substance Contamination of the Llobregat River Ecosystem (Mediterranean Area, NE Spain) Science of the Total Environment, vols. 503-504, pp. 48–57. https://doi.org/10.1016/j.scitotenv.2014.05.094.

Canada, H., 2016. Perfluorooctane Sulfonate (PFOS) Public Summary. https://www.canada.ca/en/health-canada/services/chemical-substances/fact-sheets/chemicals-glance/perfluorooctane-sulfonate-public-summary.html. Accessed 2017.

Cao, D., et al., 2017. Organophosphate esters in sediment of the. Great Lakes Environ Sci Technol 51, 1441–1449.

Cao, Y., Cao, X., Wang, H., Wan, Y., Wang, S., 2015. Assessment on the distribution and partitioning of perfluorinated compounds in the water and sediment of Nansi Lake. China Environmental Monitoring and Assessment 187, 611. https://doi.org/10.1007/s10661-015-4831-9.

Codling, G., Hosseini, S., Corcoran, M.B., Bonina, S., Lin, T., Li, A., Sturchio, N.C., Rockne, K.J., Ji, K., Peng, H., Giesy, J.P., 2018. Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes-Superior, Huron, and Michigan. Environ. Pollut. (Barking, Essex: 1987) 236, 373–381.

Codling, G., et al., 2014. Historical trends of inorganic and organic fluorine in sediments of Lake. Michigan Chemosphere 114, 203–209. https://doi.org/10.1016/j.chemosphere.2014.03.080.

Custer, T.W., Custer, C.M., Dummer, P.M., Goldberg, D., Franson, J.C., Erickson, R.A., 2016. Organic Contamination in Tree Swallow (Tachycineta Bicolor) Nestlings at United States and Binational Great Lakes Areas of Concern Environmental Toxicology and Chemistry n/a-n/a doi:10.1002/etc.3598.

Fakouri, B.S., Crimmins, B.S., Hopke, P.K., Holsen, T.M., 2016. Comprehensive emerging chemical discovery: novel polyfluorinated compounds in Lake Michigan Trout. Environ. Sci. Technol. 50, 9460–9468. https://doi.org/10.1021/acs.est.6b01349.

Gebbink, W.A., Hebert, C.E., Letcher, R.J., 2009. Perfluorinated carboxylates and sulfonates and precursor compounds in herring gull eggs from colonies spanning the Laurentian. Great Lakes of North America Environmental science & technology 43, 7443–7449.

Gewurtz, S.B., et al., 2013. Perfluoroalkyl acids in the Canadian environment: Multimedia assessment of current status and trends. Environ. Int. 59, 183–200. https://doi.org/10.1016/j.envint.2013.05.008.

Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environmental science & technology 35, 1339–1342.

Giesy, J.P., Kannan, K., 2002. Peer Reviewed: Perfluorochemical Surfactants in the Environment Environmental Science & Technology 36, 146A–152A. https://doi.org/10.1021/es022253t.

Guo, J., 2015. Spatial Distribution and Time Trend of Organic Pollutant Chemicals in the Sediments of Upper Great Lakes. University of Illinois at Chicago.

Guo, J., et al., 2016. Occurrence of atrazine and related compounds in sediments of upper great. Lakes Environ Sci Technol 50, 7335–7343.

Hermanson, M.H., Christensen, E.R., Buser, D.J., Chen, L.-M., 1991. Polychlorinated biphenyls in dated sediment cores from Green Bay and Lake Michigan. J. Great Lake. Res. 17, 94–108.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments†. Environmental Science & Technology 40, 7251–7256. https://doi.org/10.1021/es061000n.

Hornbuckle, K.C., Carlson, D.L., Swackhamer, D.L., Baker, J.E., Eisenreich, S.J., 2006. Polychlorinated biphenyls in the great lakes. In: Persistent Organic Pollutants in the Great Lakes. Springer, pp. 13–70.

Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., Muir, D.C.G., 2006. Biological monitoring of polyfluoroalkyl substances. A review Environmental Science and Technology 40, 3463–3473. https://doi.org/10.1021/es052580b.

Hughes, K.D., Martin, P.A., de Solla, S.R., 2014. Contaminants in overwintering canvasbacks (Aythya valisineria) and resident mallards (Anas platyrhynchos) in the lake St. Clair/St. Clair river area.

Johnson, T.C., 1984. Sedimentation in large lakes. Annual Review of Earth Planet Science Annual Reviews Inc. In: Kannan, K., Ridal, J., Struger, J. (Eds.), (2006) Pesticides in the Great Lakes. in: Persistent Organic Pollutants in the Great Lakes, vol. 12. Springer, pp. 151–199.

Kannan, K., Ridal, J., Struger, J., 2006. Pesticides in the Great Lakes. In: Persistent Organic Pollutants in the Great Lakes. Springer, pp. 151–199.

Lang, J.R., Allred, B.M., Peaslee, G.F., Field, J.A., Barlaz, M.A., 2016. Release of per-and polyfluoroalkyl Substances (PFASs) from carpet and clothing in model anaerobic landfill reactors. Environmental science & technology 50, 5024–5032.

Letcher, R.J., Su, G., Moore, J.N., Williams, L.L., Martin, P.A., de Solla, S.R., Bowerman, W.W., 2015. Perfluorinated sulfonate and carboxylate compounds and precursors in herring gull eggs from across the Laurentian Great Lakes of North America: temporal and recent spatial comparisons and exposure implications. Sci. Total Environ. 538, 468–477.

Li, A., Rockne, K.J., Sturchio, N., Song, W., Ford, J.C., Wei, H., 2009. PCBs in sediments of the Great Lakes–Distribution and trends, homolog and chlorine patterns, and in situ degradation. Environ. Pollut. 157, 141–147.

Marvin, C., Painter, S., Rossmann, R., 2004. Spatial and temporal patterns in mercury contamination in sediments of the Laurentian Great Lakes. Environ. Res. 95, 351–362. https://doi.org/10.1016/j.envres.2003.09.007.

Marvin, C.H., et al., 2002. Surficial sediment contamination in Lakes Erie and Ontario: a comparative analysis. J. Great Lake. Res. 28, 437–450.

McGoldrick, D.J., Murphy, E.W., 2016. Concentration and distribution of contaminants in lake trout and walleye from the Laurentian Great Lakes (2008–2012). Environ. Pollut. 217, 85–96. https://doi.org/10.1016/j.envpol.2015.12.019.

Mittal, M., Rockne, K.J., 2010. Diffusional losses of amended anaerobic electron acceptors in sediment field microcosms. Mar. Pollut. Bull. 60, 1217–1225. https://doi.org/10.1016/j.marpolbul.2010.03.026.

Naile, J.E., et al., 2010. Distributions and bioconcentration characteristics of perfluorinated compounds in environmental samples collected from the west coast of Korea. Chemosphere 90, 387–394. https://doi.org/10.1016/j.chemosphere.2012.07.033.

Oliver, B.G., Bourbonniere, R.A., 1985. Chlorinated contaminants in surficial sediments of lakes Huron, St. Clair, and Erie: implications regarding sources along the St. Clair and Detroit Rivers Journal of Great Lakes Research 11, 366–372. https://doi.org/10.1016/S0380-1330(85)71780-7.

Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environmental Science & Technology 43, 386–392. https://doi.org/10.1021/es802216n.

Peng, H., Wei, Q., Wan, Y., Giesy, J.P., Li, L., Hu, J., 2010. Tissue distribution and maternal transfer of poly- and perfluorinated compounds in Chinese sturgeon (Acipenser sinensis): implications for reproductive risk. Environmental Science & Technology 44, 1868–1874. https://doi.org/10.1021/es903248d.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology 40, 32–44. https://doi.org/10.1021/es0512475.

Robbins, J.A., Edgington, D.N., Kemp, A.L.W., 1978. Comparative 210Pb, 137Cs, and Pollen Geochronologies of Sediments from Lakes Ontario and Erie Quaternary Research, vol 10, pp. 256–278.

Stahl, L.L., Snyder, B.D., Olsen, A.R., Kincaid, T.M., Wathen, J.B., McCarty, H.B., 2014. Perfluorinated Compounds in Fish from U.S. Urban Rivers and the Great Lakes Science of the Total Environment, vol 499, pp. 185–195. https://doi.org/10.1016/j.scitotenv.2014.07.126.

Stock, N.L., Furdui, V.I., Muir, D.C.G., Mabury, S.A., 2007. Perfluoroalkyl contaminants in the canadian Arctic: evidence of atmospheric transport and local contamination. Environmental Science & Technology 41, 3529–3536. https://doi.org/10.1021/es062709x.

UNEP, 2009. SC-4/17: listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride UNEP/POPS/COP.4/17.

USEPA, 2016. PFOA stewardship program United States environmental protection agency, Viana PZ, Yin K, Rockne KJ (2012) field measurements and modeling of ebullition-facilitated flux of heavy metals and polycyclic aromatic hydrocarbons from sediments to the water column. Environmental Science & Technology 46, 12046–12054. https://doi.org/10.1021/es302579e.

Viana, P.Z., Yin, K., Rockne, K.J., 2012. Field measurements and modeling of ebullition-facilitated flux of heavy metals and polycyclic aromatic hydrocarbons from sediments to the water column. Environ. Sci. Technol. 46, 12046—12054. https://doi.org/10.1021/es302579e.

Wang, X., et al., 2014. Accumulation of perfluoroalkyl compounds in Tibetan mountain snow: temporal patterns from 1980 to 2010. Environmental Science & Technology 48, 173—181. https://doi.org/10.1021/es4044775.

Yeung, L.W., et al., 2006. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. Environmental Science & Technology 40, 715—720.

Yeung, L.W., Yamashita, N., Taniyasu, S., Lam, P.K., Sinha, R.K., Borole, D.V., Kannan, K., 2009. A survey of perfluorinated compounds in surface water and biota including dolphins from the Ganges River and in other waterbodies in India. Chemosphere 76, 55—62.

Young, C.J., Furdui, V.I., Franklin, J., Koerner, R.M., Muir, D.C., Mabury, S.A., 2007. Perfluorinated acids in arctic snow: new evidence for atmospheric formation. Environmental science & technology 41, 3455—3461.

Zhang, X., Wania, F., 2012. Modeling the uptake of semivolatile organic compounds by passive air samplers: importance of mass transfer processes within the porous sampling media. Environmental Science & Technology 46, 9563—9570. https://doi.org/10.1021/es302334r.

Zhao, L., Zhu, L., Yang, L., Liu, Z., Zhang, Y., 2012. Distribution and desorption of perfluorinated compounds in fractionated sediments. Chemosphere 88, 1390—1397. https://doi.org/10.1016/j.chemosphere.2012.05.062.

Zushi, Y., Tamada, M., Kanai, Y., Masunaga, S., 2010. Time trends of perfluorinated compounds from the sediment core of Tokyo Bay, Japan (1950s-2004). Environ. Pollut. 158, 756—763. https://doi.org/10.1016/j.envpol.2009.10.012.

Supporting Information

Spatial and temporal trends in poly- and per-fluorinated compounds in the Laurentian Great Lakes Erie, Ontario and St. Clair

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Tables:

Table S1: Location from which samples were collected, giving time and depths of water columns for Lakes Ontario, Erie and St. Clair. The time is given in Eastern Standard Time. PG represent Ponar grab samples and MC represent core samples.

Stations	Sample	Date Time (EDT)	Latitude	Longitude	Depth (m)	Stations	Sample	Date Time (EDT)	Latitude	Longitude	Depth (m)
Lake Ontario						**Lake Erie**					
ON24	PG	7/23/2013 9:30	43.3621	-77.5008	121	ER26	PG	5/27/2014 19:25	41.6729	-82.1004	20
ON25	PG, MC	7/23/2013 10:55	43.4180	-77.3762	200	ER06	PG	5/27/2014 20:45	41.4762	-82.1842	7.15
ON22	PG	7/23/2013 13:00	43.6093	-77.3759	149	ER23	PG	5/27/2014 22:23	41.5746	-82.5184	13.9
ON21	PG	7/23/2013 14:30	43.5414	-77.6859	173	ER98	PG	5/28/2014 0:18	41.5833	-82.9163	7.54
ON19	PG	7/23/2013 15:32	43.3993	-77.8194	73	ER58	PG	5/28/2014 0:57	41.6847	-82.9335	9.83
ON17	PG, MC	7/23/2013 17:30	43.5902	-78.0111	183	ER59	PG	5/28/2014 2:00	41.7269	-83.1494	8.43
ON15	PG	7/23/2013 19:35	43.5598	-78.1656	186	ER20	PG	5/28/2014 2:43	41.7604	-83.3065	6.69
ON13	PG, MC	7/23/2013 21:10	43.5414	-78.3143	181	ER04	PG	5/28/2014 3:27	41.7019	-83.4488	10.3
ON12	PG	7/23/2013 21:10	43.4306	-78.4144	86	ER05	PG	5/28/2014 5:10	41.8915	-83.3074	5.62
ON10	PG	7/23/2013 23:35	43.4856	-78.6554	155	ER60	PG	5/28/2014 5:52	41.8922	-83.1959	8.76
ON08	PG	7/24/2013 1:00	43.3575	-78.9396	79	ER21	PG	5/28/2014 6:40	41.9783	-83.1879	5.9
ON06	PG, MC	7/24/2013 2:10	43.3360	-79.0700	69	ER61	PG	5/28/2014 7:40	41.9466	-83.0454	9.49
ON04	PG	7/24/2013 4:05	43.2478	-79.4188		ER22	PG	5/28/2014 8:45	41.8210	-83.0769	10.1
ON01	PG	7/24/2013 5:30	43.3039	-79.7340	25	ER91	PG	5/28/2014 9:30	41.8418	-82.9163	10.8
ON03	PG	7/24/2013 7:30	43.5829	-79.4167	52	ER92	PG, MC	5/28/2014 11:10:00	41.9506	-82.6867	11.6
ON02	PG, MC	7/24/2013 9:15	43.3713	-79.3533	101	ER25	PG	5/28/2014 13:46	41.8760	-82.3292	16.9
ON05	PG	7/24/2013 11:10	43.5166	-79.0803	136	ER42	PG	5/28/2014 15:11	41.9654	-82.0410	23.3
ON07	PG	7/24/2013 12:00	43.6486	-79.0407	114	ER43	PG	5/28/2014 16:30	41.7885	-81.9461	23.2
ON09	PG	7/24/2013 13:05	43.5975	-78.8016	137	ER73	PG, MC	5/28/2014 6:05:00	41.9778	-81.7571	25.3
ON11	PG	7/24/2013 14:40	43.7587	-78.5158	84	ER36	PG	5/28/2014 20:18	41.9353	-81.4779	24.3
ON14	PG	7/24/2013 16:00	43.8342	-78.2063	82	ER37	PG, MC	5/28/2014 9:40:00	42.1097	-81.5748	25.2
ON16	PG	7/24/2013 17:05	43.7172	-78.0267	128	ER38	PG	5/28/2014 23:22	42.2820	-81.6717	23
ON18	PG	7/24/2013 18:00	43.6819	-77.8487	146	ER30	PG	5/29/2014 1:31	42.4298	-81.2055	21.9
ON20	PG	7/24/2013 19:21	43.8722	-77.7130	52	ER31	PG	5/29/2014 2:40	42.2536	-81.1075	23
ON23	PG	7/24/2013 20:30	43.7938	-77.4648	57	ER81	PG	5/29/2014 4:50	42.3542	-80.8079	21.8
ON27	PG	7/24/2013 22:20	43.7312	-77.0169	88	ER82	PG	5/29/2014 7:05	42.4648	-80.3604	19.5
ON34	PG	7/25/2013 0:30	43.8958	-76.5487	56	ER15	PG, MC	5/29/2014 9:10:00	42.5171	-79.8930	65
ON35	PG	7/25/2013 1:15	43.9926	-76.4901	49	ER93	PG	5/29/2014 11:52	42.6164	-80.0002	43
ON36	PG, MC	7/25/2013 2:20	44.0780	-76.4125	26	ER10	PG	5/29/2014 13:11	42.6803	-79.6922	34
ON31	PG	7/25/2013 4:30	43.7474	-76.6018	80	ER83	PG	5/29/2014 14:10	42.8236	-79.5808	16.7
ON37	PG	7/25/2013 6:02	43.5832	-76.3334	46	ER85	PG	5/29/2014 15:31	42.8499	-79.2503	16
ON33	PG	7/25/2013 7:05	43.5982	-76.5484	156	ER86	PG	5/29/2014 17:03	42.8787	-78.9037	6.96
ON32	PG	7/25/2013 7:47	43.4921	-76.5820	61	ER84	PG	5/29/2014 19:16	42.7052	-79.2665	23.2
ON28	PG	7/25/2013 8:32	43.5638	-76.7081	208	ER09	PG, MC	5/29/2014 9:37:00	42.5387	-79.6163	51
ON30	PG, MC	7/25/2013 11:50	43.5429	-76.9066	220	ER99	PG	5/29/2014 22:54	42.4170	-79.5834	33
ON29	PG	7/25/2013 14:14	43.3952	-76.8645	73	ER63	PG	5/30/2014 0:01	42.4173	-79.7991	49
ON26	PG	7/25/2013 15:10	43.4583	-77.0697	230	ER03	PG	5/30/2014 1:54	42.1357	-80.1106	7.57
Lake St. Clair						ER95	PG	5/30/2014 5:25	42.0000	-80.6666	17.5
C-102	PG, MC	9/25/2014 13:17	42.43802	82.76418	5.2	ER07	PG	5/30/2014 6:22	41.9126	-80.7964	8.24
C-101	PG	9/27/2014 9:00	42.42932	82.66676	6.4	ER32	PG	5/30/2014 7:42	42.0817	-81.0113	23.4
C-086	PG	9/27/2014 17:45	42.40212	82.85213	5.4	ER78	PG, MC	5/30/2014 8:43:00	42.1168	-81.2501	24
C-093	PG	9/28/2014 8:46	42.34930	82.63938	5.6	ER29	PG	5/30/2014 11:08	41.8237	-81.3076	19.1
C-104	PG	9/28/2014 10:25	42.32860	82.54491	3.2	ER28	PG	5/30/2014 12:22	41.8061	-81.6075	23.1
C-105	PG	9/28/2014 15:56	42.49310	82.69196	5.5	ER27	PG	5/30/2014 13:22	41.6756	-81.7518	21.1
C-090	PG	9/30/2014 16:35	42.62801	82.78120	2.9	ER02	PG	5/30/2014 14:25	41.5091	-81.7135	7.51
C-087	PG	9/30/2014 17:35	42.57870	82.72063	1.7						
C-002	PG	10/1/2014 17:00	42.70337	82.48347	1.4						
C-091	PG	10/2/2014 14:40	42.55996	82.82099	3.9						

Name	Carbon Number	Abbreviation	Molecular Formula	Molecular Weight	Ions (Mz)
Table S2: Perfluorinated acids measured in this study and ESI(−)–MS/MS ions monitored					
Perfluoro-n-alkyl					
Perfluoro-n-butanoic acid	C4	PFBA	$C_4HF_7O_2$	214.0396	213.0/168.9
Perfluoro-n-pentanoic acid	C5	PFPeA	$C_5HF_9O_2$	264.0474	262.8/218.9
Perfluoro-n-hexanoic acid	C6	PFHxA	$C_6HF_{11}O_2$	314.0552	312.934/268.8
Perfluoro-n-heptanoic acid	C7	PFHpA	$C_7HF_{13}O_2$	364.0630	362.950/318.9
Perfluoro-n-octanoic acid	C8	PFOA	$C8HF15O2$	414.0708	412.987/368.9
Perfluoro-n-nonanoic acid	C9	PFNA	$C_9HF_{17}O_2$	464.0786	462.908/418.9
Perfluoro-n-decanoic acid	C10	PFDA	$C_{10}HF_{19}O_2$	514.0864	512.876/469.0
Perfluoro-n-undecanoic acid	C11	PFUdA	$C_{11}HF_{21}O_2$	564.0942	562.865/519.0
Perfluoro-n-tridecanoic acid	C13	PFTrDA	$C_{13}HF_{25}O_2$	664.1098	663.094/618.9
Perfluoro-n-tetradecanoic acid	C14	PFTeDA	$C_{14}HF_{27}O_2$	714.1176	713.036/669.0
Perfluoro-n-hexadecanoic acid	C16	PFHxDA	$C_{16}HF_{31}O_2$	814.1332	812.840/769.1
Potassium Perfluoro-1-butanesulfonate	C4	PFBS	$C_4F_9SO_3K$	338.1901	298.877/ 79.8
Sodium Perfluoro-1-hexanesulfonate	C6	PFHxS	$C_6F_{13}SO_3Na$	422.0972	398.894/ 79.8
Sodium Perfluoro-1-octanesulfonate	C8	PFOS	$C_8F_{17}SO_3Na$	522.1129	498.971/ 79.7
Sodium Perfluoro-1-decanesulfonate	C10	PFDS	$C_{10}F_{21}SO_3Na$	622.1285	598.896/ 79.5
Perfluoro-n-Sulfonates					
Perfluoro-1-octanesulfonamide	C8	FOSA	$C_8H_2F_{17}NO_2S$	499.15	497.896/ 77.9
2-N-ethylperfluoro-1-octanesulfonamido-ethanol	C12	EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	571.25	630.109/ 58.8
2-N-methylperfluoro-1-octanesulfonamido – ethanol	C11	MeFOSE	$C_{11}H_8F_{17}NO_3S$	557.23	616.004/ 58.9
Perfluoro-1-octanesulfonamide	C8	FOSA	$C_8H_2F_{17}NO_2S$	499.15	497.8/77.8
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	525.8/168.8
N-ethylperfluoro-1-octanesulfonamidoacetic acid	C12	EtFOSAA	$C_{12}H_8F_{17}NO_4S$	585.24	583.9/418.7
Mass Labelled Recovery Standards					
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	502.899/ 79.5
perfluoro-n-[1,2,3,4-$^{13}C_4$] butanoic acid	C4	PFBA [M+4]	$^{13}C_4HF_7O_2$	218.0090	216.8/171.8
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	416.9/371.9
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	467.8/422.9
perfluoro-n-[1,2-$^{13}C_2$] decanoic acid	C10	PFDA [M+2]	$^{13}C_2^{12}C_8HF_{19}O_2$	516.0711	514.9/469.9
perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid	C11	PFUDA [M+2]	$^{13}C_2^{12}C_9HF_{21}O_2$	566.0789	564.959/ 519.8
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	614.913/ 569.9

Table S3: Concentrations of PFASs (ng g^{-1} dm) in Lake Ontario, Erie and St. Clair surface sediment.

	PFOS	PFOA	PFPEA	PFHXA	PFHPA	PFNA	PFDA	PFUdA	PFDoA	PFBS	PFHxS	PFBA	PFDS	PFTrDA	PFTeDA	PFHxDA	FOSAA	NMeFOSAA	NeTFOSAA	FOSA	Sum
Limit of Detection (LOD)																					
Ontario	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	
Erie																					
St. Clair	0.1	0.1	0.4	0.0	0.0	0.1	0.1	0.0	0.0	0.6	0.0	0.7	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.1	
Lake Ontario																					
OH14		1.2		2.8						1.2	0.3	13.1									18.6
ON01	1.4	0.4		0.7			1.0			1.5		15.5		0.4							20.9
ON02	0.2		0.1	0.8	0.1		0.3			2.3		20.4									24.2
ON03	1.5			0.2			0.9	0.4				0.2					0.2			0.2	3.6
ON03	0.6	0.2		0.3									0.6	0.3	0.2	0.3	0.0			0.2	2.6
ON04	0.1	0.1		1.9							0.2	4.6									7.4
ON05	0.3	0.1		1.2	0.1		1.5	1.4		3.2	1.9										9.8
ON06	0.4			0.7	0.1			1.1		10.7	4.1	0.9	11.4	0.1							29.5
ON07	0.8	0.3		0.5		0.2		2.6			0.2	5.5									10.0
ON08	1.1	0.5		0.2			1.0					36.6							<LOQ		39.4
ON09	0.4			1.4	0.1		4.0			2.0		0.9									8.8
ON101	0.9	0.2		0.3		0.2	0.2	1.4		0.3		15.3		0.3							18.9
ON11	1.7	0.3	0.1	2.3	0.5		0.7	6.9	11.8	0.3		2.9				1.7	4.3	3.9			37.4
ON12	0.1						1.5	0.8		42.2		20.5									65.1
ON13	2.8			0.3																	3.1
ON14	13.2	1.4	5.2	2.7	6.8		10.4			2.0	0.4	41.0	3.7				2.0				88.7
ON15	0.6			0.3	0.1		2.6				0.7										4.2
ON16	2.2		<LOQ	1.1			21.2			1.0		30.2									55.7
ON17	0.4	0.1		0.3			2.0						6.0								8.7
ON18	1.4			0.4			0.2	0.1	0.3											0.3	2.7
ON19	4.0		0.1	1.0	0.1		10.2			6.4	3.3	0.4									25.5
ON20		0.5	1.1	0.7																	2.3
ON21	4.2	0.8		0.6	0.3			0.5		1.0	0.4	20.4	1.7				0.8				30.6
ON22	0.6	0.1		0.2			1.2	0.2				3.2		0.1			0.1		<LOQ		5.8
ON23	0.1	1.1		4.2	0.1					0.4	0.1	1.8									7.8
ON24	0.5			0.7	0.1		1.7			11.5	2.5		10.3							3.1	30.3
ON25	0.5	0.1		1.1	0.1	0.4	0.7	1.4		18.7	5.2									9.3	37.6
ON26	2.2	0.4		0.3																0.2	3.1
ON27	3.0			0.3				0.0					0.6				0.2	0.3	0.7	0.3	5.5
ON28	1.7			0.3			0.4	0.0				15.4					0.1			0.2	18.1
ON29				3.0				2.9				8.1									14.0
ON30	0.3	0.0		0.6						13.6	4.2								4.7	<LOQ	23.5
ON31	1.1	0.3		0.2		0.2	0.3	0.5				15.3	1.3	0.1	0.1		0.0				19.4
ON31	0.3	0.3		0.4		0.2	0.5	1.1	<LOQ			11.6	2.0	0.4	0.2	<LOQ					17.0
ON32	5.8	0.3		0.7					1.0	4.5	0.2	14.5	2.5			0.5	3.5			0.4	33.9
ON33	2.0			0.2			0.0													0.2	2.4
ON34	0.9			0.3	0.1		0.5	0.2									0.1				2.1
ON35	6.4	0.6		0.2		0.4	0.6	0.1					3.2	0.4	0.2	0.3	0.3		1.3	0.7	14.7
ON36	0.7			0.2			0.3	0.3						0.1					<LOQ		1.7
ON36	2.9	0.4		0.3		0.3	0.3				0.2		1.0	0.3	0.2		0.1		0.1	0.2	6.3
ON37				1.2								10.4	3.6								15.2
ON92	1.5	0.3		0.3			0.2					20.2	0.4	0.3	0.2	0.3				0.2	23.9
Lake St. Clair																					
LHL02	0.2			0.2			3.6	9.0			1.3	48.9		0.2	0.2						63.7
LHL101	0.4			0.3	0.1						2.2	14.7	0.3	0.2		0.3				0.2	18.6
LHL102	1.0			1.2			1.4			19.3	0.2	3.1									26.2
LHL104	0.9	0.3		0.3		0.2	0.3				0.4	44.5		0.3	0.2					0.2	47.5
LHL105	0.4			0.3		0.2					1.2	25.1	0.6	0.2							28.0
LHL86	0.3	0.5		0.1	0.1	0.2	0.8				1.1			0.3	0.3				0.0	0.3	4.0
LHL86	0.3			0.3	0.1						1.1										1.8
LHL87			1.5	0.3			1.1	0.3		0.2		13.7		0.3							17.4
LHL90		0.3		0.1							0.3				0.3						1.0
LHL90	0.3	0.5		0.1		0.2	1.4		0.1	0.1				0.3	0.3	0.3					3.5
LHL91	0.9			0.1	0.0		3.2						1.0	0.3	0.4	0.2				0.3	6.4
LHL91	0.7			0.8			2.3	3.3	0.0					0.3	0.4	0.0				0.3	8.1
LHL93	0.9	0.3		0.3		0.2	0.2				0.2			0.3	0.2					0.2	2.7
LHL95	0.3		0.8	0.1		0.2			0.0		0.3				0.3	0.1	0.3				2.4
LHL95	0.6	0.6		0.2			1.1				1.1			0.3							3.8
LHL95	0.1		0.8	0.5			1.8	10.7	<LOQ								0.1				14.0
Lake Erie																					
ER10			3.3	0.2		0.4	0.6	0.0			0.6			0.3							5.5
ER10	3.4		2.8	0.1		0.3		0.7	0.0		0.5			0.3			0.3			0.4	8.8
ER02	1.3	0.5		0.1	0.4						0.1		0.8	0.3	0.4					0.3	4.2
ER02	1.4	1.5		0.1	0.3				0.0		0.4		0.8		0.3	0.0	0.2			0.3	5.4
ER03	0.4	1.0					0.2	0.0			1.7	1.7					0.2		0.0	0.3	5.7
ER03	0.6	0.5		0.3							0.2		0.7	0.4	0.3	0.3	0.0		<LOQ	0.2	3.5
ER03		1.7		0.4						8.2	2.7										13.0
ER04	1.9	0.4		0.4		0.2	0.7	0.2			0.2	31.7	1.5						0.3	0.2	37.6
ER05				1.3	0.1						0.4	9.3									11.1
ER06	0.9			0.3	0.2		0.2			10.8	0.3	28.0	0.3	0.3	0.2	0.3				0.2	41.9
ER07	1.0	0.6		0.2	0.1	0.2	1.5	1.0			0.1		0.6	0.3			0.2			0.3	6.3
ER07	1.3	0.3		0.2	0.1		1.6		0.0		0.3				0.3	0.0				0.3	4.5
ER09	3.1	0.9		0.2		0.3	0.7	0.3	0.0		0.4		1.2	0.3			0.2			0.3	8.0
ER15	2.1	0.3		0.3		0.2	0.4				0.2	24.3	0.6	0.3			0.1			0.2	28.8
ER18	3.0	1.3	3.4	0.2		0.6	2.5	0.8			1.4			0.4	0.3	0.0	0.2			0.3	14.5
ER18	4.0			0.5		1.0	1.3	0.7	0.0		0.4		1.3	0.4	0.4	0.0				0.3	10.4
ER20	1.1			0.6			0.3				0.2	56.3									58.5
ER21	0.5			0.3		0.2	0.1				0.2	13.3	1.3	0.2	0.2				<LOQ	0.2	16.5
ER22		0.8		0.3		0.5		0.7			1.4		0.6	0.3	0.3						4.9
ER23	1.2	0.3		0.3		0.2	0.2					33.5	0.6	0.3		0.3	0.0		<LOQ	0.2	37.1
ER25	2.8	0.3		0.4			0.3					27.8									31.6
ER26	2.2	0.5		0.3		0.3	1.1		0.3	0.2		39.1	0.8	0.4	0.2		0.1		0.1	0.2	45.8
ER27	1.9			0.4							0.3	8.3									10.9
ER28	2.5	0.4		0.3		0.4	0.5	0.1			0.3		0.7	0.3	0.2		0.1			0.2	6.0
ER29	1.5	0.3		0.3			0.2					16.2	0.9	0.3	0.2		0.1	0.0	<LOQ	0.2	20.2
ER30	2.1	0.3		0.3		0.2	0.2				0.2	20.6	0.4	0.3	0.2	0.3				0.2	25.4
ER31	2.2	0.3		0.3		0.2	0.3		0.3		0.3	16.9	0.4	0.3	0.2	0.3	0.1	0.1	<LOQ	0.2	22.3
ER32	1.8	0.7		0.2		0.2	0.4	0.4	0.0		0.6		0.6	0.3			0.2		0.0	0.3	5.9
ER37	1.9	0.7		0.3			0.3	0.0					1.7	0.3	0.2				0.0	0.3	5.7
ER38	3.2	0.5		0.2		0.3	8.2				0.3	52.0		0.7	0.3						64.8
ER42		0.8	2.2	0.2		0.3	1.3	0.7			0.3		0.7	0.3							6.8
ER43	1.5	0.4		0.3		0.3	0.2				0.3		0.3			0.3			<LOQ	0.2	3.7
ER58	1.5	1.2		0.3			0.4				1.2		0.5	0.4						0.3	5.8
ER58	1.3			0.1	0.8				0.0		0.6			0.3	0.3	0.0				0.3	3.8
ER59	2.1	1.0		0.2			0.5				0.5		0.9	0.3	0.3			0.2			6.0
ER59	1.8	0.6		0.3		0.5	0.4		0.0		0.6		0.6	0.4	0.3					0.3	5.9
ER60	0.3			0.6				0.4				49.7								0.2	51.3
ER61	0.7			0.4				0.5			0.2	44.8	0.3	0.3							47.2

ER63	1.2	0.3		0.2		0.2	0.2					22.4	0.2	0.3	0.2					0.2	25.4
ER73	2.0	0.3		0.2		0.3	0.3	0.0	0.3		0.3		1.3	0.4	0.2	0.3	0.1		<LOQ	0.2	6.2
ER78	1.0	0.3		0.4				2.1			0.2	19.7		0.3			0.2				23.7
ER84	0.7	0.4		0.2			0.5				0.1			0.3			0.2				2.4
ER84	0.6	0.3	2.0	0.5		0.2	0.6		0.0	4.9	0.7	9.0				0.0					18.8
ER91	1.8			0.9			0.8	5.2			0.4	21.4									30.4
ER93	1.7	0.3		0.3		0.2	0.2					10.2	0.4	0.3	0.2		0.1		<LOQ	0.2	14.0
ER95	0.2	0.4	1.0	0.2		0.2				12.3	0.1			0.3						0.3	14.7
ER98	2.6	1.2	2.7	0.1		0.4	0.5		0.0		0.5			0.3						0.3	8.6
ER98	1.5	1.2		0.5	0.0	0.4			0.0		0.8			0.3	0.3					0.3	5.3
ER99	1.2	0.3		0.3		0.3	1.0		0.3	20.0		21.5	0.2	0.3	0.2	0.3	0.1	0.3		0.2	46.5

Figures:

Figure S1: Temporal trends of individual, ionic PFASs identified in 12 sediment cores in Lakes Ontario, St. Clair and Erie from 1800 to 2014..
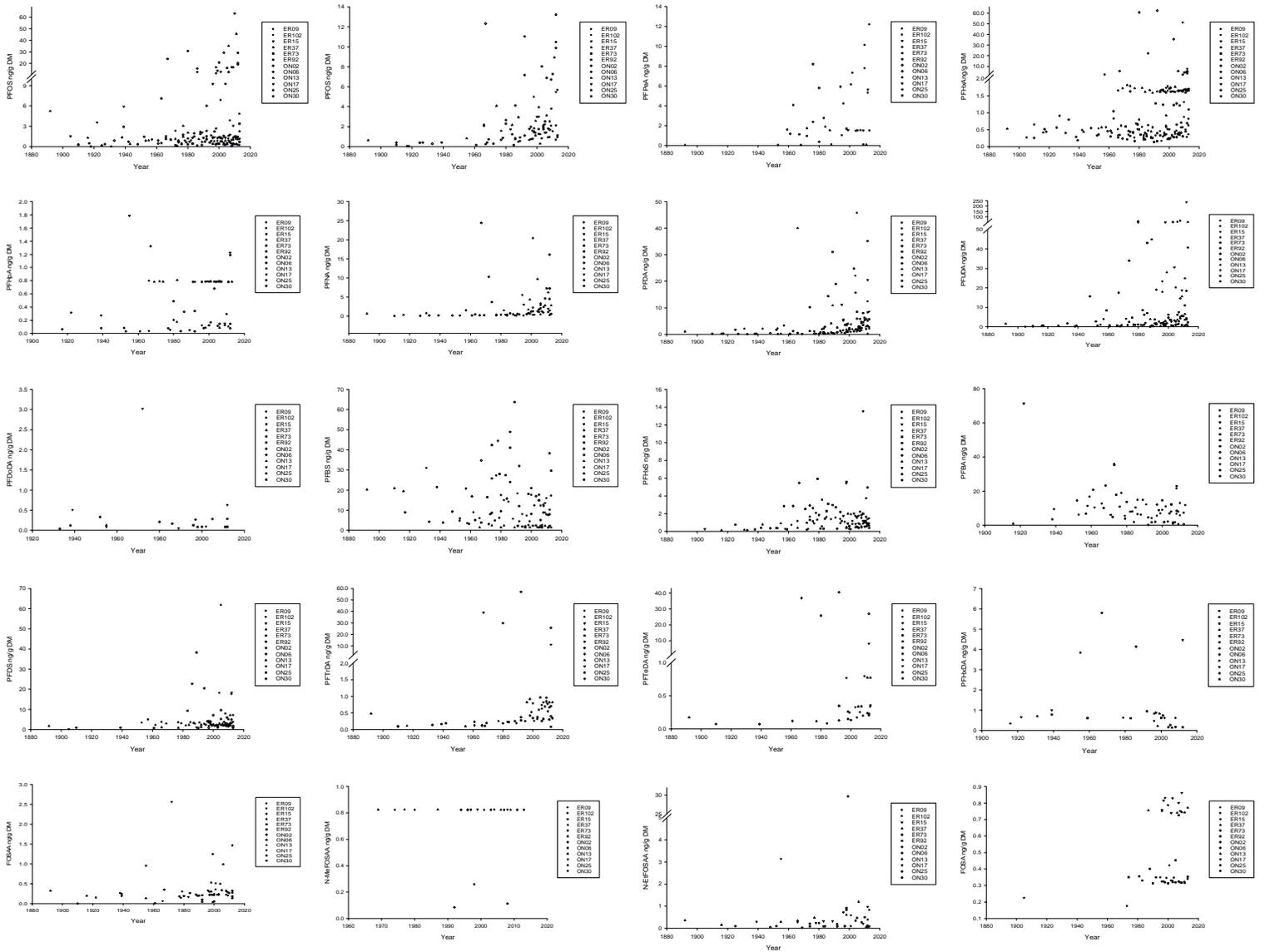
Figure S2: Temporal trends for $\sum_{20}$PFASs identified in sediment cores.
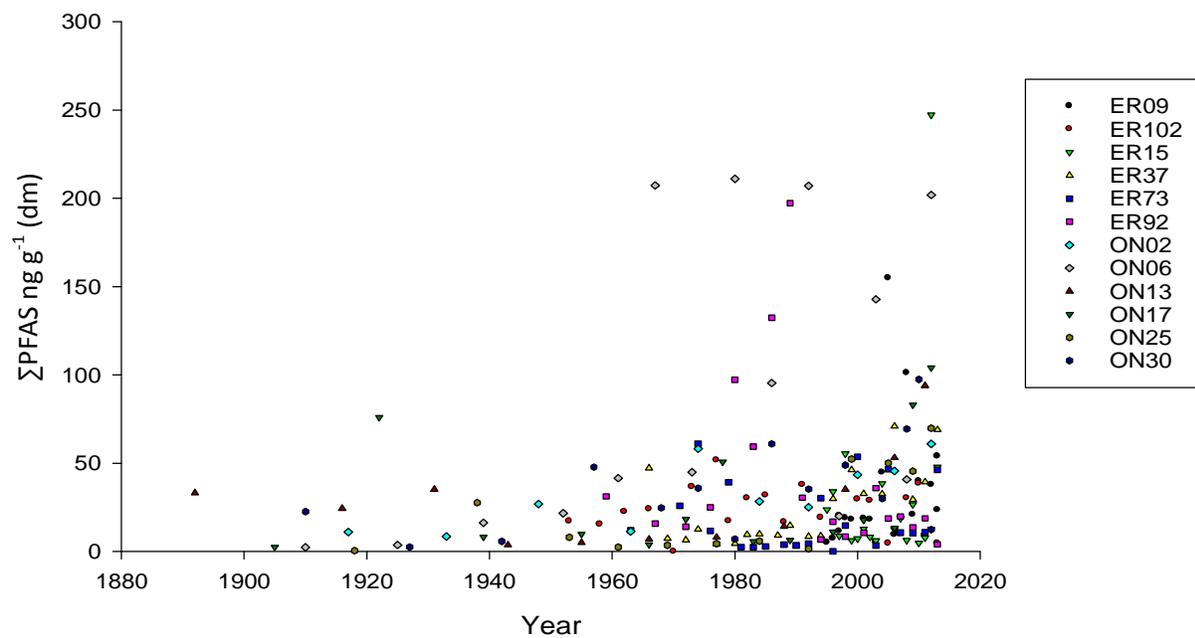
Figure S3: Concentrations (mg g^{-1} dm) of organic matter (OM) total nitrogen (TN) and black carbon (BC) in sediment cores from Lakes Erie (A-OM, B-TN, C-BC) and Ontario (D-OM, E-TN, F-BC).
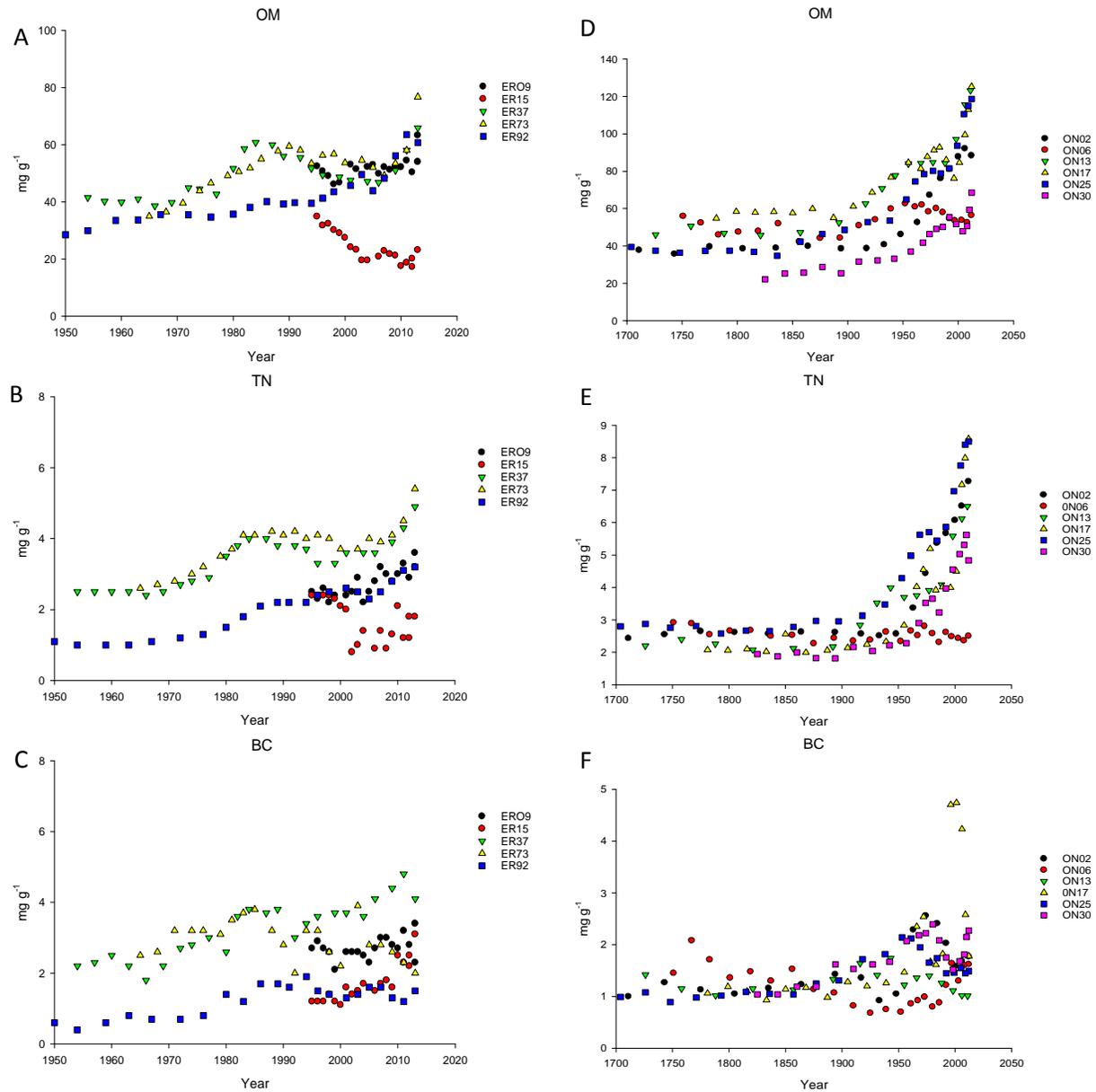
Figure S4: Extractable organic fluorine (EOF) in mg g^{-1} dm of sediment in Lake Ontario (A) and Lake Erie (B) for two core sample sets in each Lake (ON30 and ON17 and ER09 and ER15) and the total fluorine mg g^{-1} dm (TF) in Lake Ontario (C) and Lake Erie (D) for four core sample sets on lake Ontario (ON30, ON17, ON13 and ON25) and two Lake Erie sites (ER09 and ER15).
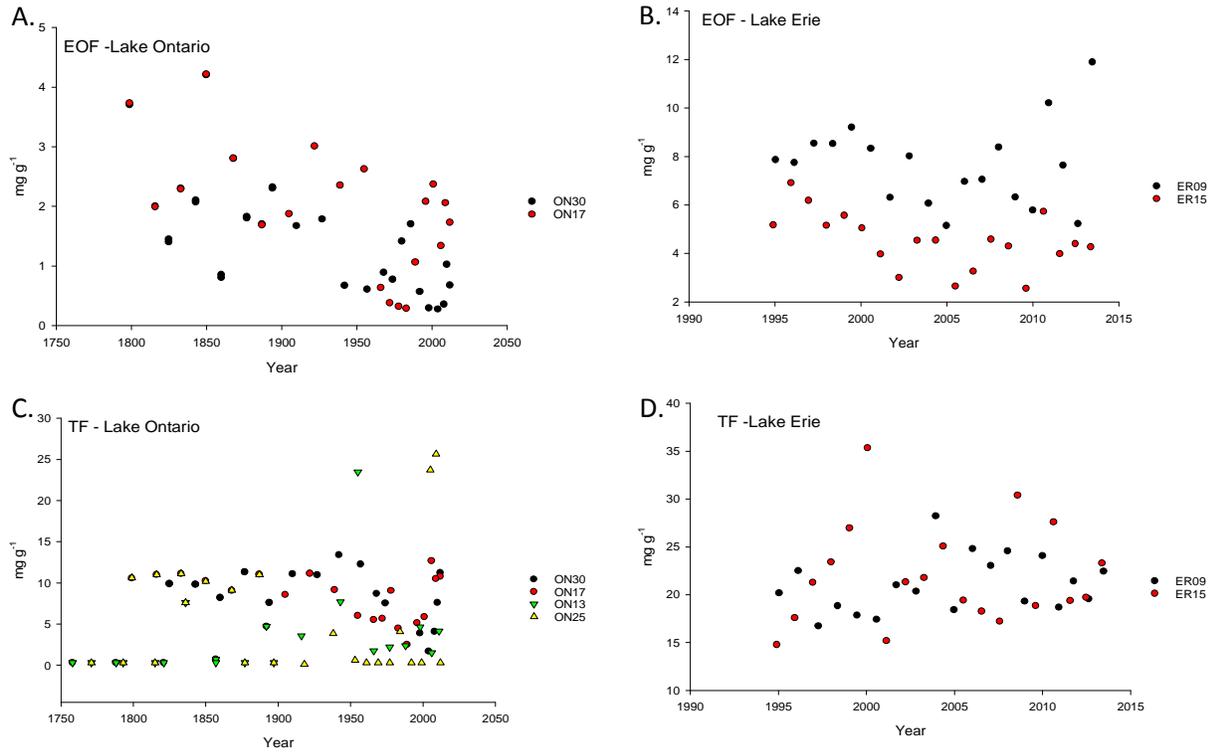
SI Figure 5: The total (n=6) and extractable (n=3) fluorine from core samples of Lake Erie and Lake Ontario.
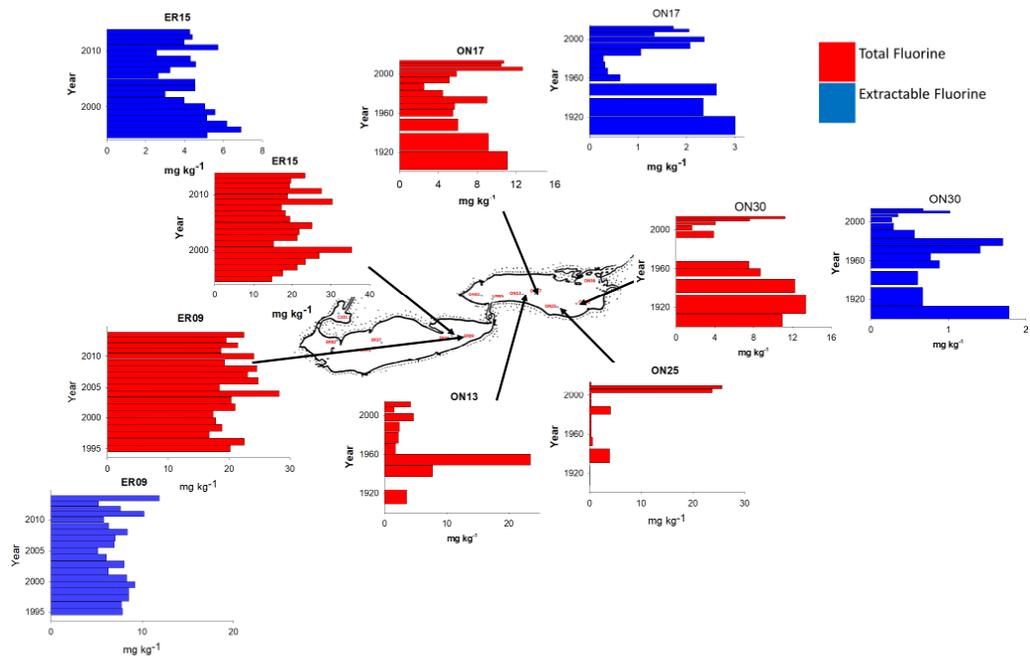
Figure S6: Extractable organic fluorine (EOF; A) in surficial sediments collected from Lakes Ontario (2013) and Erie (2014) by use of a Ponar grab sampler, and total concentration of fluorine (TF; B) each circle represents a single sample location.