

**Application of a Comprehensive Extraction Technique for the Determination of Poly- and Perfluoroalkyl Substances (PFASs) in Great Lakes Region Sediments**

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**Abstract**

A comprehensive method to extract perfluoroalkane sulfonic acids (PFASs), perfluoroalkyl carboxylic acids (PFCAs), polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluoroalkyl phosphinic acids (PFPIAs) and perfluoroalkyl phosphonic acids (PFPAAs) from sediment and analysis by liquid chromatography tandem mass spectrometry (LC-MS/MS) was developed and applied to sediment cores from three small isolated lakes (Plastic Lake, Lake 442, Lake Tettegouche) and Lake Ontario in

the Great Lakes Region. Recoveries of the target compounds using the optimized acetonitrile/sodium hydroxide extraction ranged from 73 % to 120 %. The greatest concentrations of per- and polyfluorinated alkyl substances (PFASs) were recorded in sediment from Lake Ontario ( $\Sigma$ PFASs 13.1 ng/g), where perfluorooctane sulfonic acid (PFOS) contributed over 80% of the total. Concentrations in Lake Ontario were approximately 1 to 2 orders of magnitude greater than the more remote lakes subject to primarily atmospheric inputs. Whilst the PFAS contribution in Lake Ontario was dominated by PFOS, the more remote lakes contained sediment with higher proportions of PFCAs. Trace amounts of emerging PFASs (diPAPs and PFPiAs) were found in very recent surface Lake Ontario and remote lake sediments.

#### **Key words**

PFASs, PFCAs, diPAPs, PFPiAs, PFPAs, sediment

### **1. Introduction**

Poly- and perfluorinated alkyl substances (PFASs) have been produced and used in various industries and consumer products for over fifty years because of their water and oil repellency, thermal stability, and surfactant properties that make them extremely useful. Since the first report on the worldwide contamination by PFASs (Giesy and Kannan, 2001), they have been detected in humans, air, sediment, sludge, fish, and wildlife all over the globe, including the Arctic (Giesy and Kannan, 2001; Dietz et al. 2008; Kelly et al. 2009; Lau et al. 2007; Zushi et al. 2010).

Perfluoroalkane sulfonic acids (PFSA)s and perfluoroalkyl carboxylic acids (PFCAs) are two classes of PFASs that have been the focus of environmental research, monitoring, and regulatory efforts due to their occurrence, persistence and potential toxicity. Several studies have shown that some PFASs can be classified as multisystem toxicants as well as developmental toxicants (DeWitt. 2015). PFOA and PFOS may be carcinogenic at relatively high doses (Lau et al. 2007), and repeated oral exposures may exert toxic effects including impacts on the liver, gastrointestinal and thyroid hormone. Developmental effects have also been reported in the offspring of animals exposed to PFOS or PFOA (Lau et al. 2007). One of the few toxicity studies on polyfluoroalkyl phosphoric acid diesters (diPAPs) showed that 8:2 diPAP can inhibit male sex hormone synthesis (Rosenmai et al. 2013). Considering the persistence and potential toxicity of PFASs, 3M, the dominant producer of perfluorooctane sulfonyl fluoride (POSF) based products, including PFOS, phased out production between 2000 and 2002 (3M, 2000). Further measures have been taken by industry following the designation of PFOS and POSF to the Stockholm Convention in 2009. More recently in 2006 eight major fluoropolymer and fluorotelomer manufacturers participated in a global PFOA Stewardship program to achieve a 95% reduction of PFOA by 2010, together with precursor chemicals and to have complete elimination of these chemicals in emission and products by 2015 (US EPA, 2006). As a result of the phase out of POSF-based products and PFOA, concentrations of PFASs in the environment were expected to decline (Holmstrom et al 2005; Kannan et al. 2006; Butt et al. 2007; Young et al. 2007; Hart et al. 2009; Hart et al. 2008; Olsen et

al. 2008). It is important to note that there is currently no global phase-out of PFOA, if a phase-out in production does occur there will be a lag time in the use and disposal phase. This may explain why some higher homologue chemicals (e.g., perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA)) have actually showed an increase in environmental concentrations (Loi et al. 2013).

Although most of the focus of PFASs research has been on perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), two emerging groups of fluorinated phosphate surfactants, perfluoroalkyl phosphonic acids (PFPAs) and perfluoroalkyl phosphinic acids (PFPIAs) have recently attracted the attention of a number of researchers (D'eon et al. 2009a; D'eon et al. 2009b; Esparza et al. 2011; Guo et al. 2012; Loi et al. 2013; Trier et al. 2011; Yeung and Mabury. 2016). PFPAs and PFPIAs are commonly used as levelling and wetting agents in waxes and coatings, and as foam-dampening agents in the textile industry, pharmaceutical industry and metal industry (Mason Chemical Co, 2012; Begley et al. 2008). They were also historically incorporated as inert ingredients in United States pesticide formulations until 2008 (Lee. 2013). PFPAs and PFPIAs have now been detected in a variety of different environmental media. For example PFPAs were detected in Canadian surface water and wastewater treatment plant effluents with concentrations ranging from 0.026 to 3.4 ng/L in surface water and 0.33 to 6.5 ng/L in wastewater (D'eon et al. 2009), Perfluorooctyl phosphonic acid (C8-PFPA) was reported at a concentration of 1 ng/L in Dutch surface waters (Esparza et al. 2011), and two PFPIAs congeners (C6/C6 and C6/C8) were detected in over 50% of U.S. human sera donors with the

mean concentrations ranging from 4 to 38 ng/L (Lee and Mabury, 2011). PFPAs (C6, C8) and PFPiAs (C6/C6, C6/C8, C8/C8) have also been detected in German and Chinese human sera (Yeung and Mabury, 2016). PFPiAs were identified in Ontario lake trout at concentrations 1-2 orders of magnitude lower than PFCAs and PFSAAs (Guo et al. 2012). A review on the comparative assessment of the environmental hazards and exposure to PFPAs and PFPiAs was undertaken by Wang et al. (2016), who noted that although risks from individual PFPAs/PFPiAs are currently low, their ongoing production and use and high persistence will lead to increasing exposure and risks over time.

Another class of fluorinated phosphate surfactants attracting attention are diPAPs. They have been used as wetting and levelling agents (Begley et al. 2008); however, their primary use is in food-contact paper products, even though they have been found to leach from the packaging into food (Begley et al. 2005). The diPAPs have also been used in many other products, like cosmetics, shampoo, conditioner, penetrating sealer, floor finishing, and paints (Klepeis et al. 2001). DiPAPs have been observed in human sera, wastewater treatment plant sludge and paper fibers (D'eon et al. 2009). Lee and Mabury (2011) also reported detectable diPAPs in pooled human sera samples from the U.S. at mean concentrations of  $130 \pm 40$  ng/L. High concentrations of diPAPs (frequency of detection 100%,  $\Sigma$ diPAPs 7637 and 2215 ng/g mean and median respectively) were detected in 102 residential dust samples collected from Vancouver, Canada, (De Silva et al. 2012). Similar levels have also been reported in dust from the Faroe Islands, Sweden, Greece, Spain, Nepal, Japan, and Australia (Eriksson and

Karrman. 2015). PFCAs can be formed from diPAPs through many transformation processes, such as degradation in wastewater treatment plants (Lee et al. 2010; Lee et al. 2014), and through biotransformation in rats (D'eon et al. 2007). Therefore, diPAPs are important both as a precursor to PFCAs and potentially as a fluorinated contaminant in their own right. Although there is considerable information available on PFSA and PFCAs in the environment, there is much less information on the other PFASs which include diPAPs, PFPiAs and PFPAs. The limited amount of research undertaken to date has focused on levels in water (D'eon et al. 2009a; D'eon et al. 2009b; Lee et al. 2010; Lee et al. 2014) and biota (D'eon et al. 2007; Lee and Mabury. 2011; Guo et al. 2012), with only a few studies that have investigated either diPAPs, PFPiAs or PFPAs in sediments (Esparza et al. 2011; Loi et al, 2013). In Hong Kong diPAPs, fluorotelomer sulfonic acids (FTSAs) and PFPiAs were minor contributors to the total PFASs in animals but accounted for over 95% in sewage sludge (Loi et al. 2013).

Sediment cores can provide a means of examining environmental occurrence and assessing historical inputs of persistent organic pollutants (POPs) to aquatic systems like the Great Lakes region (Gewurtz et al. 2013). Comparison of sediment deposition fluxes in remote lakes can also provide information regarding the atmospheric fate and transport of POPs (Muir et al., 2009), and this may be the case for PFSA, PFCAs, diPAPs, PFPiAs and PFPAs. However, an analytical method for the simultaneous determination of these compounds in sediments is lacking. This is largely due to the differences in  $pK_{a1}$  and  $pK_{a2}$  of PFPAs that range from 2.1 to 3.4 and 4.4 to 5.6,

respectively (Wellington Laboratories. 2009) resulting in the dianionic form of PFPAs under traditional ion-pair extraction conditions (pH=10).

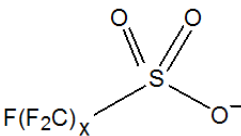
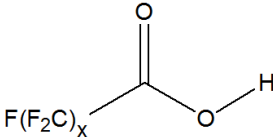
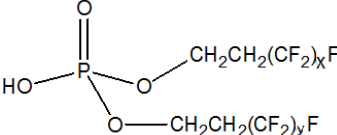
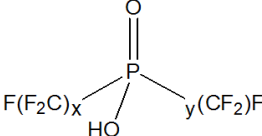
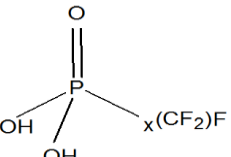
The goals of this study were to establish an analytical protocol to extract PFSA, PFCAs, diPAPs, PFPiAs and PFPAs from sediments simultaneously, to apply the method to examine the role of atmospheric inputs of PFASs in the Great Lakes region, and to explore whether other PFASs (diPAPs, PFPiAs, PFPAs) are present in the sedimentary record.

## **2. Materials and methods**

### *2.1. Chemicals and reagents*

The full name, structures, and acronyms of the target compounds are shown in Table 1, which was modified from Guo et al. (2012). Native target analytes were obtained from Wellington Laboratories (Guelph, Canada), except for the diPAPs which were obtained from Chiron AS (Trondheim, Norway). Mass-labelled PFSA and PFCAs including  $^{13}\text{C}_2$ -PFHxA,  $^{13}\text{C}_4$ -PFOA,  $^{13}\text{C}_5$ -PFNA,  $^{13}\text{C}_2$ -PFDA,  $^{13}\text{C}_2$ -PFUnDA,  $^{13}\text{C}_2$ -PFDODA,  $^{18}\text{O}_2$ -PFHxS, and  $^{13}\text{C}_4$ -PFOS, and mass-labelled  $^{13}\text{C}_2$ -6:2 diPAP and  $^{13}\text{C}_2$ -8:2 diPAP were all obtained from Wellington Laboratories. Organic reagents including HPLC grade methanol, acetonitrile, water and methyl tert-butyl ether (MTBE) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Tetrabutyl ammonium hydrogen sulphate (TBAS) was purchased from J.T. Baker (Phillipsburg, NJ, USA). Ammonium acetate and sodium hydroxide were purchased from EMD Chemicals Inc. (Darmstadt, Germany).

155 **Table 1.** Name, structure, and acronyms of target compounds

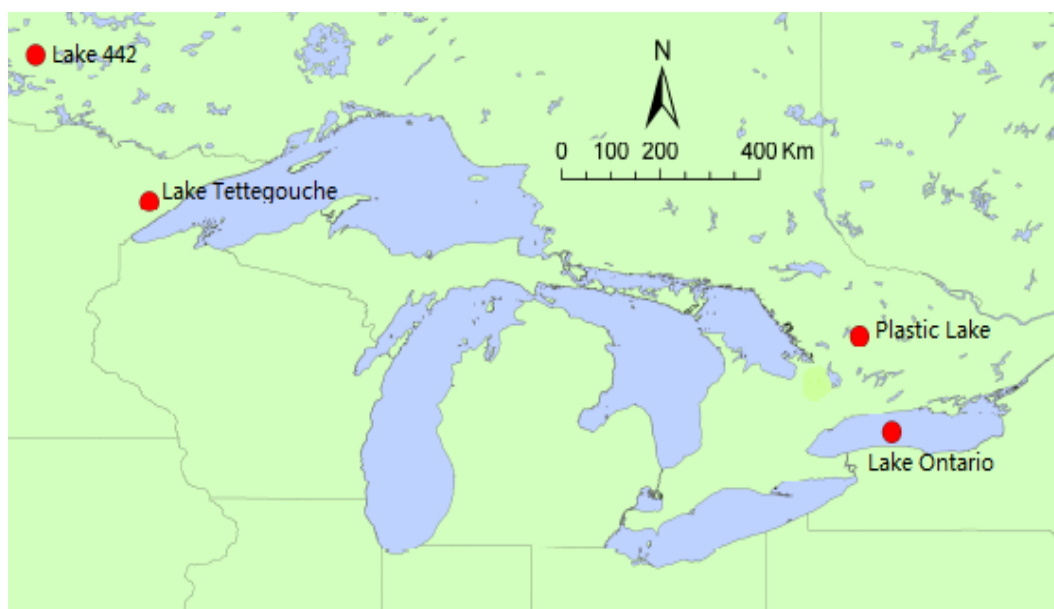
Name	Structure	Acronym
Perfluoroalkane sulfonic acid (PFSAs)		x=6, PFHxS; x=8, PFOS; x=10, PFDS
Perfluoroalkyl carboxylic acid (PFCAs)		x=5, PFHxA; x=6, PFHpA; x=7, PFOA; x=8, PFNA; x=9, PFDA; x=10, PFUnDA; x=11, PFDoDA; x=12, PFTTrDA; x=13, PFTeDA
polyfluoroalkyl phosphoric acid diester (diPAPs)		x=6, y=x 6:2 diPAP x=8, y=x 8:2 diPAP x=10, y=x 10:2 diPAP
Perfluoroalkyl phosphinic acid (PFPiAs)		x=6, y=x C6/C6-PFPiA; x=8, y=x C8/C8-PFPiA; x=6, y=8 C6/C8-PFPiA
Perfluoroalkyl phosphonic acid (PFPAAs)		x=6, C6-PFPA; x=8, C8-PFPA; x=10, C10-PFPA

156 *2.2. Sample collection*

157 Four sample sites were chosen to contrast contaminant sedimentation fluxes  
 158 associated with atmospheric-dominated inputs in remote lakes within the Great Lakes  
 159 region, to a large lake with multi-source input pathways (Figure 1). In 2009, gravity  
 160 corers were used to collect sediment from Plastic Lake (area: 32.3 Ha; max. depth:  
 161 16.0 m), L442 (Experimental Lakes Area (<https://www.iisd.org/ela/>); area: 16 Ha;  
 162 max. depth: 17.8 m), and Lake Tettegouche (area: 26.7 Ha; max. depth: 4.6 m). These



represent remote lakes that are within the Laurentian Great Lakes region but that have little or no development in their watersheds. Therefore, any inputs of PFASs are likely to be predominantly through atmospheric deposition, although each have nearby access roads and small vessels are on the lakes and minor direct inputs are therefore possible. A core was also obtained from Lake Ontario in 2006 using a box corer sub-sampled with push cores. Lake Ontario has a large population base and many commercial / industrial activities in the western portion, this therefore represents a large freshwater lake impacted by urban run-off and municipal wastewater.



**Figure 1.** Sediment core sampling locations in remote lakes within the Great Lakes region and in Lake Ontario

### *2.3. Sample preparation*

Replicate cores were collected and sliced in 1 cm increments for the top 15 cm, then every 2 cm to core bottom. Cores from Lake 442 were sliced in 0.5 cm increments for the first 5 cm. One replicate core from each site was sent for dating, while the remaining cores were used for the determination of a suite of persistent organic

pollutants. For PFASs determination, only the top few centimeters (up to 10 cm in three of the lakes) were analysed for each of the lakes to focus on recent inputs and emerging substances, and recent depositional fluxes for assessing the relative role of atmospheric inputs.

Each sample was individually air dried and homogenized with mortar and pestle. Samples were extracted based on the method reported by Guo et al. (2012) with slight modifications. Briefly, a 1 g (dry weight) sediment sample was accurately weighed and extracted with 2.5 mL of 60/40 acetonitrile/0.2 M NaOH. The resulting solution was shaken, centrifuged and transferred to a 15 mL polypropylene tube. This procedure was repeated and the supernatant was combined with original extract. The acetonitrile extracts were reduced to approximately 1 mL using nitrogen evaporation. The sample was then extracted with 1 mL of 0.5 M TBAS. The acidity of the solution was adjusted to pH 4 using 8 M NaOH and 0.5 M TBAS. The sample was then extracted twice with 5 mL of MTBE. The MTBE aliquots were combined, evaporated to dryness under a gentle stream of nitrogen and reconstituted with 1 mL methanol. Prior to analysis, the extract was separated into two fractions to enhance the precision of the diPAPs determination. The first fraction was spiked with mass-labeled PFCAs and PFSAs, and HPLC-grade water was added to adjust the solvent mixture to 60% methanol and 40% water. For the second fraction, mass-labeled diPAPs were added and the final solvent was 100% methanol. Both fractions were filtered using 0.2 µm syringeless polypropylene filter. Two procedural blanks (HPLC grade water) and a spiked sediment blank (obtained from the deep core slice that was extracted, analysed

and verified to be blank) were prepared and analysed with each set of 15 or 20 sediment samples as quality control checks.

#### *2.4. Sediment dating, sedimentation rate and focusing factor*

The rates of sedimentation and age dating of the sediments were determined by Environment Canada (Aquatic Contaminants Research Division, Burlington, ON), using  $^{210}\text{Pb}$  dating undertaken by alpha counting using  $^{210}\text{Po}$ , the granddaughter product of  $^{210}\text{Pb}$ , as described by Eakins and Morrison (1978), and detailed elsewhere (e.g. Muir et al., 2009; Myers et al., 2012).

Sedimentation rates were estimated using the Constant Rate of Supply (CRS) model that assumes a variable sedimentation rate and constant flux of unsupported  $^{210}\text{Pb}$  to the sediment/water interface (Yang, 2007).

The focusing factor (FF) indicates whether the area the core was taken was depositional or erosional. A  $\text{FF} < 1$  suggests the site is erosional, but may accumulate fine sediment on transient basis, whereas a  $\text{FF} > 1$  suggests a depositional environment.

Focusing factors were calculated as described by Simcik et al. (1996) using the  $^{210}\text{Pb}$  inventory expected from atmospheric deposition and the atmospheric flux at the sediment water interface generated from the CRS model.

#### *2.5. Organic carbon content:*

Total organic carbon was calculated by subtracting the total inorganic carbon content from the total carbon content. Inorganic carbon content was determined by

colourimetry using MOECC Method E3012 (MOECC 2006a) and total carbon was measured using a LECO C-632 Carbon Determinator using MOECC Method E3142 (MOECC 2006b).

## 2.6. PFAS determination

Extracted sediment samples were analysed using liquid chromatography with tandem mass spectrometry (LC-MS/MS). This was performed on an Agilent 1200LC liquid chromatograph coupled to a 4000 QTrap triple-quadrupole mass spectrometer (Applied Biosystems/MDS Sciex) operated in negative electrospray ionization mode. Analyte separation was performed using a Restek Ultra C18 column (50 mm × 2.1 mm, 3 µm; Restek, Bellefonte, PA, USA). The optimized instrumental parameters and HPLC mobile phase gradient are described in detail by Guo et al. (2012). An overview of the MS/MS settings and multiple reaction monitoring (MRM) target ions are presented as Table 2.

**Table 2.** Overview of MS/MS settings and MDL of target compounds

Analyte			Declustering potential, DP	Collision Energy, CE	MDL	Internal standard	
Acronym		MRM	(V)	(V)	(pg/g)	Acronym	MRM
PFSA <sub>s</sub>	PFHxS	399.0>99.0	-90	-70	30	<sup>18</sup> O <sub>2</sub> -PFHxS	403.0>103.0
	PFOS	499.0>99.0	-100	-75	50	<sup>13</sup> C <sub>4</sub> -PFOS	503.0>99.0
	PFDS	599.0>99.0	-110	-85	20	<sup>13</sup> C <sub>4</sub> -PFOS	503.0>99.0
PFCAs	PFHxA	313.0>268.9	-25	-13	25	<sup>13</sup> C <sub>2</sub> -PFHxA	315.0>270.1
	PFHpA	362.8>319.0	-30	-13	40	<sup>13</sup> C <sub>4</sub> -PFOA	417.0>372.0
	PFOA	413.0>368.9	-35	-16	20	<sup>13</sup> C <sub>4</sub> -PFOA	417.0>372.1
	PFNA	462.9>419.0	-30	-15	10	<sup>13</sup> C <sub>5</sub> -PFNA	468.0>423.0
	PFDA	513.0>468.8	-35	-15	10	<sup>13</sup> C <sub>2</sub> -PFDA	515.0>470.0
	PFUnDA	562.8>519.0	-40	-18	20	<sup>13</sup> C <sub>2</sub> -PFUnDA	565.0>520.0
	PFDoDA	613.0>569.0	-45	-18	10	<sup>13</sup> C <sub>2</sub> -PFDoDA	615.0>570.0
	PFTTrDA	663.0>619.0	-40	-19	20	<sup>13</sup> C <sub>2</sub> -PFDoDA	615.0>570.0

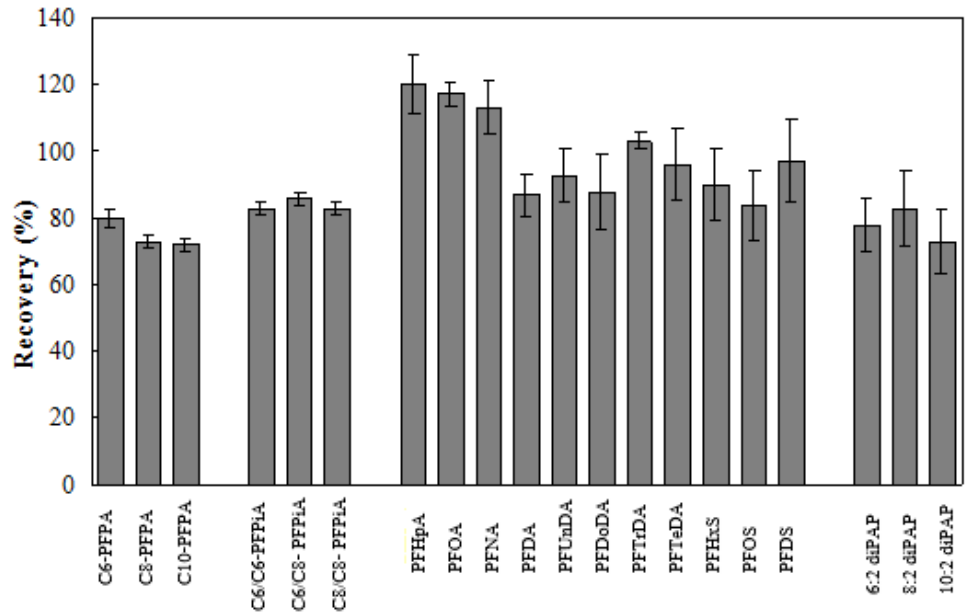
	PFTeDA	713.0>669.0	-55	-20	30	<sup>13</sup> C <sub>2</sub> -PFD <sub>2</sub> DA	615.0>570.0
diPAPs	6:2 diPAP	789.0>96.9	-85	-80	25	<sup>13</sup> C <sub>2</sub> -6:2 diPAP	793.1>96.7
		789.0>443.0	-85	-32			793.1>444.9
	8:2 diPAP	989.0>96.9	-115	-86	100	<sup>13</sup> C <sub>2</sub> -8:2 diPAP	993.1>96.9
		989.0>543.0	-115	-38			993.1>544.8
	10:2 diPAP	1189>96.9	-135	-108	200	<sup>13</sup> C <sub>2</sub> -8:2 diPAP	993.1>96.9
		1189>653.0	-135	-42			993.1>544.8
PFPIAs	C6/C6-PFPIA	701.0>401.0	-160	-74	4	No I.S.	
	C6/C8-PFPIA	801.0>501.0	-165	-82	8	No I.S.	
	C8/C8-PFPIA	901.0>501.0	-165	-88	20	No I.S.	
PFPAAs	C6-PFPA	399.0>78.9	-95	-80	150	No I.S.	
	C8-PFPA	499.0>78.9	-95	-96	90	No I.S.	
	C10-PFPA	599.0>78.9	-135	-92	100	No I.S.	

239

## 240 2.7. Quality control

241 PFSAAs, PFCAs and diPAPs were quantified using mass-labelled internal standards  
242 (specified in Table 2). PFPIAs and PFPAAs were quantified using an external standard  
243 calibration curve. Whilst matrix effects have previously been observed in dust (De  
244 Silva et al. 2012), no matrix effects were observed in matrix-matched recovery tests  
245 performed as part of this investigation. Working solutions were prepared with HPLC  
246 grade methanol and stored in a refrigerator at 4 °C. Before instrumental analysis,  
247 working solutions of PFSAAs, PFCAs, PFPAAs and PFPIAs were diluted with HPLC  
248 grade water to adjust the solvent mixture to 60% methanol and 40% water, while  
249 diPAPs working solutions were diluted with HPLC grade methanol to match the  
250 sample solution composition. Recovery tests were performed by spiking 0.5 ng of  
251 PFSAAs and PFCAs, 10 ng of PFPAAs, 5 ng of PFPIAs, 5 ng of 6:2 diPAP, 15 ng of 8:2  
252 diPAP, and 25 ng of 10:2 diPAP into four 1 g sediment samples obtained from deep

slices of each core, which pre-date the first production of PFASs in 1947 (Giesy et al. 2006). These sediments were first extracted, analysed and verified to not contain detectable concentrations of PFASs. The recovery of target compounds from four blank spiked sediment samples ranged from 73 to 120% (Figure 2). The reported concentrations in sediment samples were not recovery corrected. Method detection limits (MDL) are presented in Table 2. They were determined as three times the standard deviation of 10 parallel blank samples spiked with the lowest concentration of target compounds which could produce a signal-to-noise ratio of 10:1. Each sediment sample was extracted once, analysed twice and a randomly selected sample from each sediment core was chosen as a duplicate. The arithmetic mean concentration for each analyte in the sample was reported and any analyte below the MDL was reported as not detected (ND).



**Figure 2.** Recovery of target compounds (mean  $\pm$  standard deviation) from blank spiked deep sediment core samples (n=4) using optimized extraction solvent mix of

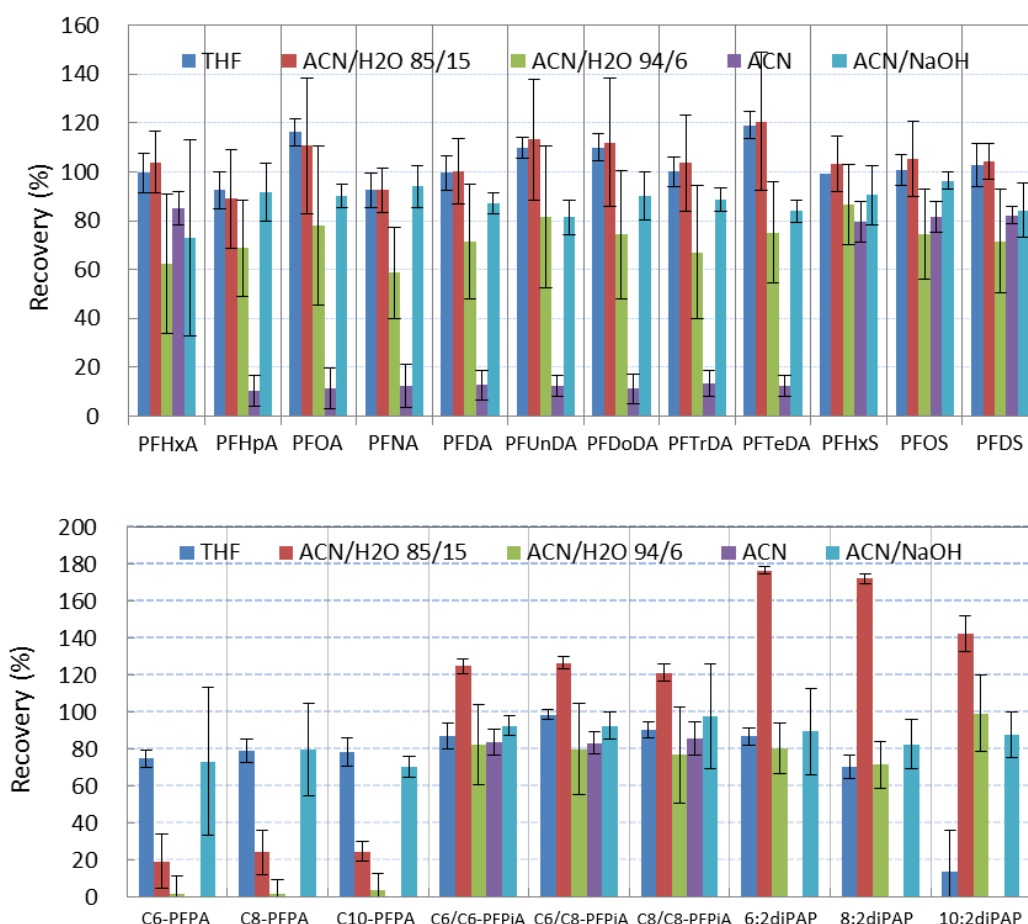
60/40 ACN/0.2 M NaOH.

### 3. Results and discussions

#### 3.1. Method optimization

Previous attempts to extract PFPAs, PFPIAs, diPAPs, PFCAs and PFSAAs have been performed using different solvents and/or separate extractions, which can deplete limited sample material and be time-consuming. There is often limited sediment material available from the sub-sampling of cores into slices, so simultaneous extraction was preferred for this project. In order to extract target compounds simultaneously, several extraction solvents were tested as part of the optimization process including; tetrahydrofuran (THF), acetonitrile (ACN), acetonitrile / water (ACN/H<sub>2</sub>O), and acetonitrile / sodium hydroxide (ACN/NaOH). Each solvent was tested using the procedure specified in the sample preparation section. The recorded recoveries of four spiked sediment blanks from deep slices of four sediment cores (corresponding to pre PFASs production) using each solvent are presented as Figure 3. ACN/NaOH proved to be the most effective at extracting all target compounds from sediment samples with recoveries ranging between 73 to 120%. Therefore ACN/NaOH was selected as the extraction solvent. After solvent extraction, ion-pair extraction is a key step to forming ion pairs with target compounds which are then extracted with MTBE. It is therefore necessary to adjust the pH value of the extract to efficiently form an ion pair. Several different pH conditions were tested and the most effective extraction was achieved at pH 4 (Guo et al. 2012). It is worthwhile

mentioning that although the extraction solvent is alkaline, some sediment sample extracts are acidic and so the pH needed to be regulated using 8 M NaOH and 0.5 M TBAS.



**Figure 3.** The recovery of target compounds (mean  $\pm$  standard deviation) from four spiked blank sediment samples with different extraction solutions.

### 3.2. PFAS concentrations and flux trends in sediments PFASs and PFCAs

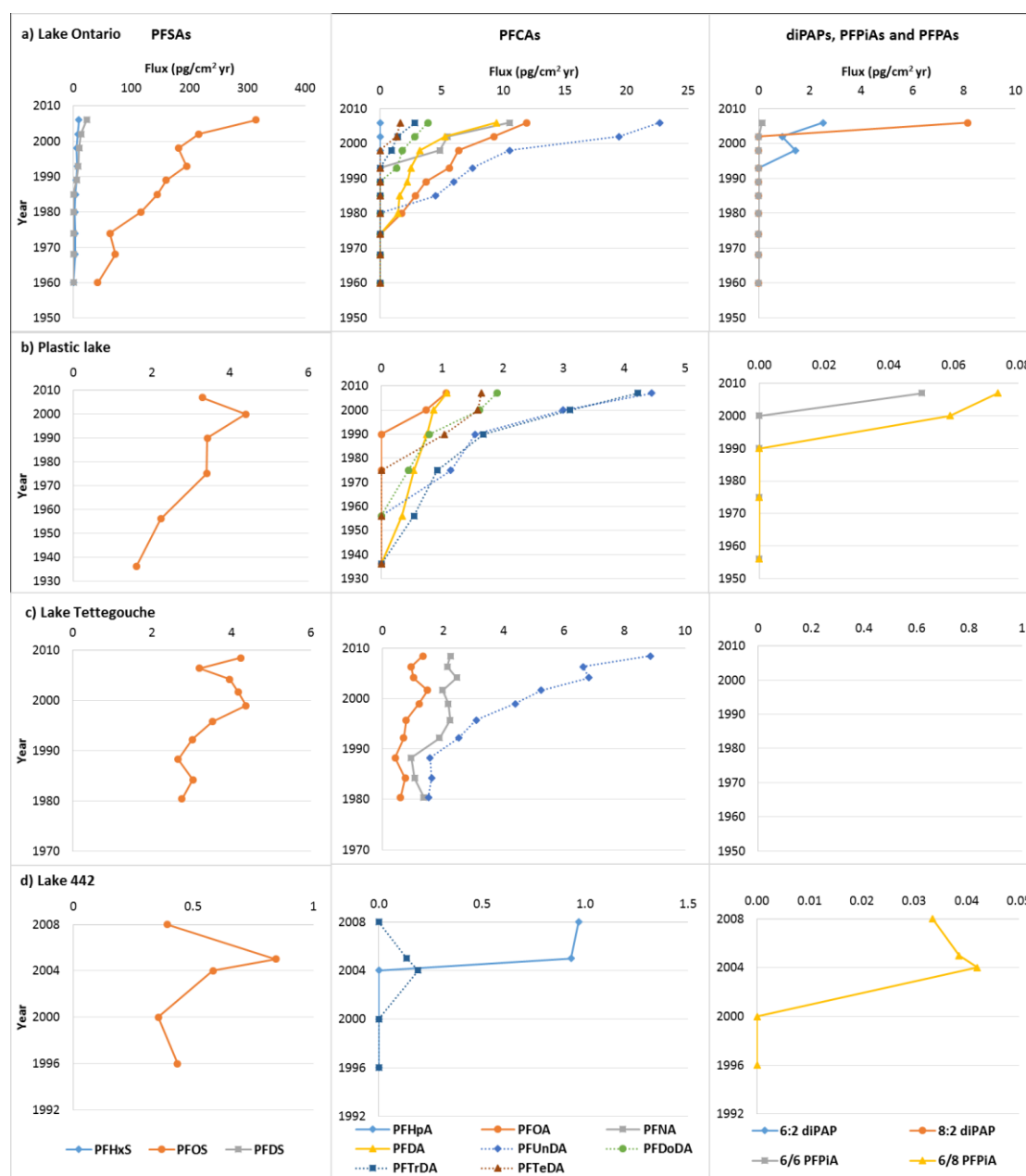
The concentration, sedimentation rate, and organic carbon data for each sample is listed in Table S1 (Supplementary Information). Total PFSA + PFCA concentrations in the surface sediments of each lake decreased in order of Lake Ontario (13.1 ng/g) > Plastic Lake (3.67 ng/g) > Lake Tettegouche (1.65 ng/g) > L442 (0.51 ng/g), which



coincided with a decreased order in the surrounding population density, indicating that direct inputs were the main source of PFAS.

Concentrations and resultant fluxes (Figure 4) were a factor of 2-3 higher for PFASs (PFOS and PFDS) and within approximately 30% for PFCAs (PFOA, PFNA, PFDA, and PFUnDA) reported from the same Lake Ontario site 1034 core samples using a different extraction method (Myers et al., 2012). Yoo et al., (2009) found that alkaline digestion increased extraction of PFAS compounds in sludges, and Yeung et al. (2013) suggested that the use of alkaline digestion may have resulted in greater concentrations observed in their sediment analysis compared to Myers et al (2012) for the same box core samples. The alkaline extraction utilized here may have similarly increased extraction efficiency for the PFOS and PFDA. PFSA and PFCA flux and concentration trends were consistent with those of Myers et al. (2012) and Yeung et al. (2013) for samples from the same box core, indicating that the extraction method used here produces good consistent results. The trends increased in recent years, which is consistent with production history and the increased use of PFASs products.

Interestingly, PFOS concentrations in Lake Ontario were over an order of magnitude greater than in Tokyo bay, Japan (Zushi et al. 2010) and Taihu Lake, China (Yang et al. 2011), even though both these areas are also densely populated and industrialized. The differences may be due to environmental processes such as residence time and dilution factors (Tokyo bay is open to the Pacific Ocean) or a difference in emission history and total loads.



**Figure 4.** Time trends of PFAS flux in the sediment (A) Lake Ontario, (B) Plastic Lake, (C) Lake Tettegouche and (D) Lake 442 (only PFASs in concentrations above the MDLs are displayed). Raw concentration data is presented in the supplementary information (Table S1)

Concentrations and flux trends for Plastic Lake and Lake Tettegouche are also shown (Table S1 and Figure 4). In the case of Plastic Lake, the low sedimentation

rate results in only a few slices that fall into the time period of production. For Lake Tettegouche, the top 10 slices go back to 1980. Concentrations of PFOS were much lower (2 orders of magnitude) in both Plastic Lake and Lake Tettegouche compared to the Lake Ontario core on a dry weight basis. However, PFCA concentrations (dry weight) were generally similar to those in Lake Ontario (within one order of magnitude), although only PFOA, PFNA and PFUnDA were detected in Lake Tettegouche. Flux trends showed less pronounced declines with core depth than in the Lake Ontario core. The Plastic Lake core exhibited a confounding result for PFHpA as core slices pre-dating the 1900s had unreasonably high amounts present (noted in Table S1; values exceeded the calibration range). The PFHpA in sediment from these time periods predate PFASs production and therefore indicate either down core migration (which is considered unlikely due to the high concentrations) or the presence of an interfering contaminant in those samples. Only surface sediments (top 2.5 cm) were examined in Lake 442, so time trends were not considered for this lake.

### *3.3. diPAPs, PFPiAs and PFPAs*

Detectable concentrations of diPAPs and PFPiAs were only recorded in the top layers of sediments from Lake Ontario, Plastic Lake and L442, and were lower than those recorded for the other PFASs. The highest concentrations were recorded in sediments from Lake Ontario. The concentrations of 6:2 diPAPs in the top three layers of sediment samples were 80.4, 33.9, and 56.1 pg/g. The 8:2 diPAP was only detected

in the surface sample, but at a concentration of 261 pg/g, which was much greater than that of 6:2 diPAPs. The relatively low level of diPAPs detected is likely due to their late production, use and also degradation to PFOA (Lee and Mabury, 2011). No diPAPs were detected in samples from Lake Tettegouche, Plastic Lake or L442, however samples from Plastic Lake and L442 did contain PFPiAs. 6/8 PFPiA was detected in the top two layers of sediment (2000-2007) from Plastic Lake and top three layers of sediment (2004-2008) from L442. The concentration of 6/8 PFPiA in each sample was recorded between 8.2 and 13 pg/g. 6/6 PFPiA was also detected in surface sediment samples from Lake Ontario and Plastic Lake, where concentrations were 4.4 and 8.9 pg/g, respectively.

D'eon et al. (2009b) identified PFPAs in 80% of the 30 Canadian surface water creeks and rivers they sampled, with C8-PFPA concentrations ranging from  $88 \pm 33$  to  $3400 \pm 900$  pg/L. However, PFPAs were not evident in any sediment samples in this current study (Table 3 and S1). Although a peak was present at the retention time for C6-PFPA in Lake Ontario sediments, it was not quantified as the peak shape was poor and subsequent standard addition tests indicated it was not C6-PFPA (Table S1). No PFPAs were detected in Lake Trout obtained from the Great Lakes region (Guo et al. 2012).

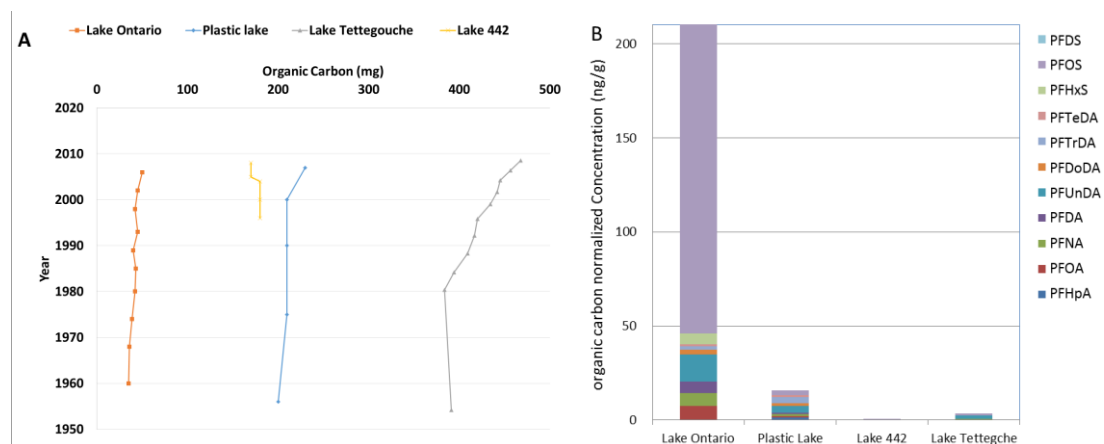
The absence of PFPAs in the sediment samples and biota indicates they are either present in low concentrations and/or they do not readily partition to sediment, as indicated by Lee (2013). D'eon et al. (2009b) suggested that high concentrations of diPAPs in wastewater treatment plant sludges may be indicative of potentially greater

partitioning of diPAPs to sediments relative to other PFASs. However, in the Hong Kong marine environment, more diPAPs were found in water than in sediment (Loi et al, 2013), suggesting either a lower affinity for sediment, or that perhaps other loss mechanisms such as salting out and microbial degradation may be important in sediment (Lee et al., 2010).

#### *3.4. Influential factors for interpreting sediment results*

There are a number of factors that can influence interpretation of sediment concentration and flux results for persistent organic contaminants, and perhaps more so for PFASs given their vastly different chemistries from non-polar organic contaminants. The mobility of the compounds within the core can be influenced by factors such as organic carbon and partitioning properties, whereas precursor compounds, transformation products, and changing market conditions can also play an important role.

The organic carbon (OC) content has been shown to have a significant impact on the PFAS concentrations in sediment (Higgins et al. 2006; Ahrens et al. 2011, Awad et al. 2011). In this study, the OC content of sediments between the four lakes varied from 35 to 468 mg/g. The OC content was temporally consistent within each lake, except for Lake Tettegouche which displayed a gradual decrease in OC down core (Figure 5).



**Figure 5. (A)** Time trends of organic carbon content in the sediment of each lake. **(B)** Organic carbon normalized PFAS concentration in the surface sediment from each lake

Although dry weight differences in concentrations were obvious for PFOS between Lake Ontario and the remote lakes, PFCA concentrations did not differ between Lake Ontario and the remote lakes on a dry weight basis. However, normalizations to OC results in stark differences for the longer-chained PFCAs (PFNA, PFDA, PFUnDA) which have a greater tendency to partition to organic carbon (Figure 5) (Higgins et al. 2006; Ahrens et al. 2011) due to increasing hydrophobicity with increasing carbon chain length.

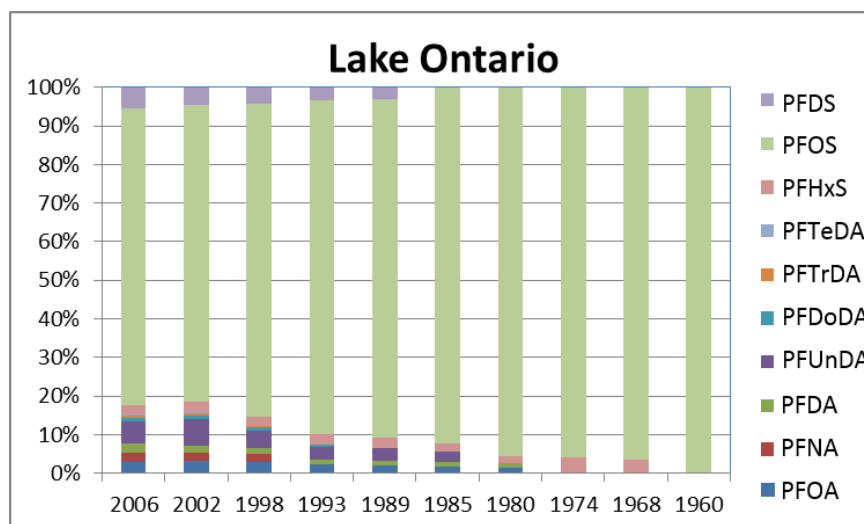
The role of organic carbon highlights the influence of partitioning properties of the PFASs on behavior in sediments. Results in this study are consistent with previous studies, where the longer chained PFCAs such as PFUnDA are the dominant PFCAs found in sediment, rather than higher use and transformation end-products such as PFOA. The dominance of long-chain PFCAs over medium and shorter chain PFCAs has also been observed previously in sediment from Tokyo bay (Zushi et al. 2010) and fine grain sediments from Lake Ontario (Myers et al. 2012). As mentioned above, short chain PFPAs have been shown to not readily partition to sediment/soils, whereas

415 longer chain PFPiAs may preferentially partition to solid matrices (Lee, 2013).  
416 DiPAPs may also partition to solid matrices, and have been detected in relatively high  
417 levels in biosolids (D'eon et al., 2009a) and house dusts (De Silva et al., 2012). This  
418 is consistent with the limited observations in sediments in this study. The  
419 partitioning properties of PFASs also lead to observations that can confound temporal  
420 assessments and flux calculations. Mobility in sediment cores may result in  
421 migration down core being observed (e.g. Ahrens et al., 2009; Myers et al., 2012).  
422 Myers et al. (2012) also questions whether migration of compounds to the top of the  
423 core (sediment-water interface), related either partitioning / solubility properties  
424 and/or bioturbation/resuspension may have a role in differences observed between  
425 core trends and lake trout trends in Lake Ontario. Although other factors such as  
426 adsorption/desorption kinetics and hydrological conditions may also play an  
427 important role. Temporal studies using peat cores have clearly demonstrated the  
428 ability of PFASs to migrate down through the peat with water penetration resulting in  
429 trends well off-set from production trends (Dreyer et al., 2012). In the Plastic Lake  
430 and Lake Ontario core results indicated the presence of some PFASs in  
431 pre-manufacturing time periods (PFHpA and PFNA in Plastic Lake and PFOS and  
432 C6-PFPA in Lake Ontario) (Table S1). Although as mentioned in Table S1 these  
433 detections were more likely due to interfering compounds with PFHpA, PFNA  
434 (Plastic Lake) and C6-PFPA (Lake Ontario).  
435 The roles of precursors of PFSAAs and PFCAs in their environmental occurrence is  
436 well documented (e.g. review by Young and Mabury, 2010). What remains less

certain is the role of such compounds in the observed trends in environmental compartments like sediment cores. Compounds such as diPAPs, have been shown to transform to PFCAs (Lee et al., 2010). If there are significant sources to the environment of such compounds, and degradation/transformation is sufficiently quick, than there may be the potential for observations of PFCAs to be influenced by such inputs.

Despite many of the challenges in interpreting PFAS trends listed above, influencing factors such as market changes and regulatory action can be observed in trends of some sediment cores. For example, although PFOS concentrations are much greater than other PFAS compounds in Lake Ontario, and their concentration profiles have continued to increase, the contributions to total PFAS of other compounds has increased in recent years (Figure 6). This may be in part to reductions in the usage of POSF chemistry and ongoing industrial transitions, but may also reflect a diversity of other sources and pre-cursors contributing to the PFAS burden. The relative proportion of PFOS to the total PFAS concentration decreased steadily from 100% PFOS in 1960 to less than 80% in 2006.





**Figure 6.** Composition of PFSA and PFCA in sediments of Lake Ontario

### 3.5 Deposition fluxes indicative of atmospheric role

Recent depositional fluxes to lake sediments can provide a good indication of the role of atmospheric transport and other processes in contaminant delivery across regions (e.g. Muir et al., 2009). In this study, deposition fluxes can be contrasted between a Laurentian Great Lake (Lake Ontario) subject to multiple inputs from a large population and commercial/industrial base, and remote primarily atmospherically-influenced lakes within the geographical region. The deposition fluxes of the PFASs in each lake are presented in Table 3 for surficial sediments, which typically represent the most recent inputs for persistent organic contaminants. The deposition flux was calculated by multiplying the surface layer concentrations (dry weight) recorded at each lake by the sedimentation rate and dividing by the focusing factor (described in Section 2.4).

**Table 3.** Deposition flux (pg/cm<sup>2</sup>yr) of selected compounds to the sediment surface

(reported to 2 significant figures). Flux is presented for surface sediments (top slice) from each core

	Lake Ontario	Plastic Lake	Lake Tettegouche	Lake 442
<b>Sedimentation Rate</b> (g/cm <sup>2</sup> /yr)	0.045	0.004	0.027	0.012
<b>Focusing Factor</b>	1.44	0.71	2.68	2.93
<b>Deposition flux (pg/cm<sup>2</sup>/yr)</b>	PFHxS	-	-	-
	PFOS	3.3	4.23	0.39
	PFDS	-	-	-
	PFHpA	1.64	-	0.97
	PFOA	1.06	1.33	-
	PFNA	1.5	2.24	-
	PFDA	1.08	-	-
	PFUnDA	4.45	8.85	-
	PFDODA	1.90	-	-
	PFTTrDA	4.22	-	-
	PFTeDA	1.64	-	-
	6:2 diPAP	-	-	-
	8:2 diPAP	-	-	-
	10:2 diPAP	-	-	-
	C6/C6-PFPiA	0.05	-	-
	C6/C8-PFPiA	0.07	-	0.03
	C8/C8-PFPiA	-	-	-
	C6-PFPA	-	-	-
	C8-PFPA	-	-	-
	C10-PFPA	-	-	-

- Not detected in surface sediment sample

Large differences in flux (2 orders of magnitude) for PFOS in Lake Ontario sediment relative to the remote lakes were observed, reflecting the past broad use of the compound and it's precursors in proximity to populated and commercially-developed areas.

In each of the remote lakes, the greatest deposition rates were for PFCAs, specifically PFUnDA in Lake Tettegouche and Plastic Lake and PFHpA in Lake 442. This indicates the remote lakes are primarily influenced by atmospheric deposition, which

may be the result of precursor compounds or atmospheric contributions of PFCAs directly. These results are consistent with observations in sediments of Arctic lakes where PFOS was the dominant compound in a lake influenced by wastewater and airport run-off, whereas a nearby lake with limited inputs and a remote lake had similar much lower concentrations that were dominated by PFCAs (Stock et al., 2007). The same study found numerous precursors of PFASs in air, in addition to PFCAs and PFSAAs themselves which would contribute to background levels in sediments. The presence of PFASs, including emerging PFASs such as diPAPs and PFPiAs, in particulate matter and dusts (e.g. De Silva et al., 2012, Liu et al., 2015; Yao et al., 2016), gives rise to the potential for atmospheric transport. The significance of atmospheric transport of such compounds will depend on factors such as deposition rate, and its impact will become more apparent with further future studies. However, the similarity in concentrations among remote lakes, weather temperate in the Great Lakes region (this study) or in remote Arctic lakes (Stock et al., 2007; Lescord et al., 2015), indicates that atmospheric transport is widespread and acts at a similar magnitude across regions. Currently the major pathway for PFASs to sediments in populated / commercialized areas is through inputs such as wastewater effluent and runoff, however the distribution of some of the lower level PFASs to remote regions by atmospheric transport is important. Although issues remain with interpreting sedimentation results using sediment cores, atmospheric transport has the potential to form a pathway for the distribution of PFASs for years to come.

#### 4. Conclusions

The analytical method presented here was able to effectively extract PFASs, PFCAs, diPAPs, PFPiAs and PFPAs from sediment cores simultaneously. This allowed for the analysis of sediment cores obtained from four lakes in the Great Lakes region (Lake Ontario, Plastic Lake, L442 and Lake Tettegouche). The greatest flux of PFASs in the four lakes were recorded in the sediment obtained from Lake Ontario ( $\Sigma$ PFASs 460  $\text{pg}/\text{cm}^2\text{yr}^{-1}$ ), where PFOS contributed to over 80% of the total concentrations. Concentrations in Lake Ontario were approximately 1 to 2 orders of magnitude greater than those recorded from the other smaller lakes with no significant urban or industrial inputs. Whilst the PFAS contribution in Lake Ontario was dominated by PFOS, the more remote lakes contained sediment with higher proportions of PFCAs. The PFAS contribution in Lake Ontario appeared to change over time as the proportion of PFOS decreased. This, along with the detection of diPAPs in the surface sediments indicated an increase in the use of alternative PFASs in recent years. Although, biodegradation and physicochemical factors have also been shown to influence PFAS temporal trends in sediment cores. The presence of diPAPs in sediments from Plastic Lake and L442 indicates that they may be undergoing atmospheric transport through dust and particulates, although the influence of potential localized sources cannot be discounted. Although PFPAs have been detected in water samples across Canada, no PFPAs were detected in the sediment from the four lakes indicating that PFPAs do not readily partition to sediments. The results of this study show that the PFAS load to watercourses continues to change with time. It

is therefore imperative to monitor the levels, distribution, fate and behavior of these compounds.

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