

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

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15

16 **Abstract**

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

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

33

34 **Key words**

35 PFASs, PFCAs, diPAPs, PFPiAs, PFPAs, sediment

36

37 **1. Introduction**

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

45 Perfluoroalkane sulfonic acids (PFSA) and perfluoroalkyl carboxylic acids (PFCA)
46 are two classes of PFASs that have been the focus of environmental research,
47 monitoring, and regulatory efforts due to their occurrence, persistence and potential
48 toxicity. Several studies have shown that some PFASs can be classified as
49 multisystem toxicants as well as developmental toxicants (DeWitt. 2015). PFOA and
50 PFOS may be carcinogenic at relatively high doses (Lau et al. 2007), and repeated
51 oral exposures may exert toxic effects including impacts on the liver, gastrointestinal
52 and thyroid hormone. Developmental effects have also been reported in the offspring
53 of animals exposed to PFOS or PFOA (Lau et al. 2007). One of the few toxicity
54 studies on polyfluoroalkyl phosphoric acid diesters (diPAPs) showed that 8:2 diPAP
55 can inhibit male sex hormone synthesis (Rosenmai et al. 2013). Considering the
56 persistence and potential toxicity of PFASs, 3M, the dominant producer of
57 perfluorooctane sulfonyl fluoride (POSF) based products, including PFOS, phased out
58 production between 2000 and 2002 (3M, 2000). Further measures have been taken by
59 industry following the designation of PFOS and POSF to the Stockholm Convention
60 in 2009. More recently in 2006 eight major fluoropolymer and fluorotelomer
61 manufacturers participated in a global PFOA Stewardship program to achieve a 95%
62 reduction of PFOA by 2010, together with precursor chemicals and to have complete
63 elimination of these chemicals in emission and products by 2015 (US EPA, 2006). As
64 a result of the phase out of POSF-based products and PFOA, concentrations of PFASs
65 in the environment were expected to decline (Holmstrom et al 2005; Kannan et al.
66 2006; Butt et al. 2007; Young et al. 2007; Hart et al. 2009; Hart et al. 2008; Olsen et

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

72 Although most of the focus of PFASs research has been on perfluoroalkane sulfonic
73 acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), two emerging groups of
74 fluorinated phosphate surfactants, perfluoroalkyl phosphonic acids (PFPAs) and
75 perfluoroalkyl phosphinic acids (PFPIAs) have recently attracted the attention of a
76 number of researchers (D'eon et al. 2009a; D'eon et al. 2009b; Esparza et al. 2011;
77 Guo et al. 2012; Loi et al. 2013; Trier et al. 2011; Yeung and Mabury. 2016). PFPAs
78 and PFPIAs are commonly used as levelling and wetting agents in waxes and coatings,
79 and as foam-dampening agents in the textile industry, pharmaceutical industry and
80 metal industry (Mason Chemical Co, 2012; Begley et al. 2008). They were also
81 historically incorporated as inert ingredients in United States pesticide formulations
82 until 2008 (Lee. 2013). PFPAs and PFPIAs have now been detected in a variety of
83 different environmental media. For example PFPAs were detected in Canadian surface
84 water and wastewater treatment plant effluents with concentrations ranging from
85 0.026 to 3.4 ng/L in surface water and 0.33 to 6.5 ng/L in wastewater (D'eon et al.
86 2009), Perfluorooctyl phosphonic acid (C8-PFPA) was reported at a concentration of
87 1 ng/L in Dutch surface waters (Esparza et al. 2011), and two PFPIAs congeners
88 (C6/C6 and C6/C8) were detected in over 50% of U.S. human sera donors with the

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

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

111 Karrman. 2015). PFCAs can be formed from diPAPs through many transformation
112 processes, such as degradation in wastewater treatment plants (Lee et al. 2010; Lee et
113 al. 2014), and through biotransformation in rats (D'eon et al. 2007). Therefore,
114 diPAPs are important both as a precursor to PFCAs and potentially as a fluorinated
115 contaminant in their own right. Although there is considerable information available
116 on PFSA and PFCAs in the environment, there is much less information on the other
117 PFASs which include diPAPs, PFPiAs and PFPAs. The limited amount of research
118 undertaken to date has focused on levels in water (D'eon et al. 2009a; D'eon et al.
119 2009b; Lee et al. 2010; Lee et al. 2014) and biota (D'eon et al. 2007; Lee and Mabury.
120 2011; Guo et al. 2012), with only a few studies that have investigated either diPAPs,
121 PFPiAs or PFPAs in sediments (Esparza et al. 2011; Loi et al, 2013). In Hong Kong
122 diPAPs, fluorotelomer sulfonic acids (FTSAs) and PFPiAs were minor contributors to
123 the total PFASs in animals but accounted for over 95% in sewage sludge (Loi et al.
124 2013).

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

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

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

140 **2. Materials and methods**

141 *2.1. Chemicals and reagents*

142 The full name, structures, and acronyms of the target compounds are shown in Table
143 1, which was modified from Guo et al. (2012). Native target analytes were obtained
144 from Wellington Laboratories (Guelph, Canada), except for the diPAPs which were
145 obtained from Chiron AS (Trondheim, Norway). Mass-labelled PFSAs and PFCAs
146 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,
147 $^{13}\text{C}_2$ -PFDoDA, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -PFOS, and mass-labelled $^{13}\text{C}_2$ -6:2 diPAP and
148 $^{13}\text{C}_2$ -8:2 diPAP were all obtained from Wellington Laboratories. Organic reagents
149 including HPLC grade methanol, acetonitrile, water and methyl tert-butyl ether
150 (MTBE) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Tetrabutyl
151 ammonium hydrogen sulphate (TBAS) was purchased from J.T. Baker (Phillipsburg,
152 NJ, USA). Ammonium acetate and sodium hydroxide were purchased from EMD
153 Chemicals Inc. (Darmstadt, Germany).

154

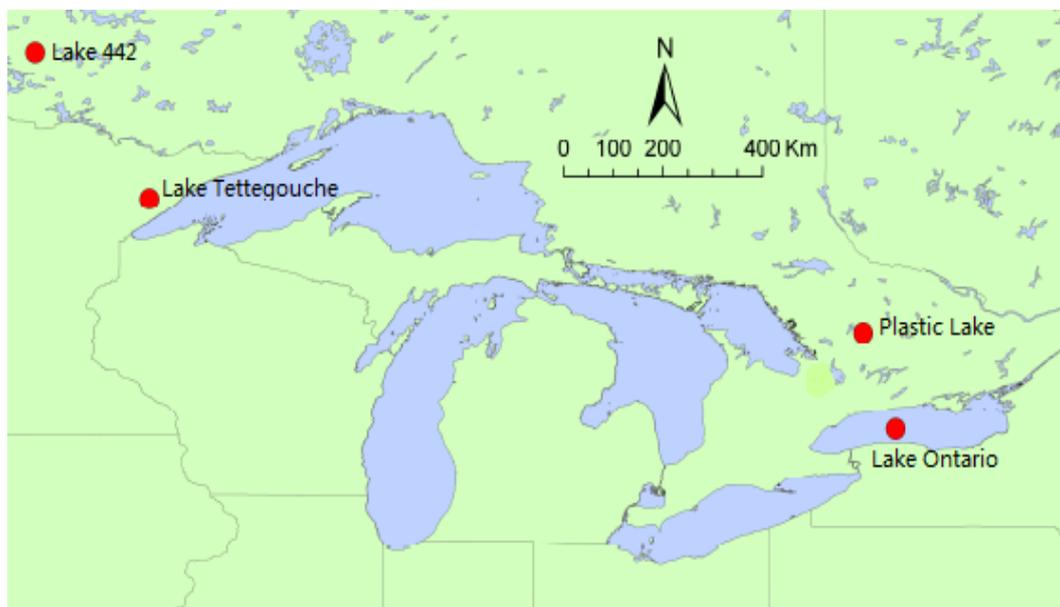
155 **Table 1.** Name, structure, and acronyms of target compounds

Name	Structure	Acronym
Perfluoroalkane sulfonic acid (PFSAAs)		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

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



171
172 **Figure 1.** Sediment core sampling locations in remote lakes within the Great Lakes
173 region and in Lake Ontario
174

175 2.3. Sample preparation

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

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

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

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

204

205 *2.4. Sediment dating, sedimentation rate and focusing factor*

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

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

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

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

220

221 *2.5. Organic carbon content:*

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

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

227

228 2.6. PFAS determination

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

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

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

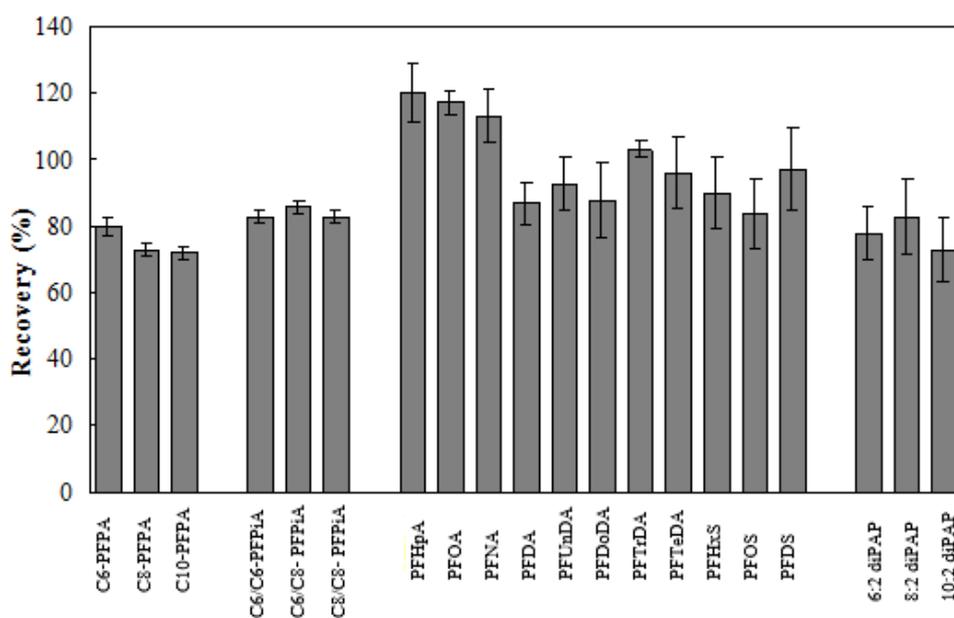
	PFTeDA	713.0>669.0	-55	-20	30	¹³ C ₂ -PFDoDA	615.0>570.0
diPAPs	6:2 diPAP	789.0>96.9	-85	-80	25	¹³ C ₂ -6:2 diPAP	793.1>96.7
		789.0>443.0	-85	-32			793.1>444.9
	8:2 diPAP	989.0>96.9	-115	-86	100	¹³ C ₂ -8:2 diPAP	993.1>96.9
		989.0>543.0	-115	-38			993.1>544.8
	10:2 diPAP	1189>96.9	-135	-108	200	¹³ C ₂ -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.
PFPA	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 PFSA, PFCA and diPAP were quantified using mass-labelled internal standards
242 (specified in Table 2). PFPiA and PFPA 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 PFSA, PFCA, PFPA and PFPiA were diluted with HPLC
248 grade water to adjust the solvent mixture to 60% methanol and 40% water, while
249 diPAP 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 PFSA and PFCA, 10 ng of PFPA, 5 ng of PFPiA, 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

253 slices of each core, which pre-date the first production of PFASs in 1947 (Giesy et al.
 254 2006). These sediments were first extracted, analysed and verified to not contain
 255 detectable concentrations of PFASs. The recovery of target compounds from four
 256 blank spiked sediment samples ranged from 73 to 120% (Figure 2). The reported
 257 concentrations in sediment samples were not recovery corrected. Method detection
 258 limits (MDL) are presented in Table 2. They were determined as three times the
 259 standard deviation of 10 parallel blank samples spiked with the lowest concentration
 260 of target compounds which could produce a signal-to-noise ratio of 10:1. Each
 261 sediment sample was extracted once, analysed twice and a randomly selected sample
 262 from each sediment core was chosen as a duplicate. The arithmetic mean
 263 concentration for each analyte in the sample was reported and any analyte below the
 264 MDL was reported as not detected (ND).



265
 266 **Figure 2.** Recovery of target compounds (mean \pm standard deviation) from blank
 267 spiked deep sediment core samples (n=4) using optimized extraction solvent mix of

60/40 ACN/0.2 M NaOH.

268

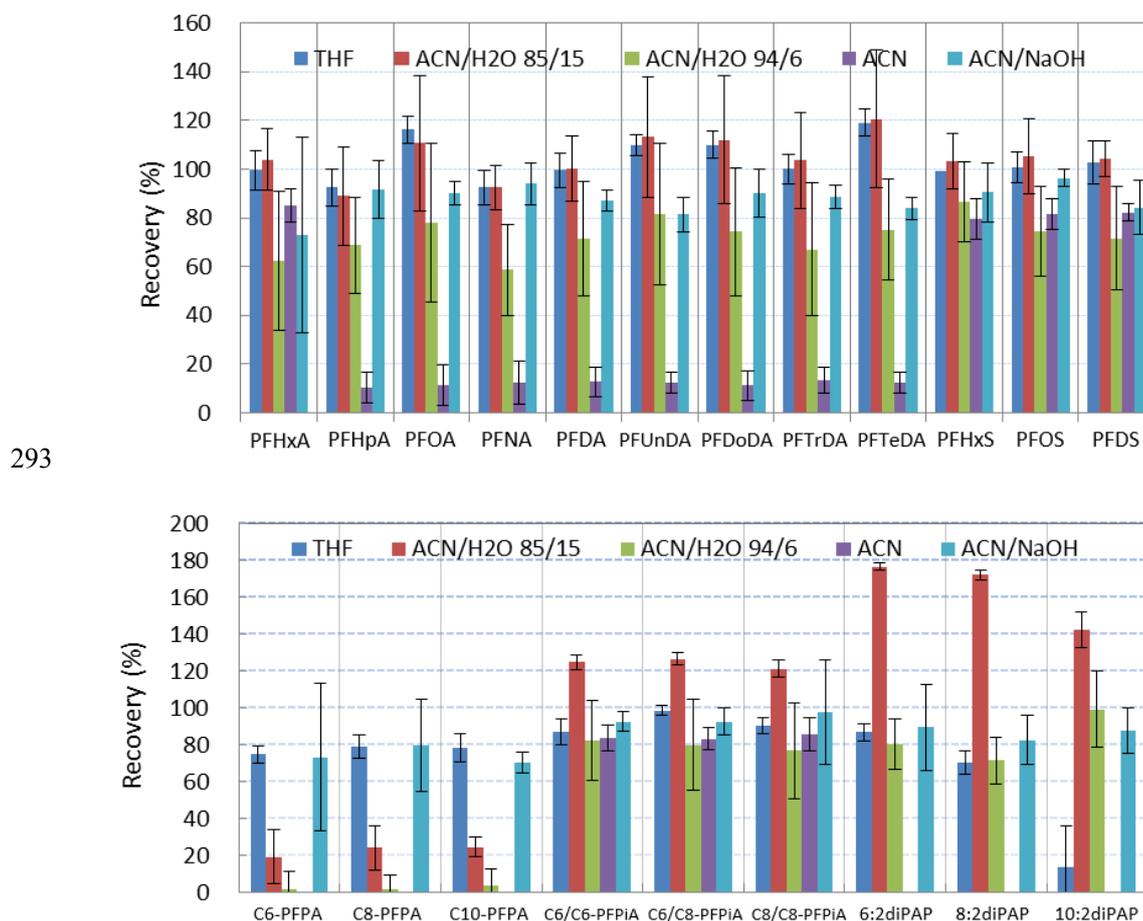
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270 **3. Results and discussions**

271 *3.1. Method optimization*

272 Previous attempts to extract PFPAs, PFPiAs, diPAPs, PFCAs and PFSAAs have been
273 performed using different solvents and/or separate extractions, which can deplete
274 limited sample material and be time-consuming. There is often limited sediment
275 material available from the sub-sampling of cores into slices, so simultaneous
276 extraction was preferred for this project. In order to extract target compounds
277 simultaneously, several extraction solvents were tested as part of the optimization
278 process including; tetrahydrofuran (THF), acetonitrile (ACN), acetonitrile / water
279 (ACN/H₂O), and acetonitrile / sodium hydroxide (ACN/NaOH). Each solvent was
280 tested using the procedure specified in the sample preparation section. The recorded
281 recoveries of four spiked sediment blanks from deep slices of four sediment cores
282 (corresponding to pre PFASs production) using each solvent are presented as Figure 3.
283 ACN/NaOH proved to be the most effective at extracting all target compounds from
284 sediment samples with recoveries ranging between 73 to 120%. Therefore
285 ACN/NaOH was selected as the extraction solvent. After solvent extraction, ion-pair
286 extraction is a key step to forming ion pairs with target compounds which are then
287 extracted with MTBE. It is therefore necessary to adjust the pH value of the extract to
288 efficiently form an ion pair. Several different pH conditions were tested and the most
289 effective extraction was achieved at pH 4 (Guo et al. 2012). It is worthwhile

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



294
 295 **Figure 3.** The recovery of target compounds (mean \pm standard deviation) from four
 296 spiked blank sediment samples with different extraction solutions.

297 *3.2. PFAS concentrations and flux trends in sediments PFASs and PFCAs*

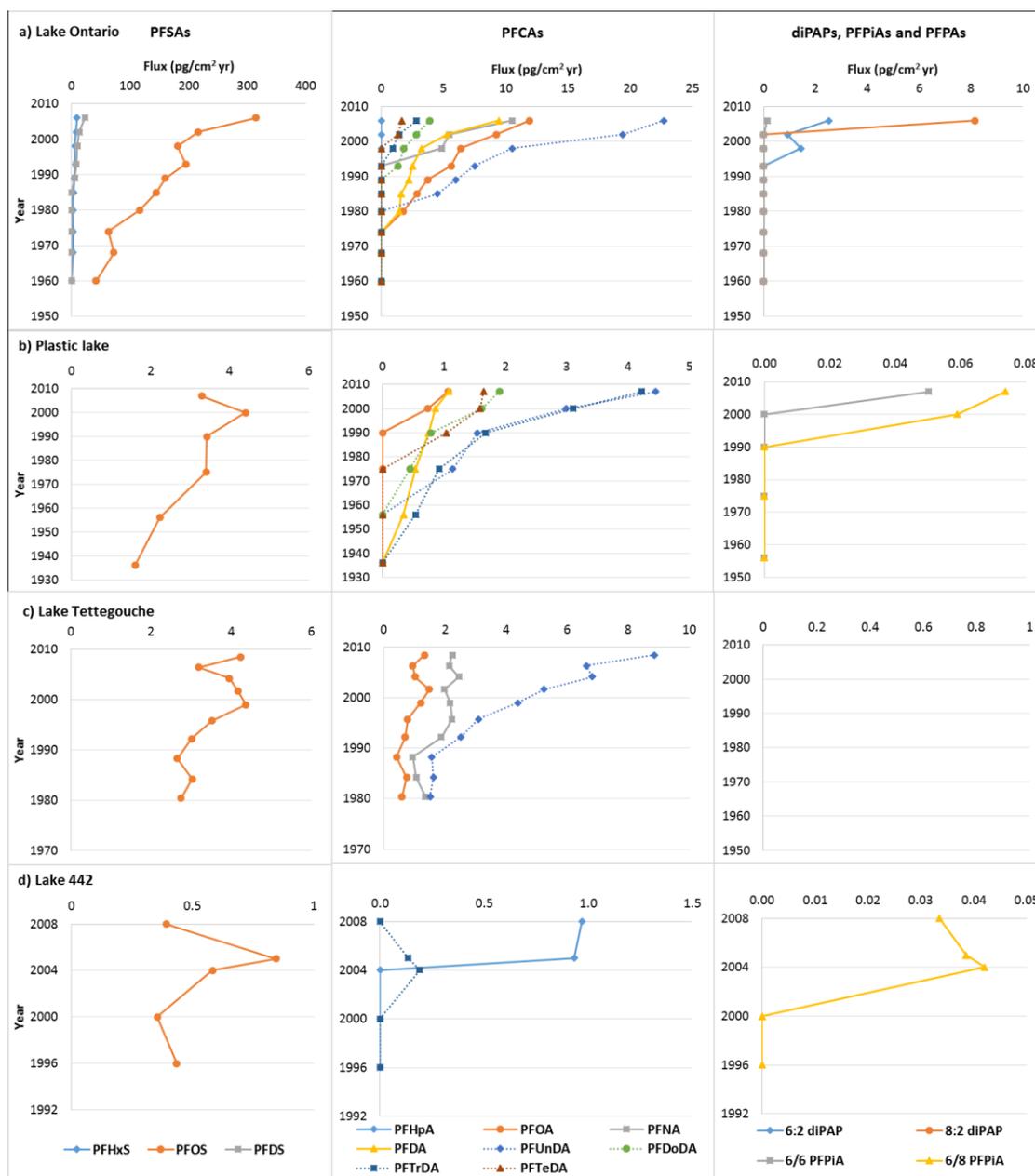
298 The concentration, sedimentation rate, and organic carbon data for each sample is
 299 listed in Table S1 (Supplementary Information). Total PFSA + PFCA concentrations
 300 in the surface sediments of each lake decreased in order of Lake Ontario (13.1 ng/g) >
 301 Plastic Lake (3.67 ng/g) > Lake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

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

304 Concentrations and resultant fluxes (Figure 4) were a factor of 2-3 higher for PFASs
305 (PFOS and PFDS) and within approximately 30% for PFCAs (PFOA, PFNA, PFDA,
306 and PFUnDA) reported from the same Lake Ontario site 1034 core samples using a
307 different extraction method (Myers et al., 2012). Yoo et al., (2009) found that
308 alkaline digestion increased extraction of PFAS compounds in sludges, and Yeung et
309 al. (2013) suggested that the use of alkaline digestion may have resulted in greater
310 concentrations observed in their sediment analysis compared to Myers et al (2012) for
311 the same box core samples. The alkaline extraction utilized here may have similarly
312 increased extraction efficiency for the PFOS and PFDA. PFSA and PFCA flux and
313 concentration trends were consistent with those of Myers et al. (2012) and Yeung et al.
314 (2013) for samples from the same box core, indicating that the extraction method used
315 here produces good consistent results. The trends increased in recent years, which is
316 consistent with production history and the increased use of PFASs products.

317 Interestingly, PFOS concentrations in Lake Ontario were over an order of magnitude
318 greater than in Tokyo bay, Japan (Zushi et al. 2010) and Taihu Lake, China (Yang et al.
319 2011), even though both these areas are also densely populated and industrialized. The
320 differences may be due to environmental processes such as residence time and
321 dilution factors (Tokyo bay is open to the Pacific Ocean) or a difference in emission
322 history and total loads.

323



324

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

329

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

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

347

348 *3.3. diPAPs, PFPiAs and PFPAs*

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

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

364 D'eon et al. (2009b) identified PFPAs in 80% of the 30 Canadian surface water creeks
365 and rivers they sampled, with C8-PFPA concentrations ranging from 88 ± 33 to
366 3400 ± 900 pg/L. However, PFPAs were not evident in any sediment samples in this
367 current study (Table 3 and S1). Although a peak was present at the retention time
368 for C6-PFPA in Lake Ontario sediments, it was not quantified as the peak shape was
369 poor and subsequent standard addition tests indicated it was not C6-PFPA (Table S1).
370 No PFPAs were detected in Lake Trout obtained from the Great Lakes region (Guo et
371 al. 2012).

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

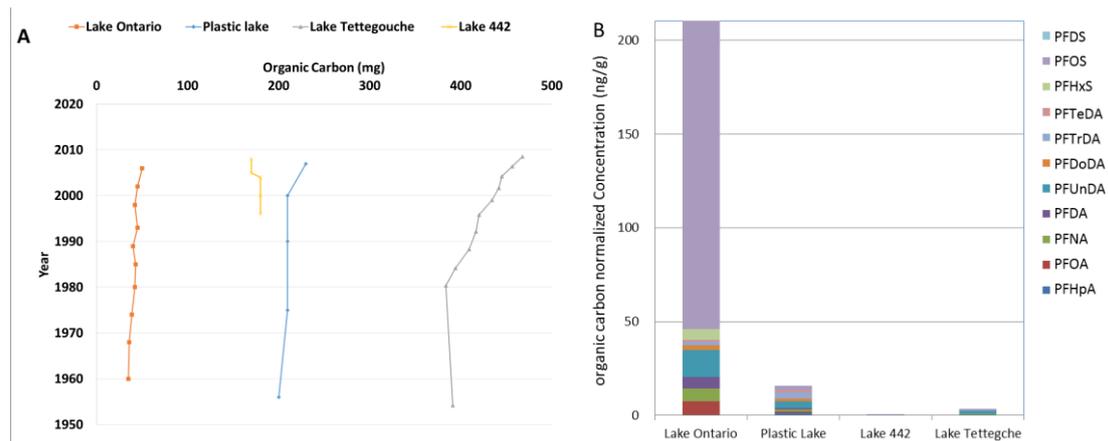
376 partitioning of diPAPs to sediments relative to other PFASs. However, in the Hong
377 Kong marine environment, more diPAPs were found in water than in sediment (Loi et
378 al, 2013), suggesting either a lower affinity for sediment, or that perhaps other loss
379 mechanisms such as salting out and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

381

382 *3.4. Influential factors for interpreting sediment results*

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

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



396

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

400 Although dry weight differences in concentrations were obvious for PFOS between
 401 Lake Ontario and the remote lakes, PFCA concentrations did not differ between Lake
 402 Ontario and the remote lakes on a dry weight basis. However, normalizations to OC
 403 results in stark differences for the longer-chained PFCAs (PFNA, PFDA, PFUnDA)
 404 which have a greater tendency to partition to organic carbon (Figure 5) (Higgins et al.
 405 2006; Ahrens et al. 2011) due to increasing hydrophobicity with increasing carbon
 406 chain length.

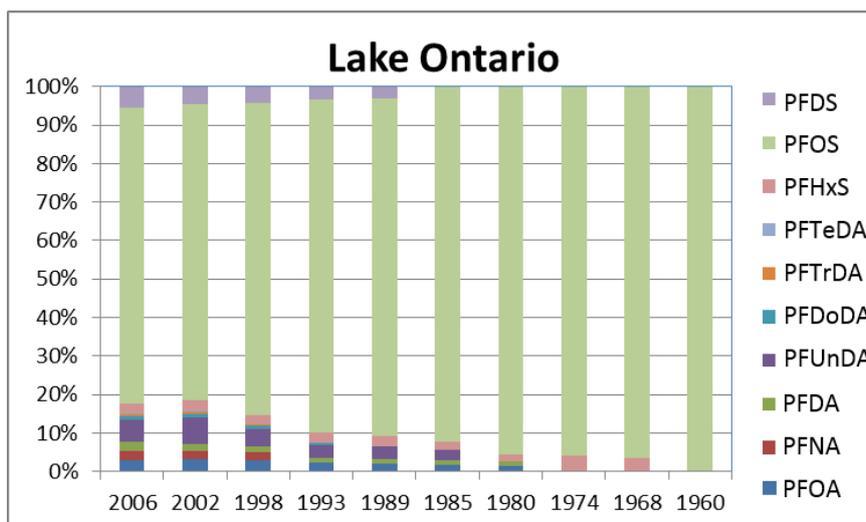
407 The role of organic carbon highlights the influence of partitioning properties of the
 408 PFASs on behavior in sediments. Results in this study are consistent with previous
 409 studies, where the longer chained PFCAs such as PFUnDA are the dominant PFCAs
 410 found in sediment, rather than higher use and transformation end-products such as
 411 PFOA. The dominance of long-chain PFCAs over medium and shorter chain PFCAs
 412 has also been observed previously in sediment from Tokyo bay (Zushi et al. 2010)
 413 and fine grain sediments from Lake Ontario (Myers et al. 2012). As mentioned above,
 414 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 PFASs and PFCAs in their environmental occurrence is
436 well documented (e.g. review by Young and Mabury, 2010). What remains less

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

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



453

454 **Figure 6.** Composition of PFASs and PFCAs in sediments of Lake Ontario

455

456 *3.5 Deposition fluxes indicative of atmospheric role*

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

468

469 **Table 3.** Deposition flux (pg/cm²yr) of selected compounds to the sediment surface

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

	Lake Ontario	Plastic Lake	Lake Tettegouche	Lake 442
Sedimentation Rate (g/cm ² /yr)	0.045	0.004	0.027	0.012
Focusing Factor	1.44	0.71	2.68	2.93
PFHxS	9.22	-	-	-
PFOS	315	3.3	4.23	0.39
PFDS	22.8	-	-	-
PFHpA	-	1.64	-	0.97
PFOA	11.9	1.06	1.33	-
PFNA	10.5	1.5	2.24	-
PFDA	9.44	1.08	-	-
PFA	22.7	4.45	8.85	-
PFD _o DA	3.86	1.90	-	-
PFT _r DA	2.82	4.22	-	-
PFT _e DA	1.65	1.64	-	-
6:2 diPAP	2.51	-	-	-
8:2 diPAP	8.15	-	-	-
10:2 diPAP	-	-	-	-
C6/C6-PFPiA	0.14	0.05	-	-
C6/C8-PFPiA	-	0.07	-	0.03
C8/C8-PFPiA	-	-	-	-
C6-PFPA	-	-	-	-
C8-PFPA	-	-	-	-
C10-PFPA	-	-	-	-

472 - Not detected in surface sediment sample

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

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

480 may be the result of precursor compounds or atmospheric contributions of PFCAs
481 directly. These results are consistent with observations in sediments of Arctic lakes
482 where PFOS was the dominant compound in a lake influenced by wastewater and
483 airport run-off, whereas a nearby lake with limited inputs and a remote lake had
484 similar much lower concentrations that were dominated by PFCAs (Stock et al., 2007).
485 The same study found numerous precursors of PFASs in air, in addition to PFCAs and
486 PFSAAs themselves which would contribute to background levels in sediments. The
487 presence of PFASs, including emerging PFASs such as diPAPs and PFPiAs, in
488 particulate matter and dusts (e.g. De Silva et al., 2012, Liu et al., 2015; Yao et al.,
489 2016), gives rise to the potential for atmospheric transport. The significance of
490 atmospheric transport of such compounds will depend on factors such as deposition
491 rate, and its impact will become more apparent with further future studies. However,
492 the similarity in concentrations among remote lakes, weather temperate in the Great
493 Lakes region (this study) or in remote Arctic lakes (Stock et al., 2007; Lescord et al.,
494 2015), indicates that atmospheric transport is widespread and acts at a similar
495 magnitude across regions. Currently the major pathway for PFASs to sediments in
496 populated / commercialized areas is through inputs such as wastewater effluent and
497 runoff, however the distribution of some of the lower level PFASs to remote regions
498 by atmospheric transport is important. Although issues remain with interpreting
499 sedimentation results using sediment cores, atmospheric transport has the potential to
500 form a pathway for the distribution of PFASs for years to come.

501

502 4. Conclusions

503 The analytical method presented here was able to effectively extract PFASs, PFCAs,
504 diPAPs, PFPiAs and PFPAs from sediment cores simultaneously. This allowed for the
505 analysis of sediment cores obtained from four lakes in the Great Lakes region (Lake
506 Ontario, Plastic Lake, L442 and Lake Tettegouche). The greatest flux of PFASs in the
507 four lakes were recorded in the sediment obtained from Lake Ontario (Σ PFASs 460
508 $\text{pg}/\text{cm}^2\text{yr}^{-1}$), where PFOS contributed to over 80% of the total concentrations.
509 Concentrations in Lake Ontario were approximately 1 to 2 orders of magnitude
510 greater than those recorded from the other smaller lakes with no significant urban or
511 industrial inputs. Whilst the PFAS contribution in Lake Ontario was dominated by
512 PFOS, the more remote lakes contained sediment with higher proportions of PFCAs.
513 The PFAS contribution in Lake Ontario appeared to change over time as the
514 proportion of PFOS decreased. This, along with the detection of diPAPs in the surface
515 sediments indicated an increase in the use of alternative PFASs in recent years.
516 Although, biodegradation and physicochemical factors have also been shown to
517 influence PFAS temporal trends in sediment cores. The presence of diPAPs in
518 sediments from Plastic Lake and L442 indicates that they may be undergoing
519 atmospheric transport through dust and particulates, although the influence of
520 potential localized sources cannot be discounted. Although PFPAs have been detected
521 in water samples across Canada, no PFPAs were detected in the sediment from the
522 four lakes indicating that PFPAs do not readily partition to sediments. The results of
523 this study show that the PFAS load to watercourses continues to change with time. It

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

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537

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