



Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario



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ABSTRACT

Fourteen perfluoroalkyl substances (PFASs) including short-chain perfluorocarboxylates (PFCAs, C4–C6) and perfluoroalkane sulfonates (PFSAs, C4 and C6) were measured in surface sediment samples from 26 stations collected in 2008 and sediment core samples from three stations (Niagara, Mississauga, and Rochester basins) collected in 2006 in Lake Ontario. Perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA) were detected in all 26 surface sediment samples, whereas perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonamide (FOSA), perfluorododecanoate (PFDoDA) and perfluorobutanoate (PFBA) were detected in over 70% of the surface sediment samples. PFOS was detected in all of the sediment core samples (range: 0.492–30.1 ng g⁻¹ d.w.) over the period 1952–2005. The C8 to C11 PFCAs, FOSA, and PFBA increased in early 1970s. An overall increasing trend in sediment PFAS concentrations/fluxes from older to more recently deposited sediments was evident in the three sediment cores. The known PFCAs and PFSAs accounted for 2–44% of the anionic fraction of the extractable organic fluorine in surface sediment, suggesting that a large proportion of fluorine in this fraction remained unknown. Sediment core samples collected from Niagara basin showed an increase in unidentified organic fluorine in recent years (1995–2006). These results suggest that the use and manufacture of fluorinated organic compounds other than known PFCAs and PFSAs has diversified and increased.

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1. Introduction

Polyfluoroalkyl/perfluoroalkyl substances (PFASs) are widely used anthropogenic chemicals. These chemicals are produced via two major manufacturing processes: electrochemical fluorination (ECF) since 1947 and telomerization since 1970 (Kissa, 2001). A mixture of linear, branched and cyclic perfluorooctanesulfonyl fluoride (POSF) with various carbon chain lengths is produced as the major ECF products (3M, 1999; Kissa, 2001); while telomerization yields a mixture with typically linear and even-numbered perfluorocarbon chains, although branched and odd chain products are possible if the starting materials are in this form. The strength of the carbon-fluorine bond accounts for the thermal and chemical stability of these compounds, rendering many of the PFASs (e.g., perfluorinated acids) resistant to hydrolysis, photolysis, biodegradation, and metabolism. These unique properties resulted in production for industrial and consumer applications, imparting them

excellent surfactants, water- or stain-proofing agents, grease or water resistant paper packaging materials (3M, 1999; Kissa, 2001; Korzeniowski, 2012). However, since the discovery of elevated perfluorooctane sulfonate (PFOS) in human and wildlife tissues (Giesy and Kannan, 2001), PFASs have been subjected to many monitoring studies. Detection of these compounds in major oceans (Benskin et al., 2012a; Yamashita et al., 2005, 2008), Arctic icecaps (Kwok et al., 2013; Young et al., 2007), in Arctic wildlife (Butt et al., 2007, 2010; Young et al., 2007), and in human tissues (Kannan et al., 2004; Yeung et al., 2013a, 2013b) has illustrated their global distribution and bioaccumulation.

Due to environmental concerns (persistence and toxicity), POSF-/ECF-based production by the 3M Company, one of the major fluorocarbon manufacturing companies, ceased in 2001/2002 (3M, 1998). In 2006, eight major fluorocarbon manufacturers agreed to participate in the perfluorooctanoate (PFOA) Stewardship program proposed by the USEPA (US EPA, 2006). The participants committed to 1) have a 95% reduction, measured from a year 2000 baseline, in emission of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals by 2010; and 2) eliminate the production of these chemicals by 2015. In Canada, PFOS-related compounds have been declared toxic under the Canadian Environmental Protection Act

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(Canada Gazette 2008). In May 2009, PFOS and related salts were included on the global list of persistent organic pollutants (POPs) under the Stockholm Convention. However, PFOS and POSF were listed in Annex B of the Convention, allowing the production and use of PFOS for many applications.

A study of PFAS concentrations in 38 Canadian rivers and creeks across Canada showed that PFOS values ranged from <0.02 to 34.6 ng L⁻¹ and that the highest concentrations occurred in waters downstream of areas with high population density (Scott et al., 2009). Another study has investigated the PFAS concentrations and biomagnification in the Lake Ontario food web (Martin et al., 2004). In that study 10-fold higher PFAS concentrations were found in the benthic invertebrate, *Diporeia*, compared to *Mysis*, a predominantly pelagic feeder. Their findings suggest that sediment was a major source of PFAS to this food web as opposed to water.

Elevated PFOS concentrations were found in Etobicoke Creek, Ontario, following a spill of aqueous film forming foams (AFFFs) at Toronto's airport (Moody et al., 2002). Elevated PFOS in the Welland River, near Hamilton airport, may also have reached Lake Ontario (de Solla et al., 2012). A recent study has investigated different fluorinated compounds present in commercially available AFFFs (Weiner et al., submitted for publication). The results showed that the known PFASs (e.g., C4–C14 perfluorocarboxylates (PFCAs), C4, C6, C8, C10 perfluorosulfonates (PFSAs)) accounted for 0.04–54% of the total organic fluorine in the foam samples, which suggested the presence of unidentified organic fluorine present in commercially available AFFFs. Sediment has been suggested as an important sink and reservoir of POPs, and it is also suggested to be a sink for long-chain PFASs. This unidentified organic fluorine may also be absorbed or adsorbed onto sediment. More importantly, a recent study has demonstrated the trophic biomagnifications of unidentified organic fluorine in a sub-tropical food web (Loi et al., 2011). It is thus pertinent to evaluate the extent of pollution in Lake Ontario by measuring both PFAS and extractable organic fluorine concentrations in sediment.

A recent study provided the first results of PFAS (C6, C8 and C10 PFSAs, FOSA, and C7–C11 PFCAs) concentrations in surface sediment and sediment core samples from Lake Ontario (Myers et al., 2012). The objectives of the present study were, firstly, to re-analyze some of the surface sediment and sediment core samples from three stations in the previous study (Niagara, Mississauga, and Rochester basins in Lake Ontario) for a wider suite of PFASs including short-chain PFCAs (C4–C6) and PFSAs (C4) to give a more comprehensive picture of PFAS pollution profiles; and secondly, to evaluate the extent of unidentified organic fluorine, if any, in the samples using combustion ion chromatography (CIC) to better understand the source(s) of contamination (Miyake et al., 2007).

2. Materials and methods

2.1. Standards and chemicals

Perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), ¹³C₂-PFBA, ¹³C₂-PFHxA, ¹³C₄-PFOA, ¹³C₅-PFNA, ¹³C₂-PFDA, ¹³C₂-PFUnDA, ¹³C₂-PFDoDA, perfluorooctanesulfonamide (FOSA), potassium salts of perfluorobutane sulfonate (PFBS), PFOS and ¹³C₄ PFOS, sodium salts of perfluorodecane sulfonate (PFDS), perfluorohexane sulfonate (PFHxS) and ¹⁸O₂-PFHxS, were purchased from the Wellington Laboratories (Guelph, ON). The purity of all standards was over 98%. Sodium fluoride (99%) and methanesulfonic acid were obtained from Wako Pure Chemical Industries (Osaka, Japan). Methanol (MeOH, LCMS grade), methyl-*tert*-butyl ether (MTBE, Omnisolv, >99%), ammonium acetate (>99%), and ammonia (NH₃, 30%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, >99%), and acetic acid (>95%) were acquired from EMD Chemicals Inc. (Mississauga, ON). OASIS solid phase extraction-weak anion exchange (SPE-WAX) cartridge (6 cm³, 150 mg, 30 μm) was

purchased from Waters Corporation (Milford, MA). ENVI-Carb graphitized carbon (100 mg) was purchased from Supelco (Supelco, Bellefonte, PA). Milli-Q water was used throughout the study.

2.2. Sample collection

Lake Ontario surface sediments (top 3 cm) were collected by Environment Canada (EC) personnel using a mini box corer in November in 2008. Sediment cores (10 cm diameter, 35 cm long) were obtained each of the 3 major depositional basins by EC personnel on board the Canadian Coast Guard ship (CCGS) *Limnos* using a large box core in July 2006. The details of the sampling campaign can be found elsewhere (Myers et al., 2012). In this study, surface sediment samples from 26 stations and sediment core samples from 3 stations were analyzed (Supplementary Information (SI) Fig. S1). Approximately 1 g (dry weight (d.w.)) was used for PFAS analysis.

2.3. Dating of the sediment core and flux calculation

Radiometric dating of the cores was conducted by EC (Aquatic Contaminants Research Division, Burlington, ON) by measuring the specific activities of ²¹⁰Pb using the polonium distillation procedure and alpha counting; the counting was conducted using an alpha spectrometer (Eakins and Morrison, 1978). The ²¹⁰Pb activity profile of the sediment core was used to determine the sedimentation rate using the constant rate of supply (CRS) model (Oldfield and Appleby, 1984), which gave mass sedimentation rates ranging from 0.020 to 0.069 g cm⁻² yr⁻¹ among the three stations (SI Table S1). Focusing factors of the three depositional basins were calculated as the ratio of the accumulated ²¹⁰Pb activity (unsupported ²¹⁰Pb inventory) to that expected from regional atmosphere input (Simcik et al., 1996). The focusing factors for stations 1004, 1034, and 1046 were calculated as 1.1, 1.4, and 1.3, respectively (SI). The flux was calculated using Eq. (1); this approach has been used in similar studies (Qiu et al., 2007; Wong et al., 1995).

$$\text{Flux}_i = \frac{C_i R}{\text{FF}} \quad (1)$$

where,

Flux_i the flux in sediment segment 1 (ng cm⁻² yr⁻¹)
 C_i the analyte concentration in sediment segment i (ng g⁻¹ d.w.)
 R the sedimentation rate as calculated by the CRS model (g cm⁻² yr⁻¹)
 FF the focusing factor.

2.4. Sample extraction

Surface sediment samples were extracted in triplicate, while sediment core samples were extracted in duplicate. Internal standards were only spiked onto one of the replicates before alkaline digestion. Both spiked and non-spiked samples were analyzed for PFASs, whereas only the non-spiked samples are applicable for extractable organic fluorine analysis. The schematic diagram for the extraction is given in the SI Fig. S2. In brief, 1 g sediment was mixed with 2 mL of 200 mM NaOH in MeOH and sonicated for 30 min. Then, 20 mL of MeOH was added to the mixture and then shaken at 250 rpm for 30 min. After that, 0.05 mL of 4 M HCl was added. The sediment and the methanol extract were separated by centrifugation at 6000 rpm for 15 min. The supernatant was transferred into a new 50 mL polypropylene (PP) tube. The above procedures were repeated except that 10 mL of MeOH was used instead of 20 mL. The total volume of the final extract was 30 mL of MeOH. 10 mL of the extract was used for further analysis. The 10 mL of MeOH extract was then reduced to 3 mL under a gentle stream of high purity nitrogen gas

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