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Application of a comprehensive extraction technique for the determination of poly- and perfluoroalkyl substances (PFASs) in Great Lakes Region sediments

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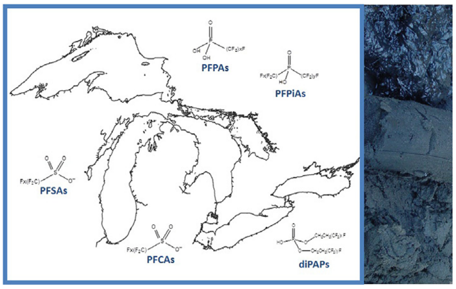
HIGHLIGHTS

- Simultaneous extraction of PFSAs, PFCAs, diPAPs, PFPiAs and PFPAs from sediment.
- PFAS contribution in Lake Ontario was dominated by PFOS.
- Remote lakes contained sediment with higher proportions of PFCAs and diPAPs.
- PFAS concentrations increased with time but proportion of PFOS to ΣPFAS decreased.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive method to extract perfluoroalkane sulfonic acids (PFSAs), perfluoroalkyl carboxylic acids (PFCAs), polyfluoroalkyl phosphoric acid diesters (diPAPs), perfluoroalkyl phosphinic acids (PFPiAs) and perfluoroalkyl phosphonic acids (PFPAs) 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 (ΣPFASs 13.1 ng/g), where perfluorooctane sulfonic acid (PFOS) contributed over 80% of the total. Concentrations in Lake Ontario were approximately 1–2 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

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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.

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 (PFSAs) 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, 3 M, the dominant producer of perfluorooctane sulfonyl fluoride (POSF) based products, including PFOS, phased out production between 2000 and 2002 (3 M, 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. 2008, 2009; 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, b; 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 0.33–6.5 ng/L in wastewater (D'eon et al., 2009a, b), 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 PFSAs (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., 2009a, b). Lee and Mabury (2011) also reported detectable diPAPs in pooled human sera samples from the U.S. at mean concentrations of 130 ± 40 ng/L. High concentrations of diPAPs (frequency of detection 100%, ΣdiPAPs 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, 2014), and through biotransformation in rats (D'eon and Mabury, 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 PFSAs 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, b; Lee et al., 2010; Lee et al. 2014) and biota (D'eon and Mabury, 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