



Historical trends of inorganic and organic fluorine in sediments of Lake Michigan



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HIGHLIGHTS

- We took 8 sediment cores and 27 ponar grabs from Lake Michigan in 2010.
- Samples were extracted for total fluorine, extractable fluorine and 25 PFCs.
- PFOS and PFOA are the predominant PFCs in sediment cores.
- PFBS and PFBA are appearing in upper sections at concentrations similar to PFOS and PFOA.
- TF and EOF concentrations are orders of magnitude higher than PFCs.

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ABSTRACT

Total fluorine (TF), extractable organic fluorine (EOF) and poly- and per-fluorinated compounds (PFCs) were measured in eight dated cores of sediment taken along with 27 surface sediments from Lake Michigan in 2010. Based on rates of sedimentation, total concentrations of PFCs (\sum PFCs) reached a maximum in the later 1990s and early 2000s. This result is consistent with rapid changes in production and subsequent sedimentation. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are still the predominant PFCs in the cores, but in surface sediments, concentrations of perfluorobutane sulfonate (PFBS) and perfluorobutanoic acid (PFBA) are now occurring at concentrations comparable to those of PFOS and PFOA. This observation is consistent with shifts in patterns of production and use in the US and Canada. Concentrations of TF in sediments were greater than those of EOF. This result is consistent with a larger proportion of un-extractable fluorinated material in both surface sediments and in cores.

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1. Introduction

Per- and poly-fluorinated compounds (PFCs) are chemically and thermal stable and have the ability to lessen surface tension and

create stable foams, which make them ideal for a range of industrial and home uses (Prevedouros et al., 2005). Though first manufactured in the late 1940s, production of PFCs began to increase dramatically in the 1970s with global production of per-fluorosulfonate (PFOS) based compounds increasing from ~500 tonnes per annum in the 1970s to an annual production of ~4500 tonnes by the 1990s (Paul et al., 2008).

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Advances in mass spectrometry in the 1990s allowed identification and quantification of PFCs in the environment. Giesy and Kannan (2001) showed that PFC contamination in biota is a global issue, and some degradation products are toxic at environmentally relevant concentrations. This resulted in ever-increasing interest in the environmental occurrence, chemodynamics and potential effects of perfluorinated alkyl carboxylates and sulphonates (Renner, 2001). Presence of PFCs in air (Ahrens et al., 2011), water (Ahrens et al., 2010), snow (Young et al., 2007), and humans (Yeung et al., 2005) have been reported, which has improved understanding of chemical transport of PFCs. But there is limited understanding of their long-term environmental fate, although they are found to have been deposited into sediments of natural rivers, lakes and estuaries (Stock et al., 2007; Naile et al., 2010).

In Europe, North America and Japan, PSOF and its related compounds has come under restriction (USEPA, 2000; CEC, 2002). Since the production was reduced, concentrations in some environmental matrices have decreased (Kannan et al., 2005; Young et al., 2007).

Temporal trends in concentrations of PFCs have been characterized in human blood serum (Harada et al., 2007; Haug et al., 2009), biota (Holmström et al., 2004; 2010), snow (Young et al., 2007), and sediment (Stock et al., 2007; Zushi et al., 2010). In all matrices specific PFCs such as PFOA and PFOS have increased until the late 1990s. In Japan, PFCs in human blood samples from 1983–1999 on average increased by 3.5 times while in guillemot eggs from 1960 to 2003 showed a 50 fold increase (Haug et al., 2009).

This study is one of the most detailed investigations of PFCs, total fluorine (TF) and extractable organic fluorine (EOF) in the sediment of Lake Michigan. The objectives of this work were to reveal the spatial and temporal trends of PFC contamination recorded in the sediment of this freshwater lake of the North America.

2. Methods

2.1. Chemicals

Omni-Solv grade methanol (MeOH), methyl *tert*-butyl ether (MTBE), and sodium thiosulphate were purchased from EMD Chemicals (Gibbstown, NJ, USA), HPLC grade ammonium acetate was purchased from J.T. Baker (Phillipsburg, NJ, USA). Perfluorinated standards were purchased from Wellington Laboratories, and included 9 mass labelled recovery standards. A list of native and mass labelled PFC compounds is given in the [Supporting Information](#) along with compound name abbreviations (SI Table S1).

2.2. Sample collection

Both Ponar and core samplers were used during September 2010 to collect sediments from the *R/V Lake Guardian*. See [Supporting Information](#) for detailed sampling methods (SI 1.1). The sampling locations are shown in [Fig. 1](#), (additional location information is given in [Table SI. 2](#)).

2.3. Sample extraction, identification and quantification of PFCs

A total of 192 samples were analysed, including 159 core layers, 27 Ponar samples and 6 blanks, using the method described by Naile et al. (2010). Briefly Each sample was lyophilized, and homogenized, fortified with surrogate standard extracted by replicates of MTBE. Samples were cleaned using Envi Carb and reconstituted in MeOH, before analysis by LC-MSMS (See [SI 1.2](#) for detailed extraction method, and [SI 1.3](#) for instrumental operating conditions). Selection of PFCs in this study was based environmental

relevance and physical chemical properties that imply their potential presence in the overlying water and some propensity for particles (Ahrens et al., 2009).

2.4. TF and EOF analysis

Total fluorine and extractable fluorine were measured by use of combustion ion chromatography (CIC). TF was measured using a 0.01 g aliquot of dried sediment and EOF a fraction of the extracted sample used for PFC identification (additional detail is given in the [SI 1.4](#)).

2.5. Rate of sedimentation

Gamma spectroscopy using two well-type HPGe detectors yielded radioactivity profiles for ^{210}Pb , ^{241}Am , ^{226}Ra , and ^{137}Cs for all cores. Rates of sedimentation were calculated by use of methods described by Appleby (2001), and are within the range of those obtained in previous studies (Robbins and Edgington, 1975; Hermanson et al., 1991; Zhang et al., 1993). See [SI 1.5](#) and [SI Table S3](#) for further information.

2.6. Quality control and assurances

Background contamination was assessed through the use of field and travel blanks. Individual PFCs in the blanks were below the limits of detection, which were calculated as $5\times$ the background method detection limits (MDLs) and ranged from 1 to 0.1 ng mL^{-1} ([SI Table S4](#)). Matrix spike recoveries were calculated from the mean response of the mass labelled standard, and averaged 82% for individual compounds with a range of 31–130% and low standard deviations ([SI Table S4](#)).

Statistical modelling to determine interrelationships between surface Ponar grabs ($n = 27$) using standardized squared Euclidean cluster analysis to calculate distance between samples, and clustered by nearest neighbour (single linkage) and analysis of variance (ANOVA), was performed using software Statgraphics Centurion XVI of StatPoint Technologies, Inc. (Warrenton, Virginia).

3. Results and discussion

Of the 25 PFCs characterized in this study, PFODA, N-MeFOSA, and N-EtFOSA were not detected in either Ponar grab samples or cores. FOSA and FOSAA were observed in <20% of samples, at concentrations near or less than the MDL.

3.1. PFCs in surface sediments

Dry weight (dw) based concentrations of PFCs which were detected in >60% of Ponar grab sediments are summarized in [Table 1](#). The concentrations are comparable to those previously reported from other locations in the Northern Hemisphere with the exception of Resolute Lake, Cornwallis Island Canada, where local discharge sources were suspected (Stock et al., 2007) (See [SI Table S5](#)). While not exhaustive, this comparison indicates the paucity of information on PFCs in sediments. Differences in measured concentrations among studies, especially for individual compounds, may be related to geographical locations, different methods used during sample collection, chemical analysis, and the sampling time periods. During 1997–2003, a reduction in production and use of both PFOA and PFOS as well as their precursor chemicals was implemented alongside the increased use of the 4-C PFCs (Prevedouros et al., 2005; Paul et al., 2008).

The spatial distribution of selected PFCs in surface sediments of Lake Michigan is illustrated in [Fig. 2](#). Concentrations of $\sum_{25}\text{PFCs}$

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