



Spatial and temporal trends in poly- and per-fluorinated compounds in the Laurentian Great Lakes Erie, Ontario and St. Clair[☆]

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ABSTRACT

The temporal and spatial trends in sediment of 22 poly- and perfluorinated (PFAS) compounds were investigated in the southern Great Lakes Erie and Ontario as well as Lake St. Clair. Surface concentrations measured by Ponar grab samples indicated a trend for greater concentrations near to urban sites. Mean concentrations \sum_{22} PFAS were 15.6, 18.2 and 19 ng g⁻¹ dm for Lakes St. Clair, Erie and Ontario, respectively. Perfluoro-n-butanoic acid (PFBA) and Perfluoro-n-hexanoic acid (PFHxA) were frequently determined in surface sediment and upper core samples indicating a shift in use patterns. Where PFBA was identified it was at relatively great concentrations typically >10 ng g⁻¹ dm. However as PFBA and PFHxA are less likely to bind to sediment they may be indicative of pore water concentrations. Sedimentation rates between Lake Erie and Lake Ontario differ greatly with greater rates observed in Lake Erie. In Lake Ontario, in general concentrations of PFAS observed in core samples closely follow the increase in use along with an observable change due to regulation implementation in the 1970s for water protection. However some of the more water soluble PFAS were observed in deeper core layers than the time of production could account for, indicating potential diffusion within the sediment. Given the greater sedimentation rates in Lake Erie, it was hoped to observe in greater resolution changes since the mid-1990s. However, though some decrease was observed at some locations the results are not clear. Many cores in Lake Erie had clearly observable gas voids, indicative of gas ebullition activity due to biogenic production, there were also observable mussel beds that could indicate mixing by bioturbation of core layers.

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1. Introduction

In 2001, perfluoro-n-octane sulfonate (PFOS) was found to be

ubiquitous in piscivorous animals, which alerted scientists and managers to the widespread and bioaccumulative behaviour of this perfluorosulfonate (Giesy and Kannan, 2001, 2002). Further studies into per- and poly-fluorinated compounds (PFASs) identified accumulation in abiotic matrices such as sediment (Codling et al., 2014) and glacial snow (Wang et al., 2014). The vector of transport for PFASs was not completely understood, because forms have been observed in the atmosphere of remote arctic locations (Ahrens et al., 2011) and in ocean water (Cai et al., 2012).

Between 1970 and 2002, an estimated 122,500 t of

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perfluorosulfonates were produced with ~37% entering the environment (Paul et al., 2009). Uses of PFASs have been varied and included, among others, carpet stain protection, clothing, fire-fighting foams, paper, aviation fluids and packaging materials (Prevedouros et al., 2006). Releases to the environment have been and continue to be via multiple routes, including air and water during manufacture, loss during consumer use and disposal via landfill and incineration (Lang et al., 2016). In humans and wildlife, concentrations in blood in industrialized regions are as great as 30,000 ng mL⁻¹, while in Arctic sites more remote from industrialization and urbanization, including open ocean, concentrations in blood have been as great as 3000 ng mL⁻¹ (Houde et al., 2006).

Concerns over the ubiquitous contamination of PFASs and the toxic potencies of longer chain (C8) chemicals have resulted in PFOS, its salts and perfluoro-n-octane sulfonyl fluoride (PFOS-F) being introduced to the Stockholm Convention on Persistent Organic Pollutants after its 4th meeting in 2009 (UNEP, 2009). In the United States, under the Toxic Substances Control Act (TSCA), two sub-categories of concern were created that include longer-chain alkyl carboxylic compounds (>C8) including perfluoro-n-octanoic carboxylic acid (PFOA) and those of >6 sulfonate carbons including PFOS and perfluoro-n-hexane sulfonic acid (PFHxS). The goals of TSCA listing include the removal of longer chain PFASs from products and emissions by 2015 (USEPA, 2016). In Canada, on January 13, 2009, PFOS and its salts were added to the virtual elimination list Part II compiled under subsection 65 (2) of CEPA 1999. The regulations demonstrate Canada is continuing in a commitment to virtually eliminate PFOS and to meet the requirements of the Perfluorooctane Sulfonate Virtual Elimination Act, that received Royal Assent on April 17, 2008 (Canada, 2016). This resulted in 87 compounds that could degrade to PFOS being banned from manufacture, use, transport or importation to Canada. To assess trends in environmental media and effectiveness of implementation of these regulations, it is important to know the environmental occurrence of these compounds at present and in the past.

There has been a large body of evidence demonstrating the accumulation of persistent compounds in sediments of the Great Lakes. Intensive surveys of sediment, have identified organochlorine pesticides (OCPs) (Kannan et al., 2006), and polychlorinated biphenyls (PCBs) (Hornbuckle et al., 2006; Li et al., 2009), along with mercury and other metals (Marvin et al., 2004). Among all five of the Laurentian Great Lakes (Superior, Huron, Ontario, Michigan and Erie) it was found that Lakes Erie and Ontario contained the greatest concentration of contaminants. In 2012, the US-Canada Great Lakes Water Quality Agreement listed 31 areas of concern (AOCs); 15 of them are within the drainage areas of Lakes Erie, Ontario, and St. Clair (USEPA, 2016). These AOCs were identified based on levels of legacy municipal and industrial contamination in the sediment and water. In Lake Erie, the Western Basin had the greatest mean concentrations of OCPs with the Detroit River having the greatest observed concentrations (Marvin et al., 2002). In Lake Ontario, sites in the southern region had the greatest concentration of contaminants for OCPs and PCBs than other sites (Marvin et al., 2004).

PFASs represent a significant fraction of total measured contaminants in fishes of the Great Lakes, and were more abundant in Lakes Erie and Ontario than in the other three lakes (McGoldrick and Murphy, 2016; Stahl et al., 2014). This pattern of contamination is mirrored in Herring gull eggs with Erie and Ontario eggs having significantly greater concentrations of PFAS than other lakes (Gebbinck et al., 2009; Letcher et al., 2015). In a study of fish by Environment Canada and the US EPA, PFOS occurred at the 6th and 10th greatest concentrations of contaminants monitored in Lake Erie (70 ± 33 ng g⁻¹ wm for Walleye) and Lake Ontario

(54 ± 30 ng g⁻¹ wm for Lake Trout), respectively. These are greater than the PFOS concentrations of 27.4 ± 2.2, 3.7 ± 2.4, and 11.6 ± 4.3 ng g⁻¹ wm measured in the fish of Lakes Huron, Superior and Michigan, respectively (McGoldrick and Murphy, 2016). Concentrations of perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorobutyric acid (PFBA), perfluorotridecanoic acid (PFTTrDA), perfluorodecanoic acid (PFDoA), perfluoro nonanoic acid (PFNA) and PFOS were all within the top 40 contaminants measured in Erie and Ontario based upon concentration and frequency of determination (McGoldrick and Murphy, 2016).

Sediments of lakes can provide a historical record of chemicals loaded to surface waters. Concentrations of PFAS have been observed to increase in sediment with time (Codling et al., 2018; Codling et al., 2014; Stock et al., 2007). In Tokyo Bay, Japan, since the change from commercial use of longer chain PFAS to those with shorter chains, compounds detected in sediments have changed rapidly (Zushi et al., 2010). The question remains whether these changes in commercial formulations have resulted in observed changes in PFAS in the lower Great Lakes such as observed previously in the upper Great Lakes (Codling et al., 2018; Codling et al., 2014). Lakes Erie and Ontario are by far the most contaminated of the Great Lakes and Lake Erie has a greater sedimentation rate. Both of these factors make the lower Great Lakes potentially ideal for identification of current and historical trends in PFAS concentrations. In this study concentrations of 22 PFAS, total fluorine (TF) and extractable organically-bound fluorine (EOF) were measured in surface sediments and cores collected during 2013–2014 in Lakes Ontario, St. Clair and Erie.

2. Materials and methods

2.1. Collection of sediments

Samples of sediments were collected on board the *R/V Lake Guardian* in Lake Ontario (ON) in 2013 and Lake Erie (ER) in 2014, and by a small boat on Lake St. Clair (C) in 2014 (Fig. 1, and Supporting Information (SI) Table S1). Cores of sediments were collected simultaneously into four polycarbonate tubes (10 cm o. d. 9.5 cm i. d. and 59.6 cm long), by use of a model MC-400 Multi-Corer (Ocean Instruments, San Diego, California). In total, six cores were collected from Lake Erie, seven from Lake Ontario, and one from Lake St. Clair. Sectioning of the cores occurred immediately after collection, and the sections at the same sediment segment depth from four sub-cores were combined and homogenized in glass bowls. Cores from Lake Erie were sectioned into 2 cm segments throughout the length of the cores. Each core from Lake Ontario was sectioned into 1 cm segments for the first 10 cm, followed by 2-cm layers thereafter. The core from Lake St. Clair was sectioned into 1 cm segments for the first 15 cm and 2-cm layers thereafter.

Surface grab samples (later referred to as Ponar) were collected using a Ponar sampler at 45 locations in Lake Erie, 11 in Lake St. Clair and 59 in Lake Ontario (Fig. 1, SI Table S1). The sampler scoop area was 152 × 152 mm. Ponar samples were homogenized using a stainless steel mixing blade attached to a power drill.

Field blanks (n = 3 per lake) were sodium sulfate in glass jars which were exposed during extraction of cores; while travel blanks (n = 3 per lake) were remained closed, during collection. Depths of overlying water at sampling locations ranged from 1.4–6.4 m, 6–65 m and 25–230 m in Lake St. Clair, Erie and Ontario, respectively (SI Table S1).

2.2. Sample preparation and analysis

Detailed analytical methods used to identify and quantify PFAS

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