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Current and historical concentrations of poly and perfluorinated compounds in sediments of the northern Great Lakes – Superior, Huron, and Michigan☆

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ABSTRACT

Current and historical concentrations of 22 poly- and perfluorinated compounds (PFASs) in sediment collected from Lake Superior and northern Lake Michigan in 2011 and Lake Huron in 2012 are reported. The sampling was performed in two ways, Ponar grabs of surface sediments for current spatial distribution across the lake and dated cores for multi-decadal temporal trends. Mean concentrations of the sum of PFASs (∑PFASs) were 1.5, 4.6 and 3.1 ng g^{-1} dry mas (dm) in surface sediments for Lakes Superior, Michigan and Huron, respectively. Of the five Laurentian Lakes, the watersheds of Superior and Huron are the less densely populated by humans, and concentrations observed were typically less and from more diffuse sources, due to lesser urbanization and industrialization. However, some regions of greater concentrations were observed and might indicate more local, point sources. In core samples concentrations ranged from <LOQ to 46.6 ng g^{-1} dm among the three lakes with concentrations typically increasing with time. Distributions of PFASs within dated cores largely corresponded with increase in use of PFASs, but with physiochemical characteristics also affecting distribution. Perfluoroalkyl sulfonates (PFSAs) with chain lengths >7 that include perfluoro-n-octane sulfonate (PFOS) bind more strongly to sediment, which resulted in more accurate analyses of temporal trends. Shorter-chain PFASs, such as perfluoro-n-butanoic acid which is the primary replacement for C8 PFASs that have been phased out, are more soluble and were identified in some core layers at depths corresponding to pre-production periods. Thus, analyses of temporal trends of these more soluble compounds in cores of sediments were less accurate. Total elemental fluorine (TF) and extractable organic fluorine (EOF) indicated that identified PFASs were not a significant fraction of fluorine containing compounds in sediment (<0.01% in EOF).

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1. Introduction

Distributions of perfluorochemicals (PFASs) have been characterized previously in a range of environmental matrices including sediment (Higgins and Luthy, 2006), snow (Codling et al., 2014a) and the atmosphere (Ahrens et al., 2011). Some PFASs are persistent in the environment and can cause toxicities (Surma and Zieliński, 2015). However, production volumes and historical distributions of PFASs are still not fully understood (Paul et al., 2009). If available archived material of the matrix of interest (e.g. water or sediment) can be used for monitoring or retrospective assessments, but such archives are either unavailable or only intermittent. In addition, some archived materials are not suitable for the assessment of some compounds of interest, or were not appropriately stored or are potentially contaminated during collection or storage. Due to widespread use of perfluorinated materials in seals, tubing and packing of samples, these effects are particularly an issue for PFASs. Therefore, to measure historical trends it is necessary to investigate materials where deposition occurs such as snow on glaciers (Wang et al., 2014) or sediment (Codling et al., 2014b). Sediments provide a matrix that preserves an historical record of releases to the environment.

High production volume compounds such as PFASs have their waste streams and atmospheric emissions monitored at source or bulk industrial use such that they are within agreed limits of discharge to the environment. However, when a compound is used it can enter the environment over the lifetime of the products containing it, so complete prevention of contamination is impossible (Prevedouros et al., 2006; Paul et al., 2009). Concern over potential effects of PFASs grew rapidly when they were found to be widespread in the environment, persistent and toxic during both *in-vitro* and *in-vivo* studies (Renner, 2001). In a comprehensive assessment of piscivorous animals from across the globe it was found that perfluorochemical surfactants were ubiquitous in biota and that aquatic systems were primary repositories (Giesy and Kannan, 2002). Further concerns about exposure of humans and potential for adverse effects on health have also been investigated for several PFASs, including perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS). A study of >600 pregnant women showed a statistically significant correlation was observed between exposure and immune system efficiency in offspring between 1 and 4 years (Dalsager et al., 2016).

The Laurentian Great Lakes of North America have been used for transport and waste disposal for hundreds of years; but it was not until the urbanization and industrialization of the region that activities of human affected more than local areas. Similar to other contaminants, PFASs may have ubiquitously contaminated the Great Lakes (Giesy et al., 2006). PFAS have been detected in the waters of these lakes (Furdui et al., 2008). The food chain in the lakes, from *Diporeia* to trout, was also contaminated (Stahl et al., 2014; Furdui et al., 2008, 2007; Kannan et al., 2005). However, information on the accumulation of PFASs in the sediment of the Great Lakes is scarce (Codling et al., 2014b). Knowing current as well as historical status and trends of concentrations in sediment cores is useful for showing current and past exposure as well as elucidating potential sources and efficacies of controls on production, changes in patterns of use and mitigation of releases.

Partitioning behaviors of PFASs in sediments have been investigated for PFOA, PFNA, PFDA, perfluoro-n-undecanoate (PFUnA), PFOS, perfluoro-n-decanesulfonate (PFDS), 2-N-methylperfluoro-n-octanesulfonamido acetic acid (N-MeFOSAA), and 2-N-ethylperfluoro-n-octanesulfonamido acetic acid (N-EtFOSAA). Results of those studies have shown sediment- and solution-specific characteristics influence sorption with organic carbon in sediment and electrostatic interactions being key factors (Higgins and Luthy, 2006). A study of partitioning behaviors between PFASs and pore water or particulates in sediment indicated that PFASs of chain length <7 carbons are more likely to remain in pore-water than to be associated with particles in sediments, and therefore could be subject to distribution to deeper sediment layers (Ahrens et al., 2010). These findings are of importance in interpreting concentrations in sediments collected from cores, because uptake might change both spatially and temporally with environmental changes and the greater use of short chain PFASs in the last decade may be more difficult to measure accurately in sediment.

Lake Superior is the most northern of the North American (Laurentian) Great Lakes, and its dominant outflow is through the St. Mary's River into Lake Huron. Lake Superior is relatively remote with low population density in its watersheds and has relatively lesser concentrations of persistent organic pollutants (POPs) in sediments, compared to the other Great Lakes (Li et al., 2006, 2009). The long residence time (171 y) of the water in Lake Superior is of concern in contaminant accumulation. Lakes Huron and Michigan share some common features, with similar elevation, latitudes, and water surface area. The southern parts of both lakes are more industrialized and densely populated than the northern parts. In the more remote regions, PFAS contamination may be primarily from atmospheric deposition.

The objective of this study was to investigate historical trends in concentrations of PFASs in the northern region of the Laurentian Great Lakes at 20 locations (9 Lake Superior, 2 Lake Michigan, 9 Lake Huron) as well as the current surface sediment (upper 40 mm; $n = 82$) as part of the Great Lakes Sediment Surveillance Program.

2. Methods

2.1. Chemicals and reagents

Distilled HPLC grade or equivalent acetonitrile (ACN; Fisher Scientific, Ottawa, ON Canada) and methanol (EMD Chemicals, Gibbstown, NJ, USA) were used during extraction. Acetic acid (99% pure) was from Sigma Aldrich. Water used during extraction and for LCMS-MS milli-rho was further purified by use of a Millipore system (18 Ω) and cleaned using Waters OASIS WAX cartridge (60 mg 6 cc) to remove PFAS contaminants. Extraction of samples used Waters HLB cartridges (60 mg 6 cc). Perfluorinated standards were purchased from Wellington Laboratories (Guelph, ON, Canada), and included 9 mass labelled recovery standards, 29 compounds were initially screened for but based upon previous investigations (Codling et al., 2014a,b) only 22 are discussed in this report (see SI Table S1). All samples were extracted in polypropylene Falcon tubes (Fisher Scientific, later referred to as tubes).

2.2. Collection and characterization of sediments

Sample collection took place on Lakes Superior and Michigan in 2011 and on Lake Huron in 2012, onboard of Research Vessel *Lake Guardian*. Two types of sediment samples were collected; Ponar-grab samples and core samplessee Fig. 1. The Ponar grab sampler collected ‘surface’ sediment with a scoop area of 152 × 152 mm. The grabbed sediment was homogenized using an electric drill fitted with a 127 mm diameter paddle. Given that the depth of penetration of the Ponar is dependent on compaction of sediments and that sedimentation rate varies, the sample therefore represents the region where water/sediment interaction occurs but can include several decades of sedimentation in any sample. Core samples were taken using the Model MC-400 Multi-corer (Ocean Instruments, San Diego, California), with samples collected