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Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America

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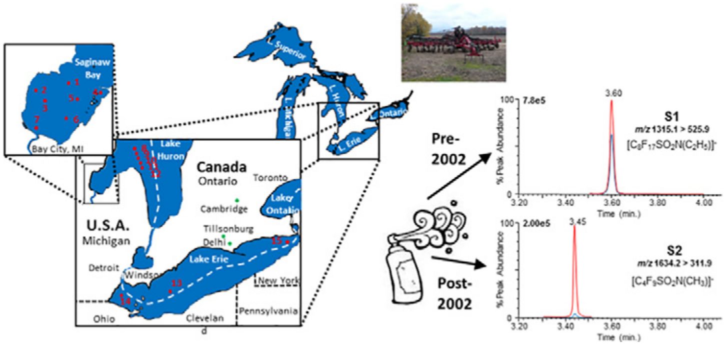
HIGHLIGHTS

- Major side-chain fluoroalkyl components found in pre- and post-2002 Scotchgard products
- High concentrations of the pre-2002 product component found in biosolid-augmented agricultural soil samples
- Both components were at greater concentrations in soil and sediment samples than all other perfluorinated compounds
- These results help to explain the low PFAS portion accountability in extractable organic fluorine content in sediments

GRAPHICAL ABSTRACT



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ABSTRACT

Side-chain fluorinated polymer surfactants are the main components of fabric protector sprays and used extensively on furniture and textiles. The composition of these commercial protector products has changed, but there is currently a total dearth of information on these novel fluorinated polymers in the environment. Using a developed analytical approach, two complementary studies examined the distribution of Scotchgard™ fabric protector components in aquatic sediment and in agricultural soils where wastewater treatment plant (WWTP) sourced biosolid application occurred, and in samples from sites in the Laurentian Great Lakes basin of North America. The main components in the pre- and post-2002 Scotchgard™ fabric protectors were identified by MS/MS and Q-TOF-MS to contain a perfluorooctane sulfonamide (S1) and perfluorobutane sulfonamide (S2) based side-chain, respectively, and bonded to a polymer backbone. In fifteen sediment samples collected in 2012–2013 from western Lake Erie and Saginaw Bay (Lake Huron), S1 was in all sediment samples (0.18 to 461.59 ng/g dry weight (d.w.)); S2 was in 80% of the sediment samples (<0.03 to 24.08 ng/g d.w.). Thirteen soil samples were collected (2015) from a biosolid applied and two non-biosolid applied farm field sites in southern Ontario (Canada). S1 was detected in 100% of the soil samples from biosolid-augmented agricultural sites (mean 236.36 ng/g d.w.; range 41.87 to 622.46 ng/g d.w.), and at concentrations much greater than in the aquatic sediment samples. The concentration of S1 and S2 in soil and sediment samples were also much greater than the total concentration of other per-and poly-fluoroalkyl substances (PFASs) that were measured.

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The ratio of S1 concentration versus $\sum_{22}$PFAS concentration was up to 1616 in sediment samples from Lake Erie. This results helps to explain why known PFASs account for low percentages of the total extractable organic fluorine (EOF) content in sediment.

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1. Introduction

Per and poly-fluoroalkyl substances (PFASs) including their precursors have been produced since mid-20th century and used in numerous industrial and commercial applications (Prevedouros et al., 2006; Lindstrom et al., 2011; Buck et al., 2011; Betts, 2007). Their widespread use has resulted in a release of PFASs into the environment either from direct sources as well as from indirect sources, such as via degradation of precursors (Prevedouros et al., 2006; Lindstrom et al., 2011; Zareitalabad et al., 2013; Benskin et al., 2012; Nadal and Domingo, 2014; Anderson et al., 2016; Liu and Avendano, 2013; Houtz et al., 2013). Worldwide investigations have shown that PFASs, particularly perfluorinated carboxylic acids (PFCAs) and sulfonic acids (PFSAs), are environmentally ubiquitous and including in humans (Buck et al., 2011; Ahrens et al., 2009; Rankin et al., 2016; Kwadijk et al., 2010; Labadie and Chevreuil, 2011; Letcher et al., 2015; Butt et al., 2010; Olsen et al., 2005; Olsen et al., 2012; Braune and Letcher, 2013; Houde et al., 2006; Houde et al., 2011; White et al., 2015).

PFAS studies have mostly targeted PFCAs (C_nF_{2n} + COOH), PFSAs (C_nF_{2n} + SO_3H) and some of their possible precursors, which are of low molecular weight. However, there has been very few studies on larger PFAS functional derivatives and polymers (Chu and Letcher, 2014; Russell et al., 2008; Washington et al., 2009). Side-chain fluorinated polymers are important industrial materials, which possess polyfluorinated chains that are chemically bonded to non-fluorinated polymer backbones (Buck et al., 2011). Side-chain fluorinated polymers represent a high percentage of all commercially available PFAS products and are used in a variety of household products such as fabric protector sprays (Buck et al., 2011; Liu and Avendano, 2013; Wang et al., 2014).

The largest producer of PFOS and its C_8 chemistry was The 3 M Company, which phased-out its PFOS-based production in 2002 (The 3M Company, 2000). For the first time, to our knowledge, we recently reported that pre- and post-2002 Scotchgard™ fabric protectors contain side-chain fluorinated polymers that could be metabolized to perfluoroalkyl sulfonamides in vitro using a rat liver microsomal based assay (Chu and Letcher, 2014). These fluorinated polymer components are widely used in commercial applications and possess strong sorption behaviour on surfaces in human indoor environments (e.g. textiles, upholstery) (Renner, 2006). It can be hypothesized that these side-chain fluorinated polymers are present in the environment, especially in receiving compartments from wastewater treatment plant (WWTP) outflows, such as sediment, sludge and soil, and result in important indirect pollution sources of PFASs (Arvaniti and Stasinakis, 2015; Buck et al., 2011; Lindstrom et al., 2011).

There are uncertainties surrounding the routes and magnitude of PFAS contamination in terrestrial soils and aquatic sediments (Prevedouros et al., 2006; Wang et al., 2014). Codling et al. (2014) measured total fluorine (TF), extractable organic fluorine (EOF) and poly- and per-fluorinated compounds (abbreviated PFCs rather than the correct PFASs) in some dated sediment cores and grab surface sediments from Lake Michigan. Of the total elemental fluorine, only 0.2% was accounted for by quantifiable PFCs in the sediment cores and surface samples. A previous study in Lake Ontario also hypothesized that significant amounts of unidentified organic fluorine might present in sediment, and this unidentified organic fluorine could include precursor and/or intermediate compounds of PFCAs and PFSAs (Yeung et al., 2013).

At present little is known about behaviour of side-chain fluorinated polymers in the environment (Buck et al., 2011; Liu and Avendano, 2013; Russell et al., 2008). In this study, using a novel developed analytical method, which included a d-SPE cleanup step and UHPLC/MS/MS determination, we investigated and compared the main components of Scotchgard™ fabric protectors, i.e. side-chain fluorinated polymer surfactants, in aquatic sediment samples and in agricultural soil samples that had been augmented with WWTP-sourced biosolids from study sites in the southern half of the Laurentian Great Lakes basin of North America.

2. Materials and methods

2.1. Chemicals and materials

Scotchgard™ pre-2002 formulation (Tech. mix) (100 μg/mL in methanol) and Scotchgard™ post-2002 formulation (Tech. mix) (100 μg/mL in methanol) were purchased from AccuStandard Inc. (New Haven, CT, USA). As detailed by the supplier, these two standard solutions were prepared from commercial products of Scotchgard™ fabric protector produced before 2002 and after 2002 by The 3 M Company. Working standard solutions (with concentration of 100 ng/mL and 1000 ng/mL) were prepared by mixing these two standard solutions and then diluting with methanol. Perfluoro-1-butane-sulfonamide (FBSA) was synthesized and purified in our lab according the method described by Benfodda et al. (2010) with some modifications as detailed in Chu et al. (Chu and Letcher, 2014). Perfluoro-1-ethylcyclohexylsulfonate (PFEtCHxS) was purchased from Campro Scientific GmbH (Berlin, Germany). All other PFAS standard solutions, including the mass-labelled internal standards, were purchased from Wellington Laboratories (Guelph, ON, Canada). The standard solutions were prepared according our previously published paper (Chu et al., 2016).

Disposable silica gel solid-phase extraction (SPE) columns (500 mg; J.T. Baker®) were purchased from VWR International (Mississauga, ON, Canada). Oasis WAX SPE cartridges (60 mg × 3 mL) were purchased from Waters Limited (Mississauga, ON, Canada). Supel QuE *Z*-Sep sorbent was purchased from Sigma-Aldrich (Oakville, ON, Canada). PVDF MicroSpin centrifuge filters (0.20 μm, 500 μL) was purchased from Fisher Scientific (Ottawa, ON, Canada).

Ammonium hydroxide solution (28–30%), Ultra CHROMASOLV grade methanol (MeOH), acetonitrile (ACN), hexane and dichloromethane (DCM) were purchased from Sigma-Aldrich. Ultrapure water was obtained from a Milli-Q system. All other reagents were the highest commercial purity and used as received. All glassware used in sample extraction and cleanup process was treated at 450 °C overnight in box furnace to destroy any possible organic contamination.

2.2. Great Lakes sample collection and preparation

The collection and sampling of all Laurentian Great Lakes sediment samples was detailed fully in our previously published paper (Trouborst et al., 2014), and listed in Table 1 and Fig. 1. Briefly, surficial sediment samples were collected by colleagues from Environment and Climate Change Canada and the United States Environmental Protection Agency (Great Lakes Environmental Center (GLEC)). Briefly, sampling was conducted using a 15 × 15 cm Petite Ponar Grab (stainless steel box) sampler (EcoEnvironmental, Perth, WA, USA), where a top 6 cm sample of surficial bottom sediment was collected. Grab samples were collected from across Lake Erie (n = 3; western, central and eastern basins) in May 2012 (n = 1) and in August 2013 (n = 2). The GLEC

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