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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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 [1,2]. Worldwide investigations have shown that PFASs, such as particularly perfluorinated carboxylic acids (PFCAs) and sulfonic acids (PFSAs), are environmentally ubiquitous and including in humans [1,3,4,5]. There are uncertainties surrounding the routes and magnitude of PFAS contamination in terrestrial soils and aquatic sediments [6,7]. For example; Codling et al. [8] analyzed dated sediment cores and grab surface sediments from Lake Michigan and found that of the total extractable elemental fluorine only 0.2 % was accounted for by quantifiable PFASs. PFAS studies have mostly targeted PFCAs (C_nF_{2n} + COOH), PFSAs (C_nF_{2n} + SO_3H) and some of their possible precursors, but there has been very few studies on larger PFAS functional derivatives and polymers [9,10]. Side-chain fluorinated polymers represent a high percentage of all commercially available PFAS products and including use in a variety of household products such as fabric protector sprays [1,10,11]. We recently reported that pre- and post-2002 Scotchgard™ fabric protectors contain side-chain fluorinated polymers, which could be metabolized to perfluoroalkyl sulfonamides *in vitro* using a rat liver microsomal based assay [9]. These side-chain fluorinated polymers are likely present in the environment, especially in receiving compartments from wastewaste treatment plant (WWTP) outflows such as sediment, sludge and soil. However, to the best of our knowledge, little is known about side-chain fluorinated polymers in the environment [1,11]. In the present study, we investigated and compared the main components of Scotchgard™ fabric protectors (side-chain fluorinated polymers) in aquatic sediment samples and in agricultural soil samples augmented with WWTP-sourced biosolids from sites in the Laurentian Great Lakes basin.

Materials and methods

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 3M Company. Perfluoro-1-butane-sulfonamide (FBSA) was synthesized and purified according the method described with some modifications as in Chu et al. [9]. All other PFAS standard solutions, including the mass-labelled internal standards, were purchased from Wellington Laboratories (Guelph, ON, Canada) or Campro Scientific GmbH (Berlin, Germany).

The collection and sampling of all Laurentian Great Lakes sediment samples was detailed fully in our previously published Trouborst et al. [12] paper (Figure 1 and Table 1). Grab samples were collected from across Lake Erie and Lake Huron in May 2012 and August 2013. Thirteen soil samples were collected in the spring of 2014 from three agricultural field locations in southern Ontario, Canada (Table 1, Figure 1). For the Cambridge (CB) site samples, dewatered biosolid product from a secondary wastewater treatment plant had been applied to the field in the fall of 2013. Soil samples also taken from fields near Tillsonburg and Delhi, Ontario had received no biosolid application.

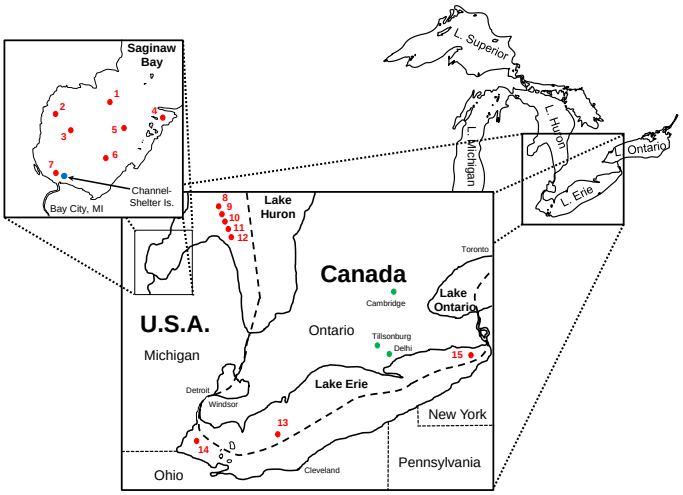

Figure 1. Sampling sites (red dots) of surficial sediments from Lakes Erie and Huron in the Laurentian Great Lakes of North America. The insert shows details of the sampling sites in Saginaw Bay. Sampling sites of the soil samples from agricultural fields in southern, Ontario (green dots).

As described in our recent paper [13], for analysis of the Scotchgard™ fabric protector components in sediment and soil samples, two grams of sample were used. Briefly, acetone/hexane (50v/50v) was added, and then ultrasonicated in a water bath at 45 °C. The supernatant solution was separated after centrifugation, this process was repeated twice more and all extracts were combined. After nitrogen evaporation the residual was reconstituted in 2 mL DCM. The sample was cleaned up using a disposable silica gel SPE column, loaded on the column, and after washing with 6 mL of DCM the target compounds were eluted with 4 mL of ACN/DCM (40v/60v) solvent. This fraction was collected and concentrated to dryness, and reconstituted in 2 mL of ACN. To reduce chemical interferences, the sample was then cleaned up by a dispersive solid-phase extraction (d-SPE) approach using 200 mg amount of Supel QuE Z-Sep sorbent. The samples were then ready for ultra-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analysis.

Quantitative analysis of the components of the Scotchgard™ fabric protectors was performed on a Waters XEVO-TQ-S UHPLC-QQQ-MS/MS (Waters Limited, Milford, MA, USA). Chromatographic separation was accomplished by a Kinetex® C8 LC Column (1.7 µm particle size, 100 Å, 2.1 × 50 mm, Phenomenex, CA, USA).The column and sample temperature were 50 °C and 20 °C, respectively. The mobile phases were water (A) and methanol (B), both containing 2 mM of ammonium acetate. The flow rate was 0.6 mL/min. The gradient started at 5 % B and increased to 95 % B in 3 min, and was then held for 3 min. The triple quadruple tandem mass spectrometer XEVO-TQ-S with an electrospray ionization source (ESI) was operated in negative mode. Nitrogen was used as nebulizing gas and desolvation gas, and argon was used as collision gas. Analyses were performed using the multiple reaction monitoring (MRM) mode, and the transitions. As described in Chu and Letcher [9], an Agilent 1200 LC system coupled to an Agilent 6520A liquid chromatography-quadrupole time of flight mass spectrometer (LC-Q-TOF-MS) system (Agilent Technologies, Mississauga, ON, Canada) was used for identification of components of Scotchgard™ fabric protectors in standard solution and confirmation the results of measured components in the environment soil and sediment samples. The analysis method for other PFASs, which includes PFCAs (13 compounds), PFSAs (5 compounds) and perfluoroalkyl sulfonamides (4 compounds), was also fully described [14] with some modifications for extraction of these compound from soil and sediment samples.

Results and discussion

The analysis of the Scotchgard™ fabric protector components in the present environmental samples was a challenge with respect to the sample cleanup as their molecular structures are not known. Regardless, using our UHPLC-

MS/MS-based method, in spiked farm soil the recoveries using our method were 101.4 % and 66.1 % for the two main fabric protector components, S1 and S2, respectively. There is no detected concentration of S1 and S2 found in blank sample. To confirm the results from the UHPLC-MS/MS analysis, a standard solution and some of the sediment and soil sample fractions were re-analyzed by LC-Q-TOF-MS. In the standard solution, the main detectable component peak, which has polyfluoroalkyl group, was detected at retention time of 15.8 min (S1) and 14.5 min (S2) in the mass chromatogram of Pre- and Post-2002 Scotchgard™ fabric protector products, respectively. The main component of Pre-2002 product (S1) had a mass spectral peak at *m/z* 1315.0591, while that of the Post-2002 product (S2) had a mass spectral peak with *m/z* 1634.3120. The product mass spectrum of *m/z* 1315.0591 (S1) had two main ions with *m/z* 418.9713 and 525.9792, which corresponded to fragment ions of $[C_8F_{17}]^-$ (*m/z* = 418.9734) and $[C_8F_{17}SO_2N(C_2H_5)]^-$ (*m/z* = 525.9775), respectively. The product mass spectrum of *m/z* 1634.3120 (S2) had two main ions with *m/z* 218.9860 and 311.9751, corresponding to $[C_4F_9]^-$ (*m/z* = 219.9862) and $[C_4F_9SO_2N(CH_3)]^-$ (*m/z* = 311.9746), respectively. Figure 2 shows the extraction ion chromatograms from a representative farm soil sample.

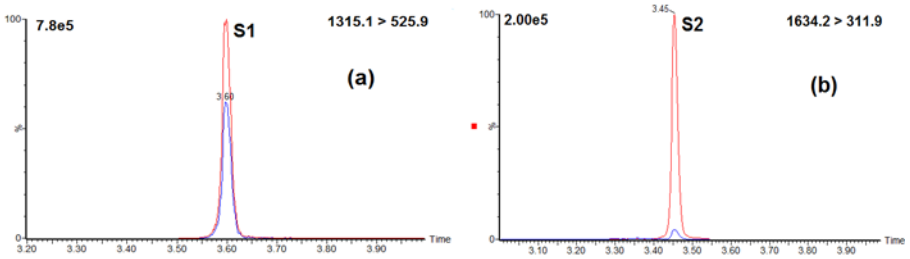

Fig. 2. UHPLC-ESI(-)-QQQ-MS/MS reconstructed mass chromatograms of the main components (S1 and S2) in the of Scotchgard™ fabric protectors in a representative agricultural soil sample from Cambridge, Ontario, Canada, with (red line) and without (blue line) internal standard spiked.

Table 1. Concentrations of the main components in the Scotchgard™ fabric protectors (S1 and S2) and other major PFASs present in the sediment and agricultural soil samples.

Sample. No.	Sample location[a]	S1	S2	PFOA[b]	PFNA[b]	PFOS[b]	Σ_{22}PFASs
Sediment							
1	Saginaw Bay, Lake Huron	167.14	2.14	0.35	0.21	1.54	3.49
2	Saginaw Bay, Lake Huron	2.08	0.23	ND	ND	ND	<MLOQ
3	Saginaw Bay, Lake Huron	129.00	2.20	<MLOQ	0.26	1.58	2.53
4	Saginaw Bay, Lake Huron	17.79	0.10	ND	ND	0.22	0.23
5	Saginaw Bay, Lake Huron	0.24	ND	ND	ND	1.25	1.41
6	Saginaw Bay, Lake Huron	0.59	ND	ND	ND	<MLOQ	<MLOQ
7	Saginaw Bay, Lake Huron	4.63	0.78	ND	ND	ND	<MLOQ
8	Lake Huron	33.12	0.11	0.75	0.61	3.47	5.71
9	Lake Huron	9.46	ND	0.18	0.18	0.63	1.87
10	Lake Huron	29.89	0.10	0.33	0.94	2.90	6.91
11	Lake Huron	27.76	0.13	0.44	0.32	1.38	4.78
12	Lake Huron	2.11	<MLOQ	<MLOQ	0.07	0.27	1.04
13	Lake Erie	461.59	14.66	ND	ND	0.20	0.29
14	Lake Erie	225.19	24.08	ND	ND	0.29	0.38
15	Lake Erie	0.62	0.25	ND	ND	ND	<MLOQ
Farm Soil		mean	mean	mean	mean	mean	mean
TI (n=9)	Tillsonburg, ON, Canada	3.02	0.16	ND	<MLOQ	<MLOQ	<MLOQ
DE (n=1)	Delhi, ON, Canada	17.36	0.52	<MLOQ	ND	ND	ND
CB (n=3)	Cambridge, ON, Canada	236.36	4.12	ND	<MLOQ	2.01	2.42

[a] See Figure 1 for sampling locations.
[b] See SI table for the full chemical name for these abbreviations.

In all of the sediment samples S1 was quantifiable and ranged from 0.24 to 461.59 ng/g d.w (Table 1). In 80 % of the samples S2 is quantifiable and ranged from < 0.04 to 24.08 ng/g d.w. The greatest concentrations of S1 and S2 were found in samples from western Lake Erie (No. 13 and No. 14), followed by two samples from Saginaw Bay (No. 1 and No. 3) with S1 concentrations of 129.0 and 167.1 ng/g d.w. The concentrations of S1 and S2 in sediment samples that were essentially sand substrate (No. 2, 5, 6 and 7) were relatively lower (ND to 4.63 ng/g d.w) as compared to the sediment samples with a silt consistency (Table 1). The greatest concentration of S1 and S2 in the western Lake Erie sediment samples is likely due to their close proximity to the Detroit River in-flow. In all of the agricultural soil samples from the southern, Ontario field sites S1 was detectable, while in 62 % of

the soil samples S2 was detectable. Among all the soil samples, the greatest S1 and S2 concentrations were in the soil samples from Cambridge, Ontario, which were the sites augmented with biosolid in the previous fall 2013 (Table 1). Cambridge sites were the only sites augmented with biosolids, indicating that the elevated S1 and S2 concentrations are sources from the WWTPs from which the biosolids came. All sediment and soil samples were also analyzed for other PFASs [14]. Possible S1 or S2 precursors, FBSA, FOSA, N-MeFOSA and N-EtFOSA were not detectable, and other PFASs were at much lower concentrations than S1 and to a lesser extent S2 (Table 1).

Scotchgard™ fabric protector components found in the present sediment and soil samples demonstrated the presence of side-chain fluoropolymers in the Great Lakes terrestrial and aquatic environments, which to our knowledge is the first such report. High concentrations of PFASs have been reported in WWTP sludge, and thus may also be a source of these fluoropolymers in the environment via WWTP discharge into water systems or via redistribution of biosolid slurry for crop field applications. The present results helps to explain why known PFCAs and PFSAs account for low percentages reported for extractable organic fluorine in sediment [7]. WWTP-sourced biosolid application to soils for agriculture purposes essentially loads fabric protector components into the human food chain.

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