

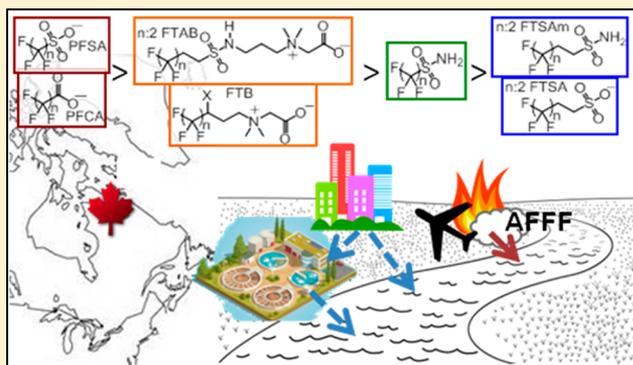
Certain Perfluoroalkyl and Polyfluoroalkyl Substances Associated with Aqueous Film Forming Foam Are Widespread in Canadian Surface Waters

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S Supporting Information

ABSTRACT: The presence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) commonly associated with aqueous film forming foams (AFFFs) at sites without known AFFF contamination is a largely unexplored area, which may reveal widespread environmental contaminants requiring further investigation. Sensitive liquid chromatography-tandem mass spectrometry (LC-MS/MS) screening for 23 classes of PFASs, followed by quantitative analysis was used to investigate surface waters from rural, urban, and AFFF-impacted sites in Canada. The PFASs detected included perfluorohexane sulfonamide (FHxSA), 6:2 fluorotelomer sulfonamide (FTSAm), fluorotelomer sulfonamide alkylbetaines (FTABs), fluorotelomer betaines (FTBs), 6:2 fluorotelomer mercaptoalkylamido sulfonate sulfone (FTSAS-SO₂), 6:2 fluorotelomerthiohydroxyl ammonium sulfoxide (FTSHA-SO), 6:2 fluorotelomer sulfonamide alkylamine (FTAA) and C3 to C6 perfluoroalkane sulfonamido amphoteric. Detection of FHxSA in all urban and AFFF-impacted sites (0.04–19 ng/L) indicates the widespread presence of rarely considered perfluorohexanesulfonate (PFHxS) precursors in Canadian waters. FTABs and FTBs were especially abundant with up to 16–33 ng/L of 6:2 FTAB in urban and AFFF-impacted water suggesting it may have additional applications, while FTBs were only in AFFF-impacted sites (qualitative; \sum FTBs 80 ng/L). The distributions of PFASs moving downstream along the AFFF-impacted Welland River and between water and sediment suggested differences in the persistence of various AFFF components and enhanced sorption of long-chain fluorotelomer betaines. Total organofluorine combustion-ion chromatography (TOF-CIC) revealed that fluorotelomer betaines were a substantial portion of the organofluorine in some waters and 36–99.7% of the total organofluorine was not measured in the targeted analysis.



INTRODUCTION

Since 1999, aqueous film forming foams (AFFFs) used to fight liquid-fuelled fires have been implicated in local environmental contamination with perfluoroalkyl and polyfluoroalkyl substances (PFASs),¹ particularly perfluoroalkyl carboxylates (PFCAs),^{1–10} perfluoroalkanesulfonates (PFSAs),^{2–7,9–11} and fluorotelomer sulfonic acids (FTSAs).^{4,12} Extremely high concentrations of PFASs have been associated with AFFF, including up to 2 210 000 ng/L of perfluorooctanesulfonate (PFOS) in Etobicoke Creek immediately after an AFFF release from Toronto Pearson Airport, Ontario in 2000³ and up to 920 000 ng/L of perfluorohexanesulfonate (PFHxS) and 14 600 000 ng/L of 6:2 FTSA in groundwater at Tyndall Air Force Base, Florida.⁴ Inputs of AFFF are also implicated in less extreme contamination of surface waters over longer time frames, including 290 ng/L of PFOS in Etobicoke Creek in 2009 near the AFFF release site from 2000,⁷ and 45–64 ng/L of PFOS in Lake Nipenco downstream of Hamilton Airport, Ontario in 2010.⁵

However, while PFOS is a major component of AFFFs prepared from electrochemical fluorination products and

PFHxS may be found in these products at concentrations less than 15% of the PFOS concentration, most of these PFCAs, PFSAs, and FTSA are not major PFASs in AFFFs relative to the primary PFAS active ingredients.^{14–16} In the past five years, over 20 additional classes of PFASs in AFFFs and commercial fluorinated surfactant concentrates^{17,18} and several additional degradation products of AFFF components^{14,19–21} have been identified. Reports of these recently identified AFFF components in the environment are limited and usually focus on sites known to have received substantial inputs of AFFF. Efforts to determine which of the AFFF-related PFASs can be detected at trace levels in surface waters without known AFFF impacts, such as urban and rural surface waters, are lacking. Only a study that estimated concentrations of fluorotelomer sulfonamide alkylamines (FTAAs) and fluorotelomer sulfonamide alkylbetaines (FTABs) in French river sediments at

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0.055–13.5 ng/g in total investigated sites without significant known impacts from AFFF or AFFF component manufacturing.¹³

The highly impacted sites that have been investigated in terms of novel AFFF-related PFASs include on and around military bases with long histories of AFFF use,^{14–19} near airport and other firefighting training areas,^{19,20} the areas surrounding large oil fires that were fought with AFFF,^{19,21–23} and near a location of PFAS manufacturing for AFFF.^{24,25} These studies have determined that a variety of AFFF-related PFASs are present in environmental samples from these sites, with one or more congeners of the following fluorotelomer PFAS classes found in various environmental media: FTABs,^{17,19–25} FTAAAs,^{17,19–23,25} fluorotelomer mercaptoalkylamido sulfonates (FTSASs),^{14,21,23} FTSAS-sulfoxides (FTSAS-SOs),^{21,23} FTSAS-sulfones (FTSAS-SO₂s),¹⁸ FTSAS-related thioether/sulfone-linked carboxylic acids,¹⁸ fluorotelomer sulfonamides (FTSAmS),²¹ fluorotelomerthiohydroxyl ammoniums (FTSHAAs),^{21,23} FTSHA-sulfoxides (FTSHA-SOs),^{21,23} demethyl-FTAAAs,²¹ and fluorotelomer betaines (FTBs).^{21,23} Perfluoroalkane sulfonamido substances found in AFFFs or their likely degradation products have also been measured on highly AFFF impacted U.S. military bases, including C4–C6 perfluoroalkane sulfonamido alkylamine acids (FASAAAs),¹⁴ C4–C6 perfluoroalkane sulfonamido alkylamines (FASAAms),^{14,15} and perfluorohexane sulfonamide (FHxSA).^{15,16} Many of these studies provided quantitative or semiquantitative results for the novel AFFF-related PFASs in environmental matrices.^{14–17,19,21–25}

However, by focusing investigations on highly AFFF impacted sites, previous studies were not able to address how widespread these contaminants are in the environment and whether the patterns in their detection and measured or estimated concentrations may suggest that they have applications outside of AFFF. For example, according to a patent, 6:2 FTAB may be used to coat ceramic surfaces to prevent deposits.²⁶ In addition, a “betaine partially fluorinated surfactant,” Capstone FS-50, is marketed for various applications, including cleaning and floor care, and has identical listed properties to Capstone 1157, which is marketed for use in AFFFs and is presumably a renamed Forafac 1157, which contained mostly 6:2 FTAB.^{20,27,28} Herein, by screening for 23 classes of PFASs with high sensitivity and quantifying, as possible, the AFFF-related PFASs found in surface water samples from rural, urban, and AFFF impacted locations in Canada, information about the environmental occurrence of PFASs typically considered AFFF-related is obtained. This shows which of these PFASs are relatively widespread in the environment due to their widespread use, high persistence, and/or environmental transport, which can help prioritize future research into the most environmentally relevant of these PFASs.

In addition to the occurrence of AFFF-related PFASs in surface waters, the total organofluorine content of surface water extracts was determined by total organofluorine combustion ion chromatography (TOF-CIC). Comparison of results of this technique with targeted, quantitative analysis can show when a substantial amount of the total organofluorine is made up of additional components containing organofluorine that were not quantified. It has been applied to numerous matrices, including sediments,²⁹ water,³⁰ and AFFF concentrates³¹ demonstrating that substantial amounts of organofluorine are not accounted for by targeted analysis. For example, the PFCAs and PFSAs

measured in the acidic fraction of Lake Ontario surface sediment extracts accounted for only 2–44% of the total organofluorine.²⁹ Using TOF-CIC, the contribution of novel AFFF-related PFASs to the total organofluorine in the surface water samples and the size of the remaining unknown fraction was investigated.

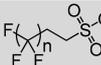
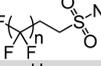
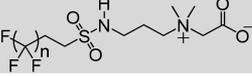
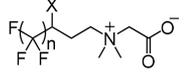
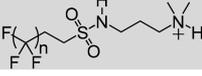
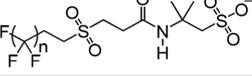
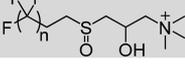
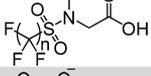
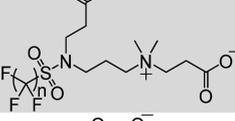
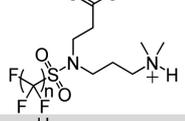
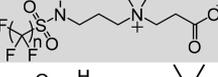
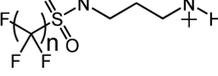
Another important aspect of the behavior of AFFF-related PFASs in surface water environments is sorption to sediment, because increased sorption can reduce the transport of PFASs downstream.^{32,33} Neither laboratory nor field determinations of the sorption behavior of the novel AFFF-related PFASs are available. With this gap in knowledge, although the focus of this investigation is surface water, sediment samples were collected concomitantly with water samples from a subset of sites along the AFFF-impacted Welland River^{5,34} and at one nearby reference site. By comparing the PFAS profiles in corresponding sediment and water samples, preliminary insights into the sorption behavior of the novel AFFF-related PFASs found in the Welland River were obtained. Where PFASs were quantified in both sediment and water at a site, field-derived sediment-water distribution coefficients ($\log K_d$) and organic carbon normalized distribution coefficients ($\log K_{OC}$) were determined. The determined field-derived $\log K_{OC}$ values for PFAAs were compared to previous field derived values in river and coastal sediments,^{8,33,35} whereas field derived $\log K_{OC}$ values and sediment concentrations of novel AFFF-related PFASs provide an indication of their sorption behavior.

■ MATERIALS AND METHODS

Materials. 6:2 FTAA, 6:2 FTAB, and 6:2 FTSAm were synthesized in house. As described in detail previously,³⁶ 6:2 fluorotelomer sulfonyl chloride (FTSO₂Cl) was prepared by a one step synthesis from 6:2 fluorotelomer thiol, using KNO₃ and SO₂Cl₂. The 6:2 FTSO₂Cl was reacted with *N,N*-dimethylamino-1-propylamine to form 6:2 FTAA or with NH₃ in tetrahydrofuran to form 6:2 FTSAm. The 6:2 FTAA was used to prepare 6:2 FTAB by refluxing it with sodium chloroacetate.³⁶ A listing of the other solvents, chemicals, and standards used is in the [Supporting Information \(SI\)](#).

Samples. Welland River (sample points 1–9) are sequential sites along the AFFF-impacted Welland River. Because it was not possible to sample upstream of the former firefighting training site on the Welland River, since this site is in the headwaters, Big Creek (two sample locations) and Welland River Reference, which are nearby rural sites not downstream of the former firefighting training site at Hamilton Airport, were sampled as rural reference sites. Water was collected in submerged 500 mL wide-mouth polypropylene bottles (Nalgene, Penfield, NY) on October 22, 2015. Water samples from two AFFF-impacted Arctic lakes, Resolute Lake and Meretta Lake, were collected in August 2012 and 2014 in 1 L polyethylene bottles (Kartell, Noviglio, Italy) by Environment and Climate Change Canada (ECCC) personnel. Rivers in Southern Ontario were sampled in conjunction with Ontario Ministry of the Environment and Climate Change (MOECC) sampling programs in 2015 with 500 mL polyethylene terephthalate jars used routinely for monitoring perfluoroalkyl acids (PFAAs). Of these rivers, Perch Creek, Thames River, Grand River, Humber River, and Don River are classified as urban; Etobicoke Creek has known prior AFFF-impacts. Additional rural samples were collected using 500 mL wide-mouth polypropylene bottles (Nalgene) from Little Rouge Creek in 2016 and Lake of Bays in 2015 some of which were

Table 1. Structures, Names, and Acronyms of PFASs Detected in Surface Waters and/or Sediments^a

Structure	Name	Acronym(s)
Perfluoroalkyl acids (PFAAs)		
	perfluoroalkyl carboxylate (PFCA)	PFPeA n = 4 ; PFHxA n = 5 PFHpA n = 6 ; PFOA n = 7
	perfluoroalkane sulfonate (PFSA)	PFBS n = 4 ; PFPeS n = 5 PFHxS n = 6 ; PFHpS n = 7 PFOS n = 8
Fluorotelomer PFASs		
	n:2 fluorotelomer sulfonic acid	n:2 FTSA (n = 4, 6, 8)
	n:2 fluorotelomer sulfonamide	n:2 FTSAm (n = 6)
	n:2 fluorotelomer sulfonamide alkylbetaine	n:2 FTAB (n = 4, 6, 8)
	fluorotelomer betaine	n:3 FTB (x = H) n:1:2 FTB (x = F) (n = 5, 7, 9)
	n:2 fluorotelomer sulfonamide alkylamine	n:2 FTAA (n = 6)
	n:2 fluorotelomer mercaptoalkylamido sulfonate sulfone	n:2 FTSAS-SO2 (n = 6)
	n:2 fluorotelomer thiohydroxylammonium sulfoxide	n:2 FTSHA-SO (n = 6)
Perfluoroalkane sulfonamido substances		
	perfluoroalkane sulfonamide	FHxSA (n = 6) FOSA (n = 8)
	N-ethyl perfluorooctane sulfonamido acetic acid	EtFOSAA (n = 8)
	perfluoroalkane sulfonamido alkylamine diacid	C3, C4, C5, C6 FASADA (n = 3–6)
	perfluoroalkane sulfonamido alkylamine acid	C3, C4, C5, C6 FASAAA (n = 3–6)
	perfluoroalkane sulfonamido alkylbetaine	C5, C6 FASAB (n = 5, 6)
	perfluoroalkane sulfonamido alkylamine	C6 FASAAM (n = 6)

^aChain-lengths for congeners for which data is quantitative through use of calibration standards are in bold. All other congeners have qualitative data with concentrations calculated based on the calibration curve for the most similar quantitative PFAS.

used for matrix spike and recovery. Samples were refrigerated at 4 °C prior to extraction. Sampling dates and locations are in SI Figure S1 and Table S1. Sediment samples were obtained in 500 mL wide-mouth polypropylene bottles (Nalgene) from four Welland River and one Big Creek site at the same time and place as water samples. Sediments were frozen at -20 °C and lyophilized prior to extraction.

Because the Welland River upstream of the Binbrook Dam flows very slowly, these sediments were likely at or near

equilibrium with the surrounding waters. The month of October 2015, prior to sampling, was relatively dry and water levels in the reservoir (Lake Niapenco) remained below the holding level of 650.5 feet throughout September and October 2015, prior to the sampling.³⁷ Therefore, the residence time of water likely was quite long prior to sampling and the water was relatively stagnant. Observations at the time of sampling support this assessment as the water was not observed to flow and the flow out of the Binbrook Dam was a trickle.

Water Extraction. Water samples were extracted in the Advanced Laboratory for Fluorinated and Other New Substances in the Environment (ALFONSE) clean laboratory (Class 100A) using Oasis WAX solid phase extraction (SPE) cartridges (6 mL, 200 mg, 30 μm ; Waters, Milford, MA). The extraction protocol used to extract the approximately 500 mL water samples was a modification of existing methods³⁸ and is described fully in the SI. The cartridges were eluted with methanol (fraction containing neutrals, zwitterions, bases, and cations) followed by 0.1% NH_4OH in methanol (fraction containing acids).

Sediment Extraction. Approximately 0.5 g subsamples of lyophilized sediment were weighed into polypropylene centrifuge tubes and extracted using 0.1% NH_4OH in methanol based on Houtz et al.¹⁵ with cleanup using 1 mL/100 mg Supelclean ENVI-Carb SPE cartridges (Supelco, Bellefonte, PA) in the ALFONSE clean laboratory. The full extraction procedure and the method for determination of organic carbon content are described in the SI.

LC-MS/MS. Analysis of sample extracts for PFASs by LC-MS/MS was performed using an Acquity UPLC–Xevo TQ-S system (Waters, Milford, MA). An Acquity UPLC BEH C18 column (1.7 μm , 2.1 mm \times 75 mm) and a mobile phase gradient of 10 mM aqueous ammonium acetate and methanol were used. The Xevo TQ-S was operated in positive and negative electrospray (ESI) mode. Further LC-MS/MS method details are in the SI. Transitions for AFFF components (SI Table S2) were optimized by infusing dilutions of suitable AFFF extracts prepared previously.³⁹ Screening LC-MS/MS runs were used to determine which PFASs (Table 1) may be present in sample extracts and included transitions for additional AFFF-components that were never detected.

The suite of PFAAs analyzed is limited to PFOS or PFOA and shorter in order to focus on those PFAAs most associated with AFFFs, which generally contain primarily PFOS and C6 or C8 perfluoroalkane sulfonamido substances or 6:2 fluorotelomer surfactants. The shortest PFCA analyzed was perfluoropentanoate (PFPeA) because perfluorobutanoate (PFBA) was poorly retained on the reverse phase column and suffered from background contamination.

TOF-CIC. Surface water extracts from each sampling location were analyzed by total organofluorine-combustion ion chromatography (TOF-CIC) using previously published procedures.^{31,40} The acid extracts were also analyzed for inorganic fluoride by combining 100 μL of extract with 6.5 mL of deionized water and directly analyzing by ion chromatography using the TOF-CIC system.

Quality Assurance of Data. Analyses by LC-MS/MS were completed in at least duplicate ($n = 2\text{--}4$). Quantification of PFASs was performed in several ways depending on the availability of standards. PFPeA, perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), PFHxS, PFOS, 4:2 FTSA, 6:2 FTSA, 8:2 FTSA, *N*-ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA), and perfluorooctane sulfonamide (FOSA) were quantified using internal calibration with isotopically labeled standards. Perfluorobutanesulfonate (PFBS), perfluoropentanesulfonate (PFPeS), perfluoroheptanesulfonate (PFHpS), FHxSA, and 6:2 FTSAm were quantified using structurally related surrogate mass-labeled internal standards: mass-labeled PFHxS for PFBS and PFPeS, mass-labeled PFOS for PFHpS, and mass-labeled FOSA for FHxSA and 6:2 FTSAm. Two multiple reaction monitoring transitions were used to confirm detection of all

PFASs, except PFPeA, PFHxA, EtFOSAA, FHxSA, and FOSA, where a single transition was used. For 6:2 FTAB and 6:2 FTAA, matrix matched calibration was used along with mass-labeled FOSA internal standard. The data are considered quantitative for the PFASs analyzed as described above with commercial analytical standards or standards prepared from neat materials. Estimation of the concentrations for qualitative analytes (novel PFASs) for which isolated standards were unavailable was performed by using matrix matched calibration curves for 6:2 FTSA for sulfonic acid-containing compounds, EtFOSAA for carboxylic acid compounds, 6:2 FTAA for amine or quaternary ammonium compounds, and 6:2 FTAB for amphoteric compounds. To confirm the detection of qualitative AFFF components, two MS/MS transitions were used and retention times were matched to AFFF extracts containing those components from a previous study.³⁹

The calibration curves had a minimum of five points and were usually constructed from 0.02 ng/mL to 10 ng/mL in the vial (range: 0.006–0.03 ng/mL to 10 ng/mL). This corresponds to 0.08 ng/L to 40 ng/L in a 500 mL water sample and 0.08 ng/g to 40 ng/g in a 0.5 g sediment sample. A quality control sample spiked at 1 ng/mL in the vial with all the PFASs being quantified was analyzed in duplicate during each analysis and analyses were accepted if the concentrations determined were within 20%. Where the concentration of a PFAS was above the highest calibration point in a sample, that sample was rerun with a suitable dilution factor. The limit of detection (LOD) was defined as the concentration giving a signal-to-noise ratio of 3 in the sample matrix and the limit of quantitation (LOQ) was the concentration giving a signal-to-noise ratio of 10 in the sample matrix. Matrix LODs and LOQs are given in SI Table S4. During each water extraction, two cartridge blanks were subjected to all portions of the extraction procedure except sample loading to evaluate contamination of the extraction solvents and contained no PFASs above the LOD. Two field blanks of deionized water that were opened to air during the collection of one Welland River sample were also extracted and found to contain no PFASs above the LOD. For the sediment extraction, two solvent blanks containing no sediment were extracted along with the sediments and contained no PFASs above the LOD. Interday duplicate extractions were performed on Welland River 1, 2, 5, 6, 7, and 9; Welland River Reference; and Big Creek 1 water samples, whereas intraday duplicate extractions were performed on all sediments and Little Rouge Creek water.

Recoveries for water extraction were determined by spiking surface water samples (~500 mL) from relatively clean environments ($n = 5$) with 2.5 ng of FTSAs, EtFOSAA, FHxSA, FOSA, 6:2 FTSAm, 6:2 FTAA, and 6:2 FTAB and 25 ng of PFCAs and PFSAs in methanol, swirling to mix, and extracting the following day. The recoveries were 71–96% for all PFASs, including recoveries of $88 \pm 24\%$ for 6:2 FTAB (zwitterionic) and $71 \pm 12\%$ for 6:2 FTAA (cationic at surface water pH; SI Table S3). Recoveries from freeze-dried sediment were determined by spiking sediment from Big Creek 1 (~0.5 g, $n = 4$) with 1 ng each of PFCAs, FTSAs, EtFOSAA, FOSA, FHxSA, 6:2 FTSAm, 6:2 FTAB, and 6:2 FTAA, and 5 ng each of PFSAs in 100 μL of methanol, vortexing to mix, and extracting the sediment the following day. Recoveries from sediment were 76–94% for the PFASs, except 6:2 FTAB ($31 \pm 2\%$; SI Table S3). Sediment concentrations are reported without correction.

Statistical Analysis. Statistical comparison of the concentrations of PFASs found at rural ($n = 5$), urban ($n = 5$), and AFFF-impacted ($n = 14$) sampling sites were performed using the two-tailed Mann–Whitney U test. For the statistical analysis, values determined between LOQ and LOD were used as determined from the calibration and concentrations below the detection limit were substituted with half the LOD. The Mann–Whitney U test was only used for PFASs detected in at least 21 out of 24 samples or 17 out of 19 urban and AFFF impacted samples to limit the impact of nondetects. The threshold for statistical significance used was $p < 0.05$. The statistical tests were performed using OriginPro 2017 software.

RESULTS AND DISCUSSION

Fluorotelomer PFASs. Maximum concentrations of fluorotelomer sulfonamide alkylbetaines (FTABs) and fluorotelomer betaines (FTBs) were higher than for other fluorotelomer substances (Figure 1a,b; SI Table S7). Welland River 1 had the highest 6:2 FTAB concentration (33 ± 4 ng/L) but 6:2 FTAB concentrations rapidly decreased downstream to under 0.25 ng/L at sites 2–9 perhaps due to 6:2 FTAB photodegradation in sunlit waters, which was demonstrated in laboratory experiments.⁴¹ Therefore, the relatively high concentrations of 6:2 FTAB (4.5–22 ng/L) and 8:2 FTAB (1.0–4.6 ng/L) in Etobicoke Creek, Don River, and Humber River are unexpected and suggest recent inputs of FTABs. Inputs may occur through runoff carrying FTABs stored in soils, wastewater treatment plant (WWTP) effluent, or AFFF use. Biodegradation of 6:2 FTAB with WWTP sludge was slow³⁶ and 6:2 FTAB was abundant in effluent from a WWTP treating industrial effluent containing 6:2 FTAB,²⁵ so FTABs can probably survive treatment. Of these rivers, only Etobicoke Creek has known AFFF inputs from Toronto Pearson Airport, while North Toronto WWTP discharges into the Don River about 1.8 km upstream of the sampling site and Humber River receives urban and industrial runoff, sewer overflows, and effluent from a small WWTP over 32 km upstream. Since 6:2 FTAB concentrations were not significantly different between urban (median 0.81 ng/L) and AFFF impacted samples (median 0.06 ng/L, $U = 17$), either AFFF use is unanticipatedly widespread or additional applications of 6:2 FTAB lead to its presence in Ontario rivers through sources including WWTP effluent, combined sewer overflows, and septic fields. This contrasts with analysis of surface waters in France that have found much higher concentrations of 6:2 FTAB downstream of firefighting training sites (up to 18,000 ng/L) and downstream of airports (up to 1800 ng/L), with relatively lower concentrations upstream of the firefighting training area on an industrially impacted river (140 ng/L).^{17,19} However, the widespread use of 6:2 FTAB is also suggested by its presence in each of 12 river sediment samples from throughout France at concentrations estimated at 0.023–3.9 ng/g.¹³ Possible additional applications of 6:2 FTAB include coating ceramic surfaces to prevent deposits²⁶ and are further suggested by Capstone FS-50, a “betaine partially fluorinated surfactant,” marketed for applications including cleaning and floor care. Capstone FS-50 lists identical properties to Capstone 1157 marketed for AFFF, which is likely the same as Forafac 1157 (mostly 6:2 FTAB).^{20,27,28}

FTBs have only been reported in fish, soil and sediments following an AFFF deployment previously^{21,23} and were detected, in this study, in high apparent concentrations (qualitative; Σ FTBs: 8–80 ng/L) in Welland River and

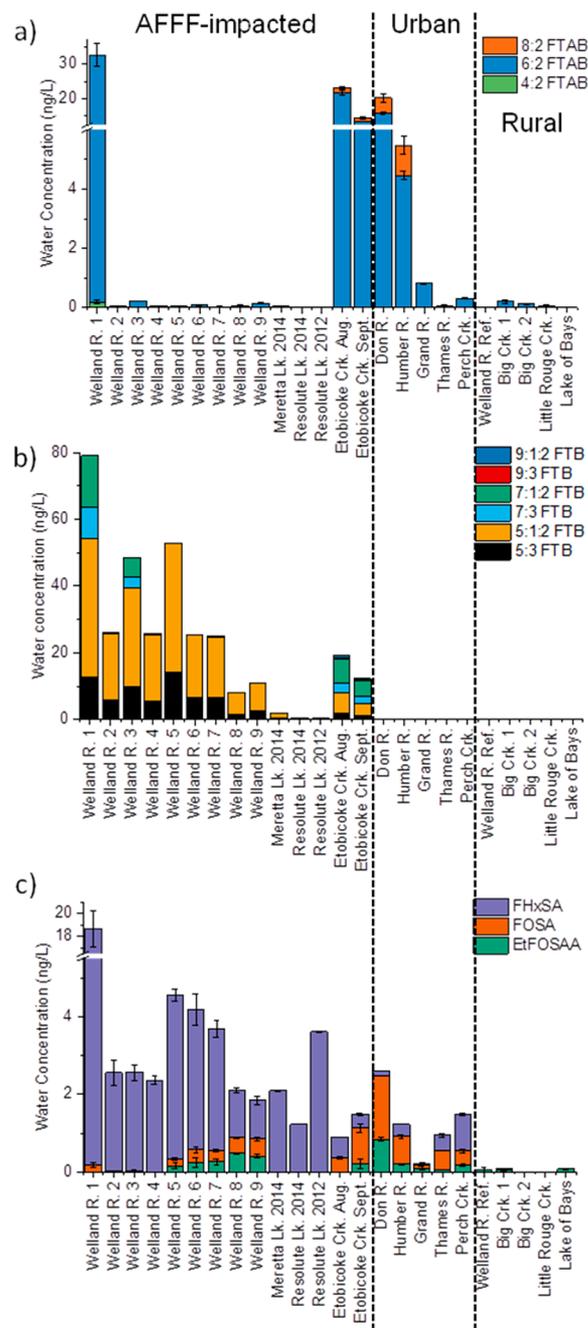


Figure 1. Concentrations of (a) FTABs, (b) FTBs, and (c) FHxSA, FOSA, and EtFOSAA in surface water samples in ng/mL. Error bars are standard deviations and are excluded for clarity from the FTBs so patterns can be seen clearly despite uncertainty in estimated concentrations for these qualitative analytes.

Etobicoke Creek samples and lower concentrations (qualitative; Σ FTBs: < 1.3–1.9 ng/L) in Resolute and Meretta Lake samples (Figure 1b). These sites have known AFFF-impacts from upstream airports, which are probably the FTB sources, perhaps through Buckeye AFFFs.^{14,15,42} However, an AFFF sample dating from an aircraft fire within meters of Etobicoke Creek in 2005¹² contained FTBs and was reportedly from Ansul.³⁹ FTB concentrations do not decrease nearly as rapidly as 6:2 FTAB concentrations downstream of Hamilton Airport. This suggests that 5:1:2 and 5:3 FTBs are less environmentally degradable and/or less sorptive than 6:2 FTAB, although there

are limitations to assuming that the grab samples are representative of the concentrations present when the downstream waters were at the upstream sites. Slower environmental degradation may be due to the lack of the sulfonamide group that may absorb sunlight and has an oxidizable nitrogen with a lone pair of electrons. The sulfonamide group likely enables some of the observed aqueous photolysis and aerobic biodegradation of 6:2 FTAB.^{36,41} Etobicoke Creek samples have a greater proportion of 7:1:2, 7:3, 9:1:2, and 9:3 FTBs than Welland River samples, which may be due to formulation differences or greater sorption of longer chain congeners from Hamilton Airport.

Fluorotelomer PFASs other than betaines were detected at lower maximum concentrations (SI Figure S2a, SI Tables S6, S8) with 6:2 FTSA having the highest maximum concentration at 2.5 ± 0.8 ng/L in Welland River 1 consistent with the association of 6:2 FTSA with AFFF-impacts.⁴ However, concentrations of FTSAs in all other surface water samples were low (<0.45 ng/L) and there was not a statistically significant difference in 6:2 FTSA concentrations between AFFF impacted (median: 0.065 ng/L) and urban water samples (median: 0.086 ng/L, $U = 32$, SI Table S10). Higher 6:2 FTSA concentrations were measured in Meretta Lake (0.42 ± 0.01 ng/L) compared to Resolute Lake (<0.12 ng/L), which is similar to measurements in 2010–11.⁴³

Detections of the 6:2 FTAB degradation product 6:2 FTSAm (<0.65 – 0.84 ng/L),³⁶ occurred alongside substantial 6:2 FTAB concentrations. The amine-containing 6:2 FTAA (<0.1 – 0.16 ng/L) and quaternary ammonium-containing 6:2 FTSOA-SO (qualitative: <0.25 – 0.29 ng/L) were detected in some urban samples, which is the first environmental detection of 6:2 FTSOA-SO outside a known AFFF-impacted area.^{21,23} Don River, Humber River, Grand River, and Thames River samples had 6:2 FTSAS-SO₂ detected at concentrations <0.1 ng/L (qualitative), while Etobicoke Creek had 6:2 FTSAS-SO₂ concentrations of 0.24–0.83 ng/L (qualitative). This is the first detection of 6:2 FTSAS-SO₂ in surface water and its relative abundance in AFFF-impacted Etobicoke Creek is consistent with a degradation product of AFFF-component 6:2 FTSAS.^{4,44}

The only fluorotelomer PFASs detected in rural samples without known AFFF-impacts were 6:2 FTAB in Big Creek (<0.2 ng/L) and Little Rouge Creek (<0.2 ng/L), and 6:2 FTSA (<0.025 ng/L) in all samples except Lake of Bays. The 6:2 FTSA has been detected in precipitation previously.⁴⁵ Concentrations of 6:2 FTSA at rural sites (median: 0.01 ng/L) were significantly lower than those at urban and AFFF impacted sites ($p < 0.05$, SI Table S10).

Perfluoroalkane Sulfonamido Substances in Surface Waters. Most PFASs reached maximum concentrations in the Welland River nearest Hamilton Airport (Welland River 1). However, FOSA and EtFOSAA had maximum concentrations at the sites furthest downstream (Figure 1c, SI Table S6), which suggests primary sources other than AFFF from Hamilton Airport. In contrast, FHxSA had maximum concentrations nearest Hamilton Airport (19 ± 2 ng/L), which suggests perfluorohexane sulfonamido precursors to FHxSA were used in AFFFs at the airport since perfluorohexane sulfonamido substances have been identified in AFFF concentrates^{18,39,42} and FHxSA has been measured in AFFF-impacted groundwater, soil, and aquifer solids.^{15,16}

In this first report of FHxSA in surface waters, FHxSA was measured outside areas with known AFFF-impacts with FHxSA

found ubiquitously in all urban waters (0.04–0.94 ng/L, median: 0.32 ng/L) at significantly lower concentrations than in AFFF impacted waters (0.35–19 ng/L, median: 2.4 ng/L, $U = 67$, $p < 0.05$, SI Table S10), but only detected in one rural sample (<0.04 ng/L). Concentrations of FHxSA at Meretta and Resolute Lakes (1.2–3.6 ng/L) were similar to downstream sections of the Welland River (1.0–4.2 ng/L). This, along with the elevated PFHxS concentrations, suggests the lakes received inputs of AFFFs containing perfluorohexane sulfonamido substances.

Indeed, Welland River, Meretta Lake, and Resolute Lake samples also contained low concentrations of C3–C6 perfluoroalkane sulfonamido substances previously identified in AFFFs^{39,42} (SI Figure S2b, Tables S8 and S9), but a broad suite of these C3–C6 compounds was only detected in Welland River 1 ($\Sigma 4$ ng/L, qualitative) with concentrations decreasing downstream. However, C6 FASADA and C6 FASAB could be detected in downstream samples at total concentrations under 0.7 ng/L (qualitative). Resolute Lake and Meretta Lake samples had less than 0.8 ng/L (qualitative) total of these perfluoroalkane sulfonamido substances. The low concentrations of these PFASs are consistent with previous studies of AFFF-impacted groundwater that found relatively low concentrations of C4 to C6 FASAAAs (≤ 660 ng/L each) compared to PFOS concentrations ($\leq 300\,000$ ng/L) in a few highly contaminated groundwater samples.^{14,15} Interestingly, FASAAAs were not detected in surface waters, while FASADAs, and FASABs make up a larger share in water than they do in AFFFs, where they are side products.^{39,46} This absence of FASAAAs may be due to enhanced sorption of amines on mineral cation exchange sites or faster degradation of amines because they have two oxidizable nitrogen atoms with lone pairs of electrons. The increased share of FASABs and FASADAs compared to FASAAAs in water may be caused by inhibition of oxidation without a tertiary amine with a lone pair.

PFAAs. Profiles of PFAAs in water samples were typically dominated by PFOS, PFPeA, PFHxA, and sometimes PFHxS (Figure 2a, SI Table S5). Higher concentrations of PFPeA and PFHxA relative to PFHpA and PFOA suggest inputs from degradation of short chain fluorotelomers due to shifts in PFAS production, although greater sorption of longer chain PFCAs may be a factor.⁴⁷ The PFHxS concentration is over half the PFOS concentration in most samples from Welland River and in samples from Resolute Lake, Meretta Lake, and Perch Creek. Since Welland River, Resolute Lake, and Meretta Lake are known to have elevated PFOS concentrations due to AFFF impacts from airports,^{5,43,48} the higher concentrations of PFHxS may be due to degradation of perfluorohexane sulfonamido substances found in 3M AFFFs.^{14,18,39,42} AFFF impacts to Perch Creek have not been reported, but Perch Creek runs alongside Sarnia Airport approximately 2.7 km upstream from the sampling site and AFFF from the airport may be a source of PFOS and PFHxS.

Etobicoke Creek PFOS concentrations (11–16 ng/L) were 2 to 3 times lower than those reported for comparable locations in 2009 (32–41 ng/L) showing continuing attenuation of PFOS concentrations since an AFFF spill in 2000.⁷ Concentrations of PFOS (24–46 ng/L), PFHxS (13–30 ng/L), and PFOA (8–14 ng/L) in Meretta and Resolute Lake samples from 2012 and 2014 were similar to measurements in 2005⁴⁸ and 2010–11,⁴³ which likely indicates slow attenuation of PFAAs from the Arctic lakes and/or ongoing inputs to the lakes, perhaps through runoff, since raw sewage inputs stopped

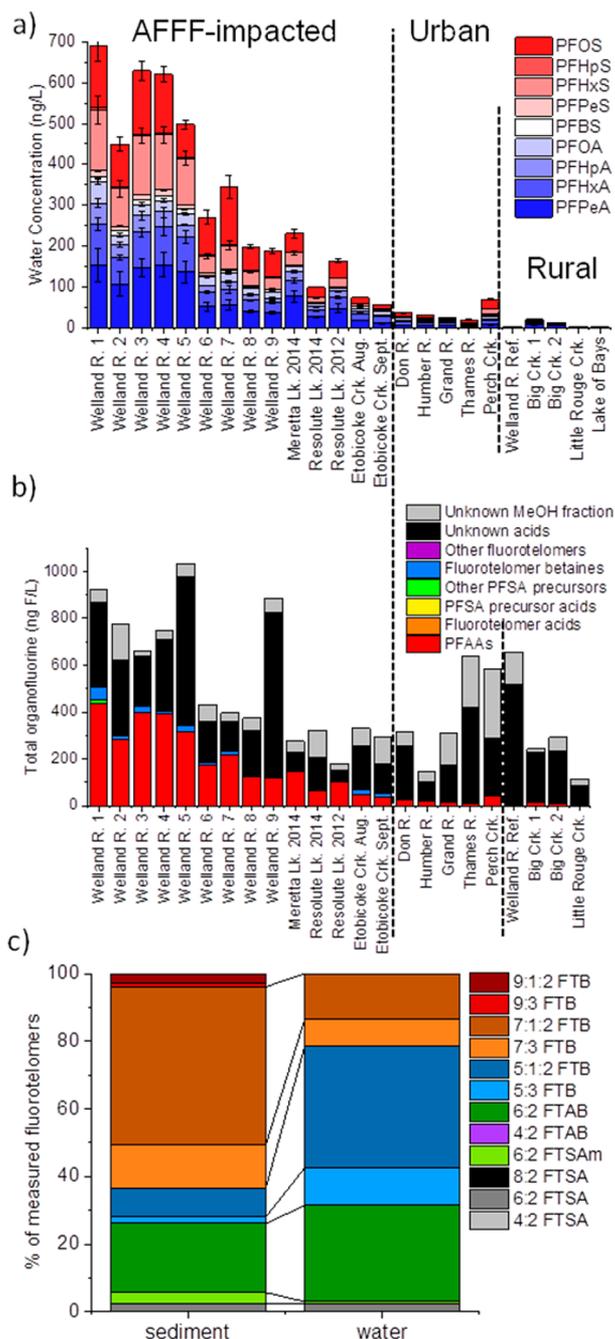


Figure 2. (a) Concentrations of PFCAs and PFSA in surface waters in ng/L with error bars showing standard deviations. (b) Total organofluorine in the surface water extracts as measured by TOF-CIC plotted with the amount of total organofluorine accounted for by measured PFASs. PFAAs include PFCAs and PFSA; fluorotelomer acids include FTSA and 6:2 FTSA-SO₂; PFSA precursor acids include FASADAs and EtFOSAA; other PFSA precursors include FHxSA, FOSA, FASAAAs, and FASABs; and fluorotelomer betaines include FTABs and FTBs. Unknown acids are organofluorine not accounted for by measured PFASs in the acids fraction and unknown MeOH fractions are organofluorine not accounted for by measured PFASs in the methanol fraction. c) Distribution of fluorotelomer substances in sediment and water from Welland River 1 sampling site.

in 1998.⁴⁹ Concentrations of PFOA and PFOS in Don River and PFOA in Humber River are 2–3-fold lower than 2007 measurements, while PFOS in Humber River decreased slightly (8.3 ng/L in 2007; 7.2 ± 0.4 ng/L in 2015).⁵⁰ These decreases

likely show effects of the PFOS phase-out⁵¹ and the PFOA stewardship program.⁵² It is notable that concentrations of all PFAAs except PFBS were significantly higher ($p < 0.05$) in AFFF-impacted samples than in urban samples (SI Table S10).

Compared to PFOS, PFBS, and PFCA concentrations reported for Welland River water in 2010,⁵ water sampled in 2015 has lower concentrations of PFAAs nearest Hamilton Airport and higher concentrations downstream. For example, Welland River 1 had PFPeA concentrations of 270 ng/L in 2010⁵ and 150 ± 40 ng/L in 2015, while Welland River 5 had PFPeA concentrations of 2.4 ng/L in 2010⁵ and 140 ± 30 ng/L in 2015. This may be due to ongoing transport of PFSA and PFCA downstream of the airport, continuing degradation of PFAA precursors from AFFFs, and/or differences in river flow between the sampling times.

Among the rural sites without known AFFF-impacts, the Big Creek samples contained short-chain PFCA and PFHxS concentrations (<5–6.6 ng/L PFPeA, < 1.2–1.3 ng/L PFHxS) similar to urban sites without known AFFF-impacts (<5–7.3 ng/L PFPeA, < 1.2–13 ng/L PFHxS), which suggests these sites may have a local PFAS source. At the remaining rural sites, PFOA (<0.6–0.7 ng/L) and PFOS (<0.2–2.5 ng/L) were always detected, whereas PFPeA, PFHxA, PFHpA, PFBS, and PFPeS were detected in one or two rural samples each at or below their respective LOQs. These PFAAs, including PFOS and PFOA, are known to be present in rainwater due to atmospheric oxidation of PFAA precursors^{45,53,54} and may also be deposited through dry deposition of atmospheric particles containing PFAAs.⁵⁵ The concentrations of PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS were significantly lower in rural samples than in urban samples ($p < 0.05$, SI Table S10), while insufficient detections of odd-chain PFSA were obtained in rural samples.

Total Organofluorine. Any measured inorganic fluoride was subtracted from the total fluoride measured by TOF-CIC in the acid fractions to obtain the total organofluorine concentrations in the acid fractions shown in Figure 2b. The percentage of the total organofluorine in the acid fraction that was not accounted for by the measured PFASs, the unknown acids, ranged from 30% to 99.7% (44–700 ngF/L). The only significant contributors to the acid fraction organofluorine were PFAAs. Shorter chain-lengths of PFAAs, which are inadequately retained in reverse phase liquid chromatography, may account for some unknown acids. In particular, trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA) were the two most abundant PFCAs in precipitation samples from Tsukuba, Japan⁵⁴ and Canada,⁵³ with TFA most abundant by a large margin. Since TFA has been measured at variable concentrations up to hundreds of ng/L in surface waters,^{56,57} TFA may account for a significant portion of the unknown acid fraction organofluorine. Because PFBA was not measured due to analytical challenges, it may also represent a significant source of organofluorine in the surface water extracts since it is sometimes a major PFCA in water samples.^{58–60}

In the methanol fraction, fluorotelomer betaines (FTBs and FTABs) accounted for the largest portion of the total organofluorine of any measured PFASs at up to 44%, while perfluoroalkane sulfonamido substances accounted for up to 10%, and other fluorotelomer substances accounted for 1% or less. The portion of methanol fraction organofluorine not accounted for by measured PFASs was 45 to 100%. Due to the lack of isolated standards, concentrations of FTBs have

significant uncertainty and the share of organofluorine accounted for by FTBs may be larger or smaller than estimated.

A study of AFFF-impacted groundwater using the oxidation of precursors assay found that unknown PFAA precursors accounted for 9% of total PFASs in highly contaminated groundwater,¹⁵ which is substantially less unidentified organofluorine than was found in surface waters here. This may be partially due to the sensitivity of TOF-CIC to short chain PFCAs, including TFA. While 6:2 FTSA was 11% of the total PFASs in the groundwater study,¹⁵ the total fluorotelomer acids accounted for at most 0.15% of the total organofluorine here. Perhaps the low relative proportion of FTSAs in surface waters compared to groundwater is related to surface water only loss processes, such as aqueous photolysis or aerobic biodegradation. Perfluoroalkane sulfonamido substances, categorized as PFSA precursors, account at most 1.4% of the total organofluorine at Welland River 1, which is close to the 3% of groundwater PFASs accounted for by FHxSA.¹⁵ The FTABs and FTBs, which contribute 2.5–6.2% of total organofluorine in eight samples are a unique finding of this study. Recently, Barzen-Hanson et al. identified 40 additional classes of PFASs in AFFF concentrates, commercial products, and AFFF-impacted groundwater, which may account for some of the unidentified organofluorine, particularly at AFFF impacted sites.¹⁸

PFASs in Sediments. The concentrations of PFAAs determined in sediment samples from the Welland River were similar to those reported for river sediment from around France.¹³ Previous studies have reported relatively high 6:2 FTAB concentrations in sediments from rivers in France (0.02–4 ng/g) and upstream (8 ng/g) and downstream (81 ng/g) of a firefighting training area in France,^{13,17} in comparison to the results determined here (<LOD–0.44 ng/g). This is not unexpected given the high 6:2 FTAB concentrations measured in water upstream (18,000 ng/L) and downstream (140 ng/L) of the firefighting training area¹⁷ relative to the water concentrations at the relevant sites in this study (<0.2–33 ng/L).

As Welland River 1 had the highest PFAS concentrations, it best illustrates the different PFAS profiles in sediment and water (SI Table S11). The PFAA profile in sediment is dominated by PFOS, whereas the PFAA profile in water also has substantial PFHxS, PFHxA, and PFPeA (SI Figure S2c), due to the greater sorption of long-chain PFSAs, such as PFOS, compared to short-chain PFAAs, especially PFCAs. The sediment water distribution coefficient (K_d) was calculated site by site for quantitative and qualitative analytes detected above the LOQ in both sediment and water according to

$$K_d = \frac{c_s}{c_w} \quad (1)$$

where c_s is the concentration in sediment in ng/kg and c_w is the concentration in water in ng/L. These were converted to organic carbon normalized distribution coefficients (K_{oc}) by dividing by the fraction of organic carbon in each sediment and average $\log K_d$ and $\log K_{oc}$ were calculated for each PFAS. The results are tabulated in SI Table S12. The determined $\log K_{oc}$ for PFOS (3.67 ± 0.28) is similar to that derived from field sediments in the Netherlands (3.18 ± 0.44)⁸ and Tokyo Bay (3.8 ± 0.1),³³ while the $\log K_{oc}$ for PFHxS (2.40 ± 0.27) is within the range of values reported previously following an AFFF release in the Netherlands (1.98)⁸ and in Tokyo Bay (3.6 ± 0.1).³³ Trends that have been reported in the literature

previously are seen as PFOS is more sorptive than PFHxS, while FHxSA ($\log K_{oc}$: 2.71 ± 0.25) is more sorptive than PFHxS as has been seen for FOSA and PFOS.⁶¹ The $\log K_{oc}$ for EtFOSAA (4.33) is also greater than for PFOS and close to that determined in Tokyo Bay sediments (4.8 ± 0.1)³³ and river sediments in Vietnam (4.4 ± 0.3).³⁵ Thus, the data reflect the expected trends in distribution coefficients for PFASs with previously reported data.

Therefore, comparing the distribution of the fluorotelomer substances between water and sediment nearest Hamilton Airport (Figure 2c) may suggest trends in sorption of novel fluorotelomer substances. These trends could be further investigated for confirmation, which is outside the scope of this work. In sediment there are increased contributions of some PFASs, particularly 7:1:2, 7:3, 9:1:2, and 9:3 FTBs and 6:2 FTSAm compared to water. These are likely relatively more sorptive compounds, which is as expected given the uncharged, less water-soluble nature of 6:2 FTSAm and the longer chain-lengths of the FTBs. Fluorotelomer substances that make up a smaller share of the profile in sediment than in water include 5:1:2 and 5:3 FTBs and 6:2 FTAB. The calculated $\log K_{oc}$ values for 6:2 FTAB, 7:1:2 FTB, and 7:3 FTB, which should be interpreted only qualitatively due to the poor recovery of 6:2 FTAB from sediment and lack of standards for FTBs, are 2.7, 3.0, and 3.3, respectively, in order of increasing number of fluorines. While it is limited by the comparison of three different fluorotelomer betaine structures, this sediment analysis suggests that sorption increases with increasing fluorinated chain-length of fluorotelomer betaines. This is consistent with trends observed for PFCAs and PFSAs, at least above a threshold chain-length.^{32,33,47}

The only perfluoroalkane sulfonamido AFFF component detected in sediment was a low concentration of C6 FASAAm below the LOQ in Welland River 1 sediment. Combined with the lack of detection of FASAAs in water, it appears FASAAs may be more sorptive than FASABs, FASAAAs, and FASADAs, which were all detected in water and not in sediment.

ENVIRONMENTAL IMPLICATIONS

This study shows that some PFASs associated with AFFFs are broadly distributed in Canadian surface waters and may be found in relatively high concentrations. In terms of compounds associated with perfluoroalkane sulfonamido AFFF components, FHxSA was detected in all the urban and AFFF-impacted sites investigated. This indicates that precursors to PFHxS are broadly present in urban and AFFF-impacted Canadian surface waters, while these classes of PFASs are rarely considered given that FHxSA has only been measured previously at highly AFFF-impacted U.S. military sites. Little is known about the biological or toxicological effects of FHxSA other than that it is a carbonic anhydrase inhibitor⁶² and is toxic to red imported fire ants.⁶³ The detection of several perfluoroalkane sulfonamido AFFF components in AFFF-impacted surface waters in the Welland River, Resolute Lake, and Meretta Lake suggests that these precursors likely contribute to FHxSA, PFHxS, PFPeS, and PFBS concentrations in these waters. However, it is likely that other as yet unidentified precursors contribute to the presence of FHxSA in urban surface waters, which may include PFHxS precursors involved in the high serum PFHxS concentrations observed in a Canadian family who frequently used carpet treatments.⁶⁴ If the biodegradation of various perfluorohexane sulfonamido substances is similar to that of EtFOSE where

FOSA is the longest lived intermediate,⁶⁵ FHxSA may be a particularly long-lived intermediate and useful in environmental monitoring.

The FTABs represent a large proportion of the PFASs characterized in some samples, including Don River where 6:2 and 8:2 FTAB constituted 36% of the known organofluorine, which is remarkable since 6:2 FTAB degrades by aqueous photolysis and biodegradation,^{36,41} while PFCAs and PFSAs are fully persistent. The presence of 8:2 FTAB at 20–30% of the 6:2 FTAB concentration in Don River and Humber River water samples is significant because it is a potential PFOA precursor and elimination of such compounds in emissions and products by 2015 was a goal of the PFOA Stewardship Program.⁵² The FTBs were also detected in high apparent concentrations (\sum FTBs \leq 80 ng/L, qualitative) in AFFF-impacted waters. Since, FTABs and FTBs represent significant sources of PFAS contamination in some surface waters, more research is required on their potential sources in addition to AFFF, toxicology, and environmental fate, including the degradability of FTBs.

The relatively low concentrations (<3.5 ng/L total) of fluorotelomer PFASs that are not betaines, including FTSA, may indicate that these compounds are degraded relatively quickly in surface waters. This may be why levels of 6:2 FTSA were under 1.5 ng/L in surface water samples from Albany, NY,⁴⁵ the River Elbe in Germany,⁶⁶ and in 13 rivers in China.⁶⁷

A large proportion of total organofluorine in surface water extracts determined by TOF-CIC was not characterized by measuring AFFF-related PFASs (36–99.7% of total organofluorine). Although a significant proportion of this may be made up of very short-chain PFCAs in the acid fraction, between 4 and 51% of the unidentified organofluorine was in the methanol fraction and may consist of commercial PFASs other than those investigated here, degradation products of commercial PFASs, or other molecules containing organofluorine. This highlights the range of PFASs found in environmental samples and the difficulty of closing the mass balance of organofluorine by quantifying all the significantly contributing compounds. Because of this, general approaches to fluorine quantitation, such as TOF-CIC or the total oxidizable precursor assay^{15,68} may be needed to fully assess the extent of PFAS contamination in the environment.

Analysis of Welland River sediments suggested that longer perfluoroalkyl chain-length is associated with increased sorption of fluorotelomer betaines. There is a need for research to systematically examine the sorption of various chain-lengths of FTBs, FTABs, FTAAAs, and other AFFF components to different soils and sediments and compare them to other PFASs. These experiments may elucidate the impact of factors such as pH and cation exchange capacity on sorption of these PFASs and will show whether basic and cationic PFASs are preferentially sorbed as suggested by the detection of C6 FASAAm exclusively in sediment.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b03994.

Details about materials, standards, extraction and LC-MS/MS methods, sampling locations, recoveries, LODs, LOQs, concentrations of PFASs in samples, statistical test results, and log K_d values are available (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Moody, C.; Field, J. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.* **1999**, *33* (16), 2800–2806.
- (2) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and ¹⁹F NMR. *Anal. Chem.* **2001**, *73* (10), 2200–2206.
- (3) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. A. Monitoring Perfluorinated Surfactants in Biota and Surface Water Samples Following an Accidental Release of Fire-Fighting Foam into Etobicoke Creek. *Environ. Sci. Technol.* **2002**, *36* (4), 545–551.
- (4) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS. *Environ. Sci. Technol.* **2004**, *38* (6), 1828–1835.
- (5) de Solla, S. R.; De Silva, A. O.; Letcher, R. J. Highly elevated levels of perfluorooctane sulfonate and other perfluorinated acids found in biota and surface water downstream of an international airport, Hamilton, Ontario, Canada. *Environ. Int.* **2012**, *39* (1), 19–26.
- (6) Karrman, A.; Elgh-Dalgren, K.; Lafossas, C.; Moskeland, T. Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination. *Environ. Chem.* **2011**, *8* (4), 372–380.
- (7) Awad, E.; Zhang, X.; Bhavsar, S. P.; Petro, S.; Crozier, P. W.; Reiner, E. J.; Fletcher, R.; Tittlemier, S. A.; Braekevelt, E. Long-Term Environmental Fate of Perfluorinated Compounds after Accidental Release at Toronto Airport. *Environ. Sci. Technol.* **2011**, *45* (19), 8081–8089.
- (8) Kwadijk, C. J. A. F.; Kotterman, M.; Koelmans, A. A. Partitioning of Perfluorooctanesulfonate and Perfluorohexanesulfonate in the Aquatic Environment After an Accidental Release of Aqueous Film Forming Foam at Schiphol Amsterdam Airport. *Environ. Toxicol. Chem.* **2014**, *33* (8), 1761–1765.
- (9) Anderson, R. H.; Long, G. C.; Porter, R. C.; Anderson, J. K. Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties. *Chemosphere* **2016**, *150*, 678–685.
- (10) Filipovic, M.; Woldegiorgis, A.; Norström, K.; Bibi, M.; Lindberg, M.; Österås, A.-H. Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl

acids from a military airport to groundwater, lakes, soils and fish. *Chemosphere* **2015**, *129*, 39–45.

(11) Moody, C.; Hebert, G.; Strauss, S.; Field, J. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *J. Environ. Monit.* **2003**, *5* (2), 341–345.

(12) Oakes, K. D.; Benskin, J. P.; Martin, J. W.; Ings, J. S.; Heinrichs, J. Y.; Dixon, D. G.; Servos, M. R. Biomonitoring of perfluorochemicals and toxicity to the downstream fish community of Etobicoke Creek following deployment of aqueous film-forming foam. *Aquat. Toxicol.* **2010**, *98* (2), 120–129.

(13) Munoz, G.; Duy, S. V.; Labadie, P.; Botta, F.; Budzinski, H.; Lestremay, F.; Liu, J.; Sauv e, S. Analysis of zwitterionic, cationic, and anionic poly- and perfluoroalkyl surfactants in sediments by liquid chromatography polarity-switching electrospray ionization coupled to high resolution mass spectrometry. *Talanta* **2016**, *152*, 447–456.

(14) Backe, W. J.; Day, T. C.; Field, J. A. Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, *47* (10), 5226–5234.

(15) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.* **2013**, *47* (15), 8187–8195.

(16) McGuire, M. E.; Schaefer, C.; Richards, T.; Backe, W. J.; Field, J. A.; Houtz, E.; Sedlak, D. L.; Guelfo, J. L.; Wunsch, A.; Higgins, C. P. Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area. *Environ. Sci. Technol.* **2014**, *48* (12), 6644–6652.

(17) Boiteux, V.; Bach, C.; Sagres, V.; Hemard, J.; Colin, A.; Rosin, C.; Munoz, J.-F.; Dauchy, X. Analysis of 29 per- and polyfluorinated compounds in water, sediment, soil and sludge by liquid chromatography–tandem mass spectrometry. *Int. J. Environ. Anal. Chem.* **2016**, *96* (8), 705–728.

(18) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* **2017**, *51* (4), 2047–2057.

(19) Dauchy, X.; Boiteux, V.; Bach, C.; Rosin, C.; Munoz, J.-F. Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams. *Chemosphere* **2017**, *183*, 53–61.

(20) Moe, M. K.; Huber, S.; Svenson, J.; Hagenaars, A.; Pabon, M.; Tr umper, M.; Berger, U.; Knapen, D.; Herzke, D. The structure of the fire fighting foam surfactant Forafac®1157 and its biological and photolytic transformation products. *Chemosphere* **2012**, *89* (7), 869–875.

(21) Munoz, G.; Desrosiers, M.; Duy, S. V.; Labadie, P.; Budzinski, H.; Liu, J.; Sauv e, S. Environmental Occurrence of Perfluoroalkyl Acids and Novel Fluorotelomer Surfactants in the Freshwater Fish *Catostomus commersonii* and Sediments Following Firefighting Foam Deployment at the Lac-M egantic Railway Accident. *Environ. Sci. Technol.* **2017**, *51* (3), 1231–1240.

(22) Mejia-Avenida, S.; Munoz, G.; Sauv e, S.; Liu, J. Assessment of the Influence of Soil Characteristics and Hydrocarbon Fuel Cocontamination on the Solvent Extraction of Perfluoroalkyl and Polyfluoroalkyl Substances. *Anal. Chem.* **2017**, *89* (4), 2539–2546.

(23) Mejia-Avenida, S.; Munoz, G.; Vo Duy, S.; Desrosiers, M.; Beno t, P.; Sauv e, S.; Liu, J. Novel Fluoroalkylated Surfactants in Soils Following Firefighting Foam Deployment During the Lac-M egantic Railway Accident. *Environ. Sci. Technol.* **2017**, *51* (15), 8313–8323.

(24) Boiteux, V.; Dauchy, X.; Bach, C.; Colin, A.; Hemard, J.; Sagres, V.; Rosin, C.; Munoz, J.-F. Concentrations and patterns of perfluoroalkyl and polyfluoroalkyl substances in a river and three drinking water treatment plants near and far from a major production source. *Sci. Total Environ.* **2017**, *583*, 393–400.

(25) Dauchy, X.; Boiteux, V.; Bach, C.; Colin, A.; Hemard, J.; Rosin, C.; Munoz, J.-F. Mass flows and fate of per- and polyfluoroalkyl substances (PFASs) in the wastewater treatment plant of a fluorochemical manufacturing facility. *Sci. Total Environ.* **2017**, *576*, 549–558.

(26) Erkenbrecher, C. W.; Longoria, J. M.; Reynolds, R. A.; Julian, J. C.; DeLeo, M.; Ochomogo, M. G. Prevention of deposits on ceramics. US20060094623, May 4, 2006.

(27) DuPont. Dupont Capstone Fluorosurfactant FS-50 Technical Information https://www.chemours.com/Capstone/en_US/assets/downloads/K-02043-2_Capstone_FS-50.pdf (accessed Oct 4, 2016).

(28) DuPont. Dupont Capston Fluorosurfactant 1157 Water-soluble additive for firefighting foam Technical Information https://www.chemours.com/Capstone/en_US/assets/downloads/H-97584-2_Capstone_1157.pdf (accessed October 4, 2016).

(29) Yeung, L. W. Y.; De Silva, A. O.; Loi, E. I. H.; Marvin, C. H.; Taniyasu, S.; Yamashita, N.; Mabury, S. A.; Muir, D. C. G.; Lam, P. K. S. Perfluoroalkyl substances and extractable organic fluorine in surface sediments and cores from Lake Ontario. *Environ. Int.* **2013**, *59*, 389–397.

(30) Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K. S.; Kannan, K. Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water. *J. Chromatogr. A* **2007**, *1143* (1–2), 98–104.

(31) Weiner, B.; Yeung, L. W. Y.; Marchington, E. B.; D’Agostino, L. A.; Mabury, S. A. Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS). *Environ. Chem.* **2013**, *10* (6), 486–493.

(32) Higgins, C. P.; Luthy, R. G. Sorption of Perfluorinated Surfactants on Sediments†. *Environ. Sci. Technol.* **2006**, *40* (23), 7251–7256.

(33) Ahrens, L.; Taniyasu, S.; Yeung, L. W. Y.; Yamashita, N.; Lam, P. K. S.; Ebinghaus, R. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere* **2010**, *79* (3), 266–272.

(34) Gewurtz, S. B.; Bhavsar, S. P.; Petro, S.; Mahon, C. G.; Zhao, X.; Morse, D.; Reiner, E. J.; Tittlemier, S. A.; Braekevelt, E.; Drouillard, K. High levels of perfluoroalkyl acids in sport fish species downstream of a firefighting training facility at Hamilton International Airport, Ontario, Canada. *Environ. Int.* **2014**, *67*, 1–11.

(35) Nguyen, T. V.; Reinhard, M.; Chen, H.; Gin, K. Y.-H. Fate and transport of perfluoro- and polyfluoroalkyl substances including perfluorooctane sulfonamides in a managed urban water body. *Environ. Sci. Pollut. Res.* **2016**, *23* (11), 10382–10392.

(36) D’Agostino, L. A.; Mabury, S. A. Aerobic biodegradation of 2 fluorotelomer sulfonamide–based aqueous film–forming foam components produces perfluoroalkyl carboxylates. *Environ. Toxicol. Chem.* **2017**, *36* (8), 2012–2021.

(37) Niagara Peninsula Conservation Authority. Stream Flow Monitoring https://npca.ca/stream-flow-monitoring?has_js=1&_ga=GA1.2.548630345.1496865763&_gid=GA1.2.506441281.1497016862&_atuv=6123&_atuv=593aaa2d7af09c33001 (accessed June 9, 2017).

(38) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* **2005**, *1093* (1–2), 89–97.

(39) D’Agostino, L. A.; Mabury, S. A. Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates. *Environ. Sci. Technol.* **2014**, *48* (1), 121–129.

(40) Rand, A. A.; Mabury, S. A. Vitro Interactions of Biological Nucleophiles with Fluorotelomer Unsaturated Acids and Aldehydes: Fate and Consequences. *Environ. Sci. Technol.* **2012**, *46* (13), 7398–7406.

- (41) Trouborst, L. Aqueous photolysis of 6:2 fluorotelomer sulfonamide alkylbetaine. M.Sc. Thesis, University of Toronto: Toronto, ON, 2015.
- (42) Place, B. J.; Field, J. A. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US Military. *Environ. Sci. Technol.* **2012**, *46* (13), 7120–7127.
- (43) Lescord, G. L.; Kidd, K. A.; De Silva, A. O.; Williamson, M.; Spencer, C.; Wang, X.; Muir, D. C. G. Perfluorinated and Polyfluorinated Compounds in Lake Food Webs from the Canadian High Arctic. *Environ. Sci. Technol.* **2015**, *49* (5), 2694–2702.
- (44) Harding-Marjanovic, K. C.; Houtz, E. F.; Yi, S.; Field, J. A.; Sedlak, D. L.; Alvarez-Cohen, L. Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ. Sci. Technol.* **2015**, *49* (13), 7666–7674.
- (45) Kim, S.-K.; Kannan, K. Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes. *Environ. Sci. Technol.* **2007**, *41* (24), 8328–8334.
- (46) Stern, R. M.; Guenther, R. A.; Alm, R. R.; Wilkinson, T. K. Process for the Preparation of Fluoroaliphatic Aminocarboxylate Surfactants. U.S. 5,144,069, September 1, 1992.
- (47) Guelfo, J. L.; Higgins, C. P. Subsurface Transport Potential of Perfluoroalkyl Acids at Aqueous Film-Forming Foam (AFFF)-Impacted Sites. *Environ. Sci. Technol.* **2013**, *47* (9), 4164–4171.
- (48) Stock, N. L.; Furdul, V. I.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl Contaminants in the Canadian Arctic: Evidence of Atmospheric Transport and Local Contamination. *Environ. Sci. Technol.* **2007**, *41* (10), 3529–3536.
- (49) Douglas, M. S. V.; Smol, J. P. Eutrophication and recovery in the High Arctic: Meretta Lake (Cornwallis Island, Nunavut, Canada) revisited. *Hydrobiologia* **2000**, *431* (2–3), 193–204.
- (50) D'eon, J. C.; Crozier, P. W.; Furdul, V. I.; Reiner, E. J.; Libelo, E. L.; Mabury, S. A. Perfluorinated phosphonic acids in Canadian surface waters and wastewater treatment plant effluent: Discovery of a new class of perfluorinated acids. *Environ. Toxicol. Chem.* **2009**, *28* (10), 2101–2107.
- (51) Weppner, W. Letter by William Weppner, 3M, to Charles Auer, EPA OPPT, regarding the Phase-out Plan for POSF-Based Products; US EPA Public Docket EPA-HQ-OPPT-2002–0043–0009; 3M General Offices: St. Paul, MN, 2000.
- (52) Johnson, S. L. PFOA Stewardship Program Invitation Letter, **2006**.
- (53) Scott, B. F.; Moody, C. A.; Spencer, C.; Small, J. M.; Muir, D. C. G.; Mabury, S. A. Analysis for Perfluorocarboxylic Acids/Anions in Surface Waters and Precipitation Using GC–MS and Analysis of PFOA from Large-Volume Samples. *Environ. Sci. Technol.* **2006**, *40* (20), 6405–6410.
- (54) Taniyasu, S.; Kannan, K.; Yeung, L. W. Y.; Kwok, K. Y.; Lam, P. K. S.; Yamashita, N. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C₂–C₄) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C₅–C₁₈). *Anal. Chim. Acta* **2008**, *619* (2), 221–230.
- (55) Müller, C. E.; Spiess, N.; Gerecke, A. C.; Scheringer, M.; Hungerbühler, K. Quantifying Diffuse and Point Inputs of Perfluoroalkyl Acids in a Nonindustrial River Catchment. *Environ. Sci. Technol.* **2011**, *45* (23), 9901–9909.
- (56) Scott, B. F.; MacTavish, D.; Spencer, C.; Strachan, W. M. J.; Muir, D. C. G. Haloacetic Acids in Canadian Lake Waters and Precipitation. *Environ. Sci. Technol.* **2000**, *34* (20), 4266–4272.
- (57) Wujcik, C. E.; Cahill, T. M.; Seiber, J. N. Determination of Trifluoroacetic Acid in 1996–1997 Precipitation and Surface Waters in California and Nevada. *Environ. Sci. Technol.* **1999**, *33* (10), 1747–1751.
- (58) Möller, A.; Ahrens, L.; Surm, R.; Westerveld, J.; van der Wielen, F.; Ebinghaus, R.; de Voogt, P. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. *Environ. Pollut.* **2010**, *158* (10), 3243–3250.
- (59) Kwok, K. Y.; Yamazaki, E.; Yamashita, N.; Taniyasu, S.; Murphy, M. B.; Horii, Y.; Petrick, G.; Kallerborn, R.; Kannan, K.; Murano, K.; et al. Transport of Perfluoroalkyl substances (PFAS) from an arctic glacier to downstream locations: Implications for sources. *Sci. Total Environ.* **2013**, *447*, 46–55.
- (60) MacInnis, J. J.; French, K.; Muir, D. C. G.; Spencer, C.; Criscitiello, A.; Silva, A. O. D.; Young, C. J. Emerging investigator series: a 14-year depositional ice record of perfluoroalkyl substances in the High Arctic. *Environ. Sci. Process. Impacts* **2017**, *19* (1), 22–30.
- (61) Ahrens, L. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. *Chemosphere* **2011**, *85* (5), 731–737.
- (62) Benfodda, Z.; Guillen, F.; Romestand, B.; Dahmani, A.; Blancou, H. Synthesis and investigation of inhibition effect of fluorinated sulfonamide derivatives on carbonic anhydrase. *Eur. J. Med. Chem.* **2010**, *45* (3), 1225–1229.
- (63) Meer, R. K. V.; Lofgren, C. S.; Williams, D. F. Fluoroaliphatic Sulfones: A New Class of Delayed-action Insecticides for Control of *Solenopsis invicta* (Hymenoptera: Formicidae). *J. Econ. Entomol.* **1985**, *78* (6), 1190–1197.
- (64) Beesoon, S.; Genuis, S. J.; Benskin, J. P.; Martin, J. W. Exceptionally High Serum Concentrations of Perfluorohexanesulfonate in a Canadian Family are Linked to Home Carpet Treatment Applications. *Environ. Sci. Technol.* **2012**, *46* (23), 12960–12967.
- (65) Rhoads, K. R.; Janssen, E. M.-L.; Luthy, R. G.; Criddle, C. S. Aerobic Biotransformation and Fate of N-Ethyl Perfluorooctane Sulfonamidoethanol (N-EtFOSE) in Activated Sludge. *Environ. Sci. Technol.* **2008**, *42* (8), 2873–2878.
- (66) Ahrens, L.; Felizeter, S.; Sturm, R.; Xie, Z.; Ebinghaus, R. Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe. *Mar. Pollut. Bull.* **2009**, *58* (9), 1326–1333.
- (67) Lin, Y.; Liu, R.; Hu, F.; Liu, R.; Ruan, T.; Jiang, G. Simultaneous qualitative and quantitative analysis of fluoroalkyl sulfonates in riverine water by liquid chromatography coupled with Orbitrap high resolution mass spectrometry. *J. Chromatogr. A* **2016**, *1435*, 66–74.
- (68) Houtz, E. F.; Sedlak, D. L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environ. Sci. Technol.* **2012**, *46* (17), 9342–9349.