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Discovery and Implications of C_2 and C_3 Perfluoroalkyl Sulfonates in Aqueous Film-Forming Foams and Groundwater

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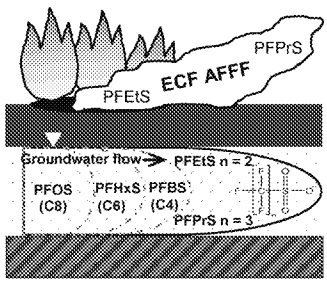
Supporting Information

ABSTRACT: Historically, 3M aqueous film-forming foams (AFFFs) were released at U.S. military and civilian sites to extinguish hydrocarbon-based fuel fires. To date, only C_4–C_{10} homologues of the perfluoroalkyl sulfonic acids (PFSAs) are documented in 3M AFFFs. Perfluoroethanesulfonate (PFEtS) and perfluoropropanesulfonate (PFPrS), two ultra-short-chain PFSAs, were discovered by liquid chromatography (LC) quadrupole time-of-flight mass spectrometry. Once they were identified, PFEtS and PFPrS were then quantified in five 3M AFFFs and in one groundwater sample from each of 11 U.S. military bases by LC tandem mass spectrometry. Concentrations of PFEtS and PFPrS in the five AFFFs ranged from 7 to 13 mg/L and from 120 to 270 mg/L, respectively. For the groundwater, PFEtS was quantified in 8 of the 11 samples (11–7500 ng/L) and PFPrS in all samples (19–63000 ng/L). The high water solubility, mobility, and detection frequency of these ultra-short-chain PFSAs indicate that groundwater contaminant plumes may be larger than previously believed, and their removal by conventional activated carbon will be challenging.



INTRODUCTION

Identifying the active ingredients in aqueous film-forming foams (AFFFs), which were repeatedly applied at firefighter training sites, is a critical first step to understanding the extent of groundwater, soil, and sediment contamination at fire-training areas on military and civilian sites. Over the past few years, efforts focused on identifying per- and polyfluorinated alkyl substances (PFASs) in AFFFs resulted in the identification of PFASs with novel headgroups (e.g., zwitterionic and cationic) attached to common chain lengths (e.g., C_4–C_{12}).[1−4]

A number of analytical tools exist for identifying unknown PFASs. Combustion ion chromatography is used to measure total and adsorbable organic fluorine but cannot be used to identify individual PFASs.[3,5,6] ^{19}F nuclear magnetic resonance (NMR)[7,8] and fast atom bombardment mass spectrometry[1] provide qualitative structural information about PFASs. The total oxidizable precursor assay, which is based on the oxidation of polyfluoroalkyl "precursor" substances to perfluoroalkyl carboxylic acids (PFCAs), is used to quantify precursors in urban runoff and groundwater.[9] Alternatively, quadrupole time-of-flight mass spectrometry (QTOF-MS) and Fourier transform cyclotron ion resonance mass spectrometry provide high-resolution, high-mass accuracy information that is critical for identifying unknown PFASs.[1,2,10]

With these analytical tools in hand, attention is now shifting to closing the mass balance on PFASs in groundwater impacted by AFFF, with emphasis on the identification of polar biodegradation intermediates.[3,4,11,12] In contrast, the existence of ultra-short-chain homologues of well-known classes [e.g., perfluoroalkyl sulfonic acids (PFSAs)] receives little attention. Notable recent work by D'Agostino et al. was the first to identify the C_3 homologues in AFFFs for a number of polyfluorinated classes.[2] A limited number of groups indicate the analytical capacity to detect the perfluoroethanesulfonate (PFEtS) and perfluoropropanesulfonate (PFPrS),[13−16] yet none report environmental levels of PFEtS and PFPrS above the analytical limits of detection (LODs). To the best of our knowledge, only two reports document low levels (≤20 ng/L) of PFEtS and PFPrS in waste and tap waters.[17,18] Short-chain (C_4–C_6) PFCAs and PFSAs, however, are gaining attention with respect to public policy. The U.S. Environmental Protection Agency's (EPA) Third Unregulated Monitoring Rule (UCMR3) includes perfluorobutanesulfonate (PFBS),[19] and the National Center for Environmental Assessment just recently established provisional peer-reviewed subchronic and chronic reference doses for PFBS.[20]

Current efforts in our laboratory to add all newly identified PFASs associated with AFFFs to analyte lists for QTOF-MS investigations resulted in the discovery of measurable levels of PFEtS and PFPrS in groundwater and AFFFs containing PFASs produced by electrofluorination (ECF). The presence of PFEtS and PFPrS was then quantified in AFFFs and groundwater by liquid chromatography–tandem mass spectrometry (LC–MS/MS).

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MATERIALS AND METHODS

Chemicals. Chemicals, reagent sources, purity information, and chemical names for standards and internal standards are provided in the Supporting Information. To the best of our knowledge, no authentic analytical standards for PFEtS and PFPrS were commercially available, whereas others received PFPrS as gifts.[17,18]

Sample Collection. *3M AFFF Formulations.* Five 3M AFFF formulations, consisting of one formulation each manufactured in 1989, 1998, and 2001 and two formulations from 1993, were reanalyzed for this study.[21] The AFFF formulations came from an archive of AFFF samples obtained from U.S. military bases as previously described.[1]

Groundwater. The groundwater samples analyzed for this study were collected between 2011 and 2014 from nine different U.S. military bases (sites A–F and H–J) by third parties as detailed elsewhere.[21] Two samples (sites G and K) that were archived at −20 °C since 1999[22] were reanalyzed to give a total of 11 groundwater samples from 11 military sites.

Sample Preparation. The AFFF formulations were diluted 39000–120000-fold in HPLC-grade water for QTOF-MS analysis and 60000–600000-fold for LC–MS/MS analysis; the dilution factors were based on previous data for C_4–C_{10} PFSAs in the same five 3M AFFF formulations.[21] Groundwater samples were diluted in reagent water 1–140-fold for QTOF-MS analysis and 1–50-fold for LC–MS/MS analysis. The 3M AFFF from 1998 and groundwater from site A were analyzed in triplicate to determine the precision of the measured values. All other samples were analyzed once.

Diluted AFFF and groundwater were extracted using a micro liquid–liquid extraction as described elsewhere;[21] a brief description is given in the Supporting Information. Given the lack of authentic PFEtS and PFPrS standards, it was assumed that the extraction and ionization efficiencies of PFEtS and PFPrS were equivalent to those of PFBS.

Discovery by Liquid Chromatography–Quadrupole Time-of-Flight Mass Spectrometry. Chromatographic separations were performed on a Shimadzu (Columbia, MD) LC-30AD instrument. A 10 μL aliquot of each sample was injected onto an orthogonal chromatographic system consisting of silica and propylamine (NH_2) guard columns placed in series with a C18 analytical column.[21] The method by Backe et al.[21] was modified to accommodate the decreased capacity of current, commercially available NH_2 guard columns (see the Supporting Information).

A quadrupole time-of-flight ABSciex (Framingham, MA) TripleTOF 5600 instrument with electrospray ionization in negative ionization mode was used to obtain QTOF-MS data. All data were collected in the information-dependent acquisition mode for nontarget analysis. Extraction blanks, consisting of water taken through the extraction process, were run throughout the sample list to ensure that there was no instrumental contamination or carryover between samples. Instrumental parameters are listed in the Supporting Information.

QTOF-MS Data Analysis Strategies. Negative mass defects (0.950–1.00)[23,24] were used to screen the QTOF-MS data collected for the groundwater at site B. A negative mass defect occurs when an ion's accurate mass (to four decimal places) is slightly smaller than its nominal (rounded to a whole number) mass.[2] PFASs sharing a common headgroup but with varying lengths of the fluorinated carbon backbone were classified by mass differences of 50 Da (-CF_2-) for perfluorinated compounds.[2]

Masses detected in the extraction blank samples were manually eliminated from the detected masses in the site B groundwater sample. Remaining masses with mass defects between 0.950 and 1.00 were extracted from the background-subtracted chromatogram. The masses of the extracted ions were first normalized to the CF_2 scale (eq 1).[23] The resulting masses (CF_2 scale) were then normalized to the mass defect (CF_2 scale, eq 2).[23] A Kendrick mass defect plot [plot of the mass-to-charge ratio (m/z) vs the mass defect (CF_2 scale)] gives rise to homologous series, each characterized by a unique mass defect.[24] The mass defect plot for the site B groundwater was inspected for multiple peaks. Any peak that was lower in intensity shared an m/z with a higher-intensity peak within 5 ppm mass error and gave a mass defect (CF_2 scale) of ±0.005, and a retention time of ±0.3 min was eliminated and attributed to branched or linear isomers. The 5 ppm error about the measured accurate mass also applies to the error about the mass defect [CF_2 scale (see the Supporting Information)].

$$\text{mass}(CF_2\ \text{scale}) = \left[\text{mass}(\text{extracted ion}) \times \frac{50}{49.99681}\right] \quad (1)$$

$$\text{mass defect}(CF_2\ \text{scale}) = \text{mass}(CF_2\ \text{scale}) - \text{nominal mass}(\text{rounded down}, CF_2\ \text{scale}) \quad (2)$$

The extracted ion chromatogram (XIC) manager in PeakView 2.1 (ABSciex) was used to generate XICs for each AFFF and groundwater sample based on the entered list of exact masses and chemical formulas for PFEtS (199.0782 Da, $C_2F_5SO_3H$) and PFPrS (249.0938 Da, $C_3F_7SO_3H$). PeakView 2.1 positively identified PFEtS and PFPrS in samples when the detected masses gave a mass error of <5 ppm, when compared to the exact masses, and measured isotope ratios that were within 10% of the predicted isotope ratio.

Quantification by LC–MS/MS. Details of the LC–MS/MS method, PFEtS and PFPrS limits of detection and quantification, MS/MS transitions, and quality controls are outlined in the Supporting Information.

RESULTS AND DISCUSSION

Ultrashort (C_2 and C_3) Perfluoroalkyl Sulfonate Discovery. A plot of m/z against the mass defect [CF_2 scale (Figure 1)] indicates six homologous series of PFASs in groundwater at site B. Initial attempts to identify PFASs with novel polar headgroups using the site B groundwater confirmed the three classes of PFASs known to be present[21] and provided evidence of three additional homologous series whose structures do not match any precursors present in AFFF.[2] However, the identification of PFASs with novel headgroups is beyond the scope of this study and is rather the focus of an ongoing investigation.

Two ultrashort PFSAs (PFEtS and PFPrS) were discovered during a close inspection of the masses below PFBS (solid black dots in Figure 1) in the PFSA class. The dot at m/z ~200 corresponds to PFEtS, and the dot at m/z ~250 corresponds to PFPrS. Because all homologues within a class have the same normalized mass defect,[24] the two solid black dots in the PFSA class were identified as PFEtS and PFPrS. The presence of

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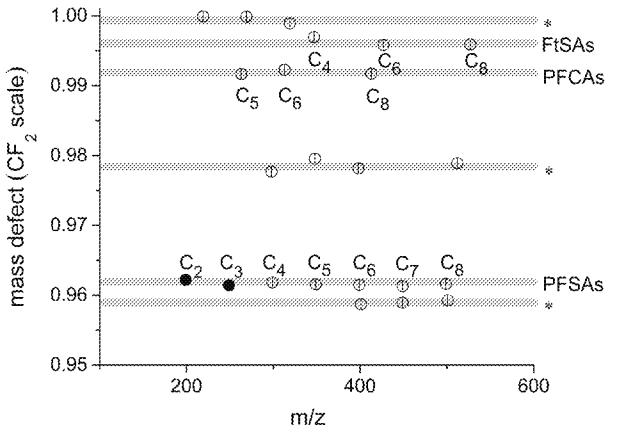

Figure 1. PFAS homologous series found in groundwater from site B. The solid black dots indicate PFEtS and PFPrS. The asterisk represents unidentified classes. FtSAs, PFCAs, and PFSAs are the fluorotelomer sulfonic acids, the perfluorocarboxylic acids, and the perfluorosulfonic acids, respectively. The width of the gray lines indicates the 5 ppm error about the normalized mass defect.

PFEtS and PFPrS was confirmed by comparing the measured and theoretical exact masses using the XIC manager. A detection frequency of 100% for PFEtS and/or PFPrS was obtained upon analyzing the five 3M AFFF and 10 remaining groundwater samples, which prompted subsequent quantification by LC–MS/MS.

3M AFFF Concentrations of PFEtS and PFPrS. Both PFEtS and PFPrS were quantified in all five 3M AFFFs manufactured over a period of 12 years [1989–2001 (Figure 2)]. Concentrations of PFEtS in AFFF formulations ranged

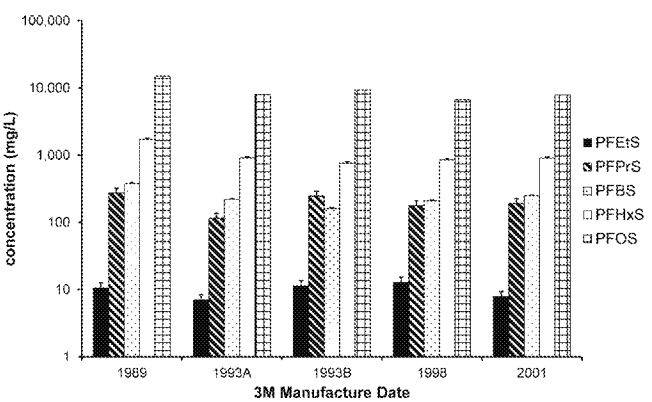

Figure 2. Concentrations of PFEtS and PFPrS relative to the three most abundant perfluoroalkyl sulfonic acids (C_4, C_6, and C_8 PFSAs) in the five 3M AFFFs manufactured over a period of 12 years. Error bars represent the relative standard deviation determined from $n = 3$ replicates of 3M AFFF manufactured in 1998. See ref 21 for PFBS, PFHxS, and PFOS concentrations.

from 7.0 to 13 mg/L and comprised 0.22% of the PFSAs on average. The concentrations of PFPrS were higher and ranged from 120 to 270 mg/L, which comprised 3.5% of the PFSAs on average. On the basis of the data from the limited AFFF sample collection, concentrations of PFEtS and PFPrS and their relative contribution to the PFSA class appear to be relatively constant over the period of 12 years. PFEtS concentrations were the lowest compared to those of the C_3, C_4, C_6, and C_8 PFSAs across the period of 12 years. On the contrary, PFPrS concentrations were similar to that of PFBS in all five AFFFs, and PFPrS was tied with PFBS as the third most abundant PFSA in 3M AFFFs over a manufacturing period of 12 years.

The identification of PFEtS and PFPrS in 3M AFFF formulations is consistent with available information about the production of sulfonic acids and salts by ECF. The ECF process produces PFSAs with 1–18 perfluorinated carbon atoms depending on the hydrocarbon starting material used.[25] The 3M Company acknowledges in their AFFF patent that the C_4–C_{10} PFSAs are present in their AFFF formulations.[26] However, PFEtS and PFPrS may be part of the "residual organic fluorochemicals" listed on materials safety data sheets for 3M AFFF formulations.[27] The presence of PFEtS and PFPrS may also result from the cleavage of carbon–carbon bonds during the ECF process, which generates PFSAs with chain lengths that are shorter than the starting material.[25] Whether PFEtS and PFPrS were present in 3M AFFFs before 1989 is unknown because no 3M AFFFs manufactured before 1989 were available at the time of the study.[1] Given the presence of PFEtS and PFPrS in 3M AFFFs, the next phase of the study was to quantify PFEtS and PFPrS in groundwater.

Groundwater Concentrations of PFEtS and PFPrS. PFEtS was quantified in 8 of the 11 groundwater samples (Figure 3 and Table S1 of the Supporting Information) at

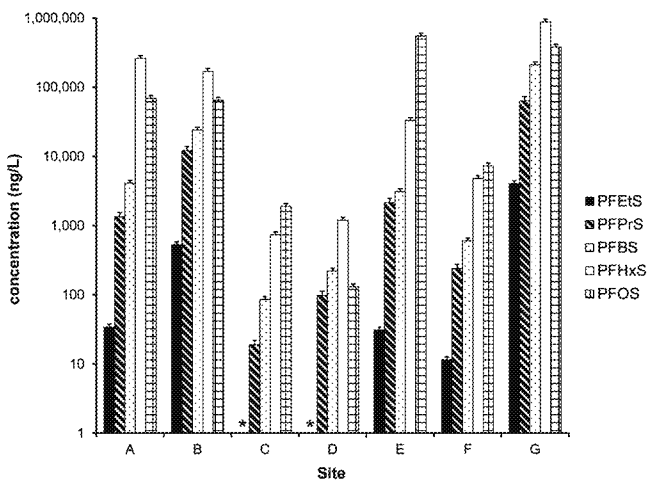

Figure 3. Concentrations of PFEtS and PFPrS relative to PFBS, PFHxS, and PFOS for a representative seven-site subset of the 11 groundwater samples. Error bars represent the relative standard deviation determined from $n = 3$ replicates of the groundwater sample from site A. The asterisk indicates PFEtS fell below the method limit of detection (0.80 ng/L).

concentrations of 11–7500 ng/L. PFPrS was quantified in all 11 groundwater samples (Figure 3 and Table S1 of the Supporting Information) with concentrations of 19–63000 ng/L. As expected, the presence of PFEtS and PFPrS at these 11 sites, some of which have been closed since 1990, clearly indicates that ultrashort PFSAs are as persistent as their long-chain homologues (e.g., PFOS).

The relative ratios of PFEtS and PFPrS to PFBS, PFHxS, and PFOS in groundwater vary among the seven sites (data for the four other sites were similar but are not shown). The variability in PFEtS, PFPrS, and PFBS ratios may be due to several factors, including site hydrogeology, sampling location relative to the points of AFFF discharge, variations in AFFF composition and use over time, the transport characteristics of each chemical, and the time between the last AFFF application and sampling.

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In addition, the composition of 3M AFFF formulations prior to 1989 may differ significantly from the composition of those examined for this study. Furthermore, PFEtS and PFPrS may result from the biodegradation of perfluoroalkyl sulfonamide-based precursors in a manner analogous to that of PFOS.[28,29] However, only one report identifies three C_3 analogues of known precursors [perfluoropropyl sulfonamido amine, perfluoropropyl sulfonamide amino carboxylate, and unnamed class (class U in ref 2)] in commercial 3M AFFFs, while no C_2-based precursors were identified.[2]

To the best of our knowledge, no health-based risk values exist for PFEtS and PFPrS. However, some health-based risk values exist for the closest related homologue in the PFSA series, PFBS. The Minnesota Department of Health (MDH) established a subchronic and chronic non-cancer health risk limit (HRL) of 7000 ng/L for PFBS,[30] and Germany set a provisional health-related indication value (HRIV) for PFBS at 3000 ng/L.[31] The concentration of PFEtS in groundwater at site K and the concentration of PFPrS at sites B, G, H, and K are above the HRL and HRIV for PFBS. Given the presence of PFEtS and PFPrS in groundwater at U.S. military bases, these ultrashort PFSAs may be present in other drinking water sources.

To the best of our knowledge, no toxicological information or occurrence data for biota are available for PFEtS and PFPrS. Only a limited number of studies have examined the toxicity[31−33] of PFBS, the closest PFSA homologue, in animals. In addition, only two reports indicate shorter serum elimination half-lives in rats, monkeys, cows, and humans compared to those of longer-chain PFSAs, primarily because of the elimination of PFBS through urine.[34,35] Despite lower serum elimination half-lives, PFBS was found in human serum and tissues.[31,36,37] By analogy, PFEtS and PFPrS may also be found in human serum and other tissues, despite their high water solubility.

Implications. The discovery of the two ultra-short-chain PFSAs in AFFFs and at a high detection frequency in groundwater from 11 military sites indicates that PFEtS and PFPrS are present and have gone unmonitored at sites where AFFFs either are currently or were historically used for firefighting and training purposes. High-mass accuracy mass spectrometry led to this discovery more than 15 years after the first early reports of PFOS and other PFASs in AFFF-contaminated groundwater.[7,22,38−40] After the 2002 phase-out of C_8-based chemistries, 3M shifted its ECF-based synthesis to C_4-based chemistries.[35,36] Given the continuation of ECF-based syntheses in the United States and abroad,[41] PFEtS and PFPrS production and use may actually increase and result in continuing human and environmental exposure. Because of their persistence, high solubility, mobility, and the potential for increasing prevalence in the marketplace, we recommend that PFEtS and PFPrS be included among the PFASs monitored in groundwater potentially impacted by AFFFs and other PFASs sources. Given their high mobility in the subsurface, PFEtS and PFPrS are most likely to be at the leading edge of PFAS-contaminated plumes. Removal of these water-soluble forms will be challenging using ex situ remedial approaches based on adsorption, such as granulated activated carbon, because an early breakthrough of perfluorobutanoic acid and PFBS relative to PFOS has already been documented.[42,43]

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, Tables S1 and S2, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) 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.

(2) 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.

(3) 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.

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

(5) 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.

(6) Wagner, A.; Raue, B.; Brauch, H. J.; Worch, E.; Lange, F. T. Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. *J. Chromatogr. A* **2013**, *1295*, 82−89.

(7) 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 ^{19}F NMR. *Anal. Chem.* **2001**, 73 (10), 2200−2206.

(8) Moody, C. A.; Field, J. A. Perfluorinated Surfactants and the Environmental Implications of Their Use in Fire-Fighting Foams. *Environ. Sci. Technol.* **2000**, *34* (18), 3864−3870.

(9) 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.

(10) Rotander, A.; Kärrman, A.; Toms, L.; Kay, M.; Mueller, J. F.; Gómez Ramos, M. J. Novel fluorinated surfactants tentatively identified in firefighters using LC-QTOF-MS/MS and a case-control approach. *Environ. Sci. Technol.* **2015**, *49* (4), 2434−2442.

DOI: 10.1021/acs.estlett.5b00049
Environ. Sci. Technol. Lett. XXXX, XXX, XXX−XXX

ED_002330_00159546-00004

(11) Harding, K. C.; Houtz, E. F.; Yi, S.; Sedlak, D. L.; Alvarez-Cohen, L. Aerobic Biotransformation of Fluorotelomer Thioamidosulfonate (Lodyne) in AFFF. Presented at Groundwater Resources Association of California Emerging Contaminants Symposium, Concord, CA, February 4−5, 2014; Poster.

(12) Yi, S.; Houtz, E. F.; Harding, K. C.; Field, J. A.; Sedlak, D. L.; Alvarez-Cohen, L. Anaerobic Biotransformation of 6:2 Fluorotelomer Thioamidosulfonate in Aqueous Film-Forming Foams. Presented at Groundwater Resources Association of California Emerging Contaminants Symposium, Concord, CA, February 4−5, 2014; Poster.

(13) Kwok, K. Y.; Yamazaki, E.; Yamashita, N.; Taniyasu, S.; Murphy, M. B.; Horii, Y.; Petrick, G.; Kallerborn, R.; Kannan, K.; Murano, K.; Lam, P. K. S. Transport of perfluoroalkyl substances (PFAS) from an arctic glacier to downstream locations: Implications for sources. *Sci. Total Environ.* **2013**, *447*, 46−55.

(14) Lu, G. H.; Yang, Y. L.; Yeung, L. W. Y.; Taniyasu, S.; Pan, J.; Lam, P. K. S.; Wang, J.; Li, X.; Yamashita, N. Level and distribution of perfluorinated compounds in river water from Shengyang, China. *Organohalogen Compd.* **2010**, *72*, 451−454.

(15) Lu, G.-h.; Shen, Y.-t.; He, J.; Yuan, F.; Yang, Y.-l.; Rao, Z. Preliminary study on perfluorinated compounds in waters from the Yellow River Estuary Area by utilizing liquid chromatography-mass spectrometry/mass spectrometry. *Yankuang Ceshi* **2012**, *31* (1), 147−153.

(16) Jeong, Y.; Yamazaki, E.; Taniyasu, S.; Yamashita, N.; Lee, S.; Moon, H. B.; Di, R.; Shi, Q.; Kannan, K. Perfluoroalkyl compounds (PFCs) in marine environment of Korea: Comparison with Tokyo Bay, Japan. *Organohalogen Compd.* **2012**, *74*, 231−234.

(17) Mak, Y. L.; Taniyasu, S.; Yeung, L. W. Y.; Lu, G. H.; Jin, L.; Yang, Y. L.; Lam, P. K. S.; Kannan, K.; Yamashita, N. Perfluorinated Compounds in Tap Water from China and Several Other Countries. *Environ. Sci. Technol.* **2009**, *43* (13), 4824−4829.

(18) Zhang, W.; Zhang, Y.; Taniyasu, S.; Yeung, L. W. Y.; Lam, P. K. S.; Wang, J.; Li, X.; Yamashita, N.; Dai, J. Distribution and fate of perfluoroalkyl substances in municipal wastewater treatment plants in economically developed areas of China. *Environ. Pollut.* **2013**, *176*, 10−17.

(19) *Third Unregulated Contaminant Monitoring Rule Data Summary*; EPA 815-S-14-004; U.S. Environmental Protection Agency: Washington, DC, 2014.

(20) Craig, E. A.; Zhao, Q. J. *Provisional Peer-Reviewed Toxicity Values for Perfluorobutane Sulfonate and Related Compound Potassium Perfluorobutane Sulfonate*; National Center for Environmental Assessment, Superfund Health Risk Technical Support Center, U.S. Environmental Protection Agency: Cincinnati, OH, 2014.

(21) 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.

(22) Moody, C. A.; Field, J. A. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.* **1999**, *33* (16), 2800−2806.

(23) Myers, A. L.; Jobst, K. J.; Mabury, S. A.; Reiner, E. J. Using mass defect plots as a discovery tool to identify novel fluoropolymer thermal decomposition products. *J. Mass Spectrom.* **2014**, *49* (4), 291−296.

(24) Roach, P. J.; Laskin, J.; Laskin, A. Higher-Order Mass Defect Analysis for Mass Spectra of Complex Organic Mixtures. *Anal. Chem.* **2011**, *83* (12), 4924−4929.

(25) Brice, T. J.; Trott, P. W. Fluorocarbon Sulfonic Acids and Derivatives. U.S. Patent 2,732,298, 1956.

(26) Alm, R. R.; Stern, R. M. Aqueous film-forming foamable solution useful as fire extinguishing concentrate. U.S. Patent 5,085,786, 1992.

(27) *FC-203CF Lightwater (TM) AFFF 3%*; MSDS No. CKQCB; 3M Company: St. Paul, MN, 1999.

(28) Ullah, S.; Huber, S.; Bignert, A.; Berger, U. Temporal trends of perfluoroalkane sulfonic acids and their sulfonamide-based precursors in herring from the Swedish west coast 1991−2011 including isomer-specific considerations. *Environ. Int.* **2014**, *65*, 63−72.

(29) 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.

(30) *2011 Health Risk Limits for Groundwater: Perfluorobutane sulfonate*; Health Risk Assessment Unit, Environmental Health Division, Minnesota Department of Health: St. Paul, MN, 2011.

(31) Wang, P.; Lu, Y.; Wang, T.; Zhu, Z.; Li, Q.; Zhang, Y.; Fu, Y.; Xiao, Y.; Giesy, J. Transport of short-chain perfluoroalkyl acids from concentrated fluoropolymer facilities to the Daling River estuary, China. *Environ. Sci. Pollut. Res.* **2015**, 1−11.

(32) Lieder, P. H.; York, R. G.; Hakes, D. C.; Chang, S.-C.; Butenhoff, J. L. A two-generation oral gavage reproduction study with potassium perfluorobutanesulfonate (K+PFBS) in Sprague Dawley rats. *Toxicology* **2009**, *259* (1−2), 33−45.

(33) Stefani, F.; Rusconi, M.; Valsecchi, S.; Marziali, L. Evolutionary ecotoxicology of perfluoralkyl substances (PFASs) inferred from multigenerational exposure: A case study with *Chironomus riparius* (Diptera, Chironomidae). *Aquat. Toxicol.* **2014**, *156*, 41−51.

(34) Kowalczyk, J.; Ehlers, S.; Oberhausen, A.; Tischer, M.; Farst, P.; Schafft, H.; Lahrssen-Wiederholt, M. Absorption, Distribution, and Milk Secretion of the Perfluoroalkyl Acids PFBS, PFHxS, PFOS, and PFOA by Dairy Cows Fed Naturally Contaminated Feed. *J. Agric. Food Chem.* **2013**, *61* (12), 2903−2912.

(35) Olsen, G. W.; Chang, S.-C.; Noker, P. E.; Gorman, G. S.; Ehresman, D. J.; Lieder, P. H.; Butenhoff, J. L. A comparison of the pharmacokinetics of perfluorobutanesulfonate (PFBS) in rats, monkeys, and humans. *Toxicology* **2009**, *256* (1−2), 65−74.

(36) Fromme, H.; Mosch, C.; Morovitz, M.; Alba-Alejandre, I.; Boehmer, S.; Kiranoglu, M.; Faber, F.; Hannibal, I.; Genzel-Boroviczény, O.; Koletzko, B.; Völkel, W. Pre- and Postnatal Exposure to Perfluorinated Compounds (PFCs). *Environ. Sci. Technol.* **2010**, *44* (18), 7123−7129.

(37) Perez, F.; Nadal, M.; Navarro-Ortega, A.; Fabrega, F.; Domingo, J. L.; Barcelo, D.; Farre, M. Accumulation of perfluoroalkyl substances in human tissues. *Environ. Int.* **2013**, *59*, 354−362.

(38) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. 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.

(39) 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.

(40) Hebert, G. N.; Odom, M. A.; Craig, P. S.; Dick, D. L.; Strauss, S. H. Method for the determination of sub-ppm concentrations of perfluoroalkylsulfonate anions in water. *J. Environ. Monit.* **2002**, *4* (1), 90−95.

(41) Xie, S.; Wang, T.; Liu, S.; Jones, K. C.; Sweetman, A. J.; Lu, Y. Industrial source identification and emission estimation of perfluorooctane sulfonate in China. *Environ. Int.* **2013**, *52*, 1−8.

(42) Appleman, T. D.; Higgins, C. P.; Quinones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C.; Dickenson, E. R. V. Treatment of poly- and perfluoroalkyl substances in US full-scale water treatment systems. *Water Res.* **2014**, *51*, 246−255.

(43) Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P. Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain. *Environ. Sci. Technol.* **2012**, *46* (3), 1708−1715.

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Environ. Sci. Technol. Lett. XXXX, XXX, XXX−XXX

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