AN ABSTRACT OF THE DISSERTATION OF

Alix E. Robel for the degree of Doctor of Philosophy in Toxicology presented on October 3, 2019.

Title: Per- and Polyfluoroalkyl Substances: From Disposition on Consumer Products and Field Materials to Treatment of Contaminated Groundwater

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Jennifer A. Field

Per- and polyfluoroalkyl substances (PFAS) are an emerging chemical class of concern. Recently in the United States, Health Advisory Limits for two PFAS in drinking water were established for perfluorooctane sulfonate and perfluorooctanoate in drinking water (set to 70 ng/L combine concentration) by the EPA. Because of PFAS mobility, persistence, and occurrence in drinking water throughout the country, it is import to understand potential sources of PFAS. In the first study, PFAS sample collection and storage and materials used in the field were examined. Sampling parameters including sampling materials, sample collection, and sample storage for the analytes represented by the new analytical method were examined. The optimal sample storage and analysis conditions were determined. Additionally, a characterization of 66 sampling materials was performed and a list of PFAS containing materials was compiled, as well as a list of materials that contain no PFAS. This study represents a comprehensive approach to over 35 PFAS actually present at an environmentally relevant site, sampling and storage, and materials that may impact analysis and cause false positives. In the second study, a subset of seventeen papers and textiles were analyzed using four techniques: liquid chromatography tandem mass spectrometry (LC-MS/MS) for 73 individual PFAS, gas chromatography mass spectrometry (GC-MS) for 7 individual PFAS, total oxidizable precursor (TOP) assay, and total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy. Total PFAS measured by LC-MS/MS, GC-MS, which represent monomeric PFAS with the potential for human exposure, only represent <2.6% of the total polymeric PFAS material bound to the surface of papers and textiles.

Environmental PFAS contaminations is leading to a direct need for remediation. In the third study, PFAS breakthrough curves resulting from a pilot-scale granular activated carbon (GAC) system were modeled to determine the efficacy for removal of individual PFAS present at a military site over 11 months. The relationship between the order of individual PFAS elution by analytical analysis by LC-MS/MS or LC-QTOF was determined to be the same as the order of breakthrough from GAC. Understanding of PFAS mass balance leads to more effective remediation with an understanding of PFAS effluent breakthrough.

Per- and Polyfluoroalkyl Substances: From Disposition on Consumer Products and Field Materials to Treatment of Contaminated Groundwater

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Alix E. Robel, Author

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Chapter 1: Introduction

Per- and polyfluoroalkyl substances (PFASs) are classified as emerging contaminants of concern, and are abundant in the environment. PFASs are anthropogenic in origin, and therefore when PFASs are observed in the environment it is a direct result of use by humans.

Characteristics & Manufacturing

PFASs are unique but share the commonality of having one or more carbons where the hydrogens are replaced with fluorine (C_nF_{2n+1}-), and are attached to a polar head group.[1] Perfluorinated substances are characterized by carbon chains in which all the original hydrogens are replaced with fluorine (e.g., $C_4F_9SO_3^-$).[1] Perfluorinated perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs) have no known biodegradation pathway such that they are persistent in the environment.[2] In contrast, polyfluorinated substances are characterized by a fluorinated carbon chain in which some of the carbons have at least one hydrogen (e.g., $C_4F_9CH_2CH_2SO_3^-$).[1] Some PFASs are considered 'precursors' because they biotransform to persistent PFCAs and PFSAs under aerobic conditions.[3-9]

PFAS manufacturing, which began in the 1940s, produces a range of C_nF_{n+1} chain lengths with varying polar head groups.[10] PFAS production is proprietary and has produced potentially 1000's of unique PFASs.[11] PFASs are manufactured by either electrochemical fluorination (ECF) or fluorotelomer (FT)-based syntheses. Manufacturing by ECF is attributed to one US manufacturer, 3M, and the process produces both odd and even chain lengths and 25% branched and 75% linear isomers.[12-14]. FT-based manufacturing is utilized by all other manufacturers and produces primarily even numbers of fluorinated carbons and only linear isomers.[15]

Regulation in the United States & Toxicology

In May of 2000, the U.S. EPA and 3M released a statement indicating that a voluntary phase out of C8-based PFAS made by ECF, which includes perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), citing a “strong tendency to accumulate in human and animal tissues, [with a potential to] pose a risk to human health and the environment over the long term.”[16] Then in 2006, a voluntary stewardship program was announced for the eight major manufacturing companies (Arkema, Asahi, Ciba, Clariant, Daikin, DuPont, 3M/Dyneon, and Solvay Solexis), which required 1] 95% reduction by 2010, and 2] a complete phase out of C8 and greater PFAS by 2015.[17] In 2009, the U.S. EPA issued a provisional health advisory for PFOA at 400 ng/L and for PFOS at 200 ng/L in drinking water.[18] However, the provisional health advisory was re-evaluated in 2016 and changed to a lifetime health advisory limit (HAL) of 70 ng/L for drinking water for both PFOA and PFOS, as individuals or when combined.[19] The HAL was established based on adverse health effects in mice and humans, including “developmental effects to fetuses during pregnancy or to breastfed infants (e.g., low birth weight, accelerated puberty, skeletal variations), cancer (e.g., testicular, kidney), liver effects (e.g., tissue damage), immune effects (e.g., antibody production and immunity), thyroid effects and other effects (e.g., cholesterol changes).”[19] The most recent development for PFASs includes a comprehensive nationwide PFASs action plan, which would include a regulatory maximum contaminant level for PFASs in drinking water.[20]

The toxicology of PFASs, like regulation, is continuing to evolve. Toxicology of PFASs is focused predominantly on PFOS and PFOA, although PFAS persistence and PFASs present in the environment are of increasing concern.[11, 21] A recent development in toxicology includes the C8 Science Panel which was an epidemiological study tracking individuals in the Mid-Ohio valley between 2005-2013 who were exposed to PFAS releases from local manufacturing.[22] The C8 study, which focused primarily on C8 PFASs, found a probable link to "diagnosed high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension.[22]" In a study by Nilsson et al., volatile PFAS were found to biotransform into PFCAs in the human body, indicating that other PFASs have the potential to impact humans.[23] Further, Perez et al. found that PFASs distribute into various tissues in the human body, but accumulate in protein rich tissues.[24] Interestingly, less is reported on shorter-chain PFASs (e.g. <C6) although shorter-chain PFASs are known to be emitted and available for exposure to both humans and other species.[25]

Other toxicological studies, which include other select PFASs (e.g. PFCAs and PFSAs), focus on species other than humans and include: fat head minnows, water-algae-zebra mussel, round goby-smallmouth bass, chinook salmon, lake whitefish, mink, bald eagles, and rats.[26-30] Lanza et al. indicates bioaccumulation in individual trophic levels, and biomagnification between trophic levels for PFOS.[29] Although this study was performed only for PFOS, the relationship is likely true for other PFASs. Phillips et al. performed an exposure study on daphnia magna, chironomus tentans, and Lemna gibba using fluorotelomer acids (FTCAs), and found FTCAs to be more toxic than PFCAs.[31] Toxicological studies such as Phillips et al.[32] indicate that inclusion of a greater range of environmentally relevant PFASs are critical for the identification of protective regulatory limits for humans and other species.

PFAS in Commerce

PFASs are used in consumer products including polymers (e.g. PTFE), additives (e.g. paper production), inks, varnishes, waxes, metal plating and cleaning, and as repellents for leather, paper and textiles.[10, 16, 33] PFASs are uniquely suited to consumer product applications because they are very effective oil repellants, as compared to silicone or hydrocarbon-based surfactants, which are only effective as water repellants.[10] PFASs are observed in many consumer products in the U.S. and around the world, but many studies only focus on a limited number of PFASs especially PFOS and PFOA.[34-38] Another type of technique, one that measures for total fluorine rather than individual PFASs has been applied.[39, 40] Fewer studies examine a larger range of PFAS or put measured PFAS into the context of total fluorine on consumer products.[39, 41, 42]

In the 1950's, PFAS production for use in aqueous film forming foams (AFFFs) began as a collaboration between the U.S. Military and manufacturers including 3M.[43] AFFFs were generated for use in extinguishing hydrocarbon-based fuel fires and polar-solvent fires.[15] AFFFs are used specifically for crash and spill events as well as for fire-fighter training purposes. Once produced, manufacturers of AFFF must have their proprietary AFFF mixtures tested in order to determine if they meet the military specification for placement on the qualified products list.[44, 45]

Typically, spill or crash events result in the use of AFFF in uncontained settings, which resulted in groundwater, soil, and sediment contamination of surrounding areas (e.g. the Lac-Mégantic train crash).[46] Fire-fighter training on military bases was conducted at a limited number of location on military bases over decades with a frequency that ranged from bi-weekly to monthly.[47] Unlike crash or spill events, for which a limited number of AFFFs were used to extinguish the fire,[46] many AFFFs were used over decades at fire-fighter training sites since the type of AFFFs available for military used changed over time.[44, 45] In order to evaluate PFAS contamination, sample collection and analysis for PFAS are necessary. It is therefore important to quantify PFASs in field sampling materials which have the potential to give a false positive. Once PFAS contamination is identified as a risk to human health (e.g.has the potential to impact a drinking water source), technologies used for remediation (e.g. granulated activated carbon) must be evaluated and implemented for PFAS removal.

In Chapter 2, the disposition of fluorine on papers and textiles was examined. Since ingestion is known as a major route of exposure, when individuals are not near a source PFAS (e.g. manufacturing),[48] papers and textiles may contribute to PFAS exposure. Previous studies examined papers and textiles for individual PFAS content by liquid chromatography-mass spectrometry or by total fluorine techniques such as particle-induced gamma ray emission spectroscopy.[36, 39, 40] However, no studies had yet examined the overall disposition of individual PFASs relative to the total fluorine on surfaces. The relationship between individual PFASs and total fluorine is of interest since not all fluorine may be available to transfer into or on other materials (e.g. food). This chapter focuses on the disposition of PFASs in 17 new and used papers and textiles by quantifying 73 non-volatile PFAS by liquid chromatography tandem mass spectrometry and an additional six volatile PFASs by gas chromatography mass spectrometry. The individual PFAS concentrations were then compared to the concentration of total fluorine by 1] the total oxidizable precursor assay which oxidizes unknown precursor PFASs into PFCAs and PFSAs and 2]particle-induced gamma ray emission spectroscopy. The resulting manuscript was publishing in *Environmental Science & Technology* in 2017.

In Chapter 3, materials used in field sampling were extracted and analyzed for 52 PFAS by LC-MS/MS. In order to inform field sampling guidance documents, PFAS concentrations on field sampling materials were used to evaluate the potential for cross-contamination between field sampling materials and samples collected in the field. Field sampling guidance documents currently list prohibited items (e.g. blue ice, permanent markers, bound notebooks, etc).[49, 50] However, many of the prohibited items have the potential to increase sampling convenience and the comfort of individuals collecting samples, and to reduce costs associated with sampling and shipping. Materials used field sampling events were assigned to categories including pre-staging, staging, sampling, and shipping. Each category was then evaluated based on the potential for the materials to come in direct contact with field samples (e.g. nitrile gloves directly touching samples). Only during sampling do materials have the potential to come into direct contact with field materials, but many materials prohibited by the guidance documents (e.g. cold packs) have no direct contact with samples (e.g. during pre-staging, staging, and shipping). Based on the PFAS concentrations in materials extracted in methanol, it is unlikely that materials could contribute to false positives in the field.

In Chapter 4, granulated activated carbon (GAC), a commonly used remediation technology, was implemented at the pilot-scale at a military base to examine PFAS breakthrough. Typically, studies which evaluate remediation technologies for PFAS removal are performed at the batch or bench scale.[51-61] Chapter 4 examines the breakthrough of PFASs from AFFF-impacted groundwater at the pilot-scale at an AFFF-contaminated site. A total of seventeen PFASs, and their branched and linear isomers, were quantified in the influent, lead vessel effluent, and lag vessel effluent; breakthrough of 13 PFASs were modeled for breakthrough in the lead and lag vessels. Chromatographic retention time for the 17 PFASs were compared to the breakthrough bed volumes when effluent concentrations reached 20% of the influent concentration; the correlation gave an R^2-value of 0.61. Chromatographic retention time is a characteristic parameter that is obtained during LC-MS/MS or high resolution mass spectrometry analysis. Once an influent of a GAC system is characterized and chromatographic retention times are known, their relative breakthrough order are also known and can be used to inform site remediation efforts.

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Chapter 2: Closing the Mass Balance of Fluorine for Papers and Textiles

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Abstract

A potential route of human exposure to per- and polyfluoroalkyl substances (PFASs) is contact with treated papers and textiles. Typically few PFASs, such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), are measured on textiles and papers. To date, none of the measurements are placed into the context of total fluorine, in part, due to a lack of methods for total fluorine. The objectives of this study were to apply gas chromatography and liquid chromatography-tandem mass spectrometry) for the quantification of volatile and ionic PFASs, respectively, as well as the total oxidizable precursor (TOP) assay for the quantification of precursors and to place the data into the context of total fluorine as determined by particle-induced gamma ray emission (PIGE) spectroscopy. Eight papers and nine textiles were extracted with solvent (methanol or ethyl acetate) and analyzed by the four different analytical techniques. The molar sum of the PFASs obtained by GC-MS, LC-MS/MS and the TOP assay was compared to total fluorine (nmol F/cm^2) by PIGE measured on the papers and textiles before and after extraction. Volatile and ionic PFASs accounted for 0-2.2% and 0-0.41%, respectively, of the total nmol F/cm^2 determined by PIGE. Unidentified precursors comprised 0.021-14% of the total nmol F/cm^2. The individual volatile, ionic PFASs, and precursors identified by TOP assay accounted for only a fraction (± 16%) of the total fluorine on papers and textiles. After extraction papers and textiles retained 64 ± 28 to 110 ± 30% of the original nmol F/cm^2 as determined by PIGE analysis, indicating that the majority of fluorine remains associated with the papers and textiles even after solvent extraction.

Introduction

Due to their unique chemical properties, per- and polyfluoroalkyl substances (PFASs) are used in fire-fighting foams, manufacturing, coatings, and in consumer products.[1, 2] PFASs are rapidly gaining attention in scientific literature due to the detection of select PFASs in humans[3-5] environmental media,[6-12] and in remote locations.[13-15] Until recently, the primary focus in the literature was on perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), the only two forms that have US EPA health advisory values.[16] However, attention is currently focused on identifying new PFASs in commerce[17, 18] that may degrade to persistent perfluoroalkyl carboxylates (PFCAs) and other forms.[17, 19] Recent reports indicate novel PFASs including ether sulfonates in municipal sludge,[20] short-chain perfluoroalkyl sulfonamides in fish,[21] and cyclic sulfonates are in the Great Lakes.[22]

There is growing evidence of a larger number of PFASs in human blood.[4, 23, 24] Given their recent discovery, few of the newly-identified PFAS forms have any toxicological data. Human exposure to PFASs include inhalation of volatiles[25-27] and ingestion of ionic PFASs[26, 27] in homes, workplaces, and automobiles.[27, 28] Consumer products such as carpets, papers, textiles, and plastics contain PFASs, but individual studies typically focus either on the volatile fluorotelomer alcohols (FTOHs) or on ionic PFASs including the C4-C14 PFCAs and only the even carbon-numbered perfluoroalkylsulfonates (C4, C6, and C8 PFSAs).[29-43] Relatively fewer studies analyze both volatile and ionic PFAS[12, 44-48] and some capture a larger array of individual PFASs including perfluoroalkyl sulfonamides and perfluoroalkyl sulfonamidoethanols, phosphorus-containing PFASs, and fluorotelomer carboxylates.[42, 49]

At present, it is difficult to determine if the individual measureable PFASs associated with consumer products have been identified or what fraction of total fluorine they comprise. Combustion ion chromatography is used to measure total fluorine in human blood,[4, 23, 24, 50] and a total adsorbable fluorine assay has been applied to water.[51, 52] Alternatively, the total oxidizable precursor (TOP) assay was developed to quantify precursors that have the potential to degrade to PFCAs or PFSAs, in urban runoff[53], groundwater and soil[54], and wastewater[11]. Gruber et al. [55] applied the TOP assay to geotextiles that are used on roofs and to create landscape barriers. However, to date, the mass of precursors determined by the TOP assay has not been compared to an independent measure of total fluorine.

A new technique, particle-induced gamma ray emission (PIGE) spectroscopy was recently described for the quantification of total fluorine on papers and textiles.[56] PIGE is a direct surface analysis technique that quantifies elemental fluorine on solids including materials[57] and more recently on papers and textiles.[56] Total fluorine determinations by PIGE do not require extraction, thus eliminating potential bias due to extraction and sample processing. The nmol F/cm^2 determined by PIGE likely represents a true measure of total fluorine on papers and textiles. To the best of our knowledge, there is a single study that compares total fluorine on food-contact papers and offers only limited data on only ionic PFASs but not on volatile PFASs or unknown precursors.[58] However, in order to close the mass balance on total fluorine on consumer products, data are needed not only on ionic PFASs but also on volatile PFASs and precursors determined by the TOP assay.

The objective of this study was to characterize the individual volatile and ionic PFASs as well as precursors that contribute to the total fluorine in papers and textiles. PIGE was applied to eight papers and nine textiles before and after solvent extraction. The papers and textiles were extracted by ethyl acetate for three volatile FTOHs and N-ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE) for analysis by gas-chromatography-mass spectrometry (GC-MS). Although none of the volatile species are actually *per*fluorinated, for brevity, volatile analytes will hereafter be referred to as volatiles PFASs. The papers and textiles were also extracted by methanol for the ionic PFASs by liquid-chromatography-mass spectrometry (LC-MS/MS). Eleven classes, totaling 73 individual ionic PFASs included the following: perfluoroalkyl carboxylates (C3-C17 PFCAs), saturated and unsaturated fluorotelomer carboxylates (n:2 FTCA C4, C6,C8, C10, n:2 FTUCAs C4, C6, C8, C10, n:3 FTCA C3,C5,C7,C9), perfluoroalkyl sulfonates (C2-C10 PFSAs), fluorotelomer sulfonates (C4,6,8,10 FtS), fluoroalkyl sulfonamido acetic acids (C4-C8 FASAA), N-methyl fluoroalkyl sulfonamide acetic acids (C4-C8 N-Me FASAA), N-ethyl fluoroalkyl sulfonamido acetic acids (C4-C8 N-EtFASAA), di-substituted perfluoroalkyl phosphinic acids (C4/C4 - C8/C8 PFPIA), di-substituted polyfluorinated phosphate esters (C4/C4-C10/C10 diPAP), fluorotelomer mercaptoalkyl phosphate esters (C6/C6-C10/C10 FTMAP), and N-ethyl perfluorooctanesulfonamido ethanol-based polyfluoroalkyl phosphate diester (C8/C8 SAmPAP). In addition, the TOP assay was used to quantify precursors on papers and textiles.[54] PIGE was applied to the papers and textiles before and after methanol extraction. Mass balance for papers and textiles was determined by comparing the sum of individual PFASs by GC-MS and LC-MS/MS and precursors by the TOP assay to total fluorine as measured by PIGE before and after solvent extraction.

Experimental Section

Standards and reagents

All reagents used for GC-MS and LC-MS/MS analysis are described in the Supporting Information (SI). For GC-MS, all native and mass-labeled standards were purchased from Wellington Laboratories (Guelph, ON, Canada). For LC-MS/MS, the native and mass-labelled standards information was the same as those used in Allred et al. with the following exceptions: 4:2, 6:2, and 8:2 FtS, EtFOSAA, MeFOSAA, 6:2 & 8:2 diPAP and mass labeled 6:2 FtS, d3-MeFOSAA, and d5-EtFOSAA, which were donated by Dr. Christopher Higgins at Colorado School of Mines.[59] For the full list of GC-MS and LC-MS/MS analytes and acronyms, see Table 2.3 and 2.4, respectively, in the SI.

Sample Collection and Storage

The papers and textiles selected for this study were samples of convenience that came from a large set of samples collected by the Washington Department of Ecology in 2015. Trip blanks consisted of copy paper placed in a quart-sized plastic bag and transported along with samples during each of the six sampling events. Trip blanks have

< LOD for volatile analytes, precursors by the TOP assay, and by PIGE. All six trip blanks contained > LOQ levels of SAMPAP but all other ionic PFASs were < LOD.

Of the eight papers selected for this study, two were new, non-food related paper products, and the remaining six were new, unused food-contact materials (Table 2.1). Paper 8 was a popcorn bag, and the remaining food contact papers were either food wrappers from fast-food establishments, or from a café. Of the nine textiles, five were from outwear (e.g. jackets, hats), two were from children's clothing, one was from a pillowcase, and one was from a used office chair (Table 2.1).

All samples were cut from the original material using methanol-rinsed scissors and distributed into two different re-sealable plastic bags. All samples, except Textile 9, were shipped to Oregon State University (OSU) or Hope College (Holland, MI). A subset of all samples received by OSU were shipped to Duke University (Durham, NC) for GC-MS analysis. All samples, at all three locations, were stored at room temperature until analysis.

Volatile Extraction and Analysis by GC-MS

At Duke University, 2 x 2 cm squares of material were cut into nine smaller pieces using acetone-rinsed scissors. All pieces were placed into a glass test tube (VWR, Radnor, PA) together with 25 ng of each M-6:2, 8:2, 10:2 FTOH and N-EtFOSE (Table 2.3). Five mL of ethyl acetate were added, vortexed briefly, and then sonicated for 15 min. The vial was then centrifuged for five min at 4000 g and the supernatant was transferred to a clean glass test tube, and the process was repeated one additional time. The combined extracts were blown down under N_2 gas in a 30 °C water bath to 1 mL.

The extract was then transferred to a 2 mL autosampler vial for analysis. All extracts were analyzed for three FTOHS and N-EtFOSE using GC-MS as described by Butt et al., 2010.[60] The experiments conducted to determine the performance of this method for the present study are described in the SI.

Extraction for Individual Ionic PFASs

Once received at OSU, **e**ach material sample was cut using methanol-rinsed scissors into pieces smaller than 2 x 2 cm^2 and that weighed 0.3 ± 0.01 g. It was necessary to measure the area and to weigh the papers and textiles due to differences in density. This information was then used to convert units of concentration (ng/g) to ug/m^2.

Sample pieces were then placed into a 15 mL HDPE centrifuge tube (VWR, Radnor, PA). Papers and textiles were extracted by adding 3.3 mL of methanol, heated to 60-65 ^{0}C, shaken on a wrist-action shaker at 10^0 of rotation (Burrell, Model 75, Pittsburg, PA) for 10 min, and centrifuged (Eppendorf, model 5810R, Hauppauge, NY) at 2808 g for 10 min at room temperature. The supernatant was poured into a secondary centrifuge tube, and the process was repeated two additional times. The optimal ratio of solvent volume to mass of paper and textile was selected as that ratio that gave the highest precision across both paper and textiles while minimizing sample size and waste (Table 2.7). Data from preliminary experiments indicated that three rounds of methanol extraction at an optimized ratio of 0.3 g paper or textile to 3.33 mL methanol per round of extraction removed >93% of individual extractable PFASs (Table 2.6). The extracted paper or textile was then frozen, air-dried for one week, and shipped to Hope College for post-extraction PIGE analysis. The extracts were also frozen overnight at -20 ^{0}C prior to analysis to precipitate any remaining particles. Extracts were then centrifuged for an additional 10 min at 2808 g. Supernatant was poured into a 10 mL-volumetric flask and brought to volume with additional methanol to 10 mL. Samples were kept frozen at -20^{0}C until analysis. The day of analysis, aliquots (60 µL) were spiked with 0.72 ng of all mass-labeled internal standards and then diluted to a final volume of 1.2 mL with methanol.

Analysis by LC-MS/MS (Individual PFASs and TOP Assay)

An Agilent 1100 series HPLC was fitted with two zirconium modified diol (Zr-diol) guard columns (Agilent, Santa Clara, CA) and a Zorbax Eclipse Plus C18 (Agilent) that was coupled to a Quattro Premier MS/MS system (Waters Corporation, Milford, MA). Operational parameters for the HPLC and for the mass spectrometer can be found in Allred et al.[59] except that the divert valve on the mass spectrometer changed to divert LC solvents to waste for the first 6 min and after 32 min, and the extractor cone was set at 4V (Table 2.4). Analyte identification and quantification were practiced as described in Allred et al.[59]

Each analytical sequence contained process blanks, which consisted of the extraction described above but with no sample present. All process blanks were spiked with 0.72 ng internal standard before extraction. All process blanks and solvent blanks were expected to fall below the limit of quantification (LOQ). Each analytical sequence contained a 7-point calibration curve (5 ng/L - 10,000 ng/L). If quantification of an analyte fell outside of the calibration curve, the sample was diluted further and reanalyzed. Sequences also contained solvent blanks, which consisted of methanol for LC-MS/MS analysis.

The data quality tiers used in this manuscript are defined in Backe et al.[59] with slight modifications. The first confidence group is quantitative (Qn), which contains analytes for which authentic analytical and internal standards were available. Semi-quantitative (Sq) analytes were those that had reference materials (e.g., donated reference materials) but did not have matched internal standards. The third group was classified as qualitative (Ql), and was assigned to those analytes whose presence were extrapolated from known homologous series or for those analytes for which there are no authentic commercial standards or reference standards (i.e. 6:2-10:2 FTMAP class, 8:2/10:2-10:2 diPAPs).

In order to compute whole method recovery and precision, one paper and one textile, previously determined to have individual PFASs less than the limit of detection (<LOD), were selected. Fourteen individual 0.3 ± 0.01 g portions were cut and placed into separate 15 mL centrifuge vials. The first n=4 replicates were spiked to give an equivalent of 8.3 ng/g of all Qn and Sq analytes (Table 2.4), and used to compute the accuracy (% recovery) and precision (% RSD) of the whole method. The remaining ten replicates were overspiked to give a range of 0.83-17 ng/g for each Qn and Sq standard for the calculation of the whole method LOD and LOQ. All 14 samples were extracted using the methanolic extraction method outlined above. Whole method LODs were calculated using the same methodology as Backe, 2013.[61] Briefly, a 1/X normalized weighted regression was used to calculate the LOD (3.3xresidual standard deviation-y-

intercept/slope).[61, 62] Whole method LOQs were determined to be 3.3x the determined LOD.

TOP Assay

The methanolic extracts generated for individual PFAS analysis by LC-MS/MS were also used for the TOP assay. The TOP assay was performed under the condition of Houtz et al.[54] with several major alterations. An aliquot (60 µL) of the methanolic extract was added to a new 15 mL centrifuge-tube and blown to dryness under nitrogen gas. To the dry vial, 3 mL of reaction solution (60 mM potassium persulfate, 125 mM sodium hydroxide in water)[53] were added and vortexed. The vial was then placed in a water bath heated to 85-90 °C for 6 h. After reaction, the sample was frozen at -20 ^{0}C until analysis. For analysis, hydrochloric acid was added to bring the solution to pH 2 and 0.72 ng of all mass labeled internal standards were added (Table 2.4). Preliminary experiments confirmed there was no difference between freezing the sample at pH 2 and freezing it in basic reaction solution before analysis. Micro liquid-liquid extraction was then carried out under conditions described in Allred, 2014.[59] Briefly, the samples were extracted in triplicate with 10:90 2,2,2-trifluoroethanol in ethyl acetate for a total extract volume of 1 mL, and then 200 µL of methanol was added for a final volume of 1.2 mL. All analytical sequences containing samples for TOP assay included solvent blanks consisting of ethyl acetate/2,2,2-trifluoroethanol/methanol spiked with 0.72 ng of all mass labeled internal standards. All extracts were analyzed by LC-MS/MS as described above.

In order to determine the accuracy of the TOP assay, separate experiments were conducted with individual polyfluorinated precursors, including 6:6PFPi, FOUEA, 8:2

diPAP, FHUEA, 6:2 FtS, 6:2 diPAP, and SAmPaP. The TOP assay, as described above, was conducted on separate vials, each spiked to give 2,000 ng/L in water of each single precursor. In addition, a mixture comprised of all Qn and Ql analytes was spiked onto blank paper (Paper2) and analyzed by the TOP assay. The accuracy of the TOP assay was determined as the percent mass of precursors recovered. To treat the TOP assay data, the nmol F/cm^2 of precursors were calculated by Equation 1. First, the concentrations of individual ionic PFASs measured by LC-MS/MS in extracts before oxidation were converted to nmol F/cm^2 and summed. That value was then subtracted from the total nmol F/cm^2 of PFCAs and PFSAs formed after oxidation (Equation 1).

$$\text{Precursors (nmol F/cm}^2\text{)} = \Sigma(\text{PFCAs} + \text{PFSAs})_{\text{after TOP Assay}} - \Sigma(\text{Individual PFASs})_{\text{before TOP Assay}}$$

Equation 1

The experiments performed to determine the accuracy and precision of the TOP assay for papers and textiles are described in detail in the SI. The LODs and LOQs of PFCAs in TOP assay samples were determined from a set of preliminary experiment (data not shown) and found to be equivalent to those determined for the individual ionic PFCAs and PFSAs on papers and textiles.

Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy

Paper and textile samples were cut, using methanol rinsed scissors, to pieces roughly 2 x 2 cm and mounted using clear adhesive tape to a stainless steel target ladder frame so the 1 x 1 cm hole for the analysis was obstructed only by the sample. In the event of the paper or textile was exposed to solvent, the material was air-dried before being cut and mounted. For thicker samples or dimensionality larger than the penetration depth (0.1mm), two samples were mounted in front and back orientations. The sample side with the higher fluorine signature, if present, was evaluated for quantification. Total fluorine nmol F/cm^{2}was determined from external calibration curves created by coating a paper and a textile in a PFOA stock solution.[56] The precision of PIGE, as indicated by RSD, is ±12% with a LOD of 13 nmol F/cm^2 for papers and 18-45 nmol F/cm^2 for fabrics. The LOQ is 42 nmol F/cm^2 for papers and ranged from 59 - 150 nmol F/cm^2 for fabrics of varying thicknesses.

Results and Discussion

Concentrations for volatile PFAS (Table 2.9) and ionic PFAS (Table 2.10) are reported in units of ug/m^2 in order to facilitate comparison of the data obtained in this study to that of others.[40, 48] To the best of our knowledge, there are no reports of precursors as determined by the TOP assay. Lastly in order to compare the concentrations of individual PFASs and precursors to that determined by PIGE, all units are reported in units of nmol F/cm^2 (Table 2.1).

Volatiles by GC/MS

Papers. Two of the papers (Papers 3 and 8), were found to be <LOQ for the volatile PFASs (Table 2.9). Conversely, six of the eight papers had one or more FTOHs that ranged from 3.0 to 30 ug/m^2, which is consistent with values found by others.[31, 45-48] Overall, 8:2 FTOH was the most frequently detected, as reported by Liu et al.[30] The only other volatile PFAS, N-EtFOSE, was not present above the LOD in any of the papers.

Textiles. Of the nine textiles, all were found to have concentrations >LOQ for one or more of the four volatile PFASs (Table 2.1). The concentrations were significantly higher than those of the papers, and ranged from 2.1 to 14,000 ug/m^2 (Table 2.9). The 8:2 FTOH was the dominant FTOH for Textiles 1-7; however, 6:2 FTOH was the most abundant in Textile 8. Long-chain 8:2 and 10:2 FTOHs are present on six out of eight papers and on all nine textiles purchased in 2015. The EPA's voluntary C8 Stewardship program targeted a 95% reduction in PFOA and PFOA precursors by 2015, but only 8 participating companies signed onto the voluntary agreement.[63] It is difficult to assess compliance with the C8 Stewardship Program from this limited sample set and because the manufacturers of surface treatments are not known.

Only Textile 9 gave measurable concentration of N-EtFOSE. To the best of our knowledge, N-EtFOSE is a target analyte in select studies, but has not been reported above the LOD/LOQ. [48, 49] Textile 9 had volatile N-EtFOSE and FTOHs, which indicates treatment of the textile with a mixture of ECF- and telomer-based chemistries. The absence of N-EtFOSE on the newer textiles is consistent with the phase-out of 3M C8-based chemistry between 2000-2002[64] and indicates no use of N-EtFOSE from other sources. Even though Textile 9 was manufactured 28 years ago in 1988, volatile PFASs persist on textiles and potentially act as sources of human exposure for decades in indoor environments. The volatile PFASs may occur as residuals from the manufacturing process[17] or from physical or biological degradation of precursors on the textile. The likelihood of biodegradation on an office chair under indoor environment conditions is low; however, there are no data on the degradation of N-EtFOSE on consumer products under indoor conditions. It is also possible that textiles act as passive samplers of volatile and particulate PFASs from other sources.

Ionic Individual PFASs by LC-MS/MS

When the concentrations of individual ionic PFASs (ug/m^2) were converted to nmol F/cm^2 and summed, ionic PFASs were significantly lower than those of the volatile PFASs on paper and textiles, with the exception of Paper 8 (Table 2.1).

Papers. Three of the eight papers (Papers 1,3, and 4) had concentrations <LOD for all 73 ionic PFASs (Table 2.9). On the remaining five papers, only five classes (PFCAs, FTUCAs, FTCAs, diPAPs, SAmPAP) comprised of 10 individual ionic PFASs were present (Table 2.9). Overall, the frequency of detection for individual ionic PFASs was very low (Table 2.9) and the concentrations were also low (0.12-19ug/m^2; Table 2.9 and Table2.1). Although, no papers gave PFOS or PFOA >LOD, C8-based 6:2/8:2; 8:2; 8:2/10:2; 10:2 diPAPs or SAmPAP (Table 2.9) were present on Papers 2 and 7 (food contact papers with recycled content), and 6 (Table 2.1). Although others have found diPAPs,[38, 39, 65] to the best of our knowledge this is the first report of a homologous series consisting of five diPAPs (Table 2.9). Two papers (Papers 2 and 7) contained SAmPAP only, and are the only two papers with recycled content.

Textiles. Concentrations of individual PFASs (0.061-190 ug/m^2) on textiles were higher than those on papers (Table 2.9), but lower than those of volatile PFASs on both paper and textiles (Table 2.1). Of the nine textiles analyzed, two were <LOQ for ionic PFASs (Paper 1 and 2). For Textiles 3-8, PFCAs and FTCAs were frequently detected (Table 2.9). This is the second report of short-chained (≤C6) fluorotelomer saturated and

unsaturated carboxylates (Table 2.9) on paper[42] and the first for textiles. The quantification of FTCAs and FTUCAs in this study indicate that they are not only intermediate products as a result of degradation,[66] but are also available on consumer goods in the current market. PFOA was detected in two textiles, in contrast to papers for which no PFOA was detected above the LOD. PFOS itself was present in two textiles in Papers 6 and 9 (Table 2.9).

The oldest Textile 9 from 1988, had the greatest diversity of individual volatile and ionic (32 total) PFASs with chain-lengths up to C18 (Table 2.9). For example, Textile 9 gave the first reported quantifiable concentrations of PFPrS (the C3 sulfonate); 8:2 FtS; C6, C7, C8 MeFASAAs; and the C8 EtFOSAA. While N-EtFOSAA may be due to the 3M product FC129,[67] there is no documented use of N-MeFASAAs as a product in commerce. The two families, MeFASAAs and EtFASAAs, are typically reported as degradation products of N-ethyl and N-methyl perfluoroalkyl sulfonamido ethanols.[68] Given the low potential for the biodegradation of the sulfonamide ethanols to the sulfonamide acetic acids under office conditions, we hypothesize that the MeFASAAs were used as products or occurred as impurities in 3M formulations.

The PFCAs on Textile 9 were branched and linear, as was PFOS (Figure 2.2), which is consistent with the finding of N-EtFOSE on this textile and the idea that ECF-based treatment was applied to this textile. In contrast, PFCAs in the other newer papers and textiles were only linear, indicating treatment with fluorotelomer-based chemistry.

TOP Assay

The recovery of individual precursor from aqueous solution was 0-45 % (Table 2.8). An overall recovery of 57 % ± 4.7 % was obtained for the mixture spiked onto paper (data not shown). The higher recovery (57%) obtained for PFASs in the presence of material may be due to competition by the material for oxidant. Others report variable and low recovery of precursor from the TOP assay.[9, 53, 69] Precision, represented by % RSD about the reported nmol F/cm^2 was 11 % for papers and 7.8 % for textiles. Regardless, it was assumed that precursors on a paper or textile were converted quantitatively upon oxidation.

While the TOP assay has relatively good precision, the accuracy is poor, and ultimately results in a bias low for quantification of precursors. Preliminary experiments using 6:2 and 8:2 FTOH spiked into a dry centrifuge tube and taken to dryness, did not give any PFCA production < LOD. Paper 4 was <LOQ for individual ionic PFASs and for precursors by the TOP assay, but had quantifiable levels of 8:2 FTOH (Table 2.1, Table 2.9, 2.10). Given the need to remove all methanol to avoid oxidant consumption, any volatile precursors not captured by GC-MS will not be captured by the TOP assay, and are not included in Equation 1 for the calculation of precursor concentrations. Additionally, of the known individual precursors poor recovery is achieved (Table 2.2, Table 2.8). For example, Paper 2 which had quantifiable levels of individual ionic PFASs (Table 2.9) but <LOQ after the TOP assay (Table 2.2, Table 2.10). For these reasons, precursor concentrations estimated by the TOP assay are likely biased low and < LOQ may represent a false negative.

However, in order to ensure that the precursors determined by TOP assay are representative of only unknown precursors all individual ionic PFASs measured are subtracted from those quantified after TOP assay (Equation 1). In order to compute precursor concentrations (Table 2.10) by Equation 1, the concentration of all measured individual precursors that can be oxidized, such as 6:2 diPAP (Table 2.9), are subtracted from the total PFCAs and PFSAs measured after oxidation. It is important to note that the unknown precursors are only representative of those loosely bound to the surface application of a paper or textiles because they are dislodged in methanol. Methanol is not used as a food simulant,[70] but could represent the potentially available fraction available for PFAS exposure. Additionally, TOP assay performed on food simulants needs to be researched further.

Papers. No precursors, determined as the net production of PFCAs and PFSAs (Σ PFASs nmol F/cm^2) by the TOP assay, were > LOQ for two of the eight papers (Table 2.10). The other six papers gave precursor concentrations ranging from 0.0046-7.8 nmol F/cm^2 (Table 2.10). The precursor concentrations, on a nmol F/cm^2 basis, were greater than the sum individual ionic PFASs, except for Paper 2 (Table 2.1). The precursor concentrations were both higher and lower than those of the volatile concentrations, and no clear trend or correlation could be identified.

When applied to papers, oxidation produced a homologous series (C3-C9) of PFCAs with C4 as the most abundant (Table 2.10, Figure 2.3a). Individual C6- and C8-based precursors oxidized for this study (Table 2.8) as well as by Houtz et al. 2012[54] yield C4-C9 PFCAs upon oxidation. Therefore, precursors on paper give a PFCA distribution after oxidation that is consistent with C6- and C8-based precursors. The PFCAs generated upon oxidation were only linear (data not shown). Linear PFCAs before and after oxidation, FTOHs, and the absence of ECF-based PFASs indicates that the papers purchased in 2015 were only treated with fluorotelomer-based chemicals.

Textiles. Of the nine textiles, all had quantifiable precursors, ranging from 0.040-73 nmol F/cm^2 (Table 2.10). Precursor concentrations were similar for papers and textiles with the exception of Textile 9 (Table 2.1). Textiles gave broader distributions of PFCAs (C4-C18) both before and upon oxidation than did papers (C4-C9)(Figure 2.3). In the case of Textile 5 and 7, PFCAS up to C18 (PFOcDA) were produced upon oxidation, which indicates precursors with chain lengths significantly longer than C8. Thus, not all producers of textile treatments are compliant with the C8 Stewardship Program.[60] Similar to papers, the concentrations of the precursors identified by TOP assay were both higher and lower than those of the volatile PFASs, and no clear correlation between the two could be made.

Textiles 1-8 produced PFCAs upon oxidation that were only linear, while Textile 9, manufactured in 1988, gave branched and linear PFCAs (Figure 2.2). In addition, Textile 9 gave a net increase in PFOS upon oxidation, indicating the presence of a precursor that oxidized to PFOS. No known precursor have yet been observed to produce PFOS or any other PFSA in this or any other study.[11, 41, 53, 54, 69] Textile 9 was clearly treated with ECF-based chemistries as indicated earlier. The concentration of unknown precursors on Textile 9 was the greater than any other paper or textiles purchased in 2015 (Table 2.1).

PIGE

Papers and Textiles. Papers tended either to be blank (Papers 1-4) or highly fluorinated (61-440 nmolF/cm^2) while all the textiles were fluorinated (370-2400 nmolF/cm^2) (Table 2). Total fluorine concentrations were converted to % fluorine by weight. Papers ranged from 0.040-0.088 wt% fluorine, while textiles ranged from 0.027-0.38 wt% fluorine. The wt% values are low relative to those reported by Kissa[2] for papers (1.0-1.5 wt %) and fabrics (2-3 wt %) but the reported values were given for a specific example, fluoroalkyl phosphates, and do not represent the wt% of fluorine alone. Total fluorine concentrations for papers were significantly lower than those for textiles; however, Ritter et al report cases where the total fluorine concentrations on papers exceed those on textile.[56] No statistically-significant correlations were found between volatile PFASs, ionic PFASs, precursors, and total fluorine by PIGE (data not shown).

The amount of fluorine remaining on the surface of paper or textiles was determined by PIGE after methanol extraction (Table 2.2). Papers 1-4 remained <LOD for total fluorine, while Papers 6-8 and all textiles gave total fluorine concentrations that was not statistically different from the original total fluorine concentrations (Table 2.2). One paper, Paper 5, gave a total fluorine concentration after solvent extraction that was significantly higher than the original concentration prior to extraction. The reason for this apparent increase after extraction is unknown; Ritter et al. described the accuracy and precision of PIGE in greater detail.[56] The lack of a significant decrease in total fluorine after methanol extraction indicates that fluorinated polymeric treatments are not extracted by methanol. In contrast, methanol removes the less strongly bound monomeric PFASs. Monomeric PFASs are described by Prevedourus et al. [71] as residual monomers of unreacted raw materials (e.g, FTOHs), residual by-products of reactions, and as

unintended manufacturing by-products (e.g., PFCAs), which are soluble in solvent such as methanol and ethyl acetate.

Closing the mass balance on fluorine

In order to determine if mass balance was achieved, we considered the original PIGE value as the total fluorine concentration for each paper and textile. Volatile PFASs only accounted for 0-2.2% of the total fluorine (Table 2.1 and 2.2). Ionic PFASs only accounted for 0-0.41% of total fluorine (Table 2.1 and 2.2). Unknown precursors accounted for 0.012-1.9% of the total fluorine of papers and textiles purchased in 2015 (Table 2.1 and 2.2). In contrast, unknown precursors accounted for a larger fraction (14%) of the total fluorine on Textile 9 from 1988 (Table 2.1 and 2.2).

For simplicity, the concentrations of volatile PFASs, ionic PFASs, and precursors were summed and accounted for a maximum of 16% total fluorine (Table 2.2). As stated earlier, the total fluorine remaining after extraction was not significantly different from the original concentration (Table 2.2).

To evaluate mass balance, the summed concentrations of volatile and ionic PFASs and precursors were added to the total fluorine after extraction (Equation 2). Mass balances ranged from 64 ± 28 % to 110 ± 30%, with the exception of Paper 5 which had a higher value for total fluorine after solvent extraction than before.

$$\text{Mass balance (\%)} = \frac{(\text{Volatile PFASs} + \text{Ionic PFASs} + \text{Precursors} + Total\ Fluorine^{\text{after extraction}})}{Total\ Fluorine^{\text{ before extraction}}} * 100$$

Equation 2

Clearly, the residual PFASs captured as volatile, ionic, and precursor are very small (within the error bounds of PIGE before and after extraction) compared to the large fraction of total fluorine that is more strongly bound to papers and textiles. While Textile 9 is not the highest measurement of total fluorine by PIGE, it has a higher relative concentration of PFASs (volatile, ionic, and precursors) that are potentially available for human exposure. The increase in solvent extractable PFASs could be a result in older surface chemistry applications being less efficiently bound to the surface of the material, the material acting as a passive sampler, or the weakening of the surface application over time.

Implications

Given the limited number of analytes in the present study, the concentration of volatile PFASs on papers and textiles is likely biased low. The presence of additional volatile PFASs should be investigated by non-target analysis, which is not yet reported in the literature. While the number of ionic PFASs analyzed by LC-MS/MS for this study is greater than typically reported, the identification of additional PFASs was attempted using non-target screening by LC quadrupole time of flight; however, this effort did not reveal any additional PFASs (data not shown). The TOP assay data clearly indicates that there are additional fluorinated substances that are not yet captured as individual PFASs. Further analytical investigations are needed to identify the PFASs in the precursor fraction.

A higher fraction of total fluorine remained of the surface of newer papers and textiles after extraction, while the older textile had a higher fraction of extractable PFASs, which suggests that either newer application techniques are more efficient or older articles have a higher fraction of monomers that may become mobile. As a result, older materials may be a greater potential source of exposure to PFASs than are newer papers and textiles. Additional research is needed on the release of PFASs from older papers and textiles and how the releases inform human exposure. For example, mass balances on the total fluorine using food simulants should be performed because solvent extraction is not a proxy for food simulants. The potential removal of unknown precursors from food-contact papers by food simulants is simply unknown. The vast majority of the total fluorine that remained on papers and textiles after extraction represents not only the fraction that remains with articles over their useful lifetimes but that enter landfills.

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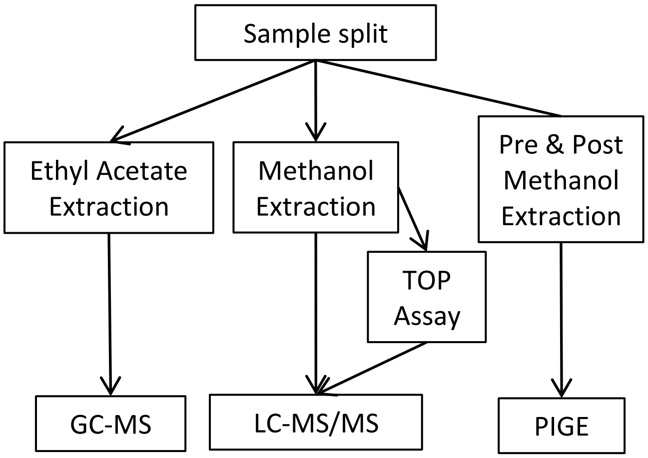

Figure 2.1 Sample processing and analysis workflow.

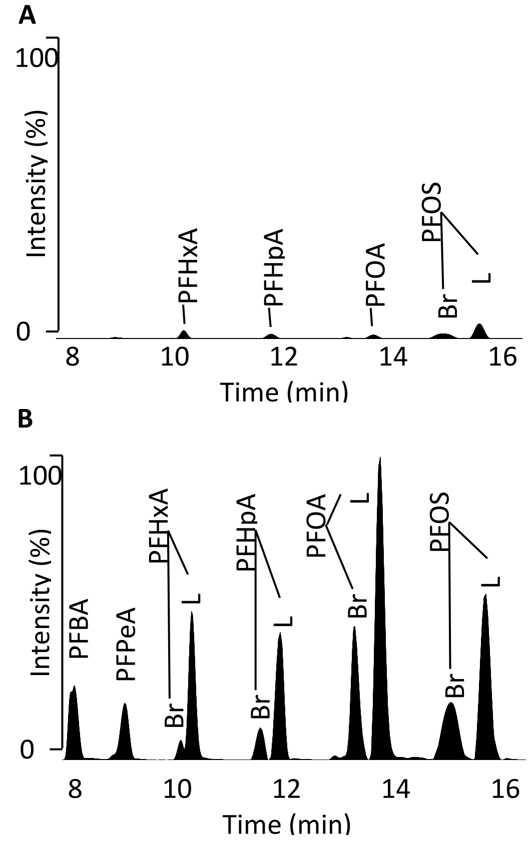

Figure 2.2 Chromatographic depiction of select branched and linear PFCAs and PFOS before (A) and after (B) oxidation by TOP assay.

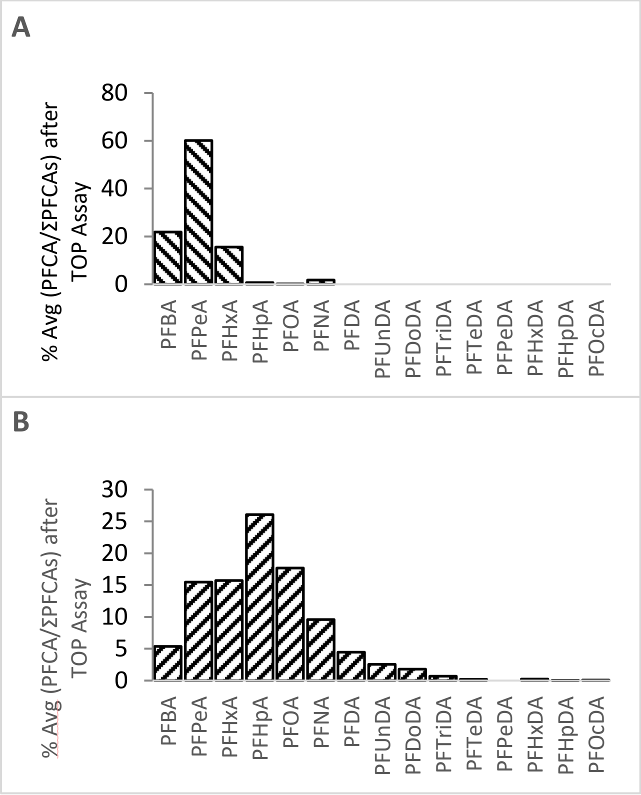

Figure 2.3 Distribution of % average contribution normalized after TOP Assay for a) eight papers and b) nine textiles.

Table 2.1 Total nmol F/cm^2 for volatile PFASs, ionic individual PFASs, and precursors from the TOP assay.[a]

		Material Type	Σ Volatile PFASs (nmol F/cm^2)	Σ Ionic PFASs (nmol F/cm^2)	Σ Precursors (nmol F/cm^2)
Papers	1	FC	0.16 ± 0.004	<LOQ	0.011 ± 0.001
	2	Copy Paper[b]	0.013 ± 0.001	0.0011 ± 0.0002	<LOQ
	3	FC	<LOQ	<LOQ	0.0046 ± 0.0006
	4	Gift Bag	0.033 ± 0.001	<LOQ	<LOQ
	5	FC	0.18 ± 0.003	0.0013 ± 0.0001	0.53 ± 0.06
	6	FC	0.055 ± 0.002	0.0062 ± 0.0004	0.36 ± 0.04
	7	FC[b]	0.13 ± 0.004	0.0004 ± 0.0002	0.0013 ± 0.0002
	8	Popcorn bag	<LOQ	0.14 ± 0.01	7.8 ± 0.9
Textiles	1	Children’s Fabric	0.40 ± 0.01	<LOQ	0.040 ± 0.003
	2	Children’s Fabric	0.66 ± 0.19	<LOQ	0.58 ± 0.05
	3	Jacket	6.7 ± 0.2	0.0030 ± 0.0001	1.7 ± 0.1
	4	Jacket	0.89 ± 0.03	0.0093 ± 0.0005	0.18 ± 0.01
	5	Jacket	0.29 ± 0.01	0.0032 ± 0.0003	0.27 ± 0.02
	6	Hat	0.082 ± 0.003	0.0048 ± 0.0002	0.15 ± 0.01
	7	Pillowcase	6.1 ± 0.2	0.025 ± 0.002	0.59 ± 0.05
	8	Jacket	53 ± 1	0.19 ± 0.01	0.28 ± 0.04
	9	Office Upholstery	11 ± 0.1	2.1 ± 0.1	73 ± 6

[a] propagated standard error computed as % RSD associated with analyte multiplied by the experimentally-derived concentration

[b] contains post-consumer recycled content

FC=food contact

LOQ = Limits of quantification

Table 2.2 The sum of volatile, ionic, and total F on solvent extracted paper/textile, total fluorine by PIGE and the % of mass balance accounted for in comparison to total fluorine by PIGE.

		Material Type	PIGE (nmol F/cm^2)[b]	The sum of volatile PFASs, ionic PFASs, and precursors (nmol F/cm^2)[a]	Total fluorine remaining on material (nmol F/cm^2)[b]	Accounted for mass (%)[c,d]
Papers	1	FC	<LOD	0.17 ± 0.004	<LOD	NC
	2	Copy Paper[e]	<LOD	0.014 ± 0.001	<LOD	NC
	3	FC	<LOD	0.0046 ± 0.0006	<LOD	NC
	4	Gift Bag	<LOD	0.033 ± 0.001	<LOD	NC
	5	FC	61 ± 14	0.71 ± 0.06	110 ± 17	180 ± 28
	6	FC	180 ± 27	0.42 ± 0.04	180 ± 25	99 ± 21
	7	FC[e]	430 ± 49	0.13 ± 0.004	330 ± 40	77 ± 17
	8	Popcorn bag	420 ± 49	7.9 ± 0.9	460 ± 52	110 ± 16
Textiles	1	Children’s Fabric	<LOQ	0.44 ± 0.01	<LOQ	NC
	2	Children’s Fabric	530 ± 98	1.2 ± 0.2	340 ± 66	64 ± 28
	3	Jacket	1100 ± 250	8.4 ± 0.2	920 ± 210	84 ± 32
	4	Jacket	840 ± 170	1.1 ± 0.03	680 ± 140	81 ± 29
	5	Jacket	370 ± 79	0.56 ± 0.02	410 ± 88	110 ± 30
	6	Hat	<LOQ	0.24 ± 0.01	<LOQ	NC
	7	Pillowcase	1600 ± 290	6.7 ± 0.2	1300 ± 250	82 ± 27
	8	Jacket	2400 ± 420	53 ± 1	2300 ± 410	98 ± 25
	9	Office Upholstery	520 ± 92	86 ± 6	480 ± 83	100 ± 26

[a] propagated standard error for the sum of ionic, volatile, and precursors data shown in Table 2.1

[b] propagated error for PIGE as discussed in Ritter et al. (2016)

[c] propagated error for data in column 1-3
[d]computed as (Column 1+ 2)/Column 3)*100
[e]contains post consumer recycled content. FC=food contact

Table 2.2 (Continued)

Limits of quantification (LOQ) for papers = 43 nmol F/cm and 150 nmol F/cm
NC = not computed

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Supporting Information

Closing the Mass Balance of Fluorine for Papers and Textiles

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Experimental Methods

Reagents

For LC-MS/MS analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (regent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Sodium hydroxide (98%, reagent grade), ethyl acetate (99.9%, reagent grade), potassium persulfate (>99%, ACS reagent), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH). For GC-MS analysis Ethyl acetate (HLPC grade) was purchased from EMD Millipore Corp (Bilerica, MA).

Volatile Analysis by GC-MS

Instrumental Analysis

Extracts were analyzed for volatile PFASs using positive chemical ionization mode gas chromatography mass spectrometry (GC-MS) operated in single ion monitoring mode (SIM), with SIM ions given in Table 2.3. The calibration range for all analytes was from 10-200 ng. Analytes were separated using a DB-WAX column (30 m x 0.250 mm, 0.25 µm film thickness, Agilent, Santa Clara, CA). The carrier gas was helium and the injection volume was 2 µl. The initial oven temperature was 60 ^{o}C, held 1 min, increased at 5 ^{o}C/min to 75 ^{o}C, increased at 10 ^{o}C/min to 130 ^{o}C, and then 50 ^{o}C/min to 240 ^{o}C. Analyte responses were normalized to internal standards as indicated in Table 2.1. If values were outside of the calibration range further dilutions were performed and the extract was re-analyzed.

Whole method performance

Spike and recovery experiments were conducted using a 2x2 cm^2 of “pre-cleaned” cotton twill fabric that served as a surrogate matrix. The cotton twill fabric was pre-cleaned with 1:1 hexane:acetone using a Soxhlet overnight and then air dried in a fume hood. The sample was then spiked with 20 ng (n=3) to give an equivalent of 50 µg m2 of each analyte (6:2, 8:2, 10:2 FTOH and N-EtFOSE) or 120 ng (n=3) to given an equivalent of 300 $\mu g/m^2$ of each analyte and allowed to dry for 10 min. Each sample was then extracted as described above in the main manuscript. Precision was determined by an n=5 analysis at a 120 ng using the spiking and extraction procedures described above. The instrumental limit of detection (LOD) was determined to be three times the standard deviation? error of the calibration curve slope and the limit of quantification (LOQ) was determined as ten times the standard deviation? error of the slope of the calibration curve Vial and Jardy 1999. Each batch of samples contained three solvent blanks that consisted of internal standards in pre-cleaned glass vials. Separate spike and recovery experiments were not performed for papers, but the performance parameters of the method were assumed to apply equally to both papers and textiles.

Ionic PFASs by LC-MS/MS

Extraction efficiency of Individual Ionic PFASs

An experiment was done to determine the number of necessary extraction cycles to remove >90% of methanol extractable mass of individual PFASs similar to van der Veen et al., 2016. A single representative paper and textile was selected based on the presence of the greatest range of individual PFASs present. Two replicates of each paper and textile were cut from the sample (0.3±0.01g) and placed in 15mL centrifuge tubes. One of the two was spiked with 0.72 ng of all labeled internal standards and allowed to dry, the other was not spiked. Both sets were then extracted in methanol as described above, but four individual rounds of extraction were performed. Rather than collecting all supernatant in one centrifuge tube, each round of extraction was collected individually. For the samples with mass labeled internal standards added before extraction, each round of extraction was diluted 1:5 in methanol and analyzed. For samples without mass labelled internal standard present, each round of extraction was diluted 1:5, 0.72 ng of mass labeled internal standard was added, and then analyzed.

TOP Assay by LC-MS/MS

Recovery for the TOP assay was determined using two sets of measurements. The mass recovery of individual polyfluorinated precursors (no paper or textile present) was determined by adding 2.4 ng each of seven oxidizable polyfluorinated precursors into seven separate 1.2mL autosampler vial containing 60 μL of methanol. The methanol was then blown to dryness, after which 3 mL of the TOP assay reaction solution was added, followed by the subsequent micro liquid-liquid extraction as described above. Known precursor experiments were performed, but showed very poor recovery when spiked into reaction solution with no paper or textile.

The second measure of accuracy for the TOP assay was determined by spiking n=4 of a paper and n=4 replicates of a single textile to give an equivalent of 8.3 ng/g of all Qn and Sq analytes. Methanolic extraction was carried out on all eight samples, as described above. The resulting extract was blown to dryness, reacted, spiked with internal standards, and extracted as described above. All extracts created for the recovery of TOP assay were analyzed for PFCAs by LC-MS/MS as described above. Concentrations of PFCAs formed after oxidation were converted to nmol F. Recovery was determined by dividing the summed nmol F formed after oxidation by the initial of the respective polyfluorinated precursor in nmol F prior to oxidation. Mass recovery was calculated by subtracting expected overspiked concentrations of PFCAs, the molar conversion equivalent of all overspiked Qn and Sq analytes, and any background present in the sample. Precision, described as % RSD, was computed from n=4 replicates of the 8.3 ng/g equivalent overspike mixture.

Results and Discussion

Ionic Individual PFASs –

Methanol was selected as the extraction solvent based on preliminary experiments, and on literature precedent.[1-9] Preliminary experiments indicated that the ratio of 0.3± 0.01g to 3.33mL methanol per round of extraction produced the lowest RSD across all analyte classes of interest for both papers and textiles (Table 2.7).

The extraction efficiency was consistent in comparison to experiments performed by van der Veen et al., 2016 and Zabaleta et al., 2016. The extraction profiles (% mass of individual PFAS recovered in each extraction/total mass) were similar, indicating that spiked and PFASs associated with the material exhibit similar extraction behavior. Three rounds of extraction removed >90% of ionic PFASs, and were applied to all subsequent analysis and data collection. TOP assay extraction efficiency experiments were not performed because TOP assay was run on the extract resulting from the methanolic extraction, and it was assumed unknown precursors behaved somewhat similarly to known precursors (i.e. diPAPs) and would also be extracted to >90% efficiency.

Tables and Figures

Table 2.3. GC-MS target analyte full name, acronym, SIM ions (quantification ion is underlined), internal standard, and data quality tier.

Full Name	Acronym	SIM	Internal Standard	Data Quality*
6:2 fluorotelomer alcohol	6:2 FTOH	$\underline{365}$, 327	$^{2}H_{2}$-,$^{13}C_{2}$-6:2 FTOH	Qn
8:2 fluorotelomer alcohol	8:2 FTOH	$\underline{465}$, 427	$^{2}H_{2}$-,$^{13}C_{2}$-8:2 FTOH	Qn
10:2 fluorotelomer alcohol	10:2 FTOH	$\underline{565,}$ 527	$^{2}H_{2}$-,$^{13}C_{2}$-8:2 FTOH	Qn
N-ethyl perfluorooctane sulfonamidoethanol	N-EtFOSE	$\underline{554,}$ 572	$^{9}H_{2}$-N-EtFOSE	Qn

*Data quality follows the same criteria as established in the ionic PFASs section.

Individual Ionic PFASs by LC-MS/MS

Table 2.4. LC-MS/MS target analyte full name, acronym, acquisition masses and parameters, internal standard, calibration reference, and data quality.

Analyte	Acronym	PI* (m/z)	CV* (V)	FI-1* (m/z)	CE* (eV)	FI-2* (m/z)	CE* (eV)	Internal Standard	Calibration Reference	Data Quality*
Perfluorobutanoic acid	PFBA	213	20	169	8	n/a	n/a	[$^{13}C_4$]PFBA	PFBA	Qn
Perfluoropentanoic acid	PFPeA	263	20	219	8	n/a	n/a	[$^{13}C_3$]PFPeA	PFPeA	Qn
Perfluorohexanoic acid	PFHxA	313	20	269	8	119	22	[$^{13}C_2$]PFHxA	PFHxA	Qn
Perfluoroheptanoic acid	PFHpA	363	20	319	8	169	14	[$^{13}C_4$]PFOA	PFHpA	Sq
Perfluorooctanoic acid	PFOA	413	20	369	8	169	18	[$^{13}C_4$]PFOA	PFOA	Qn
Perfluorononaoic acid	PFNA	463	22	419	8	169	18	[$^{13}C_5$]PFNA	PFNA	Qn
Perfluorodecanoic acid	PFDA	513	22	469	10	269	18	[$^{13}C_2$]PFDA	PFDA	Qn
Perfluoroundecanoic acid	PFUnDA	563	22	519	10	169	22	[$^{13}C_2$]PFUnDA	PFUnDA	Qn
Perfluorododecanoic acid	PFDoDA	613	22	569	10	169	24	[$^{13}C_2$]PFDoDA	PFDoDA	Qn
Perfluorortridecanoic acid	PFTriDA	663	24	619	12	169	26	[$^{13}C_2$]PFDoDA	PFTriDA	Sq
Perfluorotetradecanoic acid	PFTeDA	713	24	669	12	169	26	[$^{13}C_2$]PFDoDA	PFTeDA	Sq
Perfluoropentadecanoic acid	PFPeDA	763	25	719	12	169	28	[$^{13}C_2$]PFDoDA	PFTeDA	Ql
Perfluorohexadecanoic acid	PFHxDA	813	25	769	12	169	30	[$^{13}C_2$]PFDoDA	PFHxDA	Ql
Perfluoroheptadecanoic acid	PFHpDA	863	25	819	13	169	30	[$^{13}C_2$]PFDoDA	PFHxDA	Ql
Perfluorooctadecanoic acid	PFOcDA	913	25	869	15	169	30	[$^{13}C_2$]PFDoDA	PFOcDA	Ql
2-perfluorobutylethanoic acid	FBEA	277	20	63	7	193	23	[$^{13}C_2$]FHEA	FHEA	Ql
2-perfluorohexylethanoic acid	FHEA	377	20	293	22	63	7	[$^{13}C_2$]FHEA	FHEA	Qn
2-perfluorooctylethanoic acid	FOEA	477	20	393	20	63	10	[$^{13}C_2$]FOEA	FOEA	Qn
2-perfluorodecylethanoic acid	FDEA	577	20	493	18	63	10	[$^{13}C_2$]FDEA	FDEA	Qn
2H-perfluoro-2-hexenoic acid	FBUEA	257	19	193	16	143	33	[$^{13}C_2$]FHUEA	FHUEA	Ql
2H-perfluoro-2-octenoic acid	FHUEA	357	18	293	17	243	34	[$^{13}C_2$]FHUEA	FHUEA	Qn
2H-perfluoro-2-decenoic acid	FOUEA	457	22	393	17	343	36	[$^{13}C_2$]FOEA	FOUEA	Qn
2H-perfluoro-2-dodecenoic acid	FDUEA	557	24	493	17	443	38	[$^{13}C_2$]FDEA	FOUEA	Sq
3-Perfluoropropyl propanoic acid *(3:3)*	FPrPA	241	19	177	7	117	24	[$^{13}C_2$]FHEA	FPrPA	Sq
3-Perfluoropentyl propanoic acid *(5:3)*	FPePA	341	19	237	14	217	24	[$^{13}C_2$]FHUEA	FPePA	Sq
3-Perfluoroheptyl propanoic acid *(7:3)*	FHpPA	441	19	337	13	317	23	[$^{13}C_2$]FOEA	FHpPA	Sq

3-Perfluorononyl propanoic acid *(9:3)*	FNPA	541	19	437	14	417	23	$[^{13}C_2]$FDEA	FHpPA	Ql
Perfluoroethane sulfonate	PFEtS	199	50	80	28	99	26	$[^{18}O_2]$PFBS	PFEtS	Ql
Perfluoropropane sulfonate	PFPrS	249	50	80	30	99	26	$[^{18}O_2]$PFBS	PFPrS	Ql
Perfluorobutane sulfonate	PFBS	299	50	80	32	99	26	$[^{18}O_2]$PFBS	PFBS	Qn
Perfluoropentane sulfonate	PFPeS	349	54	80	34	99	27	$[^{18}O_2]$PFHxS	PFHxS	Sq
Branched Perfluorohexane sulfonate	Br-PFHxS	399	58	80	36	99	28	$[^{18}O_2]$PFHxS	PFHxS	Qn
Perfluorheptane sulfonate	PFHpS	449	64	80	46	99	32	$[^{13}C_2]$PFOS	PFOS	Sq
Branched Perfluorooctanesulfonic acid	Br-PFOS	499	70	80	46	99	34	$[^{13}C_2]$PFOS	PFOS	Qn
Perfluorononane sulfonate	PFNS	549	73	80	49	99	35	$[^{13}C_2]$PFOS	PFDS	Sq
Perfluorodecane sulfonate	PFDS	599	76	80	52	99	36	$[^{13}C_2]$PFOS	PFDS	Sq
4:2 fluorotelomer sulfonate	4:2 FTS	327	42	307	19	81	26	$[^{13}C_2]$ 4:2 FtS	4:2 FTS	Sq
6:2 fluorotelomer sulfonate	6:2 FTS	427	42	407	22	81	28	$[^{13}C_2]$ 6:2 FtS	6:2 FTS	Sq
8:2 fluorotelomer sulfonate	8:2 FTS	527	48	507	24	81	33	$[^{13}C_2]$ PFDA	8:2 FTS	Sq
10:2 fluorotelomer sulfonate	10:2 FTS	627	54	607	26	81	38	$[^{13}C_2]$ 6:2 FtS	8:2 FTS	Ql
Perfluorobutane sulfonamido acetic acid	FBSAA	356	35	298	20	78	30	$[^{13}C_2]$PFHxA	MeFBSAA	Ql
Perfluoropentane sulfonamido acetic acid	FPeSAA	406	37	348	22	78	32	$[^{13}C_2]$PFHxA	MeFBSAA	Ql
Perfluorohexane sulfonamido acetic acid	FHxSAA	456	40	398	24	78	35	d_3-MeFOSAA	FOSAA	Ql
Perfluoroheptane sulfonamido acetic acid	FHpSAA	506	42	448	25	78	37	d_3-MeFOSAA	FOSAA	Ql
Perfluorooctane sulfonamido acetic acid	FOSAA	556	45	498	27	78	40	d_3-MeFOSAA	FOSAA	Sq
Methyl perfluorobutane sulfonamido acetic acid	MeFBSAA	370	28	219	18	283	13	$[^{13}C_2]$PFHxA	MeFBSAA	Sq
Methylperfluoropentane sulfonamido acetic acid	MeFPeSAA	420	29	269	18	333	24	$[^{13}C_2]$PFHxA	MeFBSAA	Ql
Methyl perfluorohexane sulfonamido acetic acid	MeFHxSAA	470	31	319	19	169	26	d_3-MeFOSAA	MeFOSAA	Ql
Methyl perfluoroheptane sulfonamido acetic acid	MeFHpSAA	520	32	369	19	169	28	d_3-MeFOSAA	MeFOSAA	Ql
Methylperfluorooctane sulfonamido acetic acid	MeFOSAA	570	34	419	20	169	30	d_3-MeFOSAA	MeFOSAA	Qn
Ethylperfluorobutane sulfonamido acetic acid	EtFBSAA	384	28	219	18	326	18	$[^{13}C_2]$PFHxA	MeFBSAA	Ql
Ethylperfluoropentane sulfonamido acetic acid	EtFPeSAA	434	29	269	18	376	18	$[^{13}C_2]$PFHxA	MeFBSAA	Ql
Ethylperfluorohexane sulfonamido acetic acid	EtFHxSAA	484	31	319	19	426	19	d_5-EtFOSAA	EtFOSAA	Ql
Ethylperfluoroheptane sulfonamido acetic acid	EtFHpSAA	534	32	369	19	476	19	d_5-EtFOSAA	EtFOSAA	Ql
Ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	584	34	419	20	526	20	d_5-EtFOSAA	EtFOSAA	Qn
Bis(perfluorobutyl) phosphinate	4:4 PFPIA	501	50	301	40	101	55	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Ql

Perfluorobutyl perfluorohexyl phosphinate	4:6 PFPIA	601	60	301	42	401	43	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Ql
Bis(perfluorohexyl) phosphinate	6:6 PFPIA	701	72	401	43	101	62	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Sq
Perfluorohexylperfluorooctyl phosphinate	6:8 PFPIA	801	85	401	44	501	45	$[^{13}C_4]$-6:2DiPAP	6:6 PFPi	Sq
Bis(perfluorooctyl) phosphinate	8:8 PFPIA	901	98	501	46	101	69	$[^{13}C_4]$-6:2DiPAP	8:8 PFPi	Sq
4:2 disubstituted polyfluoroalkyl phosphate	4:2 diPAP	589	36	97	27	343	16	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Ql
4:2/6:2 disubstituted polyfluoroalkyl phosphate	4:2/6:2 diPAP	689	37	97	29	343	17	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Ql
6:2 disubstituted polyfluoroalkyl phosphate	6:2 diPAP	789	38	97	30	443	18	$[^{13}C_4]$-6:2DiPAP	6:2 diPAP	Qn
6:2/8:2 disubstituted polyfluoroalkyl phosphate	6:2/8:2 diPAP	889	39	97	33	443	19	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2 disubstituted polyfluoroalkyl phosphate	8:2 diPAP	989	40	97	35	543	20	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Sq
8:2/10:2 disubstituted polyfluoroalkyl phosphate	8:2/10:2 diPAP	1089	41	97	37	543	21	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
10:2 disubstituted polyfluoroalkyl phosphate	10:2 diPAP	1189	42	97	39	643	22	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
6:2 fluorotelomer mercaptoalkyl phosphate diester	6:2 FTMAP	921	70	79	50	575	30	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
6:2/8:2 fluorotelomer mercaptoalkyl phosphate diester	6:2/8:2 FTMAP	1021	75	79	50	575	30	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2 fluorotelomer mercaptoalkyl phosphate diester	8:2 FTMAP	1121	90	79	50	675	35	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
8:2/10:2 fluorotelomer mercaptoalkyl phosphate diester	8:2/10:2 FTMAP	1221	90	79	50	675	40	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
10:2 fluorotelomer mercaptoalkyl phosphate diester	10:2 FTMAP	1321	90	79	50	775	40	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
N-ethyl perfluorooctanesulfonamidoethanol-based phosphate diester	SAmPAP	1203	75	526	40	169	65	$[^{13}C_4]$-6:2DiPAP	8:2 diPAP	Ql
Perfluoro[1,2,3,4-$^{13}C_4$]butanoic acid	$[^{13}C_4]$ PFBA	217	20	172	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[3,4,5-$^{13}C_3$]pentanoic acid	$[^{13}C_3]$ PFPeA	266	20	222	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]hexanoic acid	$[^{13}C_2]$ PFHxA	315	20	270	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid	$[^{13}C_4]$ PFOA	417	20	372	8	n/a	n/a	n/a	n/a	n/a

Perfluoro[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$] PFNA	468	22	423	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$] PFDA	515	22	470	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$] PFUnDA	565	22	520	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$] PFDoDA	615	22	570	10	n/a	n/a	n/a	n/a	n/a
2-perfluorohexyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FHEA	379	20	294	22	n/a	n/a	n/a	n/a	n/a
2-perfluorooctyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FOEA	479	20	394	20	n/a	n/a	n/a	n/a	n/a
2-perfluorodecyl-[$^{13}C_2$]-ethanoic acid	[$^{13}C_2$] FDEA	579	20	494	18	n/a	n/a	n/a	n/a	n/a
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	[$^{13}C_2$] FHUEA	359	18	294	17	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[2,3,4-$^{13}C_3$]-butanesulfonate	[$^{13}C_2$] PFBS	302		99		n/a	n/a	n/a	n/a	n/a
Perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$] PFHxS	403	58	103	28	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octane sulfonate	[$^{13}C_2$] PFOS	503	70	99	34	n/a	n/a	n/a	n/a	n/a
4:2[1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 4:2 FTS	329		81		n/a	n/a	n/a	n/a	n/a
6:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 6:2 FTS	429	42	409	22	n/a	n/a	n/a	n/a	n/a
Methyl-d$_3$-perfluorooctane sulfonamido acetic acid	[$^{2}H_3$] MeFOSAA	573	34	419	20	n/a	n/a	n/a	n/a	n/a
Ethyl-d$_5$-perfluorooctane sulfonamido acetic acid	[$^{2}H_5$] EtFOSAA	589	34	419	20	n/a	n/a	n/a	n/a	n/a
6:2 disubstituted-[1,2-$^{13}C_2$]-polyfluoroalkyl phosphate	[$^{13}C_4$] 6:2 diPAP	794	38	97	30	n/a	n/a	n/a	n/a	n/a

*PI (precursor ion), CV (cone voltage), FI (fragmentation ion), CE (collision energy), Qn (quantitative), Sq (semiquantitative), Ql (qualitative), Sc (Screen)

Table 2.5. Analytical Validation Parameters for Recovery (Accuracy), RSD (Precision), Limit of Detection (LOD), and Limit of Quantification (LOQ) for volatile analytes.

	Recovery at 20ng (%)	Recovery at 120ng (%)	RSD (%)	LOD (µg/m^2)	LOQ (µg/m^2)
Analytes					
6:2 FTOH	87	100	2.3	0.37	1.2
8:2 FTOH	79	98	3.9	0.83	2.8
10:2 FTOH	94	92	2.7	2.4	8.1
N-EtFOSE	100	78	1.5	1.2	3.8

Table 2.6. Sample mass to methanol extraction ratio for determination of minimum material for maximum precision (RSD%) for papers and textiles.

	RSD (%) range across class											
	PFCAs		FTCAs		PFSAs		FtS		(Me,Et,)FXSAA		diPAPS	
Weight to methanol ratio	Papers	Textile	Papers	Textile	Papers	Textile	Papers	Textile	Papers	Textile	Papers	Textile
0.5g:8.33mL	2-25	6-29	5-10	<LOD	<LOQ	7-24	<LOD	14-174	<LOD	12-31	<LOD	23-43
0.3g:3.33mL	4-17	10-19	12-25	<LOD	19	5-16	<LOD	14-26	<LOD	7-24	<LOD	40-49
0.1g:1.67mL	4-16	10-29	30-40	<LOD	35	14-39	<LOD	41-131	<LOD	15-62	<LOD	30-62

Table 2.7. Analysis of individual extraction cycles for native (not spiked) ionic PFASs and isotopically-labeled ionic PFASs.

	Paper				**Paper + Internal Standard**				**Fabric**				**Fabric + Internal Standard**			
% mass recovered in each extraction/total mass	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
PFBA	65	29	5.7	<LOD	69	26	4.2	0.7	62	30	8.8	<LOD	76	19	4.1	1.5
PFPeA	73	27	<LOD	<LOD	68	27	3.8	0.7	55	28	12	5.2	77	17	4.5	1.6
PFHxA	61	31	6.3	1.5	61	36	3.7	<LOD	56	25	12	6.7	75	20	3.6	1.4
PFHpA	<LOD	<LOD	<LOD	<LOD	61	36	3.7	<LOD	65	22	8.5	4.1	75	20	3.6	1.4
PFOA	100	<LOD	<LOD	<LOD	61	34	4.9	<LOD	69	22	6.8	2.6	81	17	2.5	<LOD
PFNA	<LOD	<LOD	<LOD	<LOD	65	32	3.2	<LOD	72	21	4.4	2.9	80	17	2.1	0.4
PFDA	<LOD	<LOD	<LOD	<LOD	61	34	4.6	0.6	77	16	5.4	0.9	77	19	2.7	0.6
PFUnDA	<LOD	<LOD	<LOD	<LOD	69	26	4.9	<LOD	91	9	<LOD	<LOD	77	18	3.6	1.0
PFDoDA	<LOD	<LOD	<LOD	<LOD	65	30	3.3	0.9	83	17	<LOD	<LOD	83	14	2.8	<LOD
PFTrDA	48	44	8.0	<LOD	65	30	3.3	0.9	76	21	3.9	<LOD	83	14	2.8	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	65	30	3.3	0.9	61	29	6.0	4.3	83	14	2.8	<LOD
FHEA	59	33	7.6	<LOD	90	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	74	20	5.6	<LOD
FOEA	<LOD	<LOD	<LOD	<LOD	58	39	2.4	<LOD	<LOD	<LOD	<LOD	<LOD	82	11	5.1	1.1
FDEA	<LOD	<LOD	<LOD	<LOD	61	29	11	<LOD	<LOD	<LOD	<LOD	<LOD	83	17	<LOD	<LOD
FHUEA	57	34	6.1	2.5	67	28	4.4	1.0	<LOD	<LOD	<LOD	<LOD	70	25	4.6	0.6
FOUEA	<LOD	<LOD	<LOD	<LOD	58	39	2.4	<LOD	<LOD	<LOD	<LOD	<LOD	82	11	5.1	1.1
FPePA	58	35	6.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtS	67	33	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	41	33	15	11	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	72	19	4.9	3.9	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	70	29	1.6	<LOD	70	21	6.9	2.5	83	11	4.1	1.4
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	73	19	4.7	4.0	<LOD	<LOD	<LOD	<LOD
PFHxS	<LOD	<LOD	<LOD	<LOD	77	23	<LOD	<LOD	75	17	6.0	2.4	74	21	3.0	2.0
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	76	19	4.0	0.7	<LOD	<LOD	<LOD	<LOD

PFOS	<LOD	<LOD	<LOD	<LOD	75	25	<LOD	<LOD	77	18	4.5	1.3	80	16	4.0	0.4
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	79	18	3.5	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FtS	<LOD	<LOD	<LOD	<LOD	67	29	4.0	<LOD	<LOD	<LOD	<LOD	<LOD	68	26	4.9	1.0
6:2 FtS	<LOD	<LOD	<LOD	<LOD	65	32	3.7	<LOD	81	19	<LOD	<LOD	81	15	3.1	0.1
8:2 FtS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	76	18	3.6	2.6	<LOD	<LOD	<LOD	<LOD
10:2 FtS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	98	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	72	22	4.2	1.6	<LOD	<LOD	<LOD	<LOD
MeFBSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	75	20	5.1	<LOD	<LOD	<LOD	<LOD	<LOD
MeFHxSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	88	11	1.0	<LOD	80	15	5.2	<LOD
MeFHpSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	66	29	5.3	<LOD	80	17	2.6	<LOD
MeFOSAA	<LOD	<LOD	<LOD	<LOD	64	26	8.0	2.6	73	20	5.1	2.5	77	16	5.1	1.6
EtHxSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	63	30	5.0	2.2	66	23	7.4	3.5	77	18	4.1	0.4
6:2 DiPAP	<LOD	<LOD	<LOD	<LOD	59	35	5.0	1.3	81	15	2.9	0.6	84	13	2.2	0.7

Table 2.7. Accuracy (% Recovery), Precision (% RSD), and Limit of Detection and Quantification for Papers and Textiles

	Papers				Textiles			
	Recovery (%)	RSD (%)	LOD (µg/m^2)	LOQ (µg/m^2)	Recovery (%)	RSD (%)	LOD (µg/m^2)	LOQ (µg/m^2)
LC-MS/MS Analytes								
PFBA	74	5.9	0.056	0.18	87	4.2	0.066	0.21
PFPeA	110	8.4	0.052	0.17	90	5.8	0.066	0.22
PFHxA	78	12	0.059	0.20	89	4.1	0.029	0.091
PFHpA	97	11	0.039	0.13	87	7.8	0.081	0.26
PFOA	92	12	0.040	0.13	88	16	0.12	0.40
PFNA	92	4.8	0.028	0.089	88	4.4	0.081	0.26
PFDA	75	15	0.037	0.12	98	6.5	0.053	0.18
PFUdA	94	2.2	0.063	0.21	100	24	0.14	0.47
PFDoDA	79	6.5	0.024	0.076	93	5.1	0.029	0.096
PFTrDA	79	8.5	0.030	0.10	87	5.2	0.062	0.21
PFTeDA	73	12	0.035	0.11	85	7.1	0.066	0.21
FHEA	80	9.6	0.058	0.19	84	16	0.13	0.43
FOEA	120	9.1	0.052	0.17	96	6.8	0.12	0.38
FDEA	130	22	0.095	0.32	81	22	0.18	0.58
FHUEA	71	7.9	0.012	0.039	66	4.9	0.07	0.22
FOUEA	66	16.0	0.032	0.11	85	12	0.073	0.24
FPrPA	93	3.4	0.024	0.076	45	13	0.16	0.52
FPePA	70	6.5	0.03	0.11	54	2.4	0.086	0.28
FHpPa	69	11	0.034	0.11	80	3.4	0.093	0.31
PFBS	72	6.3	0.016	0.053	80	4.3	0.055	0.18
PFPeS	72	8.3	0.031	0.10	91	4.6	0.050	0.17
PFHxS	78	4.6	0.035	0.11	83	3.5	0.076	0.25
PFHpS	71	10	0.029	0.094	77	9.2	0.079	0.26
PFOS	90	15	0.038	0.12	92	3.0	0.15	0.48
PFNS	62	6.8	0.034	0.11	62	6.8	0.059	0.19
PFDS	72	6.2	0.027	0.090	68	9.1	0.054	0.17
4:2 FtS	71	4.8	0.028	0.092	90	3.8	0.048	0.16
6:2 FtS	76	2.9	0.019	0.063	94	5.6	0.044	0.14
8:2 FtS	120	6.5	0.016	0.055	86	4.8	0.039	0.13
FOSAA	36	5.3	0.023	0.077	170	5.9	0.029	0.096
MeFBSAA	74	8.4	0.021	0.069	87	4.3	0.082	0.27
MeFOSAA	78	5.5	0.025	0.084	100	1.6	0.047	0.15
EtFOSAA	77	6.0	0.010	0.034	87	2.3	0.045	0.15
6:6 PFPIA	42	3.1	0.016	0.053	76	4.4	0.044	0.15
8:8 PFPIA	46	11	0.022	0.070	54	12	0.080	0.26
6:2 diPAP	81	8.3	0.022	0.070	88	8.4	0.023	0.073
8:2 diPAP	120	17	0.070	0.23	110	15	0.056	0.18

Table 2.8. Known precursors % recovery (on a total nmole basis), number of perfluorinated carbons in chain, and distribution of carbon chain length after the TOP Assay (no paper or textile present).

Known Precursor	Mass recovered (%)	Number of perfluorinated carbons in precursor chain	Distribution of carbon PFCA chain length after oxidation
6:6PFPi	17	6	C5-C6
FOUEA	3.8	8	C5-C8
8:2 diPAP	45	8	C4-C9
FHUEA	41	6	C4-C7
6:2 FtS	36	6	C4-C7
6:2 diPAP	3.4	6	C5-C8
SAmPaP	0.0	8	none

Table 2.9. Concentrations ($\mu g/m^2$) of Individual Volatile and Ionic PFASs analyzed by GC-MS and LC-MS/MS.

Individual Ionic PFASs in $\mu g/m^2$

		Papers								Textiles								
	MW	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	9
Individual PFASs (Volatile)																		
6:2 FTOH	364.11	<LOD	<LOD	<LOD	<LOD	**18**	**14**	<LOD	<LOD	<LOD	**7.0**	**370**	<LOD	**2.1**	<LOD	**11**	**14000**	**130**
8:2 FTOH	464.12	**30**	**3.6**	<LOD	**9.1**	**16**	**12**	**25**	<LOD	**72**	**130**	**990**	**170**	**73**	**22**	**1300**	**340**	**170**
10:2 FTOH	564.13	**12**	<LOD	<LOD	<LOD	**15**	**3.0**	**10**	<LOD	**37**	**42**	**490**	**70**	**4.3**	<LOD	**330**	**140**	**110**
N-EtFOSE	571.25	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3100**
Individual Ionic PFASs (Non-Volatile)																		
PFBA	213.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**19**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.37**	**4.7**	**39**
PFPeA	263.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.25**	**7.0**	**14**
PFHxA	313.98	<LOD	<LOD	<LOD	<LOD	**0.27**	<LOQ	<LOD	**13**	<LOD	<LOD	**0.16**	<LOD	<LOQ	<LOD	**0.90**	**31**	**100**
PFHpA	363.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	**0.31**	**8.8**	**67**
PFOA	413.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	**0.45**	<LOD	**3.3**	<LOQ	**110**
PFNA	463.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	**0.23**	**0.93**	<LOQ	**0.17**	<LOQ	**0.24**	**7.5**
PFDA	513.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	**0.30**	**0.18**	**1.1**	<LOQ	**3.5**
PFUnDA	563.96	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.57**	<LOQ	<LOQ	<LOD	<LOD	**1.4**
PFDoDA	613.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.14**	<LOQ	**0.25**	<LOQ	**1.5**
PFTriDA	663.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	**1.8**
PFTeDA	713.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	**2.9**
PFPeDA	763.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	813.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.45**
PFHpDA	863.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOcDA	913.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.47**

FBEA	278.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHEA	377.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.8**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.82**	<LOD
FOEA	477.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.27**	**0.77**	<LOD	**0.32**	**0.59**	<LOQ	<LOQ
FDEA	577.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD
FBUEA	257.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHUEA	357.99	<LOD	<LOD	<LOD	<LOQ	**0.12**	<LOQ	<LOD	**4.1**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.2**	<LOD
FOUEA	457.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOD
FDUEA	557.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD
FPrPA	242.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FPePA	342.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHpPA	442.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FNPA	542.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtS	199.95	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	249.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.65**
PFBS	299.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**4.5**
PFPS	349.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.7**
PFHxS	399.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	**11**
PFHpS	449.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**6.3**
PFOS	499.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.69**	<LOD	<LOD	**190**
PFNS	549.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	599.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**4.2**
4:2 FtS	327.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
6:2 FtS	427.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**
8:2 FtS	527.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.49**
10:2 FtS	627.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
FBSAA	356.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FPeSAA	406.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

FHxSAA	456.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
FHpSAA	506.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	556.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**6.6**
MeFBSAA	370.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
MeFPeSAA	420.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFHxSAA	470.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.3**
MeFHpSAA	520.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1.8**
MeFOSAA	570.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**17**
EtFBSAA	385.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFPeSAA	435.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFHxSAA	485.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFHpSAA	534.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	584.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.71**
4:4 PFPiA	501.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:6 PFPiA	601.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:6 PFPiA	701.93	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:8 PFPiA	801.92	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:8 PFPiA	901.92	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 diPAP	590.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2/6:2 diPAP	689.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	789.98	<LOD	<LOD	<LOD	<LOD	<LOD	**0.17**	<LOQ	<LOD	<LOD	<LOD	<LOD	**0.31**	<LOD	<LOQ	<LOD	<LOD	**8.8**
6:2/8:2 diPAP	889.98	<LOQ	<LOQ	<LOD	<LOQ	<LOQ	**0.73**	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOQ	<LOD	<LOD	**0.43**
8:2 diPAP	989.97	<LOD	<LOD	<LOD	<LOD	<LOD	**0.35**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.9**
8:2/10:2 diPAP	1089.96	<LOD	<LOD	<LOD	<LOD	<LOQ	**0.31**	<LOQ	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**3.3**
10:2 diPAP	1189.96	<LOD	<LOQ	<LOD	<LOD	<LOD	**0.25**	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	**1.6**
6:2 FTMAP	921.99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	**1.1**
6:2/8:2 FTMAP	1021.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ

8:2 FTMAP	1121.98	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2/10:2 FTMAP	1221.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTMAP	1321.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
SAmPAP	1203.98	<LOQ	**0.39**	<LOD	<LOD	<LOD	<LOQ	**4.8**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ

<LOD=Less than limit of detection
<LOQ=Less than limit of quantification
Bolded number=above quantification

Table 2.10. Ionic PFASs after TOP assay, described as net production of PFCAs and PFSAs.

Net Production (Δ) of ionic PFASs after TOP Assay in µg/m^2

		Papers								Textiles								
	MW	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8[a]	9
PFBA	213.99	**0.81**	<LOD	**0.40**	<LOD	**42**	**29**	<LOD	**600**	<LOD	**6.8**	**40**	**2.5**	**2.8**	**1.8**	**6.1**	**16**	**781**
PFPeA	263.98	**2.2**	<LOD	**1.0**	<LOD	**100**	**70**	**1.8**	**1300**	**1.6**	**12**	**84**	**5.6**	**6.4**	**4.8**	**15**	**69**	**1186**
PFHxA	313.98	**0.23**	<LOQ	<LOQ	<LOD	**13**	**6.9**	**1.7**	**420**	**1.3**	**24**	**98**	**11**	**11**	**6.7**	**21**	**0.3**	**1900**
PFHpA	363.98	<LOQ	<LOD	<LOD	<LOD	**0.57**	**0.59**	<LOQ	**19**	**3.5**	**59**	**170**	**20**	**21**	**11**	**52**	**0.0**[b]	**1633**
PFOA	413.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	**1.9**	**17**	**43**	**6.9**	**7.8**	**5.9**	**22**	**0.54**	**14890**
PFNA	463.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.42**	<LOD	**1.5**	**22**	**41**	**4.1**	**11**	**6.1**	**20**	<LOD	**222**
PFDA	513.97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	**0.88**	**8.8**	**6.8**	**1.2**	**6.3**	**2.7**	**13**	**0.0**[b]	**47**
PFUnDA	563.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**6.5**	**0.82**	<LOQ	**4.4**	**2.2**	**7.5**	<LOD	NC[c]
PFDoDA	613.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.40**	**3.9**	<LOQ	<LOD	**2.8**	**1.1**	**6.6**	<LOD	**25**
PFTriDA	663.96	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**1.8**	<LOD	<LOD	**1.4**	**0.48**	**1.8**	<LOD	NC[c]
PFTeDA	713.95	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	**0.90**	<LOQ	<LOQ	<LOQ	**0.22**	**0.89**	<LOD	NC[c]
PFPeDA	763.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	NC[c]
PFHxDA	813.95	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.61**	<LOD	<LOD	**0.73**	**0.20**	**0.67**	<LOD	NC[c]
PFHpDA	863.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**0.22**	<LOD	<LOD	<LOD	<LOQ
PFOcDA	913.94	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOQ	**0.41**	<LOD	**0.23**	<LOD	NC[c]
PFOS	499.94	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**160**
Σ PFASs nmol F/m^2		**0.011**	**<LOQ**	**0.0046**	**<LOQ**	**0.53**	**0.36**	**0.014**	**7.8**	**0.040**	**0.58**	**1.7**	**0.18**	**0.27**	**0.15**	**0.59**	**0.28**	**73**

[a] Textile 8 had 2.2% non-converted PFASs after TOP assay (not shown).

[b] The quantity of PFHpA and PFDA showed no net production (Δ), and remained the same.

[c] Due to larger dilutions done for the TOP assay analysis, these values fell below the LOQ and no net value could be computed (NC= not computed).

Table 2.10 (Continued)

<LOD=less than the limit of detection
<LOQ=less than the limit of quantification
MW=Molecular weight

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Chapter 3: Much Ado About (Almost) Nothing: Field Sampling Materials Unlikely Source of False Positives for Per- and Polyfluoroalkyl Substances in Field Samples

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Abstract

Per-and Polyfluoroalkyl substances (PFASs) are used in numerous applications, including consumer products, oil and water repellents, and aqueous film-forming foams (AFFF). Repeat use of AFFF containing PFAS for fire-fighter training since the 1960s has resulted in a large number of military sites that are now impacted by PFASs, including perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). Given the low EPA Drinking Water Health Advisory Value of 70 ng/L for PFOS and PFOA, it is imperative that activities related to collecting and shipping samples not contribute to measurable levels of PFOS, PFOA, or other PFAS in water samples. Both the Air Force and Navy offer guidance on sampling, but there are few data to support the selection of materials for sampling and shipping of water and soil/sediment samples. Many state and federal agencies in the US and abroad offer guidance on the selection of materials for sampling and shipping of water and soil/sediment samples, but few data actually exist to support the guidance, especially the numerous restrictions placed on materials and equipment used. In order to address the lack of data and to inform the selection and use of materials during field sampling, 66 materials used during four stages of groundwater sample collection were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) for 52 individual PFAS commonly found at AFFF-contaminated sites and for total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy. Only 15% of materials had quantifiable concentrations of PFASs by LC-MS/MS, whereas 35% of the materials were fluorinated, as indicated by PIGE. Given the nature of the materials that tested positive for PFAS, the low

concentrations present and the manner in which the materials are used in the field, no plausible scenarios support the potential for cross-contamination of groundwater, soil, and sediment from field sampling materials tested in this study.

Introduction

The occurrence of per- and polyfluoroalkyl substances (PFAS) in water sources used for drinking water[1, 2] combined with toxicity evaluations, resulted in issuance of US EPA drinking water lifetime Health Advisory Levels (HAL) of 70 ng/L.[3] California recently announced a Notification Levels for drinking water of 6.5 and 5.1 ng/L for PFOs and PFOA, respectively.[4] The U.S. EPA's HAL and California's notification Limits are two orders of magnitude lower than the maximum contaminant levels (MCLs) for other common environmental contaminants (e.g., benzene 5,000 ng/L and vinyl chloride 2,000 ng/L)[3-5]. Given that ng/L concentrations are very low, combined with the ubiquitous nature of PFAS in our society from widespread usage, it is imperative to avoid creating false positives when collecting field samples, since detection of PFAS potentially has significant consequences for facility owners, the public, and other stakeholders.

Field sampling materials, especially fluorinated materials (e.g. comprised of polytetrafluoroethylene), can cause concern for false positives. For these reasons, many materials are listed as prohibited materials in guidance documents published by federal and civilian organizations, including the Navy,[6] Army,[7] and Australian organizations/entities including (CRCCare)[8], as well as civilian organizations

(NGWA).[9] However, to the best of our knowledge, the materials identified in guidance documents for exclusion are not based on published analytical data. Although there are data on PFASs associated with consumer products (e.g. papers, textiles),[10-19]}, few if any published data document PFAS on materials used in the field. Restrictions on sampling equipment (e.g., membrane interface probes (MIPs)) and materials including reusable ice packs, water-repellent field notebooks, indelible markers, sticky notes, and others increase the cost, time, and difficulty of sampling, yet with unknown benefit. Further, many materials that are prohibited from use in the field have no known direct contact with groundwater, sediment, or soil samples. Although an industry-standard level of care should keep most of those materials from ever contacting the sampled media, it is important to determine if materials that have quantifiable PFAS concentrations can realistically pose a risk for cross-contaminating field samples.

In this study, 66 materials associated with field sampling were collected between 2016 and 2019 and analyzed for 52 PFASs observed in AFFF impacted groundwater by liquid chromatography tandem mass spectrometry (LC-MS/MS), and for total fluorine by particle-induced gamma-ray emission (PIGE) spectroscopy. The materials tested include those representative of materials used during the four stages of sample collection: Group 1: used by field personnel prior to arriving at a field site, but that do not come in direct contact with samples; Group 2: used in the field during sampling or for staging a sampling event, but do not come in direct contact with samples; Group 3: used in the field and come in direct contact with field samples; and

Group 4: used in the field for shipping, but that do not come in direct contact with field samples. Materials were extracted with methanol to obtain the maximum PFAS concentration associated with a material. Materials with PFAS were then considered in the context of their use in the field to determine if they pose a risk for cross-contaminating samples. The situation is analogous to human exposure; a pathway must exist for the contaminant to reach the receptor (field sample) to conclude that the source (field sampling material) can actually contribute to exposure (e.g., cross contamination).

Experimental Method

Field Materials Selection and Extraction

Field sampling and related materials were selected based upon the authors' knowledge of materials commonly used during field sampling campaigns. A total of 66 materials were collected by Oregon State University and the University of Notre Dame between 2016-2019 (Table 3.1, Table 3.2). Of those, 11 materials used for sampling of soils and sediments (Sample ID: 41-51, Table 3.1) were donated by Geoprobe Systems and shipped to Oregon State University.

During all sample handling, nitrile gloves were worn and changed between all samples. Swatches or larger sections of each material were cut from the original material using methanol-rinsed scissors and distributed into resealable PTFE-free plastic bags. Although no field blanks were collected, some samples collected by all participating organizations (Oregon State University, University of Notre Dame, and

Geoprobe) were ND for all PFASs, indicating no PFAS contamination occurred during sample collection and shipping.

For dense plastic materials (Sample ID: 41-48, 50, 51), stainless steel cutters were used and methanol-rinsed between materials. Except for dense plastics, inks, and sealants, the sample mass was required to be 0.3 ± 0.25 g. For permanent ink from markers, a piece of copy paper known to ND for all analytes of interest was saturated with ink until the paper weighed an additional 0.3 ± 0.25 g. For the three sealants, a mass of 0.3 ± 0.25 g was weighed onto a piece of copy paper known to be ND for all analytes of interest, and allowed to dry before extraction. For dense plastics, surface area was used as the basis for sample preparation, and required to fall between 4.0 ± 0.5 cm^2. Both mass and surface area were recorded for all materials to capture differences in density and to report data in units of $\mu g/m^2$. All cut materials were place into individual 15 mL polypropylene (PP) centrifuge tubes (VWR, Radnor, PA).

Materials were extracted as in Robel et al.[11] Briefly, 3.3 mL of heated methanol (60−65 °C) were added to the 15 mL polypropylene (PP) centrifuge tube, shaken on a wrist-action shaker at 10° of rotation (Burrell, Model 75, Pittsburgh, PA) for 10 min, and then centrifuged (Eppendorf, model 5810R, Hauppauge, NY) at 2808 g for 10 min. The supernatant was collected in a secondary centrifuge tube, and the process was repeated two additional times yielding roughly 7-9.9 mL total methanol and stored at -20 °C. After at least 24 h, all extracts were removed from -20 °C, immediately centrifuged for an additional 10 min at 2808 g. The final supernatant was transferred to a 10 mL volumetric flask and brought to volume with additional methanol and then stored in 15 mL PP centrifuge tubes. Extracts were prepared for analysis as follows: 60 μL aliquots of extract were placed in PP autosampler vials, each spiked with 0.72 ng of all isotopically labeled standards (Table 3.2), and brought to a final volume of 1.5 mL with additional methanol.

Instrumental Analysis

LC-MS/MS

Extracts were analyzed by LC-MS/MS using two Zorbax DIOL guard columns (4.6 mm x 12.5 mm x 6 µm; Agilent, Santa Clara, CA), one Zorbax SIL guard column (4.6 mm x 12.5 mm x 6 µm; Agilent, Santa Clara, CA), and a Zorbax Eclipse Plus C18 analytical column (4.6 mm x 75 mm x 1.8 µm, Agilent, Santa Clara, CA) with an Agilent 1100 HPLC attached to a Triple-Quadrupole Detector MS/MS system (Waters Corporation Milford, MA). The injection volume for all extracts was 900 μL. The LC-MS/MS operating specifications were identical to those found in Robel et al.[11]

Analyte identification and quantification, data quality tiers (quantitative, Qn; qualitative (Ql), and semi-quantitative (Sq)), and the process for generating whole method blanks and solvent blank are described in Robel et al (Table 3.2).[11] All process blanks and solvent blanks were required to fall below ½ LOQ. Analytical sequences contained a 5-7-point calibration curve over the linear range 10−10,000 ng/L, with the exception of 6:2 and 8:2 FTS, which gave a linear range of 10−5000 ng/L. Whole method recovery and precision (RSD) for the Qn PFAS ranged from 62 - 130 % and 2.2 - 16%, respectively.[11] Recovery of PFAS in the Ql data tier PFAS (Table 3.2; e.g. N-TAmP-FHxSA, 6:2 FtSAB) have not been determined because analytical standards are not commercially available. Instrumental LOQs were set as the lowest calibration standard, 0.45 μg/m^2 for all analytes except for FOSA which was 2.2 μg/m^2 for the 66 materials analyzed. The instrumental limit of detection (ND), was determined to be 3x less than the LOQ (0.15 μg/m^2 for all analytes except for FOSA which was 0.75 μg/m^2).

PIGE

All materials were cut to a 2 x 2 cm^2 and adhered to an open-air stainless steel target ladder frame with a 1 cm^2 hole in the center using clear adhesive tape.[18] For the three sealants, (Sample ID # 38-40, Table 3.1) 500 mg of each sealant was spread over pre-cut 2 x 2 cm^2 of copier paper (previously determined to be ND for total fluorine) with a methanol-washed spatula and then mounted to the stainless steel target ladder frame as above. For materials known to contain very high concentrations of total fluorine or be made of PTFE, a thin strip (< 2x2 cm^2) was cut from the original material and mounted. PIGE analyses were performed as in Ritter et al.[18] and Robel et al.[11] with a ND and LOQ of 2500 µg F/m^2 and 8000 µg F/m^2 for papers and dense plastics.

For each day of PIGE analysis performed, a series of inorganic sodium fluoride (Sigma Aldrich) standards mixed with cellulose nitrate powder (Sigma Aldrich) were also analyzed to give a calibration curve relating the signal sensitivity to external standards. Normalization between different days was performed by normalizing the data to this calibration curve for each day. The calibration curve was linear in each case, but the slope varies by a few percent typically depending on the beam delivery parameters of the particular day of analysis. Roughly 10% of the materials were analyzed in duplicate and gave <10 % difference in concentration.

Results and Discussion

PFAS Composition and Concentration

Although 52 PFASs were included in analysis (Table 3.2), only 12 PFAS were observed at concentrations ≥LOQ (Table 3.1). The total fluorine concentration range of all materials was ND to 56,000,000 ± 11,000,000 µgF/m^2. Only 10 out of 66 (15%) materials gave quantifiable (> LOQ) concentrations of individual PFASs, while 23 out of 66 (35%) of the materials gave quantifiable levels of total fluorine by PIGE. The difference between the total fluorine and the sum of individual PFAS obtained by methanol extraction is likely a result of the presence of fluorinated polymers.[11, 20]

The concentrations of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates obtained by methanol extraction and total fluorine by PIGE were within the range observed by others.[10, 11, 14, 18, 19, 21] Even though leaching by water is documented for select materials, [22] there must be direct contact between the field material and water sample as well as sufficient time for PFAS transfer from the material to achieve cross contamination by a leaching mechanism. In addition, leaching is likely impacted by a number of factors including temperature, time, and water chemistry. For this reason, extraction with methanol was selected to obtain the maximum PFAS concentration(s) associated with a material. The maximum concentrations are then used with simplifying assumptions to examine the plausibility of cross contaminating field samples.

Group 1 is composed of five materials that are potentially used by field personnel prior to arriving at a field site, but that do not come in direct contact with samples. The dryer sheets were of specific interest since guidance documents indicate that no personal care products, including dryer sheets should be used by field personnel.[4, 6-8, 23, 24] The three dryer sheets were ND for PFAS and total fluorine. The packaging of the first-aid bandage gave quantifiable PFHxA. In contrast, the wrapper around the bandage gave the greatest number (six) of PFAS. Four PFCAs (PFBA, PFHxA, PFHpA, and PFOA) were present as a homologous series with branched and linear isomers evident for PFHpA and PFOA, (Table 3.1) which indicates manufacture by electrochemical fluorination (ECF).[25] In addition, PFBS and branched and linear PFOS were observed, again consistent with ECF chemistry. The First Aid bandage packaging and wrapper also gave measurable concentrations of total fluorine by PIGE. Although the first aid bandage materials in Group 1 tested positive for PFAS, there is no direct pathway for the material to come in direct contact with samples since field personnel wear gloves during sampling and shipping. Implausibly, one would have to put an entire bandage wrapper *directly* into a 1 L water sample and the PFOS could have to completely desorb in order to reach a maximum PFOS concentration of 27.5 ng/L.

Group 2 includes 24 materials that are used in the field when staging a sampling event, but are not used when actively sampling and thus, do not come in direct contact with samples. Materials in this group included PTFE tape, aluminum foil, lab tissues, labels, paper towels, various papers, adhesive note pads, and plastic shovel packaging. Six materials in Group 2 gave concentrations >LOQ for PFAS, while eight gave total fluorine >LOQ (Table 3.1). Both PTFE tape 1 and 2 had very high total fluorine, which was off scale in the case of PTFE tape 2. In contrast, PTFE tape 1 gave no PFAS >LOQ and PTFE tape 2 gave PFOA (4.4 $\mu g/m^2$) and <LOQ for PFDA and PFOS (Table 3.1). Of the three aluminum foils tested, only the non-stick aluminum foil had detectable PFAS with PFOA (27 $\mu g/m^2$) and PFBS (4.5 $\mu g/m^2$). However, the non-stick aluminum foil was <LOQ total fluorine, which indicates that the PFAS concentration was too low to be quantified by PIGE. The other two aluminum foils were ND for PFAS and ND for total fluorine.

Of the four lab tissues and packaging products tested, only tissue 3 gave a detectable PFAS concentration of 1.7 $\mu g/m^2$ PFBS (Table 3.1). Tissues 1 and 3 and the tissue packaging gave <LOQ total fluorine (Table 3.1). Only one label backing, which is a portion of the non-stick sheet beneath the label, had the only 6:2 and 8:2

FTSs detected in this study (Table 3.1). In contrast, all four label materials tested positive (≥LOQ) for total fluorine by PIGE (Table 3.1). Although FTSs are typically observed in AFFF impacted groundwater,[26-31] FTSs were previously reported papers and textiles before. [10, 11, 15, 32, 33] Three of four paper towel materials had either quantifiable PFOS (4.9 µg/m^2; Paper towel 1) or < LOQ PFOS (Table 3.1), and three of the four were <LOQ for total fluorine (Table 3.1). All 3 of these paper towel types were advertised as having some measure of "recycled content", which could contribute to PFAS content in the product.[11, 20] Paper towels, specifically listed as containing recycled content or that are chemically treated are listed on some guidance documents.[23]

While the waterproof paper was ND or <LOQ for PFAS, the lab notebook paper had measurable concentrations of PFHxA (1.4 µg/m^2) and PFOS (3.8 µg/m^2), but was <LOQ for PFHpA, PFOA, and PFHxS and ND for all others (Table 3.1). Finally, the plastic shovel packaging material was ND for PFAS but gave the measured highest concentration of total fluorine by PIGE in Group 2 (370,000 ± 45,000 µg F/m^2) and the third highest of any material, second only to the PTFE tapes.

In terms of current sampling guidance, PTFE tape, waterproof notebook, lab notebook paper, and plastic binder covers are all listed as prohibited items on guidance documents.[4, 6-8, 23, 24] As indicated for Group 2, none of the materials (e.g., paper towel, bound notebook paper, lab tissues, and aluminum foil) are likely to come into direct contact with groundwater, sediment, or soil samples. Thus, while it remains prudent to exclude material manufactured with PTFE, the data do not support the exclusion of Group 2 materials during field sampling for PFAS.

Group 3 materials are used in the field and come in direct contact with groundwater or soil/sediment when sampling. Materials in Group 3 included nitrile gloves (and glove packaging), sealants used in well development, and soil sampling materials. Of the 22 materials tested, only nitrile glove 6 had a quantifiable (5 $\mu g/m^2$) concentration of N-TAmP-FPeSA, but was ND for total fluorine (Table 3.1). In contrast, the packaging of nitrile glove 1 and 2 had total fluorine but either ND or <LOQ for PFAS (Table 3.1).

Because N-TAmP-FPeSA is present in both branched and linear forms, it derives from electrofluorination chemistry. It is not known if N-TAmP-FPeSA is a chemical in commerce or an unintended product of PFAS or fluoropolymer production. Evidence for N-TAmP-FPeSA in nitrile gloves indicates that it may be a chemical in commerce and occur in other consumer products. To the best of our knowledge, N-TAmP-FPePA has been observed in AFFF impacted groundwater,[28] but this is the first report of N-TAmP-FPePA in consumer products.

The well sealants and all but three soil sampling materials were all ND for PFAS. The three materials used for soil and sediment that gave <LOQ for some PFAS included the PVC screen, MIP membrane, and PVC liner (Table 3.1). In contrast, eight of the 11 materials for soil and sediment sampling were positive for

total fluorine and the MIP membrane, which is constructed of PTFE material, gave total fluorine that was off scale (Table 3.1).

Guidance documents[34] recommend frequent changing of gloves in the field to minimize PFAS contamination. This recommendation is prudent, not because nitrile gloves have background PFAS (Table 3.1), but because they may come in direct contact with one or more field samples and have the potential to transfer PFAS from one sample to another. Of the materials included in Group 3, only the MIP, which is constructed of PTFE, is prohibited materials on guidance documents.[4, 6-8, 23, 24] However, none of the materials in Group 3 have concentrations for the commonly measured PFAS that are >LOQ. Thus, while the materials potentially come in direct contact with field samples, they are unlikely to impact measured PFAS concentrations in field samples.

Group 4 materials are used in the field and are externally applied to or surround sample containers and include: elastic sealing film, permanent marker ink, plastic bags, various tapes, and reusable cold packs. Of the 15 materials tested, only two gave quantitative concentrations of PFAS (83 $\mu g/m^2$ PFOA in marker ink 2 and 0.77 $\mu g/m^2$ PFBS in duct tape 2; Table 3.1), and five materials gave quantitative concentrations of total fluorine (Table 3.1).

None of the Group 4 materials come in *direct* contact with groundwater, soil, or sediment samples. To examine the potential for cross contamination, reusable cold packs were selected as an example because they are convenient, reusable, and are more "green" than packing non-reusable plastic bags with ice. Despite the positive attributes, reusable cold packs are listed.[4, 6, 7, 23] as prohibited items in guidance documents. Among the Group 4 materials, all five cold packs were either ND or <LOQ for PFAS. The plausibility of cross contaminating a water sample with cold pack number 3 (Table 3.1), which was <LOQ for PFOA, was estimated. An assumed concentration equivalent to ½ of the LOQ (0.225 $\mu g/m^2$) was multiplied by the estimated area of a typical cold pack (e.g., $15x15\ cm^2$ for each of two sides), which gave a maximum of 0.0103 µg PFOA. If the entire cold pack was placed *directly into* the one liter of water sample, and all the PFOA transferred, a maximum concentration of 10.3 ng/L PFOA would be achieved. Not only is this an implausible scenario, but when cold packs are used in field shipping coolers, excess water that could serve as a transfer medium is negligible. Furthermore, guidance documents indicate that sample containers should be shipped in secondary containment (e.g., plastic bag) before being placed in coolers.[4, 6, 7, 23] Thus, there are no direct exposure pathways by which cold packs that are applied externally to or surround sample containers can plausibly cross contaminate water samples. Such arguments can be applied to all Group 4 materials and to the implausibility of them contaminating sediment and soil samples.

Conclusions

Materials utilized by personnel before going to the field or used in the field for sampling and shipping should be selected and utilized with care. It remains prudent to avoid materials that are clearly labeled as made of PFTE or labeled as having non-stick properties. However, for materials in Groups 1, 2, and 4 that are ND or <LOQ for PFAS, there are no plausible routes of exposure to support published sampling guidance documents that prohibit these materials from use.

Of the ten materials that >LOQ for individual PFAS, three (30%) were packaging and of 25 materials that gave >LOQ total fluorine, six materials (24%) were packaging. Thus, while only food packaging is addressed in guidance documents, packaging as a whole is not addressed and represents a fraction of materials used at field sites that have associated PFAS. However, as illustrated, handling of packaging in the field is unlikely to result in false positives for PFAS in field samples.

Nine out of 11 materials that tested positive for individual PFAS were also positive for total fluorine by PIGE, which indicates that PFAS are associated with fluorinated materials. Only two materials that tested positive for PFAS did not give total fluorine above the ND (2,500 µg F/m^2), which is higher than the ND of LC-MS/MS (0.14 µg/m^2). Thus, it is possible to have detectable PFAS on materials that are too low to be detected by PIGE. Despite its relative ease and lower cost, PIGE gave a higher frequency of detection among the field materials, which indicates that total fluorine is not a surrogate for individual PFAS that can be potentially transferred to field samples. However, it is possible that even with 52 analytes in the LC-MS/MS analysis used in this study, more PFASs were present in the materials but not captured. Non-target analysis by LC-high resolution mass spectrometry could potentially reveal other PFASs present in field sampling materials, but was outside of the scope of this study.

Although C8 chain length PFAS were voluntarily phased out[35] prior the purchase of the materials in this study which were purchased between 2016 and 2019, C8 chain lengths in the form of PFOA, PFOS, and 8:2 FTS (Table1) occurred in seven out of the ten materials that were >LOQ for individual PFAS. Three materials had PFAS generated by ECF chemistry as indicated by branched and linear PFOS and PFCAs, including PFHpA and PFOA. It is unclear if the ECF and C8 PFAS are due to materials that were produced prior to the 3M and C8 Stewardship phase outs but not sold until 2016-2019, or the result of imported material from countries still employing ECF and C8 chemistry or the inclusion of older recycled content.

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Table 3.1. Concentrations of individual PFASs in µg/m^2 and PIGE values in ug F/m^2 for field materials with **branched, linear** values separated when applicable (one number indicates all linear or for PFBA, PFPeA, and PFBS a lack of analytical separation between branched/linear). Bolded field material **Descriptions** indicate materials listed on a field sampling guidance document.[4, 6, 7, 23]

	Sample ID	Description	PFBA	PFHxA	PFHpA	PFOA	PFDA	PFPrS	PFBS	PFHxS	PFOS	6:2 FtS	8:2 FtS	N-TAmP-	PIGE
Group 1: Pre-staging	1	**Dryer sheet 1**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2	**Dryer sheet 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	3	**Dryer sheet3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	4	First Aid packaging	ND	**6**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	120000 ± 41000
	5	First Aid adhesive wrapper*	**0.88**	**0.68**	**0.22, 0.40**	**0.09, 3.9**	ND	ND	**1.1**	ND	**0.19, 0.32**	ND	ND	ND	660000 ± 83000
Group 2: Staging	6	**PTFE tape 1**	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	56000000 ± 11000000
	7	**PTFE tape 2**	ND	ND	ND	**4.4**	**<LOQ**	ND	ND	ND	**<LOQ**	ND	ND	ND	####
	8	**Aluminum foil 1 (non-stick)**	ND	ND	ND	**27**	ND	ND	**4.5**	ND	ND	ND	ND	ND	<LOQ
	9	**Aluminum foil 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	10	**Aluminum foil 3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11	Lab tissue 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	12	Lab tissue 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	13	Lab tissue 3	ND	ND	ND	ND	ND	ND	**1.7**	ND	ND	ND	ND	ND	<LOQ
	14	Lab tissue 4	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15	Lab tissue packaging	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ

	16	Label backing 1	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	ND	ND	**2.7**	**5.7**	ND	63000 ± 13000
	17	Label backing 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	18	Label 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28000 ± 5400
	19	Label 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	22000 ± 5200
	20	**Paper towel adhesive**	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	<LOQ
	21	**Paper towel 1**	ND	ND	ND	ND	ND	ND	ND	ND	**1.1, 3.8**	ND	ND	ND	<LOQ
	22	**Paper towel 2**	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	<LOQ
	23	**Paper towel 3**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	24	**Water-proof notepaper**	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	16000 ± 3500
	25	**Lab notebook**	ND	**1.4**	**<LOQ**	**<LOQ**	ND	ND	ND	**<LOQ**	**2.2, 1.7**	ND	ND	ND	57000 ± 10000
	26	**Adhesive notepad 1**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	27	**Adhesive notepad 2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ
	28	**Binder plastic cover**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	29	Plastic shovel packaging	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	370000 ± 45000
Group 3:	30	Nitrile glove 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	31	Nitrile glove 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

	32	Nitrile glove 3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	33	Nitrile glove 4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	34	Nitrile glove 5	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	35	Nitrile glove 6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**5**	ND
	36	Nitrile glove 1 packaging	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	160000 ± 33000
	37	Nitrile glove 2 packaging	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	ND	270000 ± 95000
	38	putty caulk	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	39	clear resin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	40	white glue	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	41	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10000 ± 3300
	42	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10000 ± 2900
	43	core catcher	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16000 ± 4100
	44	vinyl end caps	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16000 ± 3800
	45	Core catcher liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10000 ± 3100
	46	PVC liner	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16000 ± 4200
	47	PVC screen	ND	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	28000 ± 6200
	48	Polyethylene bladder	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	49	Core bag	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	50	**MIP Membrane**	ND	ND	ND	**<LOQ**	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	***
	51	PVC liner	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND
Grou-	52	Elastic sealing film	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

53	**Marker ink 1 (permanent) 1**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	**Marker ink 2 (permanent)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16000 ± 5700
55	**Marker ink 3 (permanent)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
56	Plastic bag 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	Plastic bag 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	Tape 1 (electrical)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10000 ± 3300
59	Tape 2 (duct)	ND	ND	ND	ND	ND	ND	**0.77**	ND	ND	ND	ND	ND	ND
60	Tape 3 (duct)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
61	Tape 4 (duct)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
62	**Cold pack 1 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	250000 ± 33000
63	**Cold pack 2 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
64	**Cold pack 3 (outside)**	ND	ND	**<LOQ**	ND	ND	ND	ND	ND	ND	ND	ND	ND	87000 ± 13000
65	**Cold pack 4 (outside)**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
66	**Cold pack 5 (outside)**	ND	ND	ND	ND	ND	ND	ND	**<LOQ**	ND	ND	ND	ND	81000 ± 12000
	LOQ	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	8000

* material density is lower than the average material density used to calculate the LOQ, thus the LOQ for this material is 0.22 μg/m^2
The concentration of F was too high to measure by PIGE.
ND=Below the limit of detection. <LOQ=below the limit of quantification.

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Supporting Information
Much Ado About (Almost) Nothing: Field Sampling Materials Unlikely Source of False Positives for Per and Polyfluoroalkyl Substances in Field Samples

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Experimental Methods

Table 3.2. Material origin from Oregon State University (OSU), University of Notre Dame (UND), or Geoprobe Systems® (GP).

	Sample ID	Description	Origin
Group 1: Pre-Staging	1	Dryer sheet type 1	OSU
	2	Dryer sheet type 2	OSU
	3	Dryer sheet type 3	UND
	4	First Aid cardboard packaging	UND
	5	First Aid adhesive wrapper	UND
Group 2: Staging	6	PTFE tape type 1	OSU
	7	PTFE tape type 2	OSU
	8	Foil type 1 (non-stick, aluminum)	UND
	9	Foil type 2	OSU
	10	Foil type 3	OSU
	11	Lab tissue wipe type 1	UND
	12	Lab tissue wipe type 2	OSU
	13	Lab tissue wipe type 3	UND
	14	Lab tissue wipe type 4	OSU
	15	Lab tissue wipe packaging	UND
	16	Label backing type 1	OSU
	17	Label backing type 2	UND
	18	Sticker label type 1	OSU
	19	Sticker label type 2	UND
	20	Paper towel adhesive	UND
	21	Paper towel type 1	UND
	22	Paper towel type 2	UND
	23	Paper towel type 3	UND
	24	Water-proof notepaper (bound)	OSU
	25	Lab notebook page (bound)	OSU
	26	Adhesive notepad type 1	UND
	27	Adhesive notepad type 2	UND
	28	Binder plastic (outside cover)	UND
	29	Plastic shovel plastic packaging	UND
Group	30	Nitrile glove type 1	OSU

	31	Nitrile glove type 2	OSU
	32	Nitrile glove type 3	OSU
	33	Nitrile glove type 4	UND
	34	Nitrile glove type 5	UND
	35	Nitrile glove type 6	UND
	36	Nitrile glove packaging type 1	UND
	37	Nitrile glove packaging type 2	UND
	38	putty caulk	UND
	39	clear resin	UND
	40	white glue	UND
	41	PVC liner 48”	GP*
	42	PVC liner 48”	GP*
	43	core catcher	GP*
	44	vinyl end caps	GP*
	45	Core catcher liner	GP*
	46	PVC liner 60”	GP*
	47	PVC screen	GP*
	48	Polyethylene bladder	GP*
	49	Core bag 8”	GP
	50	MIP Membrane	GP*
	51	PVC liner	GP*
Group 4: Shipping	52	Laboratory film	OSU
	53	Marker ink (permanent) type 1	UND
	54	Marker ink (permanent) type 2	UND
	55	Marker ink (permanent) type 3	UND
	56	Plastic bag type 1	UND
	57	Plastic bag type 2	UND
	58	Tape (electrical) type 1	OSU
	59	Tape (duct) type 2	UND
	60	Tape (duct) type 3	UND
	61	Tape (duct) type 4	UND
	62	Cold pack (outside) type 1	OSU
	63	Cold pack (outside) type 2	OSU
	64	Cold pack (outside) type 3	OSU

65	Cold pack (outside) type 4	OSU
66	Freezer pack packaging 5	OSU

*Indicates materials considered dense plastics.

Table 3.3. LC-MS/MS target analyte full name, acronym, acquisition masses and parameters, internal standard, calibration reference, and data quality.

Analyte	Acronym	PI* (m/z)	CV* (V)	FI-1* (m/z)	CE* (eV)	FI-2* (m/z)	CE* (eV)	Internal Standard	Calibration Reference	Data Quality*
Perfluorobutanoic acid	PFBA	213	20	169	8	n/a	n/a	$[^{13}C_4]$PFBA	PFBA	Qn
Perfluoropentanoic acid	PFPeA	263	20	219	8	n/a	n/a	$[^{13}C_3]$PFPeA	PFPeA	Qn
Perfluorohexanoic acid	PFHxA	313	20	269	8	119	22	$[^{13}C_2]$PFHxA	PFHxA	Qn
Perfluoroheptanoic acid	PFHpA	363	20	319	8	169	14	$[^{13}C_4]$PFOA	PFHpA	Ql
Perfluorooctanoic acid	PFOA	413	20	369	8	169	18	$[^{13}C_4]$PFOA	PFOA	Qn
Perfluorononaoic acid	PFNA	463	22	429	8	169	18	$[^{13}C_5]$PFNA	PFNA	Qn
Perfluorodecanoic acid	PFDA	513	22	469	10	269	18	$[^{13}C_2]$PFDA	PFDA	Qn
Perfluoroundecanoic acid	PFUnDA	563	22	519	10	169	22	$[^{13}C_2]$PFUnDA	PFUnDA	Qn
Perfluorododecanoic acid	PFDoDA	613	22	569	10	169	24	$[^{13}C_2]$PFDoDA	PFDoDA	Qn
Perfluorortridecanoic acid	PFTriDA	663	24	619	12	169	26	$[^{13}C_2]$PFDoDA	PFTriDA	Ql
Perfluorotetradecanoic acid	PFTeDA	713	24	669	12	169	26	$[^{13}C_2]$PFDoDA	PFTeDA	Ql
N-sulfo propyl perfluorobutane sulfonamide	SPr-FBSA	420	40	78	22	298	28	$[^{13}C_4]$PFOA	PFOA	Sq
N-sulfo propyl perfluoropentane sulfonamide	SPr-FPeSA	470	40	78	22	348	28	$[^{13}C_4]$PFOA	PFOA	Sq
N-sulfo propyl perfluorohexane sulfonamide	SPr-FHxSA	520	40	78	30	398	30	$[^{13}C_4]$PFOA	PFOA	Sq
Perfluoropropane sulfonate	PFPrS	249	46	80	32	99	26	$[^{18}O_2]$PFBS	PFPrS	Ql
Perfluorobutane sulfonate	PFBS	299	50	80	32	99	26	$[^{18}O_2]$PFBS	PFBS	Qn
Perfluoropentane sulfonate	PFPeS	349	56	80	34	99	28	$[^{18}O_2]$PFHxS	PFHxS	Ql
Branched Perfluorohexane sulfonate	Br-PFHxS	399	58	80	36	99	28	$[^{18}O_2]$PFHxS	PFHxS	Qn
Perfluorheptane sulfonate	PFHpS	449	64	80	46	99	32	$[^{13}C_2]$PFOS	PFOS	Ql
Branched Perfluorooctanesulfonic acid	Br-PFOS	499	70	80	46	99	34	$[^{13}C_2]$PFOS	PFOS	Qn
Perfluorononane sulfonate	PFNS	549	72	80	50	99	36	$[^{13}C_2]$PFOS	PFDS	Ql
Perfluorodecane sulfonate	PFDS	599	76	80	52	99	36	$[^{13}C_2]$PFOS	PFDS	Ql
4:2 fluorotelomer sulfonate	4:2 FTS	327	42	307	19	81	26	$[^{13}C_2]$ 4:2 FtS	4:2 FTS	Qn
6:2 fluorotelomer sulfonate	6:2 FTS	427	40	407	22	81	28	$[^{13}C_2]$ 6:2 FtS	6:2 FTS	Qn

8:2 fluorotelomer sulfonate	8:2 FTS	527	45	507	25	81	32	[$^{13}C_2$] PFDA	8:2 FTS	Qn
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaB	571	78	104	28	58	38	M-PFOS	6:2 FtSaB	Sq
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaAm	513	60	58	44	86	34	M-PFOS	PFOS	Sq
Perfluoropropane sulfonamide	FPrSA	248	40	78	32	119	26	M-PFBS	PFBS	Sq
Perfluorobutane sulfonamide	FBSA	298	50	119	26	78	32	M-PFBS	PFBS	Sq
Perfluoropentane sulfonamide	FPeSA	348	40	78	35	119	35	M-FOSA	FOSA	Sq
Perfluorohexane sulfonamide	FHxSA	398	58	78	36	119	28	M-FOSA	FHxSA	Ql
Perfluorooctane sulfonamide	FOSA	498	40	78	30	319	30	M-FOSA	FOSA	Qn
Perluorobutane sulfinate	PFBSi	283	50	83	32	119	26	M-PFBS	PFBS	Sq
Perfluoropentane sulfinate	PFPeSi	333	40	83	35	119	35	M-PFPeA	PFPeA	Sq
Perfluorohexane sulfinate	PFHxSi	383	20	319	40	83	40	M-PFHxA	PFHxA	Sq
Perfluorooctane sulfinate	PFOSi	483	40	119	40	419	40	M-PFOA	PFOA	Sq
6:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	6:2 FTSO2PrAd-DiMeEtS	618	40	203	30	152	30	M-PFOA	PFOA	Sq
8:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	8:2 FTSO2PrAd-DiMeEtS	718	40	206	30	152	30	M-PFOA	PFOA	Sq
N-sulfo propyl dimethyl ammonio propyl perfluorobutane sulfonamide	SPrAmPr-FBSA	507	40	383	40	182	40	M-FOSA	FOSA	Sq
N-sulfo propyl dimethyl ammonio propyl perfluoropentane sulfonamide	SPrAmPr-FPeSA	557	40	433	40	182	40	M-FOSA	FOSA	Sq
N-sulfo propyl dimethyl ammonio propyl perfluorohexane sulfonamide	SPrAmPr-FHxSA	607	40	483	40	182	40	M-FOSA	FOSA	Sq
N-Trimethylammoniopropyl perfluorobutane sulfonamide	TAmPr-FBSA	399	40	60	40	116	40	M-FOSA	FOSA	Sq
N-Trimethylammoniopropyl perfluoropentane sulfonamide	TAmPr-FPeSA	449	40	60	40	116	40	M-FOSA	FOSA	Sq
N-Trimethylammoniopropyl perfluorohexane sulfonamide	TAmPr-FHxSA	499	40	60	40	116	40	M-FOSA	FOSA	Sq
6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	6:2 FTTh-PrAd-DiMeEtS	586	35	135	20	80	20	M-PFOS	PFOS	Sq
N-methylperfluorooctane sulfonamido acetic acid	N-MeFOSAA	570	34	169	20	419	10	M-N-MeFOSAA	N-MeFOSAA	Qn

N-ethylperfluorooctane sulfonamido acetic acid	N-EtFOSAA	584	34	419	20	526	20	M-N-EtFOSAA	N-EtFOSAA	Qn
3-Perfluoropentyl propanoic acid *(5:3)*	FPePA	341	19	237	14	217	24	M-PFPeA	PFPeA	Qn
2H-perfluoro-2-octenoic acid	FHUEA	357	18	293	17	243	34	M-PFHxA	PFHxA	Qn
2-perfluorohexylethanoic acid	FHEA	377	20	293	22	63	7	M-PFHxA	PFHxA	Qn
Perfluorooctane sulfonamido acetic acid	FOSAA	556	45	498	27	78	40	M-PFOA	PFOA	Qn
Perfluoro[1,2,3,4-$^{13}C_4$]butanoic acid	[$^{13}C_4$] PFBA	217	20	172	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[3,4,5-$^{13}C_3$]pentanoic acid	[$^{13}C_3$] PFPeA	266	20	222	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]hexanoic acid	[$^{13}C_2$] PFHxA	315	20	270	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]heptanoic acid	[^{13}C4] PFHpA	367	15	322	11	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid	[$^{13}C_4$] PFOA	417	20	372	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]octanoic acid	[$^{13}C_2$] PFOA	415	20	370	9	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$] PFNA	468	22	423	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$] PFDA	515	22	470	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$] PFUnDA	565	22	519	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$] PFDoDA	615	22	570	10	n/a	n/a	n/a	n/a	n/a
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	[$^{13}C_2$] FHUEA	359	18	294	17	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[2,3,4-$^{13}C_3$]-butanesulfonate	[$^{13}C_2$] PFBS	302	31	99	30	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$] PFHxS	403	58	103	28	n/a	n/a	n/a	n/a	n/a

Perfluoro[1,2,3,4-$^{13}C_4$]octane sulfonate	[$^{13}C_2$] PFOS	503	70	99	34	n/a	n/a	n/a	n/a	n/a
4:2[1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 4:2 FTS	329	30	81	25	n/a	n/a	n/a	n/a	n/a
6:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 6:2 FTS	429	44	409	22	n/a	n/a	n/a	n/a	n/a
8:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 8:2 FTS	529	45	81	35	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[$^{13}C_8$]octane sulfonamide	[$^{13}C_8$] FOSA	506	40	78	30	n/a	n/a	n/a	n/a	n/a
Methyl-d_3-perfluorooctane sulfonamido acetic acid	[$^{2}H_3$] MeFOSAA	573	34	419	20	n/a	n/a	n/a	n/a	n/a
Ethyl-d_5-perfluorooctane sulfonamido acetic acid	[$^{2}H_5$] EtFOSAA	589	34	419	20	n/a	n/a	n/a	n/a	n/a

*PI (precursor ion), CV (cone voltage), FI (fragmentation ion), CE (collision energy), Qn (quantitative), Sq (semiquantitative), Ql (qualitative), Sc (Screen)[1-3]

Chapter 4: Branched and Linear Interpretation for the Removal of Per- and Polyfluoroalkyl Substances by Pilot-Scale Granulated Activated Carbon System in Groundwater at a Military Site

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Abstract

Per- and polyfluoroalkyl substances (PFASs) are components in aqueous film-forming foams (AFFF), which are applied to hydrocarbon-based fuel fires as part of fire-fighter training. Repeat use of AFFF at fire-fighter training areas results in PFAS contamination in groundwater, soils, and, sediments. Granular activated carbon (GAC) adsorption is a remediation alternative for PFAS removal from water. To identify factors controlling PFAS adsorption from AFFF-impacted groundwater containing µg/L concentrations of PFAS and organic co-contaminants, a pilot study was conducted with two GAC adsorbers in a lead-lag configuration over an 11 month period. The system was designed to evaluate the PFAS order of breakthrough, concentrations of individual PFASs, and of branched and linear distributions. Breakthrough was quantified for branched and linear isomers of fifteen individual PFASs: C4-C8 perfluoroalkyl carboxylates (PFCAs), C4-C8 perfluoroalkyl sulfonates (PFSAs), C6 and C8 perfluoroalkyl sulfonamides (FASAs) along with 4:2-8:2 fluorotelomer sulfonates. A predominance of linear PFCA isomers over branched isomers in groundwater (influent) indicated the use of fluorotelomer-based AFFF and the transformation fluorotelomer precursors at this site. The total oxidizable precursor (TOP) assay quantified precursors in the influent and in select effluent samples and 80 ± 30% of the total mass was accounted for by individual PFASs. The order of breakthrough on GAC was in the same relative order as analytical retention times for each PFAS. Relative retention time is a relatively fast and inexpensive approach to predict the relative order of breakthrough for a wide range of PFASs.

Introduction

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic chemicals which are ubiquitous in the environment.[1] Two PFASs, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), have U.S. EPA health advisory limits of 70 nanograms per liter (ng/L) either individually or combined.[2] Regulatory determination of establishing maximum contaminant levels (MCLs) for PFOS and PFOA is currently being proposed in the USEPA PFAS Action Plan.[3] PFASs typically occur as mixtures and are hydrophobic, oleophobic, and heat stable. PFASs are manufactured by either electrochemical fluorination (ECF) or fluorotelomerization processes.[4] ECF based manufacturing produces branched (Br) and linear (L) PFASs while fluorotelomerization based manufacturing produces only L PFASs. The exception to the latter is the production of isopropyl branched isomers of C9, C11, and C13 PFCAs.[1] However, to the best of our knowledge branched C9, C11, and C13 PFCAs have not been identified as major components in AFFF.[5-7]

One important input of PFASs into the environment is the application of aqueous film-forming foams (AFFF) for putting out hydrocarbon-based fuel fires at fire-fighter training areas and crash events.[5, 6, 8-10] Areas designated as fire-fighter training areas were used on a routine basis between 1970s-1990s to train fire fighters,[6] and several MilSpec AFFF were available for use during this time period.[11, 12] Due to the uncontained nature of AFFF applications, PFASs and other AFFF constituents (e.g. hydrocarbon surfactants) have contaminated soils,[13] groundwater,[14,García, 2019 #1234] and surface water.[15] Contaminated groundwater impacted by AFFF have the potential to be used as drinking water sources.[16, 17] Populations exposed to point-sources of PFAS contamination (e.g., industrial discharge[18] and AFFF-contaminated sites[17]) have higher blood serum levels of PFASs.[17, 18] Therefore, in order to reduce human and ecosystem exposure to PFASs, especially near AFFF-contaminated sites, remediation of contaminated groundwater is necessary.

Technologies for the treatment of PFASs are evolving quickly and include sequestration technologies, such as granulated activated carbon (GAC)[19-22] and ion-exchange resins.[19, 20, 22, 23] Other treatment technologies include reverse osmosis or nanofiltration, and destruction technologies, such as chemical oxidation,[24] electrochemical oxidation[25] and reduction,[26] or sonolysis.[27] Efficacy of GAC and other sorbents are most commonly evaluated using laboratory batch or column experiments with clean laboratory water and only a select number of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs).[22, 23, 28-37] Only a few reports document the efficacy of GAC in the laboratory batch or column experiments for PFCA and PFSA removal from drinking water and municipal wastewater,[23, 38, 39] and only one bench-scale study documents the adsorptive removal of precursors from AFFF-contaminated groundwater.[34] Removal of PFCAs and PFSAs, but not precursors, by GAC at the pilot and full-scale is reported for only drinking water and municipal wastewater.[19, 29, 35, 40] Currently, no pilot-scale data are reported for the removal of PFCAs, PFSAs, and precursors in AFFF-contaminated groundwater.

Precursors can be transformed biotically or abiotically into PFCAs and PFSAs,[41] and are in AFFF-impacted groundwater[13, 42, 43] and surface water.[42, 44] One way to characterize precursors is by the total oxidizable precursor (TOP) assay.[45] The TOP assay provides a quantifiable estimate of precursors by oxidizing unknown precursors to PFCAs. However, the TOP assay does not identify the individual precursors, and is typically reported as the change in individual PFCA concentrations. In addition to the TOP assay, liquid chromatography mass-spectrometry (LC-MS/MS) is a technique for quantifying target precursors[46-49] but current US EPA methods include few precursors (e.g. perfluorooctane sulfonamide (FOSA), methylperfluorooctanesulfanamidoacetic acid, and ethylperfluorooctanesulfonamidoacetic acid).[50] Precursors not yet captured by LC-MS/MS are identified by LC high-resolution mass spectrometry (HRMS).[6, 43, 46] LC-HRMS analysis is not yet a routine analysis, however, LC-HRMS is one of the best approaches for identifying unknown precursors (e.g., non-target PFASs).

Precursors adsorption on GAC is largely unknown because of a lack of commercially available analytical standards. Although limited information is available for most precursors, the analytical retention time for a precursor on a C18 analytical column (on any of the above LC mass spectrometry systems) is one of the parameters first measured for a newly identified precursor. Xiao et al. found that the relative order of LC retention times for PFCAs, PFSAs, and precursors correlated with partition coefficients (K_d) describing PFAS adsorption from AFFF-impacted groundwater in batch kinetic tests.[34] However, the relationship between LC retention time and PFAS breakthrough on GAC at the pilot scale is not yet reported.

In this study, a pilot-scale GAC system was evaluated for the removal of 17 PFASs in AFFF-contaminated groundwater (influent) over an eleven-month period. Samples of influent, lead effluent, and lag effluent were collected weekly or bi-weekly and analyzed by LC-MS/MS. The 17 PFASs in the influent included C4-C9 PFCAs and C4-C8 PFSAs; 4:2, 6:2, and 8:2 fluorotelomer sulfonates (FTSAs); and C5,C6, C8 perfluoroalkylsulfonamides (FASAs). The TOP assay was applied to a select number of influent and effluent samples in order to indicate the breakthrough of precursors and to determine the advantages and limitations of the TOP assay for assessing GAC performance. Breakthrough curves for 15 of the 17 PFASs were constructed for each PFAS as well as for the various branched and linear isomers of the PFCAs, PFSAs, and FASAs. The relationship between breakthrough and analytical retention times is also reported.

Experimental Methods

Standards and reagents

Solvents and chemicals used are described in the Supplemental Information (SI). Native and isotopically labeled standards were the same as those used in Backe et al., but with the addition of FHxSA and FOSA (Wellington Laboratories, Guelph, ON, Canada).[5] For the full list of analytes and acronyms, see Table 4.4.

Study Site and GAC System Design

The military site selected for the pilot-scale system is a former fire-fighter training area that was in operation between 1958 and 1991. Groundwater from seven extraction wells approximately 150 m down gradient from the fire-fighter training area was blended in an equilibration tank before use as the influent for the GAC pilot system. The influent groundwater contained PFASs and a list of co-contaminants identified by a commercially available volatile organic contaminant analysis (data not shown). Co-contaminants included solvents (e.g. acetone) and other contaminants of concern (e.g.1,4-dichlorobenzene) at µg/L concentrations.

Water was passed through two 200-L steel drum vessels, plumbed in series, containing prepacked, reactivated GAC (DSR-A 8x40, Calgon Carbon Corporation, Pittsburgh, PA). GAC properties and GAC system design parameters are summarized in Table 3.1. A peristaltic pump was used to pump groundwater at a rate of 8.0 L per min into the GAC vessels under low pressure. Interconnecting piping and valves were PTFE free and fabricated of PVC. The final treated water was discharged to an effluent holding tank. The pilot system was operated from November 2016 through August 2017. For the purpose of evaluating PFAS breakthrough, there was no GAC removal or change out, but there was a four week shut down in February 2017.

Sample Collection, Transport, and Storage

Samples of the influent and effluent were collected weekly for the first nine months and then bi-weekly for the following two months. Samples were collected in 30 mL HDPE containers (VWR, Radnor, PA). Field blanks consisted of laboratory-deionized water shipped in 30 mL HDPE containers that were opened during sample collection. Trip blanks consisted of laboratory-deionized water shipped to the site in 30 mL HDPE containers, but not opened at any time during sample collection. All field and trip blanks (n=4 field blanks, n=5 trip blanks) were less than the limit of quantification (LOQ) for all PFASs. The first seven effluent samples from the lag vessel served as blank controls since they were <LOQ for all PFASs, which indicates the PFAS background in the pilot GAC system was negligible. All samples were shipped to Oregon State University (OSU) on ice and frozen until analysis.

Sample Extraction

On the day of analysis, samples were brought to room temperature and inverted several times for homogenization. A 3 mL aliquot was placed in a 15 mL centrifuge tube along with 0.97-1.0 g of NaCl, 10 µL of 6M hydrochloric acid, and 0.72 ng of all mass-labeled internal standards (Table 4.4). Samples were extracted in triplicate with 10:90 2,2,2-trifluoroethanol in ethyl acetate to give a total volume of 1 mL to which 500 µL of methanol was added for a final volume of 1.5 mL for analysis by LC-MS/MS.[5]

TOP Assay

Five pairs of influent and effluent (from the lead vessel only) were selected at 3200, 5800, 9200, 11000, and 16000 bed volumes for analysis by the TOP assay.[45] Each 15 mL centrifuge tube received 1.5 mL of sample and 1.5 mL reaction solution (60 mM potassium persulfate, 125 mM sodium hydroxide in water). Briefly, samples were placed in a water bath between 85-90 °C for 6 h and then stored at 4 °C until analysis. Prior to analysis, samples were brought to room temperature, neutralized with 10 µL of 6 M HCL and 0.72 ng of all isotopically-labeled internal standards were added and then extracted as described above.

PFAS Selection and Analysis by LC-MS/MS

In an attempt to identify the PFAS mass in the influent, an upgradient groundwater sample nearer to the source zone than the influent sample in this study was analyzed by LC-QTOF as part of a prior experiment in Barzen-Hanson et al.[6] Analysis by LC-QTOF identified 52 individual PFASs (Table 4.4), and all 52 observed PFASs are included in the LC-MS/MS method created for this study. However, when the GAC influent was screened using the 52-analyte LC-MS/MS method, only 18 individual PFASs were observed. Information on the selection criteria of analytes from the independent LC-QTOF analysis can be found in the SI.

Analyses were performed on an Agilent 1100 series (Agilent, Santa Clara, CA) HPLC attached to a Waters Triple Quadrupole Detector MS/MS system (Waters Corporation, Milford, MA). The LC-MS/MS was fitted with two zirconium modified diol (Zr-diol) and one Zorbax Silica (Sil) guard columns (Agilent) and a Zorbax

Eclipse Plus C18 analytical column (Agilent).[5, 51] Calibration curves consisted of five to seven standards ranging from 10 ng/L- 5,000 ng/L for all analytes, with the exception of FOSA (50 ng/L – 10,000 ng/L) and 6:2 FtSA (10 ng/L- 2,500 ng/L). All curves were required to be linear ($R^2 \geq 0.99$). Each PFAS was quantified by internal standard calibration and assigned a data quality tier of confidence (Table 4.4).[52] Briefly, quantitative (Qn) analytes are those which contain both authentic analytical and isotopically labeled internal standards, semi-quantitative (Sq) analytes had reference materials but unmatched internal standards, and qualitative (Ql) analytes had neither authentic or internal standards. Instrumental LOQs are 10 ng/L for all analytes (Table S1) with the exception of FHxSA and FOSA which have an LOQ of 50 ng/L. All values reported >LOQ gave signal-to-noise values greater than nine. The LOD values for all analytes were defined as 3.3x lower than the LOQ, and with a signal-to-noise value between three and nine. Branched (Br) and linear (L) concentrations were calculated by separately integrating the branched isomers and the linear peaks.

Each analytical sequence was comprised of one to three weeks of samples, a whole extraction blank, and several solvent blanks. Whole extraction process blanks consisted of spiking deionized water with all isotopically labeled standards and extracting as described above. The matrix for solvent blanks was generated by extracting a mixture of 3 mL deionized water, 0.97-1.0 g of NaCl, and 10 uL hydrochloric acid with three rounds of 2,2,2-TFE, ethyl acetate (10:90). One mL of the ethyl acetate was then combined with 500 µL methanol and spiking with isotopically labeled standards. All process and solvent blanks fell at or below half of the limit of quantification (< ½ LOQ). Replicate samples of influent (n=4) were used to calculate a standard error as a measure of precision about the reported concentrations.

Data treatment and breakthrough curves

Breakthrough curves for individual PFASs were developed by normalizing concentrations of individual PFASs in the GAC effluent with the corresponding influent concentration and plotting normalized concentrations as a function of the bed volumes of water treated. Resulting breakthrough curves were described with the pore-surface diffusion model (PSDM) using the approach described in Summers et al.[53] Adjustable model input parameters included the apparent Freundlich capacity parameter (K*), tortuosity (τ), and the surface-to-pore diffusion flux ratio (SPDFR). The Freundlich isotherm exponent (1/n) was set to one. When pore diffusion alone effectively described PFAS breakthrough curves, surface diffusion was eliminated by setting the SPDFR to 10^{-30}, and the pore diffusion coefficient was adjusted by varying tortuosity, with the constraint that tortuosity cannot be less than one. For steeper breakthrough curves, pore diffusion alone could not effectively describe the data. In that case, the tortuosity was set to its smallest allowable value (i.e., 1.0), and the SPDFR was increased from 10^{-30}. For the PSDM, the average C_0 was determined from the measured PFAS concentrations in 28 GAC influent samples over the 11-month period of the pilot study. For the lead column, K*, τ, and SPDFR (required for branched PFOA only) values for each analyte are reported in Table 4.2. [54] For the lag column, K* values were within 10% of those for the lead column. Intraparticle diffusion flux values were within a factor of 2 of those for the lead column, except for PFBA, for which the difference was a factor of 5. The latter result was likely due to uncertainty in the PFBA breakthrough curve for the lead column (Figure 4.5).

Results and Discussion

Influent Characterization

The PFASs observed in the influent included C4-C9 PFCAs, C4-C8 PFSAs, 4:2, 6:2, and 8:2 FTSAs, FPeSA, FHxSA, FOSA, and N-TAmP FHxSA (Table 2). The most prevalent PFASs in the influent were PFOS (2700 ng/L), FHxSA (2800 ng/L), PFHxS (2100 ng/L), PFOA (900 ng/L), PFHxA (740 ng/L), and 6:2 FtSA (1000 ng/L; Table 2). While the PFCAs and PFSAs are commonly observed as the most prevalent PFASs,[5, 9, 44, 55] to the best of the author’s knowledge this study is the 3rd report of FHxSA in groundwater or surface water.[46, 56] A recently reported PFAS,[6] N-TAmP-FHxSA, was present initially in the influent but was not detected after the 4 week shut-down and thus is not discussed further. Fluorotelomer-based PFASs observed in the influent include 4:2, 6:2, and 8:2 FtSAs (Table 4.2). The most prevalent fluorotelomer based PFAS in the influent was 6:2 FtSA (1000 ng/L) which is more abundant than PFOA (Table 4.2).

The presence of PFCAs, PFSAs, FASAs, and N-TAmP-FHxSA are typically associated with ECF-based 3M AFFF.[1, 6] In 3M manufactured AFFF (ECF) after 1989, PFOA is 1:100 of PFOS and PFHxA is 1:10 of PFHxS.[5] At this site, the ratio of PFOA to PFOS is 1:3 and the ratio of PFHxA to PFHxS is 1:2 (Table 4.2), which indicates greater PFOA and PFHxA concentrations than expected based on the composition of 3M AFFF. McGuire et al. attributed increased ratios to an alternate PFAS source or *in-situ* transformation of precursors.[56] The presence of FtSAs, which are linear only, are direct evidence of fluorotelomer-based AFFF use at this site since FTSAs are degredation products of fluorotelomer thioether amido sulfonate.[57, 58] However, fluorotelomer thioether amido sulfonate is was not observed in the influent.

Electrochemical fluorination (ECF) manufacturing produces both branched and linear PFASs, and fluorotelomer-based manufacturing produces only L PFASs.[4, 59] Most of the PFCAs, PFSAs, and FASAs were branched and linear in the influent which was anticipated since they are all ECF-based chemistries.[60] However, PFCAs can be derived from either ECF of fluorotelomer chemistries, and therefore you cannot directly assume PFCAs will be comprised of both Br/L isomers. In contrast, FTSAs are only linear since they are derived from a linear source. Br isomers typically are lower in abundance when concentrations are low. The Br isomers are < LOQ for PFBA, PFHxA, PFBS, PFPeS, FPeSA (Table 4.2). To the best of the authors' knowledge, this is the first report of Br FHxSA (Table 4.2) in AFFF-impacted groundwater. In the GAC influent, PFOS has a Br/L of 38:62 (Figure 4.2.1a) while PFOA has a ratio of 9:91 (Figure 2.1b; Table 2.2). However, the Br/L ratio of ECF-manufactured PFASs, including PFOS and PFOA, is 25:75.[61] No known microbial biodegradation pathway for PFOS is known to alter the Br/L ratio. Depletion of L PFOS (75% to 62%) in groundwater 150 m down gradient from a source zone is consistent with higher retardation of L PFOS relative to Br PFOS. For example, Labadie et al. found higher log K_{oc} values, thus greater a greater retardation factor, for L-PFOS compared to Br PFOS.[62] Kwadijk et al. also reported higher log K_{oc} values for L-PFOS and L-PFOA than for total PFOS and PFOA.[63] Linear PFOS and PFOA isomers have longer retention times on C18 analytical columns than do their branched counterparts (Table 4.2). As indicated for PFOS, one would expect depletion of L isomers over Br isomers for all ECF-based PFASs in the influent collected down gradient from an aged fire training area source zone. However, L PFOA is relatively enriched compared to Br PFOA, which cannot be attributed to transport alone. Unlike PFOS, there are reports of PFCA formation, including PFOA, from precursors including fluorotelomer thioether amido sulfonate[57, 58] and FtSAs.[64, 65] However, these formation studies did not separate or directly document Br/L distribution. It is important to note that PFOA, and all PFCAs, may not have the anticipated ECF-based Br/Ln distribution since through fluorotelomer degradation a L PFCA is possible. For this reason, we hypothesize that the enrichment of L PFOA and other PFCAs (Table 4.2) is due to the biotransformation of linear precursors.

TOP Assay for Characterizing Influent

The TOP assay was utilized in this study for several purposes including 1] estimating unknown precursors not captured by individual PFASs measured in this study and 2] estimating the total mass of PFASs in the GAC influent. Along with unknown precursors, the TOP assay oxidizes the known precursors identified in the influent including FASAs, FTSAs, and N-TAmP-FHxSA (Table 4.6).

The TOP assay generated a range of PFCAs including PFBA (10%), PFPeA (11%), PFHxA (73%), PFHpA (0.8%), and PFOA (5%) (Table 4.3). When present, the percentage of Br isomers was maintained before and after the TOP assay (15-18% PFOA; 32% PFHxS; 27% PFHpS; 34% PFOS). Of note, the difference in PFSA concentrations before and after the TOP assay were not statistically significant (Table S2, Equation S2). At present, no precursors produce PFSAs under TOP assay conditions. The predominant production of PFHxA (73%) generated by the TOP assay are consistent with the oxidation of the C6-based precursors[52, 66] present in the influent including 6:2 FTSA, FHxSA, N-TamP-FHxSA (Table 4.2). A more precise delineation of the chain length of precursors is not possible since the original chain length of precursors is not preserved under TOP assay conditions.[44, 52, 67-70]

For the influent, known precursors accounted for 10.4 nmol ± 3.1 nmol F (Table 4.5) of the 20 ± 1 nmol F (known and unknown) precursors (Table 4.5; Equation S1), while unknown precursors accounted for 9.6 ± 2.1 nmol (Table 4.3).

The total mass of PFASs in the influent was computed as the sum of all measured individual PFASs (PFCAs, PFSAs, FASA, FTSAs, N-TAmP-FHxSA) before oxidation divided by the sum of the PFCAs and PFSAs after oxidation

(Equation S2). The total mass of measured individual PFASs before the TOP assay (29 ± 1 nmol; Table 4.5) accounted for 75 ± 30% of the total mass of PFAS in the influent (37 ± 1 nmol). Unknown precursors measured by the TOP assay accounted for the remaining 20% (9.6 ± 2.1 nmol; Equation S1). The equations and examples for TOP assay values can be found in the SI. Although the influent was screened for ~ 450 individual suspect PFASs by LC-HRMS[6] yielded only a number of low abundance precursors. Additional precursors not captured by suspect screening may be present and would require identification by non-target LC-HRMS, which was beyond the scope of the study.

Effluent Concentrations

The effluent data from the lag vessel were used for data interpretation and breakthrough modeling because full-scale systems typically run multiple vessels in sequence and the effluent data from lag vessel are used to determine the need of GAC changeout.[19, 39, 40] The additional empty-bed contact time of the lag vessel improves the separation of PFAS homologs for interpreting breakthrough curves (Figure 4.2a,b). However, data for the lead vessel are shown in the SI (Figure 4.3), which is rarely reported.

Breakthrough Curves

Concentrations of C4-C8 PFCAs (Figure 2a), C5-8 PFSAs, FHxSA, and 6:2 FtSA (Figure 4.2b) were plotted as a function of bed volume to create breakthrough curves. The order of PFCAs breakthrough is strongly associated with fluorinated chain length: PFBA, <PFPeA, <PFHxA, <PFHpA, <PFOA (Figure 4.2a). The order of PFSA breakthrough also followed the same trend with chain length: PFPeS, <PFHxS, <PFHpS, <PFOS (Figure 4.2b). To the best of the authors' knowledge, these are the first reported breakthrough curves for PFPeS, FHxSA, and 6:2 FtSA (Figure 4.2b). Breakthrough on full-scale GAC as a function of chain length is reported for PFBA, PFHxA, PFOA, and PFOS in drinking water.[19] In an analogous manner, increasing sorption of PFASs onto GAC with increasing chain length is reported for batch experiments with AFFF-impacted groundwater.[34] To the authors' knowledge, this is the first report of breakthrough curves for a pilot-scale system treating a complex AFFF-contaminated water matrix.

Observation above the <LOQ of PFBA (9192 bed volumes) occurs significantly before PFOA (9321 bed volumes) or PFOS (14752 bed volumes), the only two PFASs with Health Advisory Limits (HALs).[2] PFBA is included in some state regulations,[71] but is not included in U.S. EPA Method 537. The use of GAC for PFBA removal would require more frequent GAC change outs, which is likely cost prohibitive.[28, 54] Concentrations of PFBA exceeded that of the influent ($C/C_0 > 1$) at 9249 bed volumes and is consistent with the observation of PFBA C/Co values > 1 for a full-scale GAC system treating drinking water (Figure 4.2a).[19] Appleman et al. hypothesized PFBA displacement by longer chained PFASs[19] or by other co-contaminants. The groundwater influent in the present study has solvents and fuels co-contaminants at ug/L concentrations as well as hydrocarbon surfactants associated with AFFF[72] that may compete for weak sorption of PFBA.

Concentrations of PFOS in effluent exceeded the health advisory limit (HAL) of 70 ng/L at 9970 bed volumes. However, concentration of PFOA exceeded the HAL much earlier at 4,681 bed volumes. Because PFOA breaks through before PFOS, the HAL for the combined concentrations of PFOS and PFOA is also 4,681 bed volumes. Comparing the bed volumes corresponding to PFOS and PFOA to those reported by others is limited due to the omission of key descriptors including influent concentration[19, 29] and breakthrough curves.[39]

Br/L Isomer Breakthrough

Earlier breakthrough of Br isomers relative to the L isomers from the lag vessel (Figure 4.3) is consistent with the effluent and with lower log K_{oc} values for Br isomers (Figure 4.2),[62, 63] and had an impact on breakthrough curves (Figure 4.3). The modeling curve for Br PFOS has a K value of 55 as compared to L PFOS which has a K value of 80, which indicates earlier breakthrough of Br PFOS. However, since L-PFOS is more abundant relative to Br-PFOS (Table 4.2), the breakthrough for total PFOS indistinguishable from L-PFOS (Figure 4.3).

The ratio of Br/L PFOS was initially 29:71 at 1500 bed volumes, but increased significantly over time to 52:48 at 11,000 bed volumes (Figure 4.2b). Observation of the enrichment of Br-PFOS at earlier bed volumes is important, because although the concentration of Br-PFOS is significantly lower than L-PFOS (Table 2), Br-PFOS breaks through faster than L-PFOS.

Breakthrough and Analytical Retention Time

The relative order of breakthrough in the pilot-scale GAC system followed the relative order of Br and L PFAS elution on the C18 analytical column (Figure 4.4, Table 4.1). Similar relative orders of breakthrough on GAC and C18 analytical media indicates similar mechanisms of retention. The C18 analytical column used in this study was endcapped, thus minimizing the potential for retention mechanisms other than van der Waals (e.g., hydrophobicity). The comparison of bed volumes to analytical retention time was performed with Br/L analytes treated as individual data points (Figure 4.4). With all modeled analytes included, the R^2 value is 0.6133; however, when the only analyte of low abundance, PFPeS, is removed the R^2 values increases to 0.7082 (Figure 4.4). The R^2 value of 0.7082 matches closely to Xiao et al., who reported an R^2 value of 0.75, indicating a reproducible relationship.[34] Importantly, Xiao et al. performed their comparison using predicted bed volume values, whereas, in this study, the bed volumes were calculated from a pilot-scale system (Table 4.6). Practically, the relationship between bed volume breakthrough and analytical retention time could be used to predict the relative breakthrough of other PFASs using only analytical retention time. For example, in this study, FHxSA had an analytical retention time of 13.6 min, which will be expected, and was observed (Figure 4.2b, 4.4) to breakthrough between PFHxS (RT 11.2 min) and PFOS (15.5 min). Although commercial laboratories who perform PFAS analysis by

EPA and modified EPA methods currently use LC-MS/MS there is a trend towards utilizing QTOF for additional PFASs.

Breakthrough and TOP Assay

The TOP assay was performed only on five discrete samples of the lead vessel effluent at varying bed volumes (Table 4.3), since concentrations of precursors were more abundant than in lag vessel effluent (data not shown). Oxidation resulted in net increases in only L C4-C7 PFCAs (Table 4.3) but the increase in PFOA was low so that changes in Br and L isomers could not be distinguished. The dominant PFCA produced, irrespective of bed volume, was PFHxA and was consistent with the breakthrough of known C6-based precursors (Figure 4.5). For the lead vessel effluent, known precursors (FASAs, FTSAs, N-TAmP-FHxSA) accounted for 0-38% of the total precursors by computing the difference between the total net production of PFCAs after oxidation minus the total mass unknown precursors (Table 4.3).

Concentrations of precursors (nmol F; Table 4.3) determined the TOP assay, were plotted against bed volume (Figure 4.5b). Since the TOP assay captures an unknown number of precursors, the breakthrough curve is more challenging to interpret since it is likely weighted by the number of precursors and their relative abundance. As an example, the TOP assay breakthrough curve is similar to those for 6:2 FtSA and FHxSA (Figure 4.5b). The breakthrough curve for the TOP assay (Figure S1b) indicates breakthrough of precursors before PFOS and PFOA. The TOP assay is useful for quantifying precursors in GAC influent and effluent since few precursors are measured in current commercial analyses. Additional unknown precursors may be present in lead vessel effluent; however, attempts to identify additional unknown precursors were unsuccessful and non-target analysis of effluent was beyond the scope of this study.

Implication and limitations

Nearly half of the observed PFASs in the GAC influent had shorter chain lengths than PFOS and PFOA (e.g. 4:2 FtSA; Table 4.2). However, breakthrough curves indicate that shorter chained PFASs (<C8) are not effectively retained by GAC compared to PFOS and PFOA and will be present in finished effluent prior to GAC if only based on PFOS and PFOA. For this reason, it is important to select commercial analysis which include short-chain PFASs such as PFBA, PFPeA, PFBS, PFPeS, and 4:2 FtSA. Analytical standards for 6:2 FtSA and FHxSA are commercially available, and should be included in monitoring programs because both precursors have the potential to degrade to PFAAs,[36, 73, 74] and because 6:2 FtSA and FHxSA are at similar concentrations to that of PFHxS and PFOA, respectively, the influent (Table 4.2).

Inclusion and differentiation of Br/L ratios should be included not only for analytical accuracy, but also for interpretation of input sources and treatment processes. In this study, the relative enrichment of L PFCA isomers indicate source inputs from linear fluorotelomer precursors. In cases where individual precursors are not directly measured, excess L PFCA isomers are likely signaling the use of fluorotelomer AFFF that have degraded to PFCAs. In the case of GAC as a treatment process, shifting isomer ratios result from preferential sorption of Br over L PFASs.

The commercially available TOP assay provides a quantitative measurement of additional precursors in GAC influent and effluents. A measure of precursors is important since they may compete for sites on GAC and have the potential to end up in treated effluent if GAC changeout is only triggered by PFOS and/or PFOA breakthrough (e.g., exceeding HALs). The TOP assay provides data on the breakthrough of precursors even though the data cannot provide information on individual the behavior of unknown precursors. The TOP assay is more expensive compared to LC-MS/MS, given the need for two analyses on a single sample. While LC-MS/MS can capture a broader array of precursors, an even larger number of suspect PFASs can be determined LC-HRMS. However, LC-HRMS is expensive, not yet commercially available, and does not guarantee mass balance for PFASs since additional non-target PFASs may be present.

The relationship between the relative order of breakthrough on GAC and retention times on C18 analytical columns will prove useful for predicting breakthrough of precursors without having to measure the actual precursor concentration in individual effluent samples. This is particularly important since commercial analyses for precursors are not yet available but are likely to become available with time. Once an influent of a treatment system is fully characterized by

LC-HRMS, the retention times of precursors can be used to predict its breakthrough relative to commonly-measured PFASs.

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Table 4.1. Design parameters for GAC pilot-scale system.

Design Parameter	**Value**
GAC, type	DSR-A 8x40 BET surface area: 750 m^2/g Micropore volume: 0.310 cm^3/g Macropore plus mesopore volume: 0.242 cm^3/g
Number of GAC vessels	2 in series
GAC quantity per vessel	91 kg
Volume per vessel	200 L
Hydraulic loading rate	8.0 L/min
Empty bed contact time	13 min (lead) 26 min (lead + lag)

Table 4.2. Average Br and L PFAS influent concentrations (ng/L) ± standard error, analytical retention time (min) and PSDM modeling parameters.

PFAS	Average Influent Concentration (ng/L)		Analytical Retention Time (min)		K (L/g),[1] τ (for Modeling)	
	Branched	Linear	Branched	Linear	Branched	Linear
PFBA	<LOD	100 ± 22	NA	6.8	NA	12, 1
PFPeA	19 ± 2.5	350 ± 47	7.5	7.9	NA	18, 3
PFHxA	<LOQ	740 ± 70	8.9	9.4	NA	18, 1
PFHpA	15 ± 2.0	150 ± 20	10.8	11.3	NA	28, 4
PFOA	81 ± 7.2	820 ± 73	12.8	13.3	18, 1*	40, 2
PFNA	<LOD	18 ± 5.7	14.8	15.6	N/A	NA
PFBS	<LOD	17 ± 3.0	7.6	8.0	N/A	NA
PFPeS	<LOD	30 ± 9.0	9.2	9.4	NA	35, 1
PFHxS	190 ± 29	1400 ± 210	10.8	11.2	30, 1	70, 5
PFHpS	29 ± 5.5	62 ± 11.9	12.7	13.3	NA	NA
PFOS	1200 ± 110	1900 ± 170	14.8	15.5	55, 1.5	85, 2.5
4:2 FtSA	NA	13 ± 3.0	NA	9.2	NA	NA
6:2 FtSA	NA	1000 ± 76	NA	13.3	NA	45, 1.5
8:2 FtSA	NA	170 ± 35	NA	17.9	NA	NA
FPeSA	<LOQ	125 ± 5.8	10.8	11.6	NA	NA
FHxSA	700 ± 48	2100 ± 140	13.1	13.6	40, 1	65, 2
FOSA	100 ± 9.4	200 ± 19	17.7	18.6	N/A	NA
N-TAmP FHxSA	51 ± 21	97 ± 40	13.5	14.1	N/A	NA

<LOD = not detected; <LOQ = less than the limit of quantification; NA = not applicable because branched isomers are not detected because they are not present in fluorotelomer AFFF, *Surface-to-pore diffusion was needed for modeling, so SPDFR was 1 rather than the 10^{-30} value used for all other analytes.

[1] K values for the lead and lag vessels were similar and are reported as a single value.

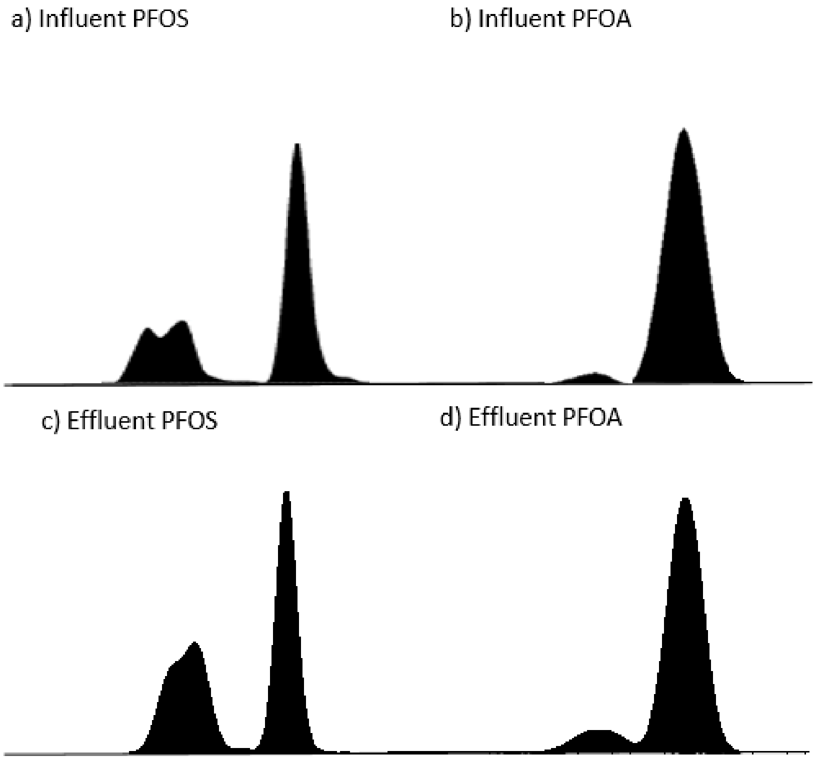

Figure 4.1. Branched (Br) and linear (L) isomers for a) PFOS and b) PFOA in GAC influent and c) PFOS and d) PFOA in GAC effluent.

Table 4.3. Net production of PFCAs by TOP assay (nmol) ± propagated relative standard error and the total mass of unknown precursors at five selected bed volumes in the lead vessel.

		Bed volumes (nmol)[1]				
	Influent[2]	**3192**	**5759**	**9192**	**10992**	**16280**
PFBA	2.0 ± 0.34	<LOQ	0.27 ± 0.046	0.36 ± 0.060	0.55 ± 0.093	1.2 ± 0.21
PFPeA	2.2 ± 0.63	0.19 ±0.05	0.31 ± 0.0019	0.63 ± 0.18	0.0064 ± 0.0019	0.41 ± 0.12
PFHxA	15 ± 1.4	0.55 ± 0.052	2.3 ± 0.22	2.7 ± 0.26	2.6 ± 0.24	5.3 ± 0.50
PFHpA	0.22 ± 0.03	<LOQ	0.065 ± 0.012	0.086 ± 0.015	<LOQ	<LOQ
PFOA	0.7 ± 0.5	<LOQ	0.52 ± 0.048	0.58 ± 0.53	<LOQ	<LOQ
Total PFCAs	20.10 ± 5.3	0.74 ± 0.12	3.5 ± 1.0	4.3 ± 1.2	3.2 ± 0.84	6.9 ± 1.6
Total mass of unknown precursors	9.6 ± 2.1	0.41 ± 0.12	3.1 ± 1.0	3.4 ± 1.1	1.4 ± 0.52	2.2 ±1.1

[1] Propagated relative standard error based on measurement of n=5 influent replicates

[2] The propagated relative standard error from the influent was applied to the single samples at each of the five bed volumes

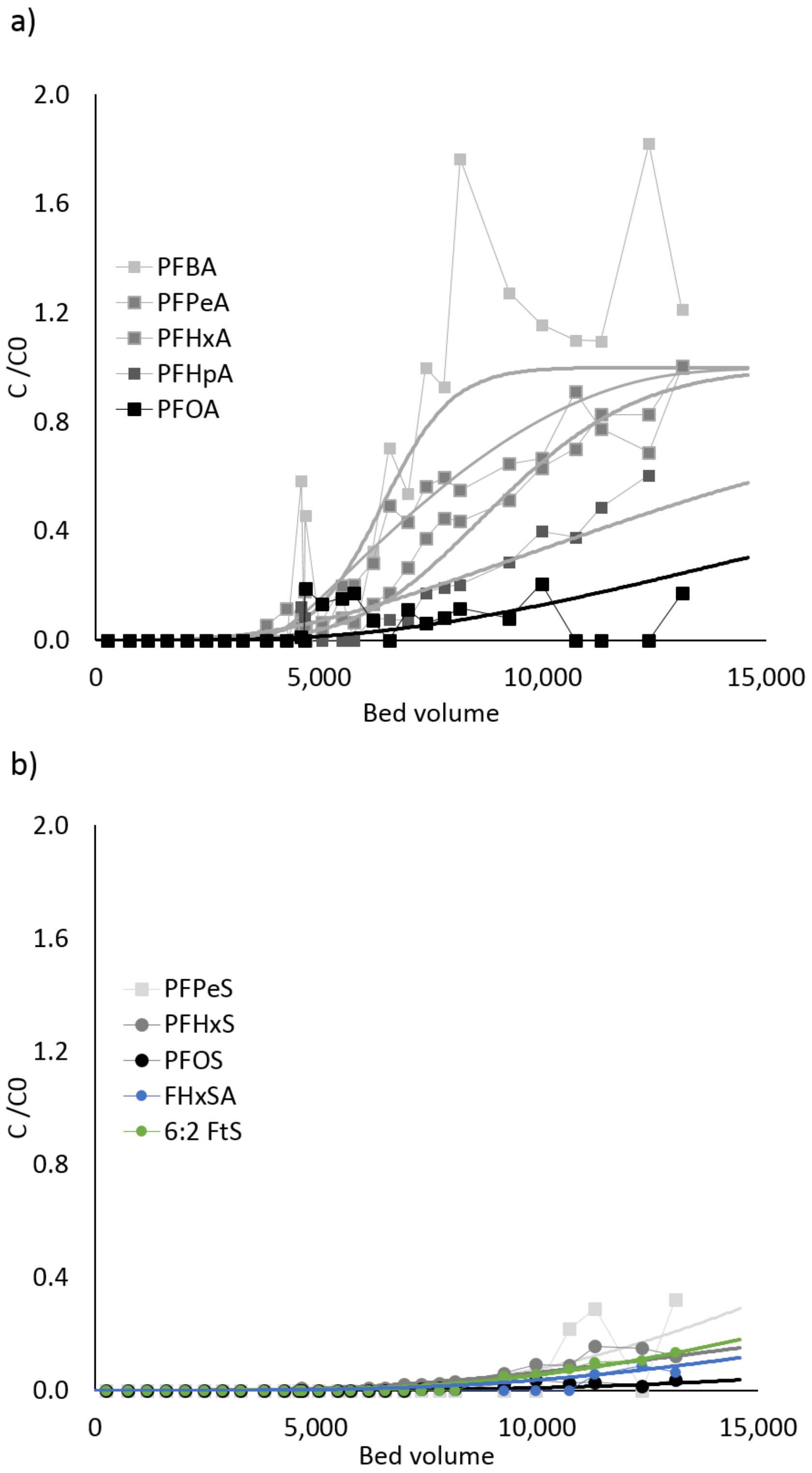

Figure 4.2. Breakthrough curves with model fits for a) PFCAs, b) PFSAs, and c) FHxSA and 6:2 FtSA.[a]

[a] Due to low concentrations PFNA, PFBS, PFHpS, 4:2 FtSA, 8:2 FtSA, FPeSA, and FOSA are not included.

[*] Two points significantly above $C/C_o > 1$ for PFBA were removed for modeling.

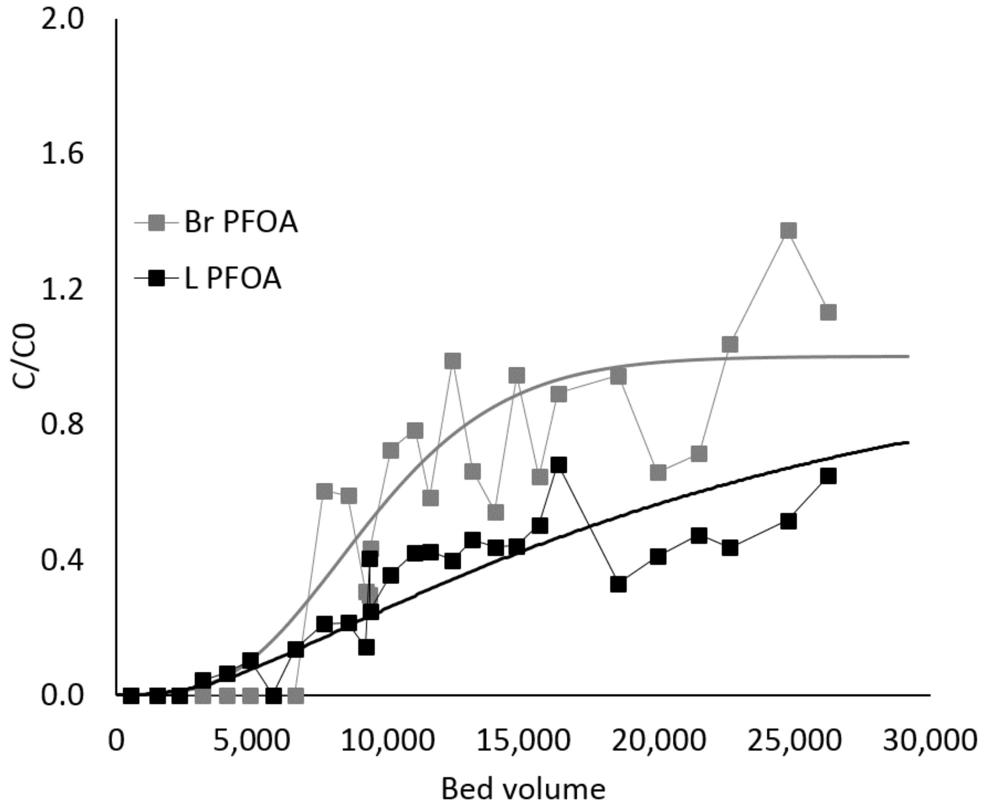

Figure 4.3.Breakthrough curves for Br and L PFOS in lag vessel effluent.

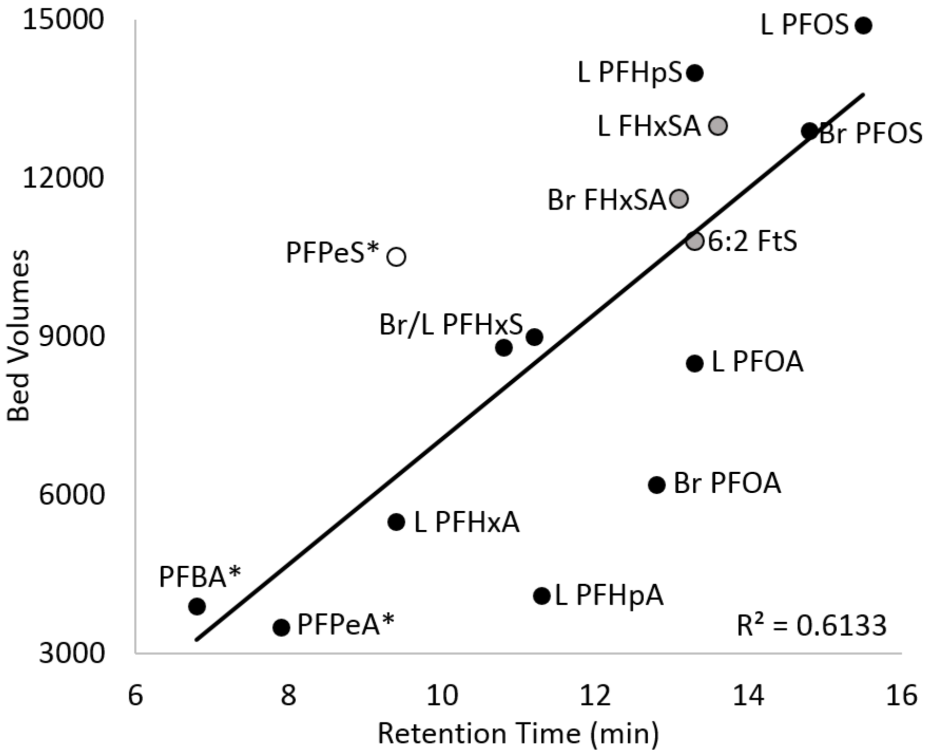

Figure 4.4. Comparison of lead vessel bed volumes required for 20% breakthrough vs. analytical retention times. The one open data point depicts PFPeS which was close to the instrumental LOQ.

*Denotes and analyte where Br/L separation was not possible.

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Supporting Information

Branched and Linear Interpretation for the Removal of Per- and Polyfluoroalkyl Substances by Pilot-Scale Granular Activated Carbon System for in Groundwater at a Military Site

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Experimental Methods

Solvents and Chemicals

For analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (reagent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Sodium hydroxide (98%, reagent grade), ethyl acetate (99.9%, reagent grade), potassium persulfate (>99%, ACS reagent), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH).

Analysis by LC-QTOF

Analysis for all individual PFASs were performed on a Shimadzu Exion HPLC (Shimadzu, Kyoto, Japan) attached to a Sciex X500R quadrupole time of flight mass spectrometer (Sciex, Concord, Canada). All instrumental conditions and parameters can be found in Barzen-Hanson et al., 2017.[3] It is important to note that analysis was performed in suspect screening mode for approximately 300 individual PFASs. Non-target analysis for additional unknown PFASs was outside of the scope of this study. In an attempt to identify the PFAS mass in the influent, an upgradient groundwater sample nearer to the source zone than the influent sample in this study was analyzed by LC-QTOF as part of a prior experiment in Barzen-Hanson et al..[3] LC-QTOF analysis identified 52 individual PFASs, and all 52 observed PFASs are included in the LC-MS/MS method created for this study. However, when the positively validated LC-MS/MS method was used to screen the influent, only 16 PFASs were routinely observed.

TOP Assay

Equation S2 assumes equal molar conversion of known precursors to PFCAs after oxidation. No attempt was made to account for expected molar concentrations of any individual precursor due to variability of precursor recovery of TOP assay in the authors' previous work and between other laboratories.[4, 5]

Table 4.4. LC-MS/MS target analyte full name, acronym, acquisition masses and parameters, internal standard, calibration reference, and data quality.

Analyte	Acronym	PI* (m/z)	CV* (V)	FI-1* (m/z)	CE* (eV)	FI-2* (m/z)	CE* (eV)	Internal Standard	Calibration Reference	Data Quali
Perfluorobutanoic acid	PFBA	213	20	169	8	n/a	n/a	$[^{13}C_4]$PFBA	PFBA	Qn
Perfluoropentanoic acid	PFPeA	263	20	219	8	n/a	n/a	$[^{13}C_3]$PFPeA	PFPeA	Qn
Perfluorohexanoic acid	PFHxA	313	20	269	8	119	22	$[^{13}C_2]$PFHxA	PFHxA	Qn
Perfluoroheptanoic acid	PFHpA	363	20	319	8	169	14	$[^{13}C_4]$PFOA	PFHpA	Sq
Perfluorooctanoic acid	PFOA	413	20	369	8	169	18	$[^{13}C_4]$PFOA	PFOA	Qn
Perfluorononaoic acid	PFNA	463	22	429	8	169	18	$[^{13}C_5]$PFNA	PFNA	Qn
Perfluorodecanoic acid	PFDA	513	22	469	10	269	18	$[^{13}C_2]$PFDA	PFDA	Qn
Perfluoroundecanoic acid	PFUnDA	563	22	519	10	169	22	$[^{13}C_2]$PFUnDA	PFUnDA	Qn
Perfluorododecanoic acid	PFDoDA	613	22	569	10	169	24	$[^{13}C_2]$PFDoDA	PFDoDA	Qn
Perfluorortridecanoic acid	PFTriDA	663	24	619	12	169	26	$[^{13}C_2]$PFDoDA	PFTriDA	Sq
Perfluorotetradecanoic acid	PFTeDA	713	24	669	12	169	26	$[^{13}C_2]$PFDoDA	PFTeDA	Sq
N-sulfo propyl perfluorobutane sulfonamide	SPr-FBSA	420	40	78	22	298	28	$[^{13}C_4]$PFOA	PFOA	Ql
N-sulfo propyl perfluoropentane sulfonamide	SPr-FPeSA	470	40	78	22	348	28	$[^{13}C_4]$PFOA	PFOA	Ql
N-sulfo propyl perfluorohexane sulfonamide	SPr-FHxSA	520	40	78	30	398	30	$[^{13}C_4]$PFOA	PFOA	Ql
Perfluoropropane sulfonate	PFPrS	249	46	80	32	99	26	$[^{18}O_2]$PFBS	PFPrS	Ql
Perfluorobutane sulfonate	PFBS	299	50	80	32	99	26	$[^{18}O_2]$PFBS	PFBS	Qn
Perfluoropentane sulfonate	PFPeS	349	56	80	34	99	28	$[^{18}O_2]$PFHxS	PFHxS	Sq
Branched Perfluorohexane sulfonate	Br-PFHxS	399	58	80	36	99	28	$[^{18}O_2]$PFHxS	PFHxS	Qn
Perfluorheptane sulfonate	PFHpS	449	64	80	46	99	32	$[^{13}C_2]$PFOS	PFOS	Sq
Branched Perfluorooctanesulfonic acid	Br-PFOS	499	70	80	46	99	34	$[^{13}C_2]$PFOS	PFOS	Qn
Perfluorononane sulfonate	PFNS	549	72	80	50	99	36	$[^{13}C_2]$PFOS	PFDS	Sq

Perfluorodecane sulfonate	PFDS	599	76	80	52	99	36	$[^{13}C_2]$PFOS	PFDS	Sq
4:2 fluorotelomer sulfonate	4:2 FTS	327	42	307	19	81	26	$[^{13}C_2]$ 4:2 FtS	4:2 FTS	Qn
6:2 fluorotelomer sulfonate	6:2 FTS	427	40	407	22	81	28	$[^{13}C_2]$ 6:2 FtS	6:2 FTS	Qn
8:2 fluorotelomer sulfonate	8:2 FTS	527	45	507	25	81	32	$[^{13}C_2]$ PFDA	8:2 FTS	Qn
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaB	571	78	104	28	58	38	M-PFOS	6:2 FtSaB	Sq
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6:2 FtSaAm	513	60	58	44	86	34	M-PFOS	PFOS	Sq
Perfluoropropane sulfonamide	FPrSA	248	40	78	32	119	26	M-PFBS	PFBS	Ql
Perfluorobutane sulfonamide	FBSA	298	50	119	26	78	32	M-PFBS	PFBS	Ql
Perfluoropentane sulfonamide	FPeSA	348	40	78	35	119	35	M-FOSA	FOSA	Ql
Perfluorohexane sulfonamide	FHxSA	398	58	78	36	119	28	M-FOSA	FHxSA	Qn
Perfluorooctane sulfonamide	FOSA	498	40	78	30	319	30	M-FOSA	FOSA	Qn
Perluorobutane sulfinate	PFBSi	283	50	83	32	119	26	M-PFBS	PFBS	Ql
Perfluoropentane sulfinate	PFPeSi	333	40	83	35	119	35	M-PFPeA	PFPeA	Ql
Perfluorohexane sulfinate	PFHxSi	383	20	319	40	83	40	M-PFHxA	PFHxA	Ql
Perfluorooctane sulfinate	PFOSi	483	40	119	40	419	40	M-PFOA	PFOA	Ql
6:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	6:2 FTSO2PrAd-DiMeEtS	618	40	203	30	152	30	M-PFOA	PFOA	Ql
8:2 fluorotelomer sulfonyl propanoamido-dimethylethyl sulfonate	8:2 FTSO2PrAd-DiMeEtS	718	40	206	30	152	30	M-PFOA	PFOA	Ql
N-sulfo propyl dimethyl ammonio propyl perfluorobutane sulfonamide	SPrAmPr-FBSA	507	40	383	40	182	40	M-FOSA	FOSA	Ql
N-sulfo propyl dimethyl ammonio propyl perfluoropentane sulfonamide	SPrAmPr-FPeSA	557	40	433	40	182	40	M-FOSA	FOSA	Ql

N-sulfo propyl dimethyl ammonio propyl perfluorohexane sulfonamide	SPrAmPr-FHxSA	607	40	483	40	182	40	M-FOSA	FOSA	Ql
N-Trimethylammoniopropyl perfluorobutane sulfonamide	TAmPr-FBSA	399	40	60	40	116	40	M-FOSA	FOSA	Ql
N-Trimethylammoniopropyl perfluoropentane sulfonamide	TAmPr-FPeSA	449	40	60	40	116	40	M-FOSA	FOSA	Ql
N-Trimethylammoniopropyl perfluorohexane sulfonamide	TAmPr-FHxSA	499	40	60	40	116	40	M-FOSA	FOSA	Ql
6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	6:2 FTTh-PrAd-DiMeEtS	586	35	135	20	80	20	M-PFOS	PFOS	Ql
N-methylperfluorooctane sulfonamido acetic acid	N-MeFOSAA	570	34	169	20	419	10	M-N-MeFOSAA	N-MeFOSAA	Qn
N-ethylperfluorooctane sulfonamido acetic acid	N-EtFOSAA	584	34	419	20	526	20	M-N-EtFOSAA	N-EtFOSAA	Qn
3-Perfluoropentyl propanoic acid *(5:3)*	FPePA	341	19	237	14	217	24	M-PFPeA	PFPeA	Sq
2H-perfluoro-2-octenoic acid	FHUEA	357	18	293	17	243	34	M-PFHxA	PFHxA	Sq
2-perfluorohexylethanoic acid	FHEA	377	20	293	22	63	7	M-PFHxA	PFHxA	Sq
Perfluorooctane sulfonamido acetic acid	FOSAA	556	45	498	27	78	40	M-PFOA	PFOA	Sq
Perfluoro[1,2,3,4-$^{13}C_4$]butanoic acid	[$^{13}C_4$] PFBA	217	20	172	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[3,4,5-$^{13}C_3$]pentanoic acid	[$^{13}C_3$] PFPeA	266	20	222	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]hexanoic acid	[$^{13}C_2$] PFHxA	315	20	270	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]heptanoic acid	[^{13}C4] PFHpA	367	15	322	11	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid	[$^{13}C_4$] PFOA	417	20	372	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]octanoic acid	[$^{13}C_2$] PFOA	415	20	370	9	n/a	n/a	n/a	n/a	n/a

Perfluoro[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$] PFNA	468	22	423	8	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$] PFDA	515	22	470	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$] PFUnDA	565	22	519	10	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2-$^{13}C_2$]dodecanoic acid	[$^{13}C_2$] PFDoDA	615	22	570	10	n/a	n/a	n/a	n/a	n/a
2H-Perfluoro-[1,2-$^{13}C_2$]-2-octenoic acid	[$^{13}C_2$] FHUEA	359	18	294	17	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[2,3,4-^{13} C_3]-butanesulfonate	[$^{13}C_2$] PFBS	302	31	99	30	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$] PFHxS	403	58	103	28	n/a	n/a	n/a	n/a	n/a
Perfluoro[1,2,3,4-$^{13}C_4$]octane sulfonate	[$^{13}C_2$] PFOS	503	70	99	34	n/a	n/a	n/a	n/a	n/a
4:2[1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 4:2 FTS	329	30	81	25	n/a	n/a	n/a	n/a	n/a
6:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 6:2 FTS	429	44	409	22	n/a	n/a	n/a	n/a	n/a
8:2 [1,2-$^{13}C_2$] fluorotelomer sulfonate	[$^{13}C_2$] 8:2 FTS	529	45	81	35	n/a	n/a	n/a	n/a	n/a
Perfluoro-1-[$^{13}C_8$]octane sulfonamide	[$^{13}C_8$] FOSA	506	40	78	30	n/a	n/a	n/a	n/a	n/a
Methyl-d_3-perfluorooctane sulfonamido acetic acid	[$^{2}H_3$] MeFOSAA	573	34	419	20	n/a	n/a	n/a	n/a	n/a
Ethyl-d_5-perfluorooctane sulfonamido acetic acid	[$^{2}H_5$] EtFOSAA	589	34	419	20	n/a	n/a	n/a	n/a	n/a

*PI (precursor ion), CV (cone voltage), FI (fragmentation ion), CE (collision energy), Qn (quantitative), Sq (semiquantitative), Ql (qualitative), Sc (Screen)[1-3]

Results and Discussion

Table 4.5. Influent analyte concentrations before and after TOP assay (ng/L and nmol) ± standard error and summed masses (nmol) ± propagated standard error.

	Analyte	MW	Before TOP Assay (ng/L)	After TOP Assay (ng/L)	Before TOP Assay (nmol)	After TOP Assay (nmol)	Net production (nmol)
Known PFCAs	PFBA	214	78 ± 14	510 ± 37	0.36 ± 0.18	2.4 ± 0.1	2.0 ± 0.1
	PFPeA	264	400 ± 83	970 ± 110	1.5 ± 0.1	3.7 ± 0.2	2.2 ± 0.2
	PFHxA	314	690 ± 140	5300 ± 460	2.2 ± 0.2	17 ± 1	15 ± 1
	PFHpA	364	150 ± 19	230 ± 16	0.41 ± 0.02	0.63 ± 0.02	0.22 ± 0.03
	PFOA	414	900 ± 210	1200 ± 390	2.2 ± 0.2	2.9 ± 0.4	0.70 ± 0.50***
	PFNA	464	23 ± 16	88 ± 7	0.050 ± 0.015	0.19 ± 0.05	0.14 ± 0.05***
Known PFSAs	PFBS	300	16 ± 3	<LOQ	0.053 ± 0.005	<LOQ	***
	PFPeS	350	28 ± 9	<LOQ	0.080 ± 0.011	<LOQ	***
	PFHxS	400	1600 ± 430	1400 ±	4.0 ± 0.5	3.5 ± 0.2	***
	PFHpS	450	87 ± 34	65 ±	0.19 ± 0.03	0.14 ± 0.02	***
	PFOS	500	3500 ± 470	2900 ±	7.0 ± 0.4	5.8 ± 0.2	***
Kn	4:2 FtSA	328	12 ± 3	<LOD	0.037 ± 0.009	<LOD	

	6:2 FtSA	428	1100 ± 130	<LOD	2.6 ± 0.1	<LOD	
	8:2 FtSA	528	180 ± 68	<LOD	0.34 ± 0.06	<LOD	
	FPeSA	348	82 ± 36	<LOD	0.24 ± 0.05	<LOD	
	FHxSA	398	2500 ± 380	<LOD	6.3 ± 0.4	<LOD	
	FOSA	448	360 ± 86	<LOD	0.80 ± 0.09	<LOD	
	N-Tamp-FHxSA	499	91 ± 29	<LOD	0.18 ± 0.05	<LOD	
Summary	ΣPFCAs (nmol)				6.7 ± 0.8	27 ± 1	20 ± 2
	ΣPFSAs (nmol)				11 ± 1	9.4 ± 0.3	***
	ΣKnown precursors (nmol)				11 ± 0	<LOD	
	ΣTotal PFASs (nmol)				29 ± 1	37 ± 1	

***The difference in the mean values of the two groups is not great enough to reject the possibility that the difference is due to random sampling variability. There is not a statistically significant difference between the TOP assay before and after oxidation.

Top Assay Calculations

a) Calculation for net production of PFCAs:

$$\text{Net Production of PFCAs (nmol)} = \Sigma((PFBA_{after\ oxid} - PFBA_{before\ oxid}) + (PFPeA_{after\ oxid} - PFPeA_{before\ oxid}) + (PFHxA_{after\ oxid} - PFHxA_{before\ oxid}) + (PFHpA_{after\ oxid} - PFHpA_{before\ oxid}) + (PFOA_{after\ oxid} - PFOA_{before\ oxid}) + (PFNA_{after\ oxid} - PFNA_{before\ oxid})$$

Example:

$$\text{Net Production of PFCAs (nmol)} = \Sigma((2.4 - 0.36) + (3.7 - 1.5) + (17 - 2.2) + (0.63 - 0.41) + (2.9 - 2.2) + (0.19 - 0.050) = 20.100\ nmol$$

b) Calculation for net production of PFCAs (simplified): $Net\ Production\ of\ PFCAs\ (nmol) = \Sigma PFCAs_{after\ oxid} - \Sigma PFCAs_{before\ oxidation}$

Example: Net Production of PFCAs $(\text{nmol}) = 27 - 6.7 = 20\ nmol$

c) **Equation S1.** Calculation of unknown precursor mass. $Unknown\ Precursor\ Mass\ (nmol) = \Sigma PFCAs_{after\ oxid} - \Sigma PFCAs_{before\ oxid} - \Sigma Known\ Precursors_{before\ oxid}$

Example: Unknown Precursor Mass $(\text{nmol}) = 27 - 6.7 - 10 = 9.6\ nmol$

d) **Equation S2**. Calculation of total mass of PFASs accounted for before the TOP assay (%).$^{\Psi}$

$$\text{Total mass accounted for by known PFAS (\%)} = \left(\frac{(\Sigma PFCAs_{before\ oxid} + \Sigma PFSAs_{before\ oxid} + \Sigma Known\ Precursors_{before\ oxid})}{(\Sigma PFCAs_{after\ oxid} + \Sigma PFSAs_{after\ oxidation})} \times 100\right)$$

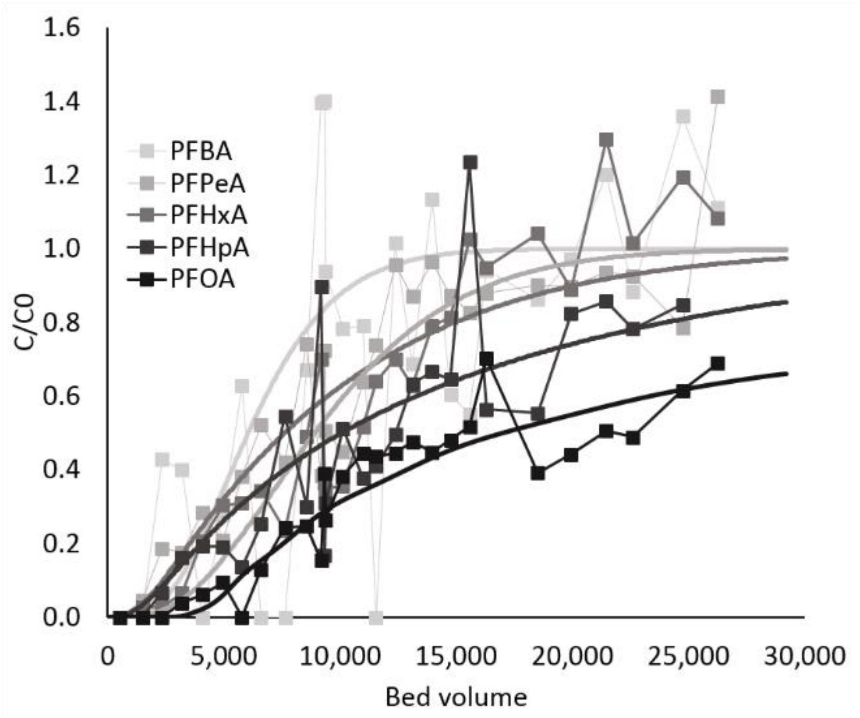
Example: $^{\Psi}$

$$\text{Total mass accounted for by known PFAS (\%)} = \left(\frac{(6.7+11+10)}{(27+11)} \times 100\right) = \left(\frac{28}{38}\ x\ 100\right) = 75\%$$

[Ψ]As a result of the insignificant, but different, values for ΣPFSAs before and after oxidation the authors' have elected to underestimate the total mass accounted for by known PFAS (%) by using ΣPFSAs before oxidation.

Figure 4.5. Breakthrough curves for lead vessel of PFCAs, PFSAs, 6:2 FtS and FHxSA. Red stars denote the C/C₀ for the TOP assay at select BVs.

a)



b)

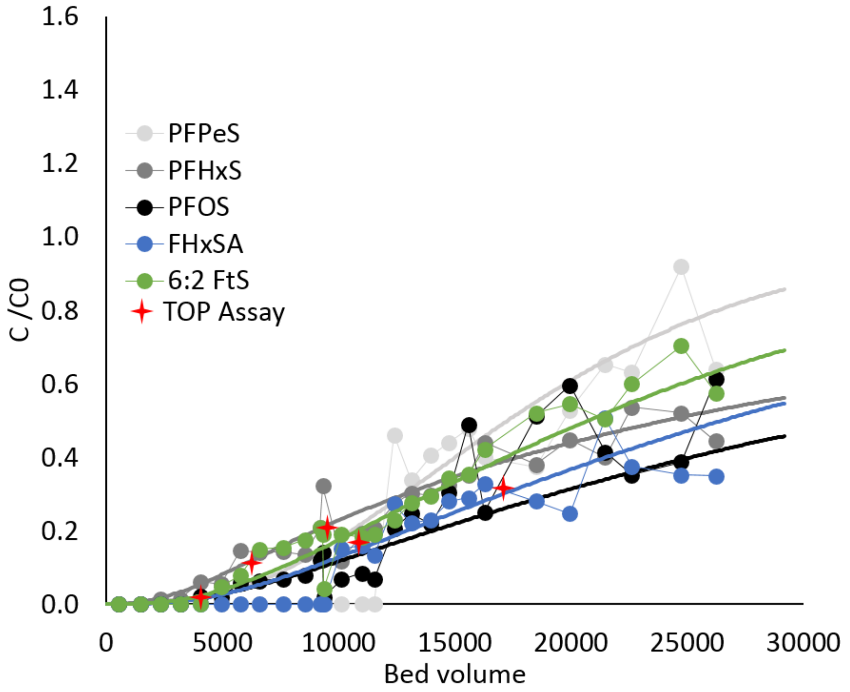


Table S2. Analyte name, bed volumes at 20% breakthrough, and analytical retention time.

	Bed Volumes	Retention Time (min)
PFBA	3900	6.8
PFPeA	3500	7.9
PFHxA	5500	9.4
PFHpA	4100	11.3
Br-PFOA	6200	12.8
L-PFOA	8500	13.3
PFPeS	10500	9.4
Br-PFHxS	8800	10.8
L-PFHxS	9000	11.2
PFHpS	14000	13.3
Br-PFOS	12900	14.8
L-PFOS	14900	15.5
6:2 FtS	10800	13.3
Br-FHxSA	11600	13.1
L-FHxSA	13000	13.6

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Chapter 6: Conclusions

Per- and polyfluoroalkyl substances (PFASs) are emerging contaminants that are abundant in the environment. The manufacturing production and application, which dates back to the 40’s, continues to evolve as a result of various attempts to phase out PFAS. Humans are exposed to PFAS from a number of sources, and this dissertation discusses two of those sources, including consumer products and aqueous film-forming foams (AFFFs). Only drinking water has lifetime health advisory values for only perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), yet many other PFASs are likely to be present in consumer products and AFFFs. The three chapters in this dissertation discuss the number, type, and disposition of PFASs in consumer products, field sampling materials, and AFFF-contaminated groundwater undergoing treatment.

In Chapter 2, 17 papers and textiles were examined for fluorinated content. Since papers and textiles can contribute to exposure to PFASs, it was important to evaluate extractable volatile and ionic PFASs by liquid chromatography mass spectrometry (LC-MS/MS) and gas chromatography mass spectrometry, respectively. In this study, methanol extraction was used as a proxy for transferable PFASs from the surface of papers and textiles. The volatile and ionic PFASs and the unknown precursors in the methanol extracts by the total oxidizable precursor (TOP) assay, were compared to the total fluorine content measured by particle-induced gamma ray emission (PIGE) spectroscopy, measured before and after methanol extraction. Volatile PFAS, ionic PFAS, and unknown precursors by TOP assay only accounted for 0.0-2.2%; 0.0-0.41%;

and 0.021-14%, respectively of the total fluorine by PIGE, prior to extraction. In the oldest material, the summed mass of volatile PFAS, ionic PFAS, and unknown precursors accounted for a maximum of 16% of the total fluorine present before extraction. The total fluorine remaining on papers and textiles after extraction, plus the individual PFAS and unknown precursors removed by methanol extraction accounted for 64 to 110% of the total fluorine originally present. Future research could examine aged materials for a wide range of PFAS and fluoropolymers, and explore the breakdown and leaching of polymeric materials under realistic landfill conditions.

In Chapter 3, 66 materials that are used during field sampling were extracted in methanol and analyzed by LC-MS/MS. The extractable PFAS content was then compared to total fluorine by PIGE. Total fluorine by PIGE was observed in 35% of field materials, where individual PFASs were only observed in 15% of materials, indicating that extractable PFASs are less abundant relative to the total fluorine. Although individual PFASs were observed at $\mu g/m^2$ concentrations, for many materials that don't come in direct contact with field samples (e.g. groundwater, surface water, soil, sediment) there are no plausible scenarios for cross contamination. However, for materials which do come in direct contact with samples, the concentrations that are <LOD and <LOQ cannot plausibly support a cross contamination scenario. Thus, many materials are unnecessarily excluded from field sampling. Future work should include a larger number of PFASs and a greater number and diversity of field sampling materials that have the potential to directly interact with field samples (e.g. acetate liners, bailers, etc).

In Chapter 4, a pilot-scale granulated activated carbon (GAC) system, containing lead and lag vessels, was operated for nine months at an AFFF-contaminated site. In weekly or bi-weekly samples, a total of 17 PFAS were routinely observed, and 13 PFAS breakthrough curves were modeled. Breakthrough of both branched and linear PFASs was reported, and the total oxidizable precursor (TOP) assay was used to quantify any unknown precursor mass. Of the net production of perfluoroalkyl carboxylates by the TOP assay, 80 ± 30% was accounted for by individual PFASs. Breakthrough of PFAS at 20% of the influent concentration correlated with chromatographic retention time ($R^2 = 0.61$) on a C18 analytical column. Practically, this relationship can be applied to other remediation efforts that rely on hydrophobic sorption processes. Chromatographic retention time is a parameter collected for individual PFAS during LC-MS/MS or LC-high resolution mass spectrometry and can be used to predict relative breakthrough order. Future work could further explore the predictive relationship between relative breakthrough order and chromatographic retention times for a larger number of environmentally relevant PFAS.

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