

Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

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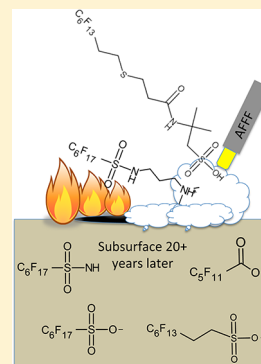
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Supporting Information

ABSTRACT: Several classes of polyfluorinated chemicals that are potential precursors to the perfluorinated carboxylates and sulfonates are present in aqueous film-forming foams (AFFF). To assess the persistence of these AFFF-derived precursors, groundwater, soil, and aquifer solids were obtained in 2011 from an unlined firefighter training area at a U.S. Air Force Base where AFFF was regularly used between 1970 and 1990. To measure the total concentration of perfluorinated carboxylate and sulfonate precursors in archived AFFF formulations and AFFF-impacted environmental samples, a previously developed assay that uses hydroxyl radical to oxidize precursors to perfluorinated carboxylates was adapted for these media. This assay was employed along with direct measurement of 22 precursors found in AFFF and a suite of other poly- and perfluoroalkyl substances (PFASs). On a molar basis, precursors accounted for 41–100% of the total concentration of PFASs in archived AFFF formulations. In the training area, precursors measured by the oxidation assay accounted for an average of 23% and 28% of total PFASs (i.e., precursors and perfluorinated carboxylates and sulfonates) in groundwater and solids samples, respectively. One precursor in AFFF, perfluorohexane sulfonamide amine, was observed on several highly contaminated soil and aquifer solids samples, but no other precursors present in AFFF formulations were detected in any samples at this field site. Suspected intermediate transformation products of precursors in AFFF that were directly measured accounted for approximately half of the total precursor concentration in samples from the training site. The fraction of PFASs consisting of perfluorinated carboxylates and sulfonates was greater in groundwater and solid samples than in any archived AFFF formulations, suggesting that much of the mass of precursors released at the site was converted to perfluorinated carboxylates and sulfonates. The precursors that have persisted at this site may generate significant amounts of additional perfluorinated carboxylates and sulfonates upon remediation of contaminated groundwater or aquifer solids.



INTRODUCTION

Aqueous film-forming foams (AFFFs) have been used since the 1960s to extinguish hydrocarbon-based fuel fires at military bases, airports, oil refineries, and municipal firefighter training facilities.¹ AFFF formulations contain both hydrocarbon and fluorocarbon surfactants to enhance the spreading of AFFF along hydrocarbon–water and air–water interfaces.¹ Where these foams have been deployed accidentally, in response to fires, or in unlined firefighter training areas, high concentrations of poly- and perfluoroalkyl substances (PFASs) have been detected in biota,^{2–5} surface water,^{2–5} and groundwater.^{6–9} For example, nine years after 22 000 L of AFFF was released at the Toronto airport, perfluorooctane sulfonate (PFOS) concentrations in fish and surface waters were 2–10 times higher than those observed in locations upstream of the release.⁴

The types of PFASs in AFFF vary by year of production and manufacturer. AFFF manufactured by the 3M Company reportedly contained perfluorinated carboxylates from the 1960s and early 1970s^{10–13} and perfluorinated sulfonates from the 1970s to 2001,^{10,13–15} when 3M ceased AFFF production. AFFF formulations manufactured by 3M between 1988 and 2001 also contained multiple polyfluorinated

surfactants with a four to six carbon perfluorinated chain linked by a sulfonamide moiety to a positively charged alkyl group (Supporting Information (SI) Figure S1).¹⁵ Notably, no polyfluorinated surfactants containing an 8-carbon perfluoroalkyl chain (i.e., C₈) were observed in these 3M formulations.¹⁵ In fluorotelomer-based AFFF manufactured by six other formulators between 1984 and 2010, the only PFASs identified were polyfluorinated surfactants containing a 4–10 carbon perfluorinated chain linked by 2–3 nonfluorinated carbons to a charged alkyl group (Figure S1).¹⁵

The fate of the polyfluorinated compounds in AFFF released to soil and groundwater is not well understood, but the nonfluorinated part of the molecule attached to the perfluorinated chain may be amenable to microbial or chemical transformation.^{16–21} These reactions could produce perfluorinated carboxylates or perfluorinated sulfonates. Therefore, we collectively refer to these polyfluorinated compounds in AFFF

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and their polyfluorinated intermediate products as perfluoroalkyl acid (PFAA) precursors, or simply precursors.

Previous studies have provided evidence of the occurrence of PFAA precursors at AFFF-impacted sites. For example, precursors in Ansul and 3M AFFF formulations were detected in groundwater from five U.S. military firefighter training areas, albeit at low concentrations relative to PFAAs.⁹ One precursor in AFFF manufactured by National Foam, 6:2 fluorotelomer sulfonamide betaine, was recently detected on soils near an airport in Norway where AFFF was used.²² The precursors may exhibit a strong affinity for soil and aquifer solids: due to the presence of anionic, cationic, and zwitterionic alkyl moieties, many of the precursors in AFFF are likely to undergo ion exchange processes. Precursors in AFFF may also partition to soil organic matter, especially those containing perfluorinated groups with more than seven carbon atoms.²³

Multiple analytical tools are needed to assess the transformation of precursors in AFFF, because the transformation products may not be readily identifiable. An assay developed for detection of PFAA precursors in stormwater²⁴ was adapted to conditions encountered in dilute AFFF, groundwater, and surficial soil and aquifer solids extracts. The assay was used to quantify the total concentration of PFAA precursors in the samples by converting them into readily measurable perfluorinated carboxylates through reactions with hydroxyl radical. The precursor assay was applied to archived AFFF formulations and groundwater, soil, and aquifer solids from a site where AFFF was used between 1970 and 1990 in conjunction with direct measurement of 22 PFAA precursors found in AFFF formulations, potential intermediate transformation products for which standards were available, and perfluorinated sulfonates and carboxylates. Results were used to assess the persistence of AFFF-derived precursors and to evaluate their in situ transformation to PFAAs.

MATERIALS AND METHODS

Materials. Structures of PFAA precursors in AFFF are depicted in Figure S1. Abbreviations for these and other PFASs are listed in Table S1. All isotopically labeled standards, perfluorinated carboxylates, perfluorinated sulfonates, perfluorooctane sulfonamide (FOSA), 6:2 fluorotelomer sulfonate (6:2 FtS), and 8:2 fluorotelomer sulfonate (8:2 FtS) were purchased from Wellington Laboratories. Commercial source materials containing 6:2 fluorotelomer sulfonamido betaine, 6:2 fluorotelomer sulfonamido amine, 6:2 fluorotelomer thioamido sulfonate, 6:2 fluorotelomer thio hydroxy ammonium and 5:1:2, 7:1:2, 9:1:2, 5:3, 7:3, and 9:3 fluorotelomer betaines were provided by the Fire Fighting Foam Coalition⁹ and were used for quantitation of those analytes. All other solvents and chemicals were purchased from Sigma Aldrich or Fisher Scientific at the highest purity available.

Archived samples of AFFF formulations manufactured by 3M, Ansul, Chemguard, National Foam, and Buckeye were obtained from U.S. military bases as described previously.¹⁵ Some of these AFFF formulations were previously used to identify the structures of PFASs in AFFF.¹⁵

Site Information. Groundwater, soil, and aquifer solids samples were collected from a location at Ellsworth Air Force Base in Piedmont, SD. Firefighter training was conducted between 1942 and 1990. As part of these activities, waste oil, solvents, and fuels were placed in an unlined pit, ignited, and subsequently extinguished using various firefighting agents, including AFFF after 1970. Remedial activities targeted at

solvent contamination, including oxygen infusion, soil vapor extraction, and groundwater extraction followed by ex situ treatment, occurred in the area where samples were collected. The subsurface at this site consists of low-to-moderate permeability clay loam and gravely sandy loam alluvial soil, underlain by Pierre Shale bedrock. Additional details on the site and firefighter training exercises are summarized elsewhere.²⁵

Records of the exact makeup of AFFF formulations used onsite during this period are not available. However, it is likely that AFFF manufactured by 3M, National Foam, and Ansul accounted for most of the materials used because they were approved for U.S. military use from 1976 to 1990.²⁶ 3M reportedly supplied most of the U.S. military's AFFF prior to its cessation of AFFF production in 2001.²⁷ As of 2004, 75% of the military's stockpiled AFFF was manufactured by 3M.²⁷

Groundwater, Soil, and Aquifer Solids Collection. Groundwater and soil samples were collected in October 2011 from a 1200 m by 600 m area encompassing the burn pit (Figures S2–S3). Groundwater was collected from permanent and temporary wells using techniques designed to minimize contamination of samples with PFASs.²⁵ The groundwater depth was 2–8 m below ground surface (bgs). Soil samples were collected 0.6 m bgs and aquifer solids were collected approximately 5–6 m bgs.²⁵

Sample Storage and Preparation for Direct Analysis. Archived AFFF samples were stored at room temperature. The number (*n*) of AFFF samples analyzed from each manufacturing category was as follows: 3M 1988, 1989: *n* = 2; 3M 1993–2001: *n* = 6; National Foam 2002–2008: *n* = 3; Buckeye 2009: *n* = 1; Chemguard 2008, 2010: *n* = 2; Ansul 1984, 1987: *n* = 2; Ansul 2009, 2010: *n* = 2. AFFF formulations were analyzed in duplicate after two sequential thousand-fold dilutions in methanol. Internal standards were added to AFFF after the final dilution.

Groundwater samples were stored at 4 °C until use and analyzed in duplicate. Twenty-two groundwater samples were analyzed. Groundwater samples were inverted five times to ensure adequate mixing before subsampling. A 500 µL aliquot of groundwater collected from 5 cm below the liquid surface was added to 500 µL of methanol in a 2 mL microcentrifuge tube. Samples were centrifuged at 15 000 rpm for 5 min to remove suspended particles. Each groundwater sample was initially analyzed in 50:50 methanol: water at 2.5 times dilution. Samples were diluted further as necessary to achieve concentrations within the working range of the calibration curve (i.e., 0.1 µg/L to 24 µg/L). Internal standards were added to groundwater after the final dilution. Whole method limits of detection (LOD) ranged from 0.1 to 0.5 µg/L (Table S2). Spike recoveries and method precision were within the range reported in previous studies^{8,9} (Table S2).

Soil and aquifer solids samples were stored at 4 °C until analysis. Sixteen soil samples and ten aquifer solids samples were analyzed. All samples were extracted in triplicate. The soil extraction method was similar to the approach used by Higgins et al.²⁸ Briefly, a 500 mg subsample of a homogenized soil sample was placed in a 15 mL LDPE centrifuge tube containing 2.5 mL of 0.1% ammonium hydroxide (NH₄OH) in methanol. Tubes were vortexed for 20 seconds, sonicated for 30 min at 30–35 °C, and shaken on a rotating table at 150 rpm for two hours. The extract was separated from the soil by centrifugation at 5000 rpm for 5 min. The supernatant was transferred to a new 15 mL centrifuge tube with a glass pipet. Extractions were repeated two more times to ensure complete removal of all

PFASs (Figure S4). The combined 7.5 mL extract was evaporated to dryness with nitrogen in a 45 °C water bath (Organomation N-EVAP 24). Three extractions in 0.1% NH₄OH/methanol were sufficient to remove all anionic, cationic, and zwitterionic PFASs; additional extractions in acidic methanol did not improve recoveries. Extracts were reconstituted in 1.5 mL of 0.1% acetic acid in methanol and kept at 45 °C for another 30 min to ensure dissolution of target analytes. The extract was transferred to a 2 mL microcentrifuge tube containing 25 mg of ENVI-CARB and centrifuged at 15 000 rpm for 5 min. The ENVI-CARB was used to remove excess organic matter that could suppress ionization of the compounds in the mass spectrometer or reduce the efficiency of the oxidative assay. Control experiments demonstrated that the ENVI-CARB did not remove any PFASs. Reconstituted soil extracts were initially diluted five times for analysis in a 50:50 methanol: water mixture and diluted further as necessary to achieve peak areas that were within the working range of the calibration curve. Internal standards were added after final dilution. Whole method LODs ranged from 0.4 to 3 µg/kg (Table S3). Spike recoveries and method precision for solid sample analysis were within the range reported in previous studies²⁸ (Table S3).

Sample Preparation for Precursor Oxidation Assay. A previously developed method for converting PFAA precursors to perfluorinated carboxylates in urban runoff was adapted to the AFFF matrix.²⁴ Under the conditions of the assay, precursors to both the perfluorinated carboxylates and the perfluorinated sulfonates are converted to perfluorinated carboxylates.²⁴ Exposure of diluted AFFF or groundwater amended with 60 mM potassium persulfate in 0.125 M NaOH followed by heating for six hours at 85 °C produced an amount of hydroxyl radical that was sufficient to convert all precursors into perfluorinated carboxylates. For soils and aquifer solids, the methanolic soil extract was evaporated to dryness with nitrogen gas and resuspended in 6 mL of 60 mM persulfate and 0.125 M NaOH before heating. The ENVI-CARB cleanup step did not remove PFAA precursors as determined by the oxidation assay (Figure S6). After reaction, all samples were neutralized with concentrated HCl and amended with methanol before they were subsampled for analysis. Detailed information on sample preparation for the oxidation assay is included in the (discussion and Figures S5–S6).

Analytical Methods. All samples were analyzed in 500 µL of 50:50 methanol: water containing 50 µL of a 20 µg/L internal standard stock solution. Analysis was conducted on an Agilent 6410 LC-MS/MS according to the method described previously.²⁴ A list of ion transitions and MS parameters is included in Table S1.

Analyte Quantification. All perfluorinated carboxylates, perfluorinated sulfonates, 6:2 FtS, 8:2 FtS, and FOSA were quantified using isotope dilution (Table S1) with certified analytical standards. The fluorotelomer precursors in AFFF formulations were quantified using commercial source materials; a source material was only available for the C₆ homologues (i.e., compounds containing a 6-carbon perfluorinated group) of Ansul, Chemguard, and National Foam fluorotelomer precursors. For non-C₆ homologues of these compounds, the calibration curve for the C₆ compound was used to estimate the concentration of the entire family of homologues, with a correction for perfluorinated chain length, as detailed in the SI.

No certified standard or commercial source material was available for perfluorohexane sulfonamide (FHxSA) or any of

the precursor compounds in 3M AFFF formulations. The concentration of FHxSA was estimated from the calibration curve of FOSA with a correction for perfluorinated chain length. The concentrations of the 3M compounds were estimated using the precursor oxidation data from 3M AFFF formulations (Table S4). Briefly, the total molar concentration of precursors for each homologue group was estimated from the concentration of the corresponding perfluorinated carboxylate homologue produced upon oxidation of the AFFF sample. Because most 3M samples contained two types of precursors per homologue, each precursor of the same chain length was assumed to yield an equal instrument response on a molar basis. A more detailed explanation and a discussion of the uncertainty associated with this approach is included in the SI.

Total Precursor Concentration and Total PFAS Concentration. The summation of the total molar concentration of perfluorinated carboxylates produced upon oxidation can be used to estimate the total concentration of PFAA precursors (i.e., the total amount of precursors to both perfluorinated carboxylates and perfluorinated sulfonates) present in a sample. Because less than 75% of the 6:2 and shorter fluorotelomer compounds initially present in a sample are converted into measurable perfluorinated carboxylates,²⁴ the total PFAA precursor concentration determined by this approach slightly underestimates the actual concentration of precursors in samples that contained a high proportion of C₆ and shorter fluorotelomer compounds. For sulfonamide-containing and 8:2 fluorotelomer compounds, this approach does not lead to a substantial error because more than 95% of these precursors are converted into measurable perfluorinated carboxylates.²⁴ The total PFAA precursor concentration combined with the concentrations of all perfluorinated sulfonates and perfluorinated carboxylates is referred to from this point forward as the total PFAS concentration.

RESULTS

Analysis of Pure AFFF Samples. AFFF samples manufactured by 3M (1988–2001), National Foam (2002–2008), Ansul (1984–2010), Chemguard (2008–2010), and Buckeye (2009) were directly analyzed for AFFF-related PFAA precursors (SI Table S5), perfluorinated sulfonates, and perfluorinated carboxylates (Figure 1a, Table S5) in addition

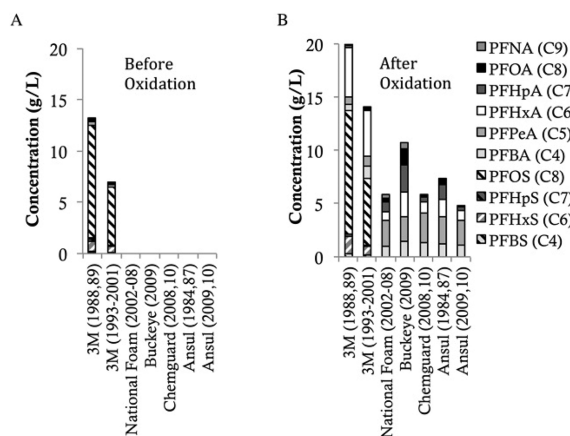


Figure 1. Average concentrations of perfluorinated sulfonates and carboxylates in AFFF formulations analyzed before (a) and after oxidation (b). Dates represent the years of manufacture of AFFF formulations analyzed in each category.

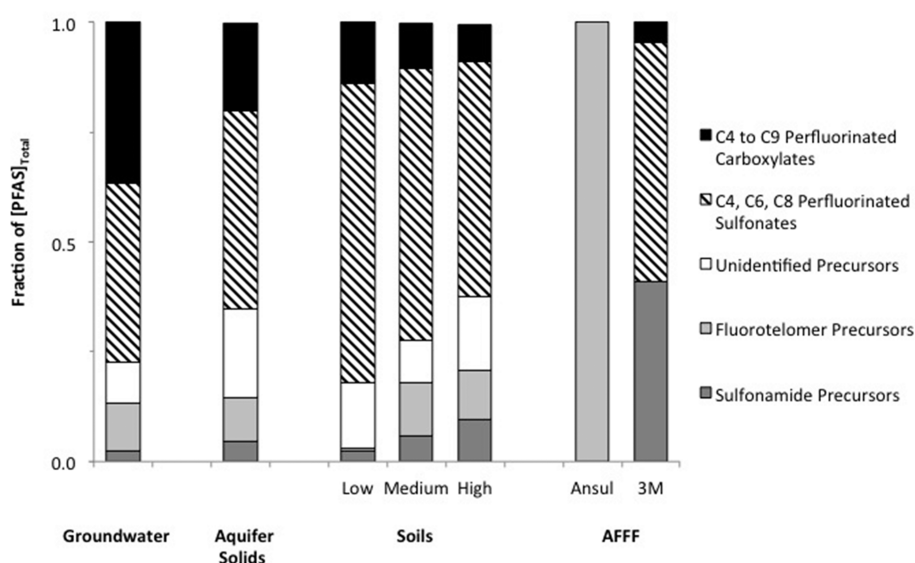


Figure 2. The average molar fraction of n samples of different classes of PFASs in groundwater ($n = 22$), aquifer solids ($n = 10$), low contamination soils ($n = 6$), medium contamination soils ($n = 5$), high contamination soils ($n = 5$) and AFFF formulations (Ansul: $n = 2$, 3M: $n = 2$) from the 1980s. The total concentration of PFASs is equal to the summation of the concentrations of perfluorinated carboxylates, perfluorinated sulfonates, and total precursors (i.e., precursors measured by LC-MS/MS plus additional precursors measured by the oxidation assay). Low, medium, and high contamination soils contained 0.1–1 $\mu\text{mol}/\text{kg}$, 1 to 10 $\mu\text{mol}/\text{kg}$, and 10–200 $\mu\text{mol}/\text{kg}$ total PFASs, respectively. Fluorotelomer and sulfonamide precursors were measured through chemical-specific analysis. Unidentified precursors are the portion of perfluorinated carboxylate production in oxidized samples that could not be attributed to the fluorotelomer and sulfonamide-based precursors.

to perfluorinated carboxylates generated upon oxidation (Figure 1b, Table S6). The perfluorinated sulfonates were the primary PFASs in the 3M formulations, with 0.1–0.2 times as much PFHxS (0.5–1.4 g/L) as PFOS (4.9–11.4 g/L). Relatively low concentrations of perfluorinated carboxylates (0.1–0.5 g/L) were also detected in the 3M formulations. Neither perfluorinated carboxylates nor perfluorinated sulfonates were detected in any of the formulations from the other manufacturers.

Upon oxidative treatment with the precursor assay, between 5.9 and 10.8 g/L of perfluorinated carboxylates were generated from oxidation of the PFAA precursors in AFFF samples (Figure 1b). As observed previously,²⁴ when a sample containing PFAA precursors was exposed to hydroxyl radical under the assay conditions, the C_n sulfonamide-containing precursor compounds (i.e., typically precursors to the perfluorinated sulfonates) were transformed to equimolar quantities of the corresponding C_n perfluorinated carboxylates. The fluorotelomer precursor compounds (i.e., typically precursors to the perfluorinated carboxylates) were transformed to a mixture of C_4 to C_{n+1} perfluorinated carboxylates.²⁴ For $n:2$ fluorotelomer sulfonates, the ratio between the C_{n+1} : C_n : C_{n-1} : C_{n-2} perfluorinated carboxylate products was approximately 0.25:1.0:1.3:1.0.²⁴ Thus, C_n precursor compounds in 3M formulations produced equimolar quantities of the corresponding C_n perfluorinated carboxylate, whereas $n:2$ precursors in the other AFFF formulations produced a mixture of perfluorinated carboxylate products, mainly C_n and lower.

All AFFF formulations except those from Buckeye produced mainly C_5 and C_6 perfluorinated carboxylates upon oxidation: in 3M formulations, PFHxA was the predominant product whereas National Foam, Chemguard, and Ansul produced substantial amounts of both PFPeA and PFHxA upon oxidation. The C_6 PFAA precursors responsible for PFHxA production in the 3M AFFF were perfluorohexane sulfonamide

amine (PFHxSA) and perfluorohexane sulfonamide amino carboxylate (Table S5, S6).¹⁵ The C_6 PFAA precursors responsible for PFHxA and PFPeA in the fluorotelomer-based AFFF formulations were 6:2 fluorotelomer sulfonamide amine and 6:2 fluorotelomer sulfonamide betaine in National Foam formulations and 6:2 fluorotelomer thioamido sulfonate in Ansul and Chemguard formulations (Table S5, S6).¹⁵ Notably, PFOA was not the major oxidation product of any of the formulations studied. Ansul AFFF formulations from 1984 and 1987 produced approximately four times as much PFOA upon oxidation as samples from 2009 and 2010, suggesting a shift away from C_8 -based compounds. AFFF manufactured by Buckeye contained a mixture of precursor compounds, all fluorotelomer betaines, with perfluorinated chains ranging in length from C_5 to C_9 . With C_7 serving as the dominant homologue in Buckeye's AFFF, PFHpA, and PFHxA were the predominant perfluorinated carboxylates produced upon oxidation.

Analysis of AFFF-Contaminated Groundwater and Soil Samples. Groundwater samples collected from the firefighter training area contained a suite of PFASs: the average PFAS composition in groundwater samples was 37% perfluorinated carboxylates, 40% perfluorinated sulfonates, and 23% PFAA precursors (Figure 2). PFAS concentrations decreased in groundwater as distance from the burn pit increased; the spatial significance of PFAS concentrations in groundwater are discussed in more depth in a companion paper.²⁵ Median concentrations of PFOS (19 $\mu\text{g}/\text{L}$) and PFOA (26 $\mu\text{g}/\text{L}$) were comparable to or lower than those of their C_6 analogs, PFHxS (71 $\mu\text{g}/\text{L}$) and PFHxA (36 $\mu\text{g}/\text{L}$) (Table S7). The measurable PFAA precursors in groundwater, which predominately consisted of C_6 -based compounds, included 6:2 FtS (median concentration = 25 $\mu\text{g}/\text{L}$), FHxSA (median concentration = 4.0 $\mu\text{g}/\text{L}$), and 8:2 FtS, which was detected in fewer than half of groundwater samples (Table S7). 6:2 and 8:2

FtS made up 11%, on average, of PFAS content of groundwater samples, and FHxSA made up 3% (Figure 2). None of the PFAA precursors in AFFF formulations were detected in groundwater at concentrations above method detection limits (0.1–0.4 $\mu\text{g}/\text{L}$) (Table S2). An average of 9% of the total PFAS concentration (approximately 40% of all PFAA precursors in groundwater) consisted of PFAA precursors not detected by direct LC-MS/MS analysis (Figure 2).

In aquifer solids and soils from the firefighter training area, perfluorinated sulfonates and PFAA precursors usually accounted for a larger fraction of total PFAS concentration relative to groundwater samples (Figure 2). PFAA precursors accounted for an average of 35% of the total PFAS concentration in aquifer solids samples (Figure 2). In surficial soils, PFAA precursors increased as a proportion of total PFAS concentration as the total PFAS concentration in the soil increased; precursors accounted for an average of 26% of the total PFAS concentration across all samples and 38% on the five most contaminated surficial soils (Figure 2).

PFOS was the PFAS species detected at the highest concentration on nearly every soil (median = 2400 $\mu\text{g}/\text{kg}$) and aquifer solid (median = 270 $\mu\text{g}/\text{kg}$) sample (Table S8). The ratio of PFHxS (median soil = 66 $\mu\text{g}/\text{kg}$, median aquifer solids = 150 $\mu\text{g}/\text{kg}$) to PFOS ranged from 0.01 to 10. The perfluorinated carboxylates were detected at significantly lower concentrations than perfluorinated sulfonates on soils and aquifer solids (Figure 2). Among the perfluorinated carboxylates, PFOA predominated on surficial soils (median = 21 $\mu\text{g}/\text{kg}$ PFOA, 11 $\mu\text{g}/\text{kg}$ PFHxA) and PFHxA predominated on aquifer solids (median = 35 $\mu\text{g}/\text{kg}$ PFOA, 45 $\mu\text{g}/\text{kg}$ PFHxA) (Table S8). A paired *t* test indicated that the log transformed total concentration of PFASs was greater on surficial soils than aquifer solids ($p < 0.05$). As observed in groundwater samples, PFAS concentrations on both soils and aquifer solids decreased with distance from the burn pit.²⁵

PFHxSAm, a PFAA precursor present in AFFF formulations manufactured by 3M, was the only PFAA precursor present in AFFF that was detected on soils and aquifer solids. The compound was detected on fewer than 30% of the samples, with most detections on samples that contained high concentrations of PFOS and other perfluorinated sulfonates present in AFFF manufactured by 3M. In addition to PFHxSAm, the other precursors detected on solids included 6:2 FtS (median = 85 $\mu\text{g}/\text{kg}$ surficial soils; 68 $\mu\text{g}/\text{kg}$ aquifer solids), 8:2 FtS (median = 81 $\mu\text{g}/\text{kg}$ surficial soils; 42 $\mu\text{g}/\text{kg}$ aquifer solids), FHxSA (median = 12 $\mu\text{g}/\text{kg}$ surficial soils; 14 $\mu\text{g}/\text{kg}$ aquifer solids), and FOSA (median = 3 $\mu\text{g}/\text{kg}$ surficial soils; 7 $\mu\text{g}/\text{kg}$ aquifer solids). Concentrations of the PFAA precursor compounds observed by direct LC-MS/MS analysis typically increased as the concentrations of the perfluorinated sulfonates increased on both surficial soils and aquifer solids.

Approximately half of the PFAA precursors on soil and aquifer solids samples measured by the oxidation assay were attributable to PFHxSAm, 6:2 FtS, 8:2 FtS, FHxSA, or FOSA. The fluorotelomer-based PFAA precursors accounted for 8% and 10% of average molar PFAS content on surficial soils and aquifer solids, respectively, and the sulfonamide-based PFAA precursors accounted for an average of 5% of total PFASs on both types of solids (Figure 2). On average, more unidentified PFAA precursors were present on aquifer solids (20% of total PFASs), than in soils (13% of total PFASs).

Many samples within each type of media contained specific PFAS analytes in similar proportions to one another. However,

due to the complex pattern of AFFF contamination at the site, statistically significant correlations were not observed among two or more analytes in groundwater, soil, or aquifer solids samples.

DISCUSSION

Identifying Likely Sources of AFFF. To gain insight into the fate of PFASs released at firefighter training sites, it is important to understand the composition of the AFFF formulations that were applied. Despite the absence of records on AFFF purchases and applications and an incomplete knowledge of the composition of AFFF manufactured prior to 1984, the archived AFFF samples and available information on the U.S. military's AFFF stockpiles provide an understanding of the likely composition of AFFF used onsite.

Most of the mass of PFASs in groundwater and solid samples resemble the PFASs in the archived 3M formulations produced between 1988 and 2001. The perfluorinated sulfonates, which were present at high concentrations in all 3M formulations (Figure 1a, Figure 2), accounted for 40–60% of the PFASs in groundwater and solid samples (Figure 2). The PFAA precursor PFHxSAm detected in archived 3M AFFF samples was also observed on soils and aquifer solids. FHxSA, which was detected frequently in groundwater and solids samples, was a probable transformation product of sulfonamide-based C_6 precursor compounds like PFHxSAm.

There is also evidence of the use of 3M formulations with a different PFAS composition than those of the archived samples. The C_8 sulfonamide-based precursor FOSA was detected at concentrations within an order of magnitude of PFOS in many soil and aquifer solids samples. This finding is inconsistent with the archived AFFF formulations manufactured by 3M between 1988 and 2001, which contained negligible concentrations of C_8 precursors (Figure 1b). A 1971 U.S. patent submitted by the 3M Company identified a C_8 sulfonamide-containing precursor in their AFFF products that may have been the source of FOSA.²⁹ Prior to 1976, 3M's AFFF formulations reportedly contained high concentrations of perfluorinated carboxylates and their derivatives.^{9–12} The perfluorinated carboxylates detected in groundwater and solid samples could have originated from these early 3M formulations. They also could have been derived from transformation of fluorotelomer precursors in AFFF formulations from other manufacturers.

Although the 3M Company provided most of the military's AFFF prior to 2001,²⁷ AFFF manufactured by National Foam and Ansul were also approved for military use starting in 1976.²⁶ AFFF formulations manufactured by one or both of these companies appear to have been used in the firefighter training area, as evidenced by the presence of transformation products of fluorotelomer compounds, such as 6:2 FtS and 8:2 FtS, in all contaminated media. These fluorotelomer compounds could not have been generated from 3M's precursors. However, fluorotelomer precursors that occur in the archived National Foam and Ansul AFFF (e.g., 6:2 FtTaOS or 6:2 FtSaB) were not detected in any contaminated samples. The absence of these AFFF-derived compounds implies that they were transformed after release. The abundance of 8:2 FtS on surficial soil samples indicates that the fluorotelomer-based AFFF applied in the firefighter training area contained a significant proportion of C_8 precursor compounds, similar to the archived Ansul AFFF formulations from 1984 and 1987 (Figure 1b).

AFFF Precursor Transformation. Despite the fact that they accounted for between 41% and 100% of the PFASs in AFFF formulations (Figure 2), the PFAA precursors observed in AFFF formulations were largely absent from groundwater, soil, and aquifer solid samples. PFHxSAM, the only precursor compound in AFFF that was detected onsite, was only detected sporadically. On average, the concentration of PFHxSAM was 5% of the molar concentration of PFHxS on soil samples. In the soil sample with the highest PFHxSAM concentration, the concentration of PFHxSAM was 25% of the concentration of PFHxS. In AFFF formulations from 1988 and 1989, the concentration of PFHxSAM was 60% of the concentration of PFHxS. In 3M formulations manufactured after 1989, PFHxSAM concentrations were five times higher than those of PFHxS. Because AFFF manufactured by 3M is the only source of these two compounds, these data suggest that most PFHxSAM released onsite was transformed.

The absence of AFFF precursors at this site is consistent with the two other studies where these compounds were measured at firefighter training areas.^{9,22} In groundwater samples collected from facilities that operated contemporaneously with this site, AFFF precursor concentrations were below detection limits or were present at concentrations several orders of magnitude lower than the other PFASs.⁹ A National Foam AFFF precursor (i.e., 6:2 fluorotelomer sulfonamido betaine) was detected on soils outside a Norwegian airport, but concurrent detection of four of its putative transformation products suggests that it may not persist.²²

Several precursor compounds that were not present in any of the AFFF samples were detected at the site, including FOSA, FHxSA, 6:2 FtS, and 8:2 FtS. It is likely that these compounds were formed from the biological or chemical transformation of precursors present in AFFF; various remedial activities that occurred onsite, including the installation of oxygen infusion wells,²⁵ may have promoted the biotransformation of these precursors. FOSA and FHxSA contain sulfonamide moieties adjacent to the perfluorinated chain, just like the precursors in AFFF formulations manufactured by 3M. FOSA is a known product of aerobic microbial transformation of sulfonamide-containing compounds such as *N*-ethyl perfluorooctane sulfonamidoethanol¹⁶ that are oxidized through carboxylation and dealkylation reactions. It has also been proposed as a metabolite of numerous sulfonamide-containing precursors in humans³⁰ and biota.³¹ FHxSA, a shorter-chain length analog of FOSA, is a potential product of biotransformation of C₆ sulfonamide compounds in AFFF manufactured by 3M. 6:2 FtS and 8:2 FtS could have been produced by one or more oxygen additions to the thio group followed by dealkylation of fluorotelomer thioamido sulfonates in Ansul AFFF or fluorotelomer sulfonamide betaines and amines in AFFF manufactured by National Foam. 6:2 FtS and 8:2 FtS have also been detected at relatively high concentrations at other sites where AFFF was used for firefighter training.^{8,9}

Data from the precursor assay indicated that most samples contained PFAA precursors that were not identified by direct LC-MS/MS measurement of specific compounds (Figure 2). The distribution of perfluorinated carboxylates produced upon oxidation provides insight into the identity of the unknown precursors (Figure 3). The left side of Figure 3 consists of a series of bars that depicts the precursors measured in the sample next to the distribution of perfluorinated carboxylates expected after the sample is subjected to the oxidation assay. The right side of the figure compares the sum and distribution

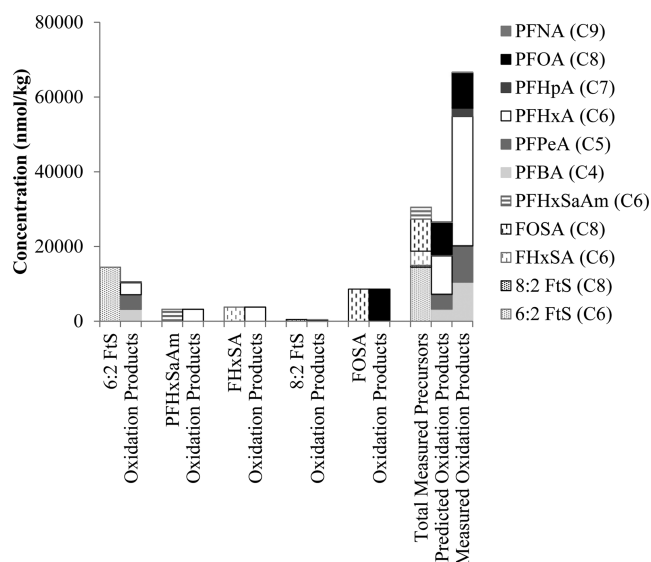


Figure 3. The measured PFAA precursor compounds in a contaminated soil sample extract (S5-S) compared with the expected and measured perfluorinated carboxylate products in the oxidized extract. The bars labeled “Total Measured Precursors” and “Predicted Oxidation Products” are summations of the respective bars to their left.

of the measured precursors and their expected perfluorinated carboxylate products with the sum and distribution of perfluorinated carboxylate products observed when the sample was oxidized. This comparison indicates that the measured precursors only accounted for 40% of the observed perfluorinated carboxylate products in the oxidized sample (Figure 3). The homologue profile of unattributed perfluorinated carboxylate production suggests that unidentified precursors mainly consisted of C₆ compounds: PFHxA measured after oxidation was 3.5 times higher than expected, whereas the concentration of PFOA produced upon oxidation was only ten percent higher. Because PFPeA and PFBA were also generated in greater concentrations than predicted, we estimate that up to 20% of the C₆ precursors had 6:2 fluorotelomer groups.²⁴ The remainder of the generated PFHxA in this sample appears to have been related to C₆ sulfonamide-containing molecules in 3M AFFF formulations.

Using the approach described for the single sample in Figure 3, the structures of the unidentified precursors in other samples were inferred by comparing the homologue pattern of the oxidation products with the precursors measured by LC-MS/MS (Figure 4). Of the perfluorinated carboxylate production that was not attributable to directly measured precursors in groundwater, PFBA and PFHxA accounted for an average of 85% (Figure 4). The absence of significant PFPeA production means that PFHxA was mainly generated from sulfonamide-containing precursor compounds.²⁴ Similarly, relatively high PFBA production compared to PFPeA production indicates the presence of C₄ PFAA precursors that were fluorotelomer-based or sulfonamide-based. Because hydrophilicity increases with decreasing perfluorinated chain length, it is unsurprising to observe a larger fraction of C₄ PFAA precursors in groundwater relative to solids.

The profile of perfluorinated carboxylates produced from unidentified precursor compounds in aquifer solids and soils was enriched with longer chain homologues (Figure 4). Like groundwater, PFHxA was the main product of unidentified precursors, but significant concentrations of PFHpA and PFOA

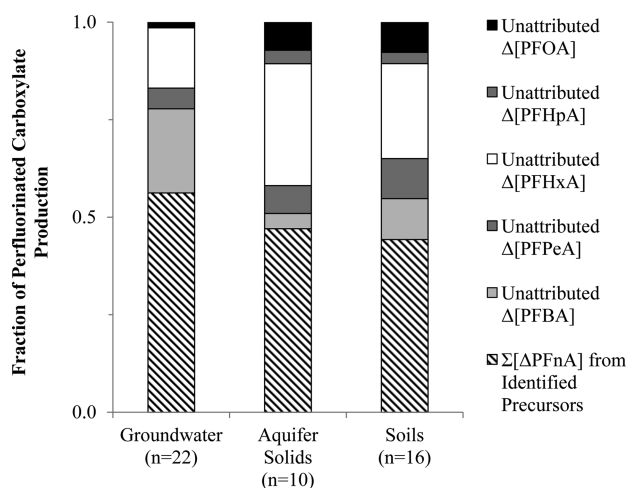


Figure 4. The average composition of perfluorinated carboxylates generated by precursor compounds in groundwater, aquifer solids, and soils from the firefighter training area.

were also generated from unidentified longer-chain precursors. The unattributed fraction of PFHxA on aquifer solids was mainly generated by sulfonamide-based C_6 precursors, as evidenced by the comparatively low production of PFPeA and PFBA. The composition of precursors on surficial soils is less certain because production of all homologues was significant.

There are two likely sources of the unidentified fraction of PFAA precursor compounds. First, the unidentified precursors could have been composed of precursors from AFFF formulations that were not present in the archived AFFF formulations. A second explanation is that the unidentified precursors were transformation products of AFFF-derived precursor compounds.

Biotransformation of fluorotelomer precursor compounds with structures similar to those in AFFF has been observed previously.^{17,18} In laboratory microcosms, fluorotelomer compounds, including 6:2 FtS, were transformed to perfluorinated carboxylates upon exposure to mixed cultures of aerobic bacteria.^{17,18} For example, 6:2 FtS underwent desulfonation followed by oxidation and decarboxylation to be converted into PFHxA and PFPeA in activated sludge microcosms.¹⁷ In most studies on biotransformation of $n:2$ fluorotelomer compounds, both the C_n and C_{n-1} perfluorinated carboxylates were produced at similar concentrations.^{17,18} As a result, the occurrence of even C_n and odd C_{n-1} perfluorinated homologues in samples would support their origination from biotransformation of fluorotelomer compounds.

Despite the presence of relatively high concentrations of PFOA observed in many soil and groundwater samples, PFHpA was rarely detected. The absence of PFHpA suggests that biotransformation of 8:2 FtS was not the main source of PFOA, assuming that 8:2 FtS follows a similar transformation pathway to 6:2 FtS.¹⁷ The ratio of PFHxA to PFPeA in most soil and groundwater samples was roughly consistent with the expected perfluorinated carboxylate product distribution from aerobic transformation of 6:2 FtS.¹⁷ Much of the PFHxA and PFPeA detected onsite could have resulted from biotransformation of 6:2 fluorotelomer compounds, but it is impossible to test this hypothesis without specific knowledge of the composition of 3M AFFF formulations containing perfluorinated carboxylates manufactured in the early 1970s.

The isomer distribution of individual perfluorinated carboxylate homologues could be used in future research to identify their source.³² 3M historically used a manufacturing process that generates a mixture of roughly 30% branched and 70% linear isomers of perfluorinated compounds,¹⁰ whereas the fluorotelomer manufacturing process only produces compounds with linear perfluorinated chains. Although the method used in this study did not quantify individual perfluorinated carboxylate isotopes, the ratio of linear to branched isomers of perfluorinated homologues could be used to distinguish the origins of perfluorinated carboxylates in an AFFF-contaminated area.

The transformation of precursors can serve as an important source of additional perfluorinated sulfonates. This is especially true for C_6 homologues. In the AFFF formulations from 3M, transformation of the precursors could have increased the concentration of PFHxS by a factor of 4 if all C_6 precursors were transformed to PFHxS (Figure 1a,b). Thus, an increase in the ratio of PFHxS to PFOS in contaminated samples relative to those observed in AFFF would imply that C_6 precursors had been transformed to PFHxS. AFFF manufactured by 3M from 1988 to 1989 exhibited a PFHxS-to-PFOS mass ratio of 0.1. On surficial soils, PFHxS to PFOS ratios varied widely, but the ratio between the median concentrations of PFHxS and PFOS was 0.23. On the most contaminated sample analyzed, the PFHxS to PFOS ratio was 0.66. Similarly, the ratio between the median concentrations of PFHxS and PFOS was greater than 0.5 on aquifer solids and greater than 2 in groundwater. In all media, there was more than a 2-fold increase in the PFHxS-to-PFOS mass ratio compared with the representative 3M formulations from 1988 to 1989, suggesting substantial transformation of 3M-derived C_6 precursors to PFHxS.

Transformation of AFFF-derived precursors to perfluorinated carboxylate and perfluorinated sulfonate products would also be indicated by a decrease in the percentage of precursor compounds relative to AFFF formulations. In all media, the average percentage of precursors as a share of total PFASs declined relative to Ansul and 3M AFFF formulations from the 1980s (Figure 2), which contained 100% and 41% PFAA precursors as a percentage of total PFAS concentrations, respectively. The declines in precursor content were more pronounced in groundwater (average = 23% precursors) than in soils and aquifer solids (average = 28% precursors). It is possible that older AFFF formulations containing smaller relative PFAA precursor concentrations than the archived AFFF accounted for some of these observations, but PFAA precursor compounds have been included in AFFF patents through the entire era of AFFF production and were likely present in older AFFF formulations.^{10-12,29,33,34}

Overall, significant production of perfluorinated sulfonates and carboxylates from AFFF-derived PFAA precursors appears to have occurred in the firefighter training area. However, the presence of PFAA precursors more than twenty years after AFFF applications ceased indicates that the rate of transformation of precursors to the terminal PFAAs has been slow.

Environmental Implications. For at least three decades, AFFF formulations have contained polyfluorinated compounds that are potential precursors of perfluorinated carboxylates and perfluorinated sulfonates. The health effects of precursors from AFFF formulations currently are unknown, but perfluorinated carboxylates and perfluorinated sulfonates have been associated with adverse health effects in humans and biota.³⁵⁻⁴⁰ The data collected in this study provide strong evidence that most of the

PFAA precursors originally present in AFFF were transformed into other precursors and PFAAs over a period of several decades in the subsurface. The transformation products may be more mobile than the compounds originally present in AFFF thereby expanding the plume of PFAS contamination.

Firefighter training sites are often contaminated with halogenated solvents and hydrocarbons. As AFFF-impacted sites are remediated for these cocontaminants or for the perfluorinated carboxylates and sulfonates, the co-occurrence of AFFF-related precursors cannot be ignored. Some remedial activities targeted at cocontaminants may inadvertently accelerate the production of PFAAs. For example, in situ chemical oxidation often generates oxidants that convert precursors into perfluorinated carboxylates through the mechanism employed in the precursor assay. Additionally, the slow biotransformation of AFFF precursors contributes to the total concentration of PFAAs even if no action is taken at a site. As a result, the mass of precursors may need to be remediated along with the PFAAs for complete site closure if PFAAs are the target of the remediation effort.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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