Supporting Information:

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

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Submitted to Environmental Science & Technology

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Figure S1: Structures of PFAA precursors found in AFFF formulations.¹



3M: Perfluoroalkyl sulfonamide amino carboxylates (PFnSAmA). n=4,5,6.



Buckeye: n:1:2 Fluorotelomer betaine. n=5,7,9.



3M: Perfluoroalkyl sulfonamido amines (PFnSAm). n= 4,5,6.



Buckeye: n:3 Fluorotelomer betaine. n=4,7,9.



Ansul, Chemguard: Fluorotelomer thioamido sulfonates (n:2 FtTAoS). n=4,6,8.



Ansul: Fluorotelomer thio hydroxy ammonium (n:2 FtTHN+). n=6.



National Foam (NF): Fluorotelomer Sulfonamido Betaines (n:2 FtSaB). n=6,8,10,12.



NF: Fluorotelomer Sulfonamido Amines (n:2 FtSaAm). n=6,8.

Electrochemical Fluorination- Based Compounds													
Compound	Internal Standard	Molecular Ion	Fragmentor Voltage (V)	Quantifier Ion (m/z)	Collision Energy (V)	Qualifier Ion (m/z)	Collision Energy (V)	Polarity					
_	Per	rfluoroalkyl s	ulfonamide an	nino carboxyl	lates (PFSA	mA)							
PFBSAmA	[¹⁸ O ₂] PFHxS	457	135	85	30	70	60	Positive					
PFPeSAmA	[¹⁸ O ₂] PFHxS	507	135	85	30	70	60	Positive					
PFHxSAmA	[¹⁸ O ₂] PFHxS	557	135	85	30	70	60	Positive					
		Perfluoro	alkyl sulfonar	nido amines ((PFSAm)								
PFBSAm	[¹⁸ O ₂] PFHxS	385	135	85	30	58	60	Positive					
PFPeSAm	[¹⁸ O ₂] PFHxS	435	135	85	30	58	60	Positive					
PFHxSAm	[¹⁸ O ₂] PFHxS	485	135	85	30	58	60	Positive					
Perfluorinated sulfonates													
PFBS	[¹⁸ O ₂] PFHxS	299	120	80	70	99	30	Negative					
PFHxS	[¹⁸ O ₂] PFHxS	399	160	80	80	99	50	Negative					
PFHpS	$[^{13}C_4]$ PFOS	449	160	80	80	99	50	Negative					
PFOS	$[^{13}C_4]$ PFOS	499	180	80	80	99	50	Negative					
PFDS	$[^{13}C_4]$ PFOS	599	150	80	50	99	50	Negative					
Perfluoroalkyl sulfonamides													
FHxSA	$[^{13}C_8]$ FOSA	398	180	78	78 40			Negative					
FOSA		Negative											
Fluorotelomer - Based Compounds													
			Fragmentor		Collision	Qualifier	Collision						
C		Molecular	Voltage	Quantifier	Energy	Ion	Energy	D.1					
Compound		lon	(V)	$\frac{100 \text{ (m/z)}}{(\text{E})}$	(v)	(m/z)	(V)	Polarity					
5.1.2 E/D	[¹³ C] 6·2 EtS	422	100	50	50			Desid					
5:1:2 FtB	$\begin{bmatrix} C_2 \end{bmatrix} 0.2$ FtS	432	180	58	50			Positive					
5:3 FtB	$\begin{bmatrix} C_2 \end{bmatrix} 0.2$ FtS	414 522	180	58	60			Positive					
7:1:2 FtB	$\begin{bmatrix} C_2 \end{bmatrix} 0.2$ FtS	552	180	58	60			Positive					
7:3 FtB	$\begin{bmatrix} C_2 \end{bmatrix} 0.2 \text{ FtS}$	622	180	58	60			Positive					
9:1:2 FLD	$\begin{bmatrix} C_2 \end{bmatrix} 0.2$ FtS	614	100	50	60			Positive					
9:3 FLD	$[C_2] 0.2 $ TtS	D14	100	38				Positive					
6.2 EtTUN	[¹³ C ₂] 6:2 EtS	106			$\frac{1}{40}$	127	20	Dogitiyo					
0.2 PtIIIN+	[02] 0.210	Fluorotal	omor thiosmid	o sulfonatos d	$(\text{EtTA} \circ \mathbf{S})$	437	30	rostuve					
$4.2 \text{ EtT} \Lambda \circ S$	$[^{13}C_{2}] 6.2 \text{ FtS}$	186		206	(FITA05) 45	135	45	Nagativa					
4.2 FtTA05	$[^{13}C_2] 6:2 \text{ FtS}$	586	100	135	45	206	43	Negative					
8.2 FtTA05	$\begin{bmatrix} 1^{13}C_2 \end{bmatrix} 6:2 \text{ FtS}$	686	190	206	50	135	50	Negative					
0.2111A05		000 Fi	uorotelomer «	ulfonates (Ft)	<u> </u>	155	50	riegative					
6:2 EtS	$[^{13}C_2] 6.2$ FtS	427	140		25	80	35	Negative					
8.2 FtS	$[^{13}C_2] 6:2 \text{ FtS}$	527	140	507	30	80	40	Negative					
0.210	1 021 0.21 0	521	140	507	50	00	40	Inegative					
		Fluorote	lomer sulfonar	nido betaines	(FtSaB)								

Table S1: Monitored ion transitions, MS Conditions, and internal standard used for quantification of each analyte.

6:2 FtSaB	[¹³ C ₂] 6:2 FtS	571	180	58	40	104	40	Positive
8:2 FtSaB	$[^{13}C_2]$ 6:2 FtS	671	180	104	40	58	60	Positive
10:2 FtSaB	$[^{13}C_2]$ 6:2 FtS	771	180	104	40	58	60	Positive
12:2 FtSaB	$[^{13}C_2]$ 6:2 FtS	871	180	104	40	58	60	Positive
		Fluorotel						
6:2 FtSaAm	$[^{13}C_2]$ 6:2 FtS	513	180	58	60	86	60	Positive
8:2 FtSaAm	$[^{13}C_2]$ 6:2 FtS	613	180	86	60	58	80	Positive
	Perfluor	inated carbox						
PFBA	$[^{13}C_4]$ PFBA	213	50	169	2			Negative
PFPeA	$[^{13}C_4]$ PFBA	263	60	219	2			Negative
PFHxA	[¹³ C ₂] PFHxA	313	80	269	2	119	15	Negative
PFHpA	[¹³ C ₂] PFHxA	363	80	319	2	169	2	Negative
PFOA	[¹³ C ₄] PFOA	413	80	369	3	169	14	Negative
PFNA	$[^{13}C_5]$ PFNA	463	80	419	2	219	15	Negative
PFDA	$[^{13}C_2]$ PFDA	513	80	469	5	169	10	Negative
PFUnA	[¹³ C ₂] PFUnA	563	80	519	10	269	15	Negative
PFDoA	[¹³ C ₂] PFDoA	613	100	569	5	169	25	Negative
PFTrdA	[¹³ C ₂] PFDoA	663	100	619	10			Negative
PFTeDA	[¹³ C ₂] PFDoA	713	100	669	10			Negative
			Internal S	tandards				
$[^{13}C_8]$ FOSA		506	150	77.8	50			Negative
[¹⁸ O ₂] PFHxS		403	150	103	40			Negative
[¹³ C ₄] PFOS		503	190	80	60			Negative
[¹³ C ₄] PFBA		217	50	172	5			Negative
[¹³ C ₂] PFHxA		315	60	270	5			Negative
[¹³ C ₄] PFOA		417	70	372	2			Negative
$[^{13}C_5]$ PFNA		468	70	423	5			Negative
$[^{13}C_2]$ PFDA		515	70	470	10			Negative
[¹³ C ₂] PFUnA		565	80	520	10			Negative
[¹³ C ₂] PFDoA		615	80	570	10			Negative
[¹³ C ₂] 6:2 FtS		429	140	409	25			Negative

Figure S2: Map of sampling area and groundwater sampling locations. The burn pit used for fire training is circled.





Figure S3: Map of sampling area and soil and aquifer solids sampling locations. The burn pit used for fire training is circled.

Description of Spike Recovery Experiments in Groundwater

A groundwater sample that did not contain any background signal for PFASs was used for spike recovery of PFASs and determination of method precision.

The perfluorinated carboxylates, perfluorinated sulfonates, and 6:2 and 8:2 fluorotelomer precursor compounds were amended from a 60 μ g/L mixed methanolic stock solution to a 6-mL aliquot of the uncontaminated groundwater sample for final concentrations of 2 μ g/L per analyte. The FtB compounds were amended to the same sample from a methanolic stock for individual final concentrations ranging from 0.5 to 2 μ g/L per analyte. Three replicates were prepared. After equilibrating overnight, the spiked samples were analyzed as described in the section on groundwater analysis in the Materials and Methods. Recovery was calculated as the average concentration measured in the spiked groundwater sample divided by the expected concentration (Table S2). Precision was calculated by taking the percent relative standard deviation of the concentrations measured in the three replicate spiked samples (Table S2). The instrumental limit of detection (LOD) of an analyte was defined as the minimum concentration that produced a signal to noise ratio of 3. Because matrix effects were minimal in groundwater, the whole method LOD (Table S2) was defined as the instrumental limit of detection multiplied by the groundwater analysis dilution factor, 2.5.

Because no quantitative standards were available for the 3M AFFF-derived PFAA precursors, spike recovery of those compounds in groundwater was conducted with an AFFF solution. A 3M AFFF formulation manufactured in 1998 was diluted 10^3 times in methanol and added to 6-mL aliquots of an uncontaminated groundwater sample for a final dilution of 10^5 , or approximately 1 to 50 µg/L per analyte. Three replicates were prepared. Preparation for LC-MS/MS analysis was identical to that described above for non-3M PFAA precursor analytes. Recovery of a 3M AFFF-derived PFAA precursor was calculated as the average instrumental response measured in the spiked groundwater sample divided by the instrumental response of the analyte in the parent AFFF formulation measured at the same total dilution factor (Table S2). Precision was calculated by taking the percent relative standard deviation of the instrumental response of the three replicate spiked samples (Table S2). The instrumental LOD and whole method LOD (Table S2) were calculated as above using the conversion from instrumental response to concentration described below and in Table S4.

			Whole
	Percentage		Method LOD,
	Recovery	Precision	µg/L
PFBA	94%	3.8%	0.5
PFPeA	130%	0.9%	0.2
PFHxA	107%	4.9%	0.1
PFHpA	116%	2.8%	0.2
PFOA	115%	5.1%	0.1
PFNA	86%	1.2%	0.2
PFDA	57%	3.8%	0.1
PFBS	90%	9.8%	0.3
PFHxS	95%	3.5%	0.1
PFHpS	102%	3.3%	0.1
PFOS	84%	4.9%	0.1
FOSA	94%	6.5%	0.1
6:2 FtS	107%	11%	0.1
8:2 FtS	90%	9.4%	0.1
6:2 FtTAoS	96%	9.2%	0.1
6:2 FtSaAm	60%	4.4%	0.3
5:1:2 FtB	114%	2.9%	0.3
5:3 FtB	109%	1.4%	0.3
7:1:2 FtB	105%	5.0%	0.3
7:3 FtB	100%	8.4%	0.3
9:1:2 FtB	56%	2.6%	0.4
PFBSAm	133%	1.3%	0.3
PFPeSAm	97%	0.9%	0.3
PFHxSAm	131%	0.0%	0.1
PFBSAmA	98%	1.6%	0.3
PFPeSAmA	160%	0.5%	0.3
PFHxSAmA	85%	0.3%	0.1

Table S2: Recovery, precision, and whole method LOD of PFASs in groundwater.

Description of Spike Recovery Experiments in Soils

A soil sample that did not contain any background signal for PFASs was used for spike recovery of PFASs and determination of method precision.

A methanol stock containing 10 ng of perfluorinated carboxylates and perfluorinated sulfonates and 50 ng of 6:2 FtS, 8:2 FtS, and FOSA was amended to 250 mg of uncontaminated soil in triplicate. Soil samples were vortexed in this methanol slurry for twenty seconds, dried under N₂ gas, and aged at room temperature for 72 hours before extraction. The spiked samples were extracted and analyzed using the methodology described in the section on soil analysis in the Materials and Methods. Recovery was calculated as the average concentration measured in the spiked groundwater sample divided by the expected concentration (Table S3). Precision was calculated by taking the percent relative standard deviation of the concentrations measured in the three replicate spiked samples (Table S3). The use of ENVI-carb minimized matrix effects, so the whole method LOD (Table S3) was defined as the instrumental LOD multiplied by the soil extract concentration factor, 15 L/kg.

To measure recoveries of Ansul and 3M PFAA precursor compounds, 10³ diluted Ansul and 3M AFFF formulations in methanol were separately added to three replicates each of uncontaminated soil samples at approximately 1 to 10 ng per compound. Soil samples were treated as in the above recovery experiment. Recovery, precision, and whole method LOD were calculated for Ansul-derived PFAA precursors (*i.e.*, 6:2 FtTAoS and 8:2 FtTAoS) as described for other PFASs above. Recovery of the 3M AFFF-derived PFAA precursor compounds was calculated as the average instrumental response measured in the spiked soil sample divided by the instrumental response of the analyte in the parent AFFF formulation measured at the same total dilution factor (Table S3). Precision was calculated by taking the percent relative standard deviation of the instrumental response of the three replicate spiked samples (Table S3). The instrumental LOD and whole method LOD (Table S3) were calculated as above using the conversion from instrumental response to concentration described below and in Table S4.



Figure S4: Fractional recovery of PFASs added to an uncontaminated soil sample. The 500 mg soil sample was extracted sequentially three times with 2.5 mL 0.1% NH_4OH in methanol per extraction. The data depict the recovery of compounds in each fraction; around 1% was recovered in the third fraction for most compounds.

Table S3: Recovery, precision, and whole method LODs of PFASs in soil and aquifer solidssamples.

	Percentage		Whole Method
Analyte	Recovery	Precision	LOD,µg/kg
6:2 FtS	110%	5%	0.4
8:2 FtS	121%	3%	0.6
FOSA	110%	6%	0.6
PFBA	95%	9%	3.0
PFPeA	105%	13%	1.1
PFHxA	110%	7%	0.8
PFHpA	113%	10%	1.1
PFOA	106%	4%	0.8
PFNA	109%	6%	1.1
PFBS	112%	8%	1.7
PFHxS	116%	13%	0.6
PFOS	104%	3%	0.4
PFDS	106%	4%	0.6
PFBSAm	100%	1%	1.5
PFBSAmA	56%	1%	1.5
PFPeSAmA	131%	1%	1.5
PFHxSAm	85%	2%	0.8
PFHxSAmA	70%	1%	0.8
6:2 FtTAoS	91%	16%	0.8
8:2 FtTAoS	98%	14%	0.8

Sample Preparation for Precursor Assay

Duplicate 140 μ L aliquots of each AFFF formulation diluted 1000x in methanol were added to 7-mL HDPE vials and evaporated under nitrogen. The evaporated samples were reconstituted in 6 mL of 60 mM potassium persulfate and 125 mM sodium hydroxide and reacted for 6 hours at 85°C. Samples were brought to room temperature, neutralized with concentrated HCl to a pH value between 4 and 10, and amended with 1 mL methanol to enhance dissolution of PFASs. The reacted AFFF samples were analyzed at 10⁶ total dilution.

Duplicate 3 mL aliquots of each groundwater sample were diluted 1:1 in a persulfate and NaOH stock solution in 7-mL HDPE tubes to achieve the same reaction conditions as in the oxidation of AFFF samples. Following reaction, samples were treated identically to AFFF and analyzed at an appropriate dilution factor previously determined in the analysis of unreacted groundwater samples.

The basic methanolic soil extracts were evaporated to dryness and subsequently reacted to measure the perfluorinated carboxylate products of precursor compounds. Complete removal of measureable precursor compounds in the methanolic extract was verified through spike recovery experiments (Table S3). Analysis of oxidized soil sample extracts was less time consuming and produced more precise data than treatment of suspended soils with persulfate followed by solid-phase extraction. To determine if the extraction method yielded lower concentrations than oxidation of suspended particulates, one sample was measured with both approaches. Reacting a whole soil sample at 2 to 4 g soil/L yielded similar concentrations of perfluorinated carboxylate products as reacting the evaporated soil extract and produced less variability (Figure S5). Using an ENVI-CARB- exposed extract did not remove any precursor compounds, as demonstrated by consistent perfluorinated carboxylate production upon reaction with and without ENVI-CARB exposure (Figure S6).

A 1 mL aliquot of each ENVI-CARB exposed soil extract was added to a 7-mL HDPE tube and evaporated for use in the oxidation assay. The evaporated extract was reconstituted in the same persulfate and NaOH mixture used in AFFF formulation analysis. Reacted soil extracts were analyzed at appropriate dilutions previously determined from the analysis of unreacted soils.



Figure S5: Comparison of whole soil sample oxidation and soil extract oxidation approach for a single sample. The unreacted soil extract is shown for comparison. Soil extracts were evaporated under N_2 prior to oxidation. All samples were reacted in triplicate in 60 mM potassium persulfate and 125 mM NaOH. Error bars represent standard deviation of three measurements.



Figure S6: Effect of ENVI-CARB on precursor recovery in soil extracts. Concentrations of PFAA analytes are shown after reaction of two AFFF-contaminated soil sample extracts (one sandy surficial soil sample and one clay-rich aquifer solids sample) with and without an ENVI-CARB addition before blow down of basic methanolic extract.

Quantification of analytes for which authentic standards were not available:

Fluorotelomer compounds where a standard was available for one homolog in a class of compounds:

For all 6:2 fluorotelomer compounds in AFFF, a commercial material was used for quantification. No commercial material was available for the longer chain versions of these compounds. All of these compounds were quantified relative to the 6:2 FtS internal standard using the calibration of the 6:2 compound of related structure. The calibration was adjusted slightly, for differences in response of compounds due to different perfluorinated chain length. The chain length adjustment factors are as follows:

8:2 FtTAoS: $\frac{8:2 FtS \ slope}{6:2 \ FtS \ slope}$ - both slopes calculated relative to 6:2 FtS IS response.	
10:2 FtSaB: $\frac{PFDA \ slope}{PFHxA \ slope}$ - both slopes calculated relative to PFHxA IS response.	
8:2 FtSaB: $\frac{8:2 \ FtS \ slope}{6:2 \ FtS \ slope}$ - both slopes calculated relative to the 6:2 FtS IS response.	

FHxSA

No reference material or standard was available for FHxSA. To quantify FHxSA, an MRM method was designed using the same ion transition as FOSA adjusted for the mass difference due to the shorter perfluorinated chain length. The retention time of FHxSA was approximated relative to FOSA using typical spacing between other C8 and C6 compounds (*i.e.* about 1 minute). FHxSA was quantified using the calibration curve for FOSA with an adjustment for chain length in the following manner:

 $[FHxSA] = \frac{FHxSA\,response}{FOSA\,IS\,response} \times FOSA\,slope \times Chain length adjustment factor)$, where the FOSA slope is calculated relative to the FOSA IS response.

Chain length adjustment factor = $\frac{PFHxS \ slope}{PFOS \ slope}$, where both slopes were calculated relative to the PFOS IS response.

3M PFAA Precursor compounds:

No quantitative standards were available for the 3M-derived C_4 to C_6 perfluorinated sulfonamide amines (PFnSAm) and C_4 to C_6 perfluorinated sulfonamide amino carboxylates (PFnSAmA). The internal standard-relative responses of these compounds in various 3M formulations were compared to the concentration of perfluorinated carboxylates generated upon oxidation of each of these formulations. As these precursors contain a sulfonamide-linkage, one mole of a precursor molecule with a perfluorinated chain length of n will generate one mole of the C_n perfluorinated carboxylate under the oxidation conditions used.² Thus, the molar concentration of PFHxA generated should be equal to the combined molar concentration of PFHxSAm and PFHxSAmA, assuming that these compounds are the only C_6 precursors present in the formulation. For environmental samples, the following procedure was used to estimate the concentration of each C_6 precursor:

3M AFFF Sample A, diluted 1 x 10^6 prior to analysis

$$\frac{PFHxSAm \ response}{PFHxS \ IS \ response} = 9.2$$
$$\frac{PFHxSAmA \ response}{PFHxS \ IS \ response} = 5.3$$

Combined PFHxS IS relative response = 14.5

3M AFFF Sample A, reacted at 10^4 dilution in the presence of 60 mM S₂O₈²⁻, 125 mM NaOH at 85C for 6 hours; analysis performed at 10^6 dilution.

$$\Delta \left[PFHxA \right] = 10.1 \, nM$$

The relative responses of PFHxSAm and PFHxSAmA were assumed to be equal on a molar basis. The production of PFHxA was distributed accordingly.

$$[PFHxSAm] = \frac{9.2}{14.5} \times 10.1 \, nM = 6.4 \, nM \times \frac{485 \, \mu g}{1000 \, nM} = 3.1 \, \mu g/l$$
$$[PFHxSAmA] = \frac{5.3}{14.5} \times 10.1 \, nM = 3.7 \, nM \, * \frac{557 \, \mu g}{1000 \, nM} = 2.0 \, \mu g/l$$
$$[PFHxSAm] = \frac{3.1 \, \mu g}{l} = 0.24 \, \mu g$$

 $\frac{[PFHxSAm]}{\frac{PFHxSAm response}{PFHxS IS response}} = \frac{5.1 \ \overline{l}}{9.2} = 0.34 \frac{\mu g}{l} PFHxSAm per relative response$

 $\frac{[PFHxSAmA]}{\frac{PFHxSAmA \ response}{PFHxS \ IS \ response}} = \frac{2.0 \frac{\mu g}{l}}{5.3} = 0.38 \frac{\mu g}{l} PFHxSAmA \ per \ relative \ response$

This procedure was also used to estimate the concentrations of the C4 and C5 precursor compounds manufactured by 3M. A total of five 3M formulations were analyzed to determine an average concentration coefficient for each of the 3M fluorochemicals. Quantitative estimates of each compound in AFFF samples, groundwater, and soils were made using the coefficients determined in Table S4.

The accuracy of this approach depends in large part on the validity of assuming that each C_n homolog produces the same instrumental response per mole. Based on the quantification of other sulfonamide-containing precursors with authentic analytical standards, this assumption seems reasonable. For example, *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA) and *N*-ethyl perfluorooctane sulfonamide acetic acid (*N*-EtFOSAA) differ by a 58 mass unit amidic- methyl carboxylate group and produce less than 15% difference in instrument signal per mole, with the smaller compound ionizing slightly more efficiently. Similarly, PFHxSAm and PFHxSAmA

differ by a 72 mass unit amidic-ethyl carboxylate group. It follows that the difference in instrumental response per mole would be comparable to the difference between *N*-EtFOSA and *N*-EtFOSAA. Thus, the PFHxSAm concentration might be underestimated by approximately 15% to 25% in samples. PFHxSAm is the only 3M precursor compound detected in environmental samples, and it is also less than 10% of the total molar precursor concentration in any sample in which it is detected. On the whole, a small error in quantification of PFHxSAm would not introduce any significant changes to the quantitative or qualitative interpretation of the data presented in this study.

Table S4: Coefficients used to compute concentrations of precursors in 3M formulations without quantitative standards. The relative response refers to the response of the analyte versus the response of the PFHxS internal standard.

μg/L per Relative Response													
PFBSAm	PFPeSAm	PFHxSAm	PFBSAmA	PFPeSAmA	PFHxSAmA								
0.62	0.40	0.35	0.74	0.47	0.40								

			Precurso	rs (g/L)			Perf	uorinated	sulfonates ((g/L)	Perfluorinated Carboxylates (g/L)					
Formulation		PFPeS-	PFHxS-	PFBS-	PFPeS-	PFHxS-										
and Year	PFBSAm ^a	Am ^a	Am ^a	AmA ^a	AmA^{a}	AmA ^a	PFBS	PFHxS	PFHpS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	
3M 1988			0.4				0.1	1.4	0.3	11		0.3	0.1		0.1	
3M 1989	0.1		1.1			0.1	0.1	0.9	0.2	11		0.5	0.3		0.1	
3M 1992	0.9	0.6	4.8	1.0	0.4	2.2	0.0	0.5	0.1	5.1		0.2	0.1		0.1	
3M 1993	1.3	0.8	5.1	1.3	0.6	2.7	0.1	0.6	0.1	5.6		0.3	0.1		0.1	
3M 1993	0.7	0.5	3.0	1.1	0.6	2.4	0.0	0.6	0.1	5.3		0.2	0.1		0.1	
3M 1998	1.3	0.9	4.7	1.4	0.6	2.6	0.1	0.8	0.1	5.7		0.5	0.1		0.1	
3M 1998	1.1	0.8	5.1	1.3	0.5	2.6	0.0	0.7	0.1	4.9		0.1	0.1		0.1	
3M 1999	0.8	0.6	3.8	1.2	0.5	2.5	0.1	0.6		4.9		0.2	0.1		0.1	
3M 2001	0.6	0.5	4.2	1.5	0.7	3.6	0.2	1.0	0.1	8.0		0.5	0.2		0.1	
	6:2	8:2														
	FtTAoS [♭]	FtTAoS ^c														
Chemguard 2008	17															
Chemguard																
2010	21															
Ansul 1986	9	3.1														
Ansul 1987	10	2.7														
Ansul 2009	18															
Ansul 2010	10															
	5:1:2 FtB ^b	7:1:2 FtB ^b	9:1:2 FtB ^b	5:3 FtB ^b	7:3 FtB ^b	9:3 FtB ^b										
Buckeye 2009	2.3	4.3	1.4	0.6	1.0	0.3										
	6:2 FtSaB ^b	8:2 FtSaB ^c	10:2 FtSaB ^c	6:2 FtSaAm ^b	6:2 FtS	8:2 FtS										
National Foam 2005	7.0	0.5	0.1	1.8	0.2	0.0										
National Foam 2005	4.8	0.3	0.0	0.4	0.1	0.0										
National Foam 2008	7.5	0.5	0.0	1.4	0.2	0.0										

Table S5: Concentrations of PFASs (g/L) in all AFFF formulations measured. Analytes that were not detected in any samples are not shown.

^a These compounds were quantified using the reference materials provided by the Fire Fighting Foam Coalition ^c These compounds were quantified using the calibration of an alternate analyte as described earlier.

Table S6: Percentage recovery of measured precursors in AFFF formulations as perfluorinated carboxylate products. Analytes that were not detected in any samples are not shown.

		Pro	ecursors Mea	sured by LC-	MS/MS, m	mol/L		Perfluo	ı, mmol/L						
	PFBS- Am	PFPeS- Am	PFHxS- Am	PFBS- AmA	PFPeS- AmA	PFHxS- AmA	Sum Measured Precursors	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Sum PFCAs Generated	% Recovery of Precursors as PFCA Products
3M 1988	0.1	0.1	0.8	0.0	0.0	0.0	1.1	2.6	1.3	15	0.5	0.7		20	N/A ^d
3M 1989	0.1	0.1	2.2	0.0	0.0	0.1	2.6	3.2	0.4	14	0.3	0.6		19	N/A ^d
3M 1992	2.3	1.5	9.8	2.1	0.8	4.0	21	4.3	2.0	13	0.2	0.4		19	95%
3M 1993	1.9	1.2	6.3	2.4	1.2	4.2	17	4.8	2.5	14	0.2	0.4		21	130%
3M 1993	3.3	1.7	11	2.8	1.1	4.9	24	4.5	2.0	11	0.1	0.3		18	75%
3M 1998	2.9	1.8	11	2.8	1.0	4.7	24	4.5	3.0	13	0.3	0.4		21	87%
3M 1998	3.3	2.1	9.7	3.0	1.1	4.7	24	4.5	1.2	11	0.2	0.2		17	73%
3M 1999	2.2	1.3	7.8	2.6	1.1	4.5	19	0.0	4.2	11	0.8	0.3		16	82%
3M 2001	1.6	1.1	8.7	3.2	1.4	6.6	23	6.6	2.8	22	0.6	0.9		33	150%
	6:2 FtTAoS	8:2 FtTAoS					Sum Measured Precursors	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Sum PFCAs Generated	% Recovery of Precursors as PFCA Products
Chemguard 2008	29						29	6.4	11	3.2	1.1	0.3	0.4	22	76%
Chemguard 2010	37						37	5.9	11	3.5	1.2	0.3	0.4	22	61%
Ansul 1986	16	4.5					20	5.7	10	5.2	4.0	1.2	0.6	27	130%
Ansul 1987	16	4.0					20	5.6	10	5.2	3.5	1.2	0.5	25	130%
Ansul 2009	30						30	6.5	11	3.9	0.9	0.3	0.1	23	76%
Ansul 2010	18						18	3.6	6	2.3	0.6	0.1	0.1	13	74%
	5:1:2 FtB	5:3 FtB	7:1:2 FtB	7:3 FtB	9:1:2 FtB	9:3 FtB	Sum Measured Precursors	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Sum PFCAs Generated	% Recovery of Precursors as PFCA Products
Buckeye 2009	5.3	1.4	8.1	1.9	2.2	0.5	19	6.9	8.9	7.1	7.3	3.4	1.4	35	180%
	6:2 FtSaB	8:2 FtSaB	10:2 FtSaB	6:2 FtSaAm	6:2 FtS	8:2 FtS	Sum Measured Precursors	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Sum PFCAs Generated	% Recovery of Precursors as PFCA Products
National Foam 2005	10	0.8	0.1	3.4	0.6	0.0	15	4.1	8.0	2.6	1.9	0.7	0.7	18	120%
National Foam 2005	7.1	0.5	0.0	0.8	0.2	0.0	8.7	4.2	7.4	2.6	2.2	0.7	0.8	18	200%
National Foam 2008	11	0.9	0.0	2.7	0.4	0.0	15	5.9	12	3.5	3.2	0.9	1.0	26	170%

^d Formulation chemistry not captured by measured analytes.

		Precurso	rs		Р	erfluorinat	ed carboxyl	ates		Р	erfluorina	ted sulfona	tes	Δ[Perfluorinated carboxylates]						
	6:2 FtS	8:2 FtS	FHxSA	C4	C5	C6	C7	C8	С9	C4	C6	C7	C8	C4	C5	C6	C7	C8		
Sample	μg/L	µg/L	μg/L	μg/L	μg/L	μg/L	µg/L	μg/L	μg/L	μg/L	μg/L	µg/L	μg/L	μg/L	μg/L	μg/L	μg/L	µg/L		
LOQ	0.06	0.1	0.1	0.5	0.3	0.1	0.2	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		
TMP 21	0.1	ND	ND	0.0	0.1	ND	ND	ND	ND	ND	ND	ND	ND	0.3	ND	ND	ND	1.2		
TMP 12	ND	ND	ND	0.2	0.3	0.3	ND	0.2	ND	ND	ND	ND	ND	0.6	ND	ND	1.7	0.9		
970101	0.5	ND	ND	ND	0.5	1.4	ND	0.2	ND	1.1	3.2	ND	ND	1.2	0.7	ND	ND	ND		
TMP 11	0.5	ND	0.5	ND	1.3	3.3	ND	2.1	ND	1.6	9.9	0.2	0.2	2.7	0.6	ND	2.0	0.2		
TMP 17	7.0	ND	ND	6.5	12.6	22	2.9	11	ND	8.4	32	0.1	1.6	ND	1.6	8.7	0.3	ND		
TMP 03	6.4	0.4	7.2	4.0	8.0	14	2.0	8.4	ND	5.8	31	0.7	16	4.4	3.4	13	0.2	1.1		
TMP 14	12	0.4	1.2	4.0	8.8	17	2.3	11	0.5	7.6	38	0.9	19	3.9	3.1	8.0	0.4	ND		
TMP 15	17	ND	0.7	4.1	7.5	14	2.6	17	ND	5.6	39	2.1	14	6.5	4.5	7.9	0.2	ND		
TMP 20	24	ND	1.3	4.2	7.2	14	2.3	14	ND	6.2	40	1.9	14	5.2	5.2	8.6	0.2	1.8		
EMW 21	11	1.7	11	4.4	8.1	16	2.0	10	ND	5.5	37	1.4	35	4.8	5.7	19	0.9	1.6		
EMW 01	13	2.1	15	3.6	8.4	16	2.4	11	0.4	5.0	37	1.0	35	7.2	5.2	21	0.6	1.6		
TMP 01	38	0.1	12	6.2	8.9	31	3.2	12	ND	9.7	40	1.5	26	13	14	31	0.3	1.8		
EMW 08	51	ND	ND	6.9	12	35	4.3	36	ND	14	77	2.6	8.8	10	8.7	11	0.9	ND		
EMW 04	18	ND	3.5	12	22	58	6.1	27	ND	25	64	0.7	1.9	22	8.0	18	0.4	4.1		
EMW 09	44	ND	ND	7.2	15	37	5.6	36	ND	18	98	2.7	7.8	13	8.3	20	ND	4.1		
TMP 02	26	0.1	21	12	18	51	7.9	28	0.3	21	99	3.9	17	31	20	34	ND	3.1		
EMW 20	48	0.9	33	12	26	61	6.8	26	0.5	21	93	3.8	55	23	15	49	1.0	1.3		
EMW 02	40	0.6	34	12	28	68	6.7	26	ND	21	92	3.6	60	27	17	50	1.3	4.4		
TMP 13	110	0.6	4.5	16	45	61	13	34	2.8	23	170	4.6	31	20	16	24	ND	0.0		
TMP 06	140	13	ND	14	24	56	6.7	48	0.2	20	120	9.2	79	27	24	76	2.5	5.6		
TMP 09	69	7.1	53	19	44	77	12	50	0.7	27	170	5.9	93	28	17	72	ND	ND		
930103	270	4.1	7.5	14	38	53	9.3	30	2.9	17	140	18	86	29	32	54	4.3	3.5		
80102	210	ND	11	27	75	130	15	52	1.4	46	300	6.3	100	53	39	49	ND	ND		
890102	17	ND	ND	87	220	320	20	40	ND	120	290	3.2	19	22	ND	ND	ND	ND		
EMW 03	96	ND	11	60	130	300	33	190	2.7	140	400	4.7	24	39	1.3	36	ND	ND		
TMP 04	150	0.6	26	56	130	250	29	120	2.7	120	530	6.3	57	35	15	42	ND	ND		
Min	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		
Median	25	ND	4.0	7.0	14	36	4.9	26	ND	15	71	2.4	19	13	6.8	19	0.2	1.0		
Max	270	13	53	87	220	320	33	190	2.9	140	530	18	100	53	39	76	4.3	5.6		

Table S7: Concentrations (μ g/l) of individual PFASs and perfluorinated carboxylates generated upon oxidation (*i.e.* Δ [perfluorinated carboxylates]) in groundwater samples. Analytes that were not detected in any samples are not shown.

Table S8: Concentrations (μ g/kg) of individual PFASs and perfluorinated carboxylates generated upon oxidation (*i.e.* Δ [perfluorinated carboxylates]) in surficial soil (0.6 m below surface) and aquifer solids (5 to 6 m below surface) samples. Analytes that were not detected in any samples are not shown.

	Precursors						Perfluorinated carboxylates						Perfluorinated sulfonates				Δ [Perfluorinated carboxylates]				
	6:2		PFHxS-	8:2																	
Sample	FtS	FHxSA	aAm	FtS	FOSA	C4	C5	C6	C7	C8	C9	C4	C6	C7	C8	C4	C5	C6	C7	C8	C9
LOQ	0.4	0.6	0.8	0.6	0.6	3	1.1	0.8	1.1	0.8	1.1	1.7	0.6	0.6	0.4	1	1	1	1	1	1
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
S-16S	ND	ND	ND	ND	ND	ND	ND	3	ND	2	ND	ND	18	ND	11	ND	ND	ND	ND	ND	ND
S-15S	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3	ND	45	ND	ND	ND	ND	ND	ND
S-12S	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	ND	41	5	1	4	ND	1	ND
S-14S	ND	2	7	ND	3	ND	4	8	ND	5	ND	3	22	ND	69	3	3	15	1	5	ND
S-13S	5	2	ND	2	ND	ND	9	4	3	7	5	ND	44	ND	190	ND	3	13	ND	7	ND
S-11S	ND	ND	ND	3	ND	4	7	10	3	17	3	4	70	ND	280	4	3	3	ND	9	1
S-7S	470	12	ND	20	3	75	290	480	51	310	ND	130	830	ND	96	73	200	160	26	100	2
S-8S	110	5	ND	800	Nd	ND	10	12	16	95	20	ND	150	ND	2400	31	130	190	220	180	20
S-6S	40	12	8	130	3	ND	4	6	3	9	7	ND	37	19	3800	30	37	200	29	30	ND
S-4S	80	23	12	780	18	ND	7	9	ND	19	5	ND	58	ND	3000	43	110	420	190	360	15
S-1S	140	870	ND	150	180	ND	0	19	ND	23	8	ND	61	ND	3100	ND	71	840	45	97	ND
S-9S	350	18	ND	790	8	ND	30	33	9	82	5	ND	270	ND	2300	38	200	1000	290	260	14
S-18S	680	1700	6	32	89	4	7	15	4	61	10	ND	140	96	2400	120	210	1500	33	78	2
S-10S	90	12	ND	730	18	ND	11	16	10	35	10	ND	160	22	8300	120	200	300	280	250	22
S-2S	1900	58	120	280	82	410	820	880	88	720	5	510	5600	89	5900	630	820	1600	290	320	13
S-5S	6200	1500	1600	240	3400	380	1300	2000	320	5200	ND	610	13000	430	20000	2200	2600	11000	830	4000	53
Min	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3	ND	11	ND	ND	ND	ND	ND	ND
Median	85	12	ND	81	3	ND	7	11	3	21	5	ND	66	ND	2400	31	91	195	31	87	2
Max	6200	1700	1600	800	3400	410	1300	2000	320	5200	20	610	13000	430	20000	2200	2600	11000	830	4000	53
			Precursors				Perf	luorinate	d carboxy	lates		Perfluorinated sulfonates				Δ [Perfluorinated carboxylates]					
	6:2		PFHxSa	8:2																-	
Sample	FtS	FHxSA	-Am	FtS	FOSA	C4	C5	C6	C7	C8	C9	C4	C6	C7	C8	C4	C5	C6	C7	C8	C9
S-14D	ND	5	ND	ND	3	3	12	23	4	25	ND	14	100	4	190	7	3	17	5	19	ND
S-6D	88	13	ND	22	3	4	14	22	3	16	ND	8	53	ND	270	ND	20	34	7	8	ND
S-1D	26	69	ND	6	28	14	18	78	22	32	ND	14	87	ND	98	ND	14	57	7	30	ND
S-9D	25	4	ND	70	2	ND	18	16	7	11	ND	2	40	ND	250	ND	25	220	42	33	2
S-4D	51	12	ND	46	11	6	21	44	3	13	ND	14	51	ND	260	ND	31	140	18	130	2
S2-D	120	16	ND	10	8	52	59	135	19	38	ND	88	200	ND	170	5	38	68	ND	15	ND
S-8D	56	11	ND	55	ND	ND	16	39	11	130	2	5	280	5	460	ND	25	580	12	10	2
S-5D	310	18	13	90	19	24	82	150	20	130	ND	60	270	ND	530	46	85	300	49	67	2
S-3D	80	110	14	86	86	11	17	46	5	67	ND	18	210	11	940	39	89	500	78	170	2
S-10D	370	110	ND	38	5	17	95	210	31	88	2	49	870	27	1000	86	97	120	20	41	1
Min	ND	4	ND	ND	ND	ND	12	16	3	11	ND	2	40	ND	98	ND	3	17	ND	8	ND
Median	68	14	ND	42	7	9	18	45	9	35	ND	14	150	ND	270	3	28	130	15	31	1
Max	370	110	14	90	86	52	95	210	31	130	2	88	870	27	1000	86	97	580	78	170	2

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