Supporting Information

Reconstructing the composition of per- and polyfluoroalkyl substances (PFAS) in contemporary aqueous film forming foams

Bridger J. Ruyle[1*], Colin P. Thackray[1], James P. McCord[2], Mark J. Strynar[2], Kevin A. Mauge-Lewis[3], Suzanne E. Fenton[3], and Elsie M. Sunderland[1,4].

[1]Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge MA USA 02138.

[2]U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park NC USA 27709.

[3]National Institute of Environmental Health Sciences, National Toxicology Program Laboratory, Research Triangle Park NC 27709.

[4]Department of Environmental Health, Harvard T.H. Chan School of Public Health, Harvard University, Boston MA USA 02115.

*bruyle@g.harvard.edu

Table of Contents

Supplemental Materials and Methods

Sample preparation and extraction. Both electrochemical fluorination (ECF) and fluorotelomer-based (FT) AFFF were diluted 3% gravimetrically in Milli-Q water (Thermo Scientific™ Barnstead™, Lake Balboa, CA). A Milli-Q water blank was included in the analyses to assess contamination from the solvent. Prior work has indicated some PFAS in AFFF may be volatile.[1] We account for contamination of the sampling equipment from volatile PFAS by a Milli-Q water dilution blank using the pipettor after pipetting the AFFF. Samples were diluted gravimetrically in Milli-Q water to a total factor of 7,500 before analysis for total fluorine (TF) and inorganic fluorine (IF), and by a total factor of 50,000 before extraction for extractable organic fluorine (EOF) and targeted analysis.

Offline solid phase extraction was performed following the method in Koch et al.[2] Briefly, 15 mL samples were extracted using mixed-mode, weak anion exchange cartridges (Waters Oasis™ WAX, Milford, MA). Samples were loaded onto the cartridges with a flow rate of 1 drop per second. After sample loading, cartridges were rinsed with 10 mL 0.01% NH_4OH to remove fluoride followed by 4 mL of Milli-Q water. Samples were eluted into 15 mL polypropylene centrifuge tubes (Corning, Corning, New York) with 4 mL of LC-MS grade methanol (J.T. Baker, Center Valley, PA) used to rinse the sample bottles followed by 4 mL 0.1% NH_4OH in LC-MS grade methanol. The extracts were blown to dryness using a N-EVAP (Organomation, Berlin, MA) nitrogen evaporator and reconstituted in 1 mL of LC-MS grade methanol and split between combustion ion chromatography (CIC) and LC-MS/MS. An isotopically labeled internal standard (IS, Wellington Laboratories, Guelph, Ontario, Canada) (Table S3) was added to the LC-MS/MS fraction after the extract was split between the two fractions.

Targeted PFAS. Extracted samples were diluted volumetrically in Milli-Q water by a factor of 100. Method detection limits (MDLs; Table S3) were calculated as the average concentration at which the sample signal-to-noise ratio was three, multiplied by the dilution factor. Blank concentrations were subtracted from samples when measured PFAS concentrations in the dilution or extraction blank were >MDL. The percent difference in the sum of targeted PFAS concentrations from duplicate extractions of the ECF AFFF was 2% and was ≤10% for most individual PFAS. A 1,000 ng L^{-1} PFAS spike in Milli-Q water was added immediately preceding extraction to assess individual analyte recovery. Recoveries for each targeted PFAS ranged from 72-130%, except for 8:2 FTSA (62%) and 10:2 FTSA (45%).

Fluorine measurements. For TF, two boat blanks were run between each set of duplicate injections of 100 μL. Relative standard deviations of duplicate injections were <8%. Samples were blank corrected using the peak areas of the boat blanks run before and after each set of injections. Two Milli-Q water blanks were run before and after the calibration and after every six samples to account for contamination from the solvents used in the analysis. Concentrations were determined from the average peak areas of duplicate injections using an eight-point calibration curve of perfluorooctanoate (PFOA, 95% purity, Sigma-Aldrich, St. Louis, MO) in Milli-Q water from 100 to 10,000 μg F L^{-1} (R^2>0.999). Concentrations above LOD were adjusted by the dilution factor and reported here. The percent difference of duplicate dilutions of the 3M AFFF was 2%. A 2,500 ug F L^{-1} as PFOA spike was added to a duplicate of FT 2 AFFF (see Table S1) before analysis. Method recovery (99%) was calculated as the difference in fluorine concentrations between the spiked and un-spiked AFFF divided by the nominal spiking concentration.

Samples were analyzed for EOF in a similar manner to TF, except LC-MS grade methanol was used as the solvent instead of Milli-Q Water. Relative standard deviations of duplicate injections were <5%. Concentrations were determined from the average peak areas of duplicate injections using an eight-point calibration curve of PFOA in methanol from 38 to 10,000 μg L^{-1} (R^2>0.999). The percent difference of dilution duplicates of the 3M AFFF was 10%. A 2,500 ug F L^{-1} as PFOA spike was added to a duplicate of FT 2 AFFF before extraction. The method recovery (101%) was calculated in the same manner as for total fluorine. The equivalent organofluorine concentration of the spiking standard was also analyzed using LC-MS/MS by measuring the concentration of PFOA. The method recovery calculated by the difference in EOF divided by the measured spiking concentration was 96%.

Preconcentration of PFAS and organofluorine is not needed in AFFF due to their high concentrations in stock formulas (Table 1, Table S7). However, detections at environmentally relevant levels of PFAS often require extraction,[2,3] which is typically performed for aqueous samples using weak anion exchange (WAX).[4] We perform extraction and measure EOF to quantify the fraction of PFAS amendable to extraction using common field techniques. We chose EOF as the metric for fluorine in AFFF in this work because concentrations of IF and non-extractable organofluorine were determined to be negligible. EOF has more sensitive detection limits than TF and can be directly compared to reported results from environmental matrices.

For inorganic fluorine, Milli-Q blanks were run before and after the calibration and every four sets of triplicate injections. Concentrations were determined from a six-point calibration curve from 0.05 to 10 mg L^{-1} (R^2 > 0.999). Inorganic fluorine was not detected above the lowest calibration point in the dilution blank or Milli-Q blanks.

Non-targeted PFAS analysis. The instrument was run in positive and negative modes using the high-flow heated electrospray ionization (HESI) source. Samples were measured using an acquisition with a scan range of 150-1500 m/z and Orbitrap resolution of 120,000 and 30,000 for MS1 and data-dependent MS2 acquisition respectively. MS2 spectra were collected with precursor isolation window of 1.6 Da, and stepped higher collisional dissociation (HCD) collision energy of 20/35/50. Chromatographic separation was performed using an attached Vanquish ultra performance liquid chromatography (UPLC) system (Thermo Fisher Scientific, Waltham, MA) at a flow rate of 300 μL/min with an Accucore C18+ (2.1 mm x 100 mm x 1.5 um particles) column heated at 50 °C, injection volumes of 3 μL, and a binary mobile phase gradient composed of Solvent A (5% MeOH in water, 0.4 mM ammonium formate) and Solvent B (95% MeOH in water, 0.4 mM ammonium formate). The separation gradient consisted as follows: 3 min pre-equilibration at 10% B, 0-1.5 min linear gradient from 10% - 50% B; 1.5-17 min linear gradient from 50% - 75% B; 17-19 min linear gradient from 75% - 100% B; 19-20 min hold at 100% B.

For nontargeted data analysis, raw instrument files were processed using Thermo Compound Discoverer 2.1. Chemical features were extracted, retention time corrected, and aligned across the batches (i.e. features were aligned between AFFF samples to allow identification of similarities). Matches were based on a maximum 60s retention time shift and 10 ppm mass accuracy match. Features were filtered out if the detected peak area abundance was less than five times the value in reference blank samples and preliminary feature identification was based on a series of potential matches. Masses were matched against the USEPA's Distributed Structure-Searchable Toxicity database (DSSTox v. Dec 2016) and a reference list of AFFF related PFAS species gathered from literature sources. MS/MS spectra were matched

against Thermo mzCloud (v. Dec 2018), and a Mass Bank of North America (MONA) mzvault library (v. January 2018). Predicted molecular compositions were assigned based on isotopic distribution with maximum allowable atom counts - C60 H120 O30 F50 N5 S5 Cl8 Br8.

Features were tentatively flagged as suspect PFAS and features above an integrated peak area of 500,000 (to limit identification to major AFFF components) were manually examined to determine structural elements if they met any of the following sets of conditions: accurate mass match or MS/MS match against a PFAS species from one of the database sources, a predicted molecular composition containing 6+ fluorine and a mass defect between 0.85 and 0.1. Features were assumed to be a PFAS if their MS/MS fragments were consistent with fluorinated moieties (e.g. CF3, CF3CF2, CF3CF2O, etc.) or neutral losses diagnostic for polyfluorinated compounds (e.g. neutral HF loss).

Total Oxidizable Precursor (TOP) Assay. The TOP assay was performed on diluted samples (15 mL) prior to extraction by combining equal parts volume of 120 mM potassium persulfate (ACS-grade $K_2S_2O_8$, Honeywell, Charlotte, NC) and 250 mM sodium hydroxide (ACS-grade NaOH, Macron Fine Chemicals, Radnor, PA) and heated for 16 hours at 85°C in a water bath. Samples were cooled and neutralized with hydrochloric acid (ACS-Plus grade 37% HCl, Fisher Scientific, Hampton, NH). The efficacy of precursor oxidation was evaluated by spiking 3 ng of 6:2 and 8:2 fluorotelomer sulfonate (6:2 FTSA, 8:2 FTSA) and perfluorooctane sulfonamide (FOSA) in Milli-Q water before performing the TOP assay. Concentrations of precursors following the TOP assay were below the method detection limit (MDL) in the spiked sample, indicating complete oxidation. The percent difference in oxidizable precursors from duplicate extractions of the ECF AFFF was 10%.

Bayesian inference method. Equation (1) predicts the original concentration of unknown PFAS grouped by perfluorinated chain length and manufacturing source (θ) given measured concentrations of oxidation products (x) in the TOP assay:

$$\pi(\theta|x) \propto \pi(\theta)p(x|\theta) \qquad \text{(Eq. 1)}$$

where:

$\pi(\theta|x)$ is the posterior, the log10-normal distribution of unknown PFAS concentrations.

$\pi(\theta)$ is the prior, the log10 uncertainty in concentrations of unknown PFAS based on known information regarding the concentrations of these compounds. We use a prior for ECF precursors based on their expected range of concentrations in AFFF based on concentrations of PFOS (0.84*[PFOS] to 2.73*[PFOS]; adapted from Tables S5 and S6 in Houtz et al.[5]) and their relative abundance in AFFF (Table S6). No prior information for unknown FT PFAS was available.

$p(x|\theta)$ is the likelihood, the log10 sum of least squares estimator:

$$p(x|\theta)=\Sigma_i[(\mu_{A,i}\theta_i-x)/\varepsilon_i]^2 \qquad \text{(Eq. 2)}$$

where:

$\mu_{A,i}$ represent the average molar oxidation yields of unknown PFAS i into perfluoroalkyl carboxylates reported in the literature (Table S5).[6–8] ε_i is the total error of the comparison for unknown PFAS i:

$$\varepsilon_i=[(\sigma_{A,i}/\mu_{A,i})^2 + \Delta_{x,i}^2]^{0.5} \qquad \text{(Eq. 3)}$$

Where, σ_{Ai} is the standard deviation of the average molar oxidation yields of unknown PFAS i into perfluoroalkyl carboxylates reported in the literature and $\Delta_{x,i}$ the relative error in the measurement (10% from duplicate analyses).

The posterior distribution was sampled by Markov chain Monte Carlo (MCMC) analysis using 32 ensemble samplers. Sequential steps in the Markov chain were determined using the

differential evolution algorithm[9] with the mean equal to 0.595 (2.38/SQRT[2*ndim]) and standard deviation equal to 1.01, following the recommendation of the software.[10] The MCMC was run until the Monte Carlo standard error was 1/SQRT(2,500) of the standard deviation of the posterior distribution.

Point-of-use EOF concentration

Before use in firefighting, AFFF concentrates are diluted to 3% or 6% (v/v%) in water. The average point-of-use EOF concentration in these AFFF was 18.0±3.72 mM F and ranged from 13 to 23 mM F for the FT-based AFFF (Table S1). No significant difference (two-sided t-test, p-value > 0.05) in point-of-use PFAS concentration was observed between the 3% and 6% products. EOF in FT 6, manufactured in 2016, agreed with estimates of organofluorine in the same product from 2004.[11] These data suggest that the AFFF-industry may target a point-of-use concentration of approximately 18 mM F to achieve ideal firefighting performance.

Table S1. List of AFFF samples and results of fluorine measurements.

AFFF	Product	Year	PFAS disclosed on MSDS	TF [mM][1]	EOF [mM][2]	IF [mM][3]	Point-of-use dilution	Point-of-use EOF [mM]
ECF	3M LightWater™ FC-203CF	2001	Amphoteric fluoroalkylamide derivative (trade secret; 5%) perfluoroalkyl sulfonate salts (trade secret; 1.5%) residual organic fluorochemicals (mixture; unknown)	810	841	26.7	0.03	25.2
ECF Dup				825	934	ND[4]	0.03	28.0
FT 1	Fomtec 3% M	2013	Undisclosed	476	622	<MRL	0.03	18.7
FT 2	Chemguard C306-MS-C	2017	Polyfluorinated alkyl polyamide (proprietary; 1-5%) Polyfluorinated alkyl quaternary amine chloride (proprietary, 0.1-1%)	739	771	<MRL	0.03	23.1
FT 3	Angus Fire Tridol® M^{C6} 6%	2016	Fluoroalkyl surfactants (proprietary; 1-5%)	295	218	ND	0.06	13.1
FT 4	Solberg Arctic™ U.S. Type 3	2016	Undisclosed	5370	586	<MRL	0.03	17.6
FT 5	Chemguard C606-MS-C	2017	Polyfluorinated alkyl polyamide (proprietary; 0.1-1%)	311	276	ND	0.06	16.6
FT 6	Angus Fire Tridol® M^{C6} 3%	2016	Fluoroalkyl surfactants (proprietary; 1-5%)	553	467	<MRL	0.03	14.0
FT 7	Solberg Arctic™ U.S. Type 6	2015	Undisclosed	294	275	ND	0.06	16.5
FT 8	Fire Service Plus FireAde MIL 3%	2017	Undisclosed	586	595	<MRL	0.03	17.8
FT 9	Fire Service Plus FireAde MIL 6%	2017	Undisclosed	337	289	ND	0.06	17.4
Class A Foam	PHOS-CHEK® WD881	2015	Undisclosed	<LOD	<LOD	<MRL	0.00	0.00
Dilution Blank				<LOD	<LOD	<MRL		
Blank				<LOD	<LOD	ND		

[1]TF limit of detection (LOD) = 0.007 mM; [2]EOF LOD = 0.01 mM; [3]IF method reporting limit (MRL) = 0.003 mM; [4]ND = not determined

196 **Table S2. Targeted PFAS analyzed by LC-MS/MS.**

Name	Acronym	Number of perfluorinated carbons
Perfluoroalkyl carboxylates (PFCA)		
Perfluorobutanoate	PFBA	3
Perfluoropentanoate	PFPeA	4
Perfluorohexanoate	PFHxA	5
Perfluoroheptanoate	PFHpA	6
Perfluorooctanoate	PFOA	7
Perfluorononanoate	PFNA	8
Perfluorodecanoate	PFDA	9
Perfluoroundecanoate	PFUnDA	10
Perfluorododecanoate	PFDoDA	11
Perfluorotridecanoate	PFTrDA	12
Perfluorotetradecanoate	PFTeDA	13
Perfluoroalkyl sulfonates (PFSA)		
Perfluorobutane sulfonate	PFBS	4
Perfluoropentane sulfonate	PFPeS	5
Linear perfluorohexane sulfonate isomer	l-PFHxS	6
Branched perfluorohexane sulfonate isomers	br-PFHxS	6
Perfluoroheptane sulfonate	PFHpS	7
Linear perfluorooctane sulfonate isomer	l-PFOS	8
Branched perfluorooctane sulfonate isomers	br-PFOS	8
Perfluorononane sulfonate	PFNS	9
Perfluorodecane sulfonate	PFDS	10
Fluorotelomer sulfonates (FTSA)		
4:2 fluorotelomer sulfonate	4:2 FTSA	4
6:2 fluorotelomer sulfonate	6:2 FTSA	6
8:2 fluorotelomer sulfonate	8:2 FTSA	8
10:2 fluorotelomer sulfonate	10:2 FTSA	10
Perfluoroalkyl sulfonamides (FASA)		
Perfluorobutane sulfonamide	FBSA	4
Perfluorohexane sulfonamide	FHxSA	6
Perfluorooctane sulfonamide	FOSA	8

197
198

199 **Table S3. LC-MS/MS parameters for targeted PFAS analysis.**

Analyte	Type	Internal Standard	Precursor Ion	Quantifier Ion	Quantifier Collision Energy (V)	Qualifier Ion	Qualifier Collision Energy (V)	Fragmentor Voltage (V)
PFPeA	Target	[$^{13}C_5$] PFPeA	262.9	218.9	2			60
PFHxA	Target	[$^{13}C_5$] PFHxA	312.9	268.9	2	118.9	14	70
PFHpA	Target	[$^{13}C_4$] PFHpA	362.9	318.9	2	168.9/118.9	10/18	70
PFOA	Target	[$^{13}C_8$] PFOA	412.9	368.9	2	168.9	10	80
PFNA	Target	[$^{13}C_9$] PFNA	462.9	418.9	2	218.9/169.0	10/14	75
PFDA	Target	[$^{13}C_6$] PFDA	512.9	468.9	6	269.0/218.9	14/14	85
PFUnDA	Target	[$^{13}C_7$] PFUnDA	562.9	518.9	6	269.0/169.0	14/22	95
PFDoDA	Target	[$^{13}C_2$] PFDoDA	612.9	569.0	6	269.0/169.0	14/26	90
PFTrDA	Target	[$^{13}C_2$] PFTeDA	662.8	618.9	6	169.0	26	95
PFTeDA	Target	[$^{13}C_2$] PFTeDA	712.9	669.0	6	169.0	25	100
PFBS	Target	[$^{13}C_3$] PFBS	298.9	80.0	38	98.9	30	95
PFPeS	Target	[$^{13}C_3$] PFHxS	348.9	80.0	38	98.9	30	140
PFHxS	Target	[$^{13}C_3$] PFHxS	398.9	80.0	58	98.9	34	135
PFHpS	Target	[$^{13}C_8$] PFOS	448.9	80.0	54	98.9	42	180
PFOS	Target	[$^{13}C_8$] PFOS	498.9	80.0	60	98.9	50	200
PFNS	Target	[$^{13}C_8$] PFOS	548.9	80.0	60	98.9	54	175
PFDS	Target	[$^{13}C_8$] PFOS	598.9	80.0	60	98.9	54	175
4:2 FTSA	Target	[$^{13}C_2$] 4:2 FTSA	326.9	307.0	10	81.0	30	130
6:2 FTSA	Target	[$^{13}C_2$] 6:2 FTSA	426.9	406.9	18	81.0	34	135
8:2 FTSA	Target	[$^{13}C_2$] 8:2 FTSA	526.9	506.9	26	81.0	42	180
10:2 FTSA	Target	[$^{13}C_2$] 8:2 FTSA	627	607	30	81.0	70	180
FBSA	Target	[$^{13}C_8$] FOSA	298.0	78.0	20			140
FHxSA	Target	[$^{13}C_8$] FOSA	398.0	78.0	40			180
FOSA	Target	[$^{13}C_8$] FOSA	497.9	78.0	38			140
[$^{13}C_4$] PFBA	ISTD		216.9	171.9	2			60
[$^{13}C_5$] PFPeA	ISTD		267.9	223.0	2			60
[$^{13}C_5$] PFHxA	ISTD		317.8	273.0	2			70
[$^{13}C_4$] PFHpA	ISTD		366.8	321.9	2			70
[$^{13}C_8$] PFOA	ISTD		420.9	376.0	2			75
[$^{13}C_9$] PFNA	ISTD		472.0	427.0	2			85
[$^{13}C_6$] PFDA	ISTD		518.9	474.0	2			90
[$^{13}C_7$] PFUnDA	ISTD		569.9	525.0	6			85
[$^{13}C_2$] PFDoDA	ISTD		614.9	569.9	6			95
[$^{13}C_2$] PFTeDA	ISTD		714.8	670.0	6			95
[$^{13}C_3$] PFBS	ISTD		301.9	99.0	26			95
[$^{13}C_3$] PFHxS	ISTD		401.9	98.9	38			180

[$^{13}C_8$] PFOS	ISTD	506.9	99.0	50	180
[$^{13}C_2$] 4:2 FTSA	ISTD	328.9	81.0	38	95
[$^{13}C_2$] 6:2 FTSA	ISTD	428.9	81.0	46	95
[$^{13}C_2$] 8:2 FTSA	ISTD	528.9	81.0	46	180
[$^{13}C_8$] FOSA	ISTD	505.9	78.0	38	95

200

Table S4. Measured change in PFCA in extracts after the TOP assay.[1]

	ΔC3	ΔC4	ΔC5	ΔC6	ΔC7	ΔC8
ECF	2598	1650	8672	116	110	0.00
ECF Dup	2833	1817	9618	131	126	0.00
FT 1	2507	4686	1955	351	2507	0.00
FT 2	2747	5102	2042	420	2747	0.00
FT 3	1393	2668	852	198	1393	0.00
FT 4	2490	5356	1384	355	2490	0.00
FT 5	1314	2480	1086	201	1314	0.00
FT 6	2323	5063	1414	299	2323	0.00
FT 7	1563	3136	787	201	1563	0.00
FT 8	3345	6327	2567	508	3345	0.00
FT 9	1645	3242	1335	258	1645	0.00
Class A Foam	0.00	0.00	0.00	0.00	0.00	0.00

[1]Measured concentrations [nM] are reported after blank subtraction.

Note: AFFF sample designations are listed in Table S1

Table S5. PFCA yields from representative precursors in the TOP assay.

Compound	Number of perfluorianted carbons (n)	Cn PFCA yield [%]					
		n	n-1	n-2	n-3	n-4	n-5
n:2 fluorotelomer precursors							
4:2 FTSA[1]	4	3	24				
6:2 FTSA[1]	6	2	17	24	21		
6:2 FTSA-PrB[1]	6	1	8	33	21		
6:2 FTSA[2]	6	2	22	27	22		
8:2 FTSA[1]	8	2	20	25	19	16	9
8:2 FTSA[2]	8	3	21	27	19	12	11
10:2 FTSA[1]	10	3	28	29	16	14	6
mean[3]		2	20	28	20	14	9
standard deviation[3]		1	7	6	2	2	3
Cn ECF precursors							
N-EtFOSAA[2,4]	8	0	92	0	0	0	0
N-MeFOSAA[2,4]	8	0	110	0	0	0	0
FOSA[2]	8	0	97	0	0	0	0
FHxSA[1]	6	0	96	1	0	0	0
FOSA[1]	8	0	88	2	0	0	0
MeFOSA[1,4]	8	0	84	1	0	0	0
EtFOSA[1,4]	8	0	76	1	0	0	0
FOSAA[1,4]	8	0	88	2	0	0	0
MeFOSAA[1,4]	8	0	94	2	0	0	0
EtFOSAA[1,4]	8	0	95	1	0	0	0
PFOSB[1,4]	8	0	73	2	0	0	0
PFOSNO[1,4]	8	0	73	2	0	0	0
PFOSAmS[1,4]	8	0	68	1	0	0	0
PFOSAm[1,4]	8	0	89	3	0	0	0
PFOAB[1,4]	8	0	71	2	0	0	0
PFOANO[1,4]	8	0	79	2	0	0	0
FEtSA[4,5]	2	0	88	0	0	0	0
FBSA[5]	4	0	65	0	0	0	0
FHxSA[5]	6	0	84	0	0	0	0
FOSA[5]	8	0	103	0	0	0	0
mean[3]		0	87	1	0	0	0
standard deviation[3]		0	12	1	0	0	0

[1]Reported by Martin et al.[7] (Table 1).

[2]Reported by Houtz and Sedlak[6] (Table 1).

[3]Random samples from a normal distribution parametrized by mean (μ_A) and standard deviation ($\sigma_A^{1/2}$) are implemented in Bayesian Inference in Eq S2

[4]N-EtFOSAA = N-ethyl perfluorooctane sulfonamido acetic acid, N-MeFOSAA = N-methyl perfluorooctane sulfonamido acetic acid, MeFOSA = methylperfluorooctane sulfonamide, EtFOSA = ethylperfluorooctane sulfonamide, FOSAA = perfluorooctane sulfonamido acetic

acid, MeFOSAA = methyl perfluorooctane sulfonamido acetic acid, EtFOSAA = ethyl perfluorooctane sulfonamido acetic acid, PFOSB = perfluorooctane sulfonamidoalkyl betaine, PFOSNO = perfluorooctane sulfonamidoalkyl amine oxide, PFOSAmS = perfluorooctane sulfonamidoalkyl ammonium salt, PFOSAm = perfluorooctane sulfonamidoalkyl amine, PFOAB = perfluorooctane amidoalkyl betaine, PFOANO = perfluorooctane amidoalkyl amine oxide, FEtSA = perfluoroethane sulfonamide.

[5]Reported in Janda et al.[8] (Table 1).

Table S6. ECF precursor prior composition

Sample[1]	ΔC3/ΔCTOT[2]	ΔC3/ΔCTOT	ΔC3/ΔCTOT	ΔC3/ΔCTOT	ΔC3/ΔCTOT
3M 1988	0.13	0.06	0.75	0.02	0.03
3M 1989	0.17	0.02	0.76	0.02	0.03
3M 1992	0.22	0.10	0.65	0.01	0.02
3M 1993	0.22	0.11	0.64	0.01	0.02
3M 1993	0.25	0.11	0.61	0.01	0.02
3M 1998	0.21	0.14	0.61	0.01	0.02
3M 1998	0.26	0.07	0.64	0.01	0.01
3M 1999	0.00	0.26	0.67	0.05	0.02
3M 2001	0.20	0.09	0.67	0.02	0.03
mean[3]	0.19	0.11	0.67	0.02	0.02
standard deviation[3]	0.08	0.07	0.05	0.01	0.01

[1]Sample names and data correspond to Table S5 and Table S6 in Houtz et al.[5]

[2]ΔCn/ΔCTOT = the ratio of the molar change in Cn PFCA to the total molar change in PFCA in the TOP assay

[3]Random samples from a normal distribution parametrized by mean (μ) and standard deviation (σ^2) are implemented in the prior in the Bayesian inference as $\pi(\theta=N(\mu,\sigma^2))$ in Eq S1.

Table S7. Organofluorine content of targeted PFAS in AFFF [mM F].[1]

Targeted PFAS	Method Detection Limit (MDL)	ECF	ECF Dup	FT 1	FT 2	FT 3	FT 4	FT 5	FT 6
	[nM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]
PFBA	12.64	1.48	1.59	<MDL	0.05	0.06	0.08	<MDL	0.08
PFPeA	9.78	2.43	2.79	<MDL	<MDL	<MDL	<MDL	<MDL	0.04
PFHxA	4.2	7.1	7.88	<MDL	0.06	0.04	0.11	0.02	0.06
PFHpA	6.38	2.12	2.43	0.12	0.04	<MDL	0.02	<MDL	0.03
PFOA	23.01	8.55	9.14	<MDL	<MDL	<MDL	<MDL	0.15	0.09
PFNA	15.4	<MDL	<MDL	<MDL	<MDL	0.27	<MDL	0.07	<MDL
PFDA	29.24	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFUnDA	6.98	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFDoDA	13.37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFTrDA	38.86	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFTeDA	116.92	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFBS	2.78	7.42	6.54	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFPeS	3.1	7.59	7.45	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Linear PFHxS	4.37	39.81	40.37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Branched PFHxS	4.3	13.05	13.83	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFHpS	3.32	9.17	8.37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Linear PFOS	16.02	226.92	217.83	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Branched PFOS	19.36	79.16	80.94	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFNS	131.88	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFDS	3.54	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4:2 FTSA	5.29	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6:2 FTSA	5.14	<MDL	<MDL	0.23	0.21	1.63	5.41	0.07	2.66
8:2 FTSA	32.59	<MDL	<MDL	0.1	<MDL	<MDL	<MDL	<MDL	<MDL
10:2 FTSA	27.52	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FBSA	4.49	0.08	0.09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FHxSA	15.18	1.86	1.34	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FOSA	4.89	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

[1]Measured concentrations are reported after blank subtraction.

Note: AFFF sample designations are listed in Table S1

Table S7 cont. Organofluorine content of targeted PFAS in AFFF [mM F].[a]

Targeted PFAS	Method Detection Limit (MDL)	FT 7	FT 8	FT 9	Class A Foam	Dilution Blank	Extraction Blank
	[nM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]	[mM F]
PFBA	12.64	0.09	0.04	<MDL	<MDL	<MDL	<MDL
PFPeA	9.78	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFHxA	4.2	0.07	0.02	<MDL	<MDL	<MDL	<MDL
PFHpA	6.38	<MDL	<MDL	0.05	<MDL	<MDL	<MDL
PFOA	23.01	0.15	<MDL	0.72	<MDL	<MDL	<MDL
PFNA	15.4	0.05	<MDL	<MDL	<MDL	<MDL	<MDL
PFDA	29.24	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFUnDA	6.98	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFDoDA	13.37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFTrDA	38.86	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFTeDA	116.92	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFBS	2.78	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFPeS	3.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Linear PFHxS	4.37	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Branched PFHxS	4.3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFHpS	3.32	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Linear PFOS	16.02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Branched PFOS	19.36	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFNS	131.88	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
PFDS	3.54	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4:2 FTSA	5.29	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6:2 FTSA	5.14	2.83	<MDL	0.16	<MDL	<MDL	<MDL
8:2 FTSA	32.59	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
10:2 FTSA	27.52	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FBSA	4.49	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FHxSA	15.18	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FOSA	4.89	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

[a]Measured concentrations are reported after blank subtraction.

Note: AFFF sample designations are listed in Table S1

Table S8. Median TOP precursor concentration [mM F] in AFFF stocks.[1]

	4:2 FT	6:2 FT	8:2 FT	C4 ECF	C5 ECF	C6 ECF	C7 ECF	C8 ECF	Fluorine
ECF	6.31E-03	1.66E-02	2.34E-03	4.93E+00	2.82E+00	1.63E+01	2.63E-01	5.13E-01	4.07E+02
ECF Dup	9.33E-03	1.58E-02	3.47E-03	5.41E+00	3.16E+00	1.91E+01	3.02E-01	5.62E-01	4.57E+02
FT 1	6.17E-03	3.61E+01	1.20E-04	1.15E-04	5.75E-05	3.80E-04	4.68E-06	1.23E-05	5.13E+02
FT 2	8.13E-03	4.55E+01	2.24E-04	1.38E-04	7.24E-05	4.57E-04	5.75E-06	1.41E-05	6.46E+02
FT 3	5.50E-03	1.70E+01	1.74E-04	1.26E-04	6.17E-05	4.27E-04	5.62E-06	1.32E-05	2.69E+02
FT 4	8.51E-03	2.77E+01	1.62E-04	1.10E-04	6.17E-05	4.47E-04	4.37E-06	1.23E-05	4.79E+02
FT 5	6.31E-03	2.23E+01	1.95E-04	1.23E-04	6.31E-05	4.79E-04	4.79E-06	1.26E-05	3.24E+02
FT 6	8.71E-03	2.82E+01	1.66E-04	1.17E-04	6.17E-05	4.68E-04	4.79E-06	1.35E-05	4.47E+02
FT 7	5.62E-03	1.67E+01	2.00E-04	1.38E-04	6.46E-05	4.57E-04	5.62E-06	1.41E-05	2.82E+02
FT 8	6.76E-03	5.01E+01	1.26E-04	1.35E-04	7.08E-05	4.68E-04	5.13E-06	1.41E-05	7.24E+02
FT 9	3.55E-03	2.67E+01	1.95E-04	1.17E-04	5.37E-05	4.47E-04	4.57E-06	1.23E-05	3.80E+02

[1]Results represent the median value of the kernel density (Fig 2, Fig S1) of precursors inferred from Bayesian inference of the TOP assay (Table S4) after substracting those identified using targeted analysis (Table S7). Concentrations were determined using Markov-chain Monte Carlo (MCMC) analysis.

Note: AFFF sample designations are listed in Table S1

Table S9. Fluorine mass balance [mM F] in AFFF stocks.

	EOF	Targeted PFAAs	Targeted precursors	Median TOP precursors	ΣTargeted+ TOP PFAS	EOF and Σtargeted+TOP PFAS (% Difference)
ECF	841	405	1.94	408	815	3.2
ECF Dup	934	399	1.44	460	860	8.2
FT 1	622	0.12	0.33	510	510	20
FT 2	771	0.15	0.21	652	652	17
FT 3	218	0.37	1.63	270	272	22
FT 4	586	0.21	5.41	477	483	19
FT 5	276	0.25	0.07	321	321	15
FT 6	467	0.31	2.66	443	446	4.6
FT 7	275	0.36	2.83	281	284	3.3
FT 8	595	0.06	0.00	725	725	20
FT 9	289	0.77	0.16	382	383	28

Note: AFFF sample designations are listed in Table S1

Table S10. HRMS identification of most abundant suspect PFAS.

	Name	CASRN	RT [min]	Identification confidence[1]	Mode(s)	Neg (m/z)	Pos (m/z)
1	6:2 fluorotelomer sulfinyl propanamido dimethyl ethyl sulfonate sulfoxide	1513864-10-2	5.138	2b	+/-	602.0346	604.0498
2	6:2 fluorotelomer thia hydroxy propyl trimethyl ammonium	88992-45-4	7.256	2b	+		496.0982
3	6:2 fluorotelomer thia propanoamido dimethyl ethyl sulfonate	88992-47-6	8.166	2b	+/-	586.0395	588.0547
4	Class 19 from Barzen-Hanson 2017[12]		8.855	3	+/-	521.0572	523.0724
5	6:2 fluorotelomer thia propanamide	64972-10-7	10.626	2b	+		452.0351
6	6:2 fluorotelomer sulfonic acid	27619-97-2	4.978	1	-	426.9674	
7	6:2 fluorotelomer sulfonamide betaine	34455-29-3	6.222	2a	+/-	569.0785	571.0937
8	6:2 fluorotelomer sulfonamido propyl hydroxy dimethyl amine	80475-32-7	6.953	2b	+/-	527.0682	529.0834
9	N-hydroxyethyl dimethylammoniopropyl perfluorohexane sulfonamido propylsulfonate	76201-56-4	5.883	2b	+/-	649.0717	651.0869
10	6:2 fluorotelomer sulfinyl hydroxypropyl trimethyl ammonium	1513864-18-0	5.612	2b	+		513.0882
11			7.523	5	+/-	663.1318	665.147
12	$C_{16}H_{22}F_{13}NO_5S$		7.066	3	-	586.0937	
13			7.849	5	+/-	592.0945	594.1097
14			7.161	5	+		736.1841

Note: Compounds are numbered corresponding to Table 1

[1]Confidence levels according to Schymanski[13]

Table S11. Peak area of most abundant suspect PFAS in Positive Ion mode.

Compound Number[1]	FT 1	FT 2	FT 3	FT 4	FT5	Class A Foam	FT 6	FT 7
1	7.15E+05	5.68E+05	1.38E+06	3.80E+05	2.63E+05	4.60E+02	1.46E+06	3.42E+05
2	4.48E+07	1.11E+07	2.98E+03	6.76E+06	3.38E+06	6.64E+02	5.28E+02	2.09E+06
3	8.88E+06	1.20E+07	3.73E+06	2.01E+06	9.13E+06	1.53E+03	8.29E+06	7.70E+05
4	8.25E+06	4.88E+06	7.94E+05	1.20E+06	2.47E+06	1.12E+03	1.55E+06	5.43E+05
5	3.21E+06	1.93E+06	1.58E+05	4.14E+05	2.02E+03	9.30E+02	4.54E+05	1.30E+05
6	ND[2]	ND	ND	ND	ND	ND	ND	ND
7	1.96E+03	1.54E+03	1.69E+04	1.40E+07	1.35E+03	8.57E+02	3.83E+04	6.92E+06
8	6.23E+02	5.42E+02	8.28E+03	6.04E+07	6.59E+03	1.09E+03	3.35E+04	3.69E+07
9	7.35E+02	7.24E+02	7.80E+06	1.03E+03	6.49E+02	1.60E+03	1.51E+07	8.84E+02
10	1.60E+06	2.66E+05	7.00E+02	6.67E+05	2.26E+05	1.22E+03	3.94E+02	5.02E+05
11	1.85E+06	8.99E+05	2.06E+05	2.77E+05	5.40E+05	6.82E+02	4.09E+05	1.15E+05
12	ND	ND	ND	ND	ND	ND	ND	ND
13	1.76E+06	1.45E+06	2.11E+05	2.87E+05	8.18E+05	6.02E+02	3.71E+05	1.38E+05
14	1.38E+06	1.23E+06	1.32E+05	1.72E+05	6.55E+05	9.88E+02	3.19E+05	7.08E+04

[1]Compound numbers correspond to fluorotelomers listed in Table 1

[2]ND = not detected in positive ion mode

Note: AFFF sample designations are listed in Table S1

Table S11 cont. Peak area of most abundant suspect PFAS in Positive Ion mode.

Compound Number[1]	FT 8	FT 9	Blank
1	2.92E+05	3.15E+05	3.52E+03
2	4.31E+07	1.66E+07	5.87E+04
3	9.00E+06	5.71E+06	5.50E+03
4	1.02E+07	4.88E+06	1.13E+04
5	4.14E+06	1.88E+06	2.40E+04
6	ND[2]	ND	ND
7	6.09E+02	9.57E+02	1.81E+03
8	7.67E+03	1.60E+03	8.70E+03
9	1.84E+03	8.21E+02	1.90E+03
10	7.61E+05	5.83E+05	2.08E+04
11	2.17E+06	1.10E+06	8.03E+02
12	ND	ND	ND
13	2.11E+06	1.17E+06	1.17E+03
14	1.81E+06	9.76E+05	7.82E+02

[1]Compound numbers correspond to fluorotelomers listed in Table 1

[2]ND = not detected in positive ion mode

Note: AFFF sample designations are listed in Table S1

Table S12. Peak area of most abundant suspect PFAS in Negative Ion mode.

Compound Number[1]	FT 1	FT 2	FT 3	FT 4	FT5	Class A Foam	FT 6	FT 7
1	1.10E+06	7.61E+05	2.81E+06	6.61E+05	4.37E+05	1.00E+03	3.34E+06	5.78E+05
2	ND[2]	ND	ND	ND	ND	ND	ND	ND
3	3.53E+07	6.17E+07	1.32E+07	7.27E+06	2.49E+07	2.22E+03	2.71E+07	2.29E+06
4	7.06E+06	4.18E+06	7.54E+05	1.11E+06	2.30E+06	2.35E+03	1.59E+06	5.39E+05
5	ND	ND	ND	ND	ND	ND	ND	ND
6	1.61E+04	4.77E+04	4.76E+05	1.45E+06	1.82E+04	3.17E+03	9.89E+05	8.82E+05
7	4.09E+02	4.21E+02	4.44E+03	5.69E+06	4.15E+02	8.80E+02	1.14E+04	2.71E+06
8	1.13E+03	7.54E+02	1.33E+03	2.56E+07	1.13E+03	2.46E+03	5.52E+03	1.35E+07
9	4.33E+02	4.27E+02	4.61E+06	1.95E+04	4.33E+02	1.49E+03	8.79E+06	1.07E+04
10	ND	ND	ND	ND	ND	ND	ND	ND
11	1.51E+06	1.15E+06	1.69E+05	2.58E+05	7.81E+05	5.23E+03	3.56E+05	1.30E+05
12	2.11E+06	6.74E+05	2.99E+02	4.35E+05	1.29E+03	1.43E+03	2.98E+02	5.88E+02
13	ND	ND	ND	ND	ND	ND	ND	ND
14	ND	ND	ND	ND	ND	ND	ND	ND

[1]Compound numbers correspond to fluorotelomers listed in Table 1

[2]ND = not detected in negative ion mode

Note: AFFF sample designations are listed in Table S1

Table S12 cont. Peak area of most abundant suspect PFAS in Negative Ion mode.[a]

Compound Number[1]	FT 8	FT 9	Blank
1	5.43E+05	5.19E+05	6.98E+03
2	ND[2]	ND	ND
3	3.66E+07	2.32E+07	2.60E+03
4	8.04E+06	4.33E+06	7.83E+03
5	ND	ND	ND
6	1.80E+04	1.76E+04	3.24E+03
7	4.77E+02	5.68E+02	6.52E+02
8	1.56E+03	8.41E+02	1.82E+03
9	1.02E+03	4.51E+02	1.26E+03
10	ND	ND	ND
11	1.72E+06	9.37E+05	1.42E+03
12	1.75E+06	1.00E+06	1.02E+03
13	ND	ND	ND
14	ND	ND	ND

[1]Compound numbers correspond to fluorotelomers listed in Table 1

[2]ND = not detected in negative ion mode

Note: AFFF sample designations are listed in Table S1

Table S13. Potential PFAS releases from fluorotelomer-containing AFFF use.

Use scenario[1]	AFFF used [ML yr^{-1}][2]	EOF released [kmol yr^{-1}]	6:2 fluorotelomers released [kmol yr^{-1}]
5%	1.43	25.8	1.78
15%	4.29	77.3	5.35

[1]Based on a stockpile of 7,559,000 gallons and minimum and maximum annual use scenarios estimated in 2011 by Darwin.[14]

[2]ML = megaliters

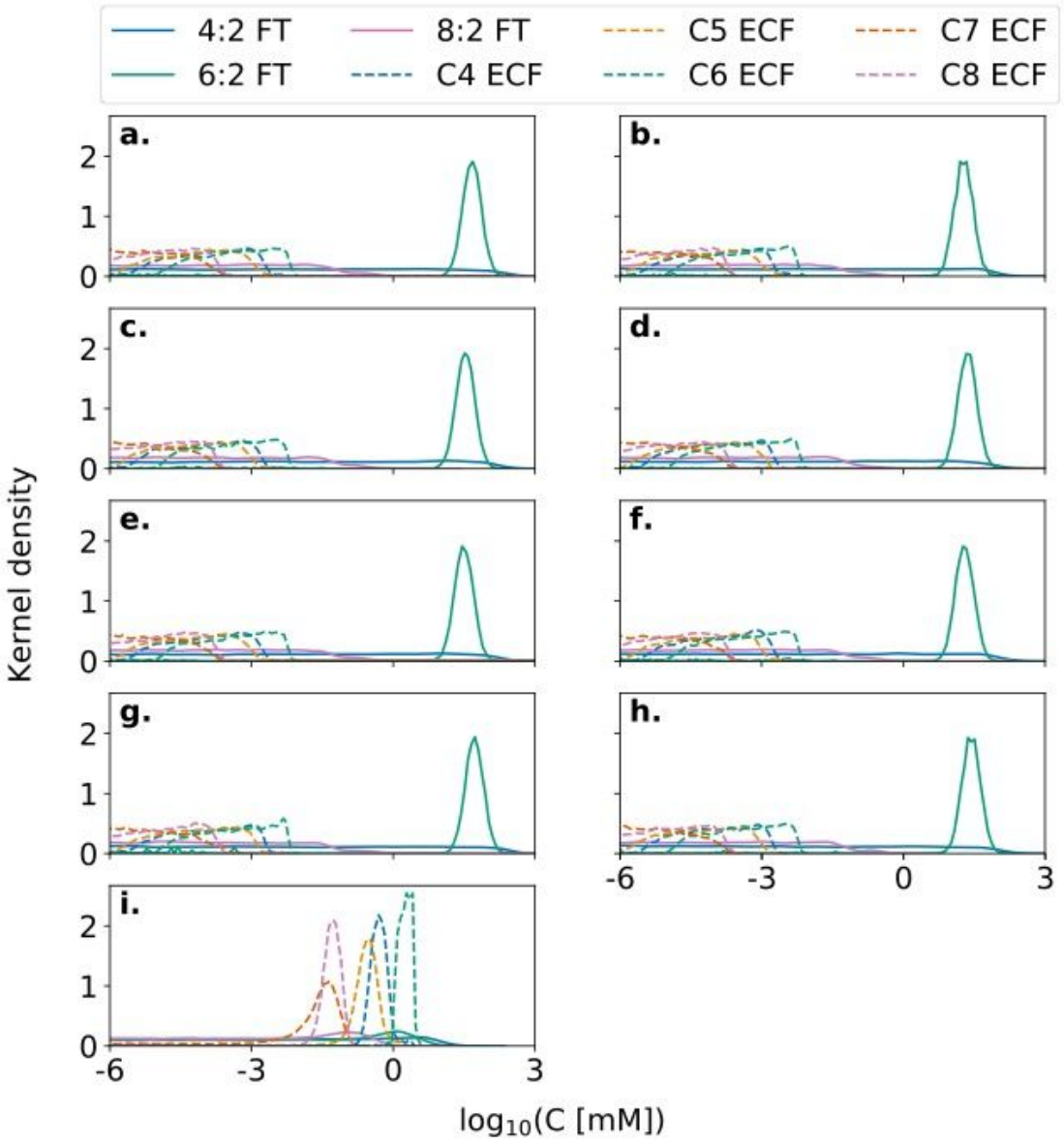

Fig S1. Inferred concentrations of oxidizable precursors and their perfluorinated chain length in AFFF using Bayesian inference and results of the TOP assay. Panels show probability density functions estimated by the non-parametric kernel density of the concentrations of oxidizable precursors in: (a) FT 2, (b) FT 3, (c) FT 4, (d) FT 5, (e) FT 6, (f) FT 7, (g) FT 8, (h) FT 9, and (i) Legacy ECF Dup. AFFF numbering corresponds to Table S1. Precursors are grouped by perfluorinated chain length and manufacturing source. ECF precursors range from 4-8 perfluorinated carbons (C4-C8) while FT precursors have *n* perfluorinated carbons followed by two aliphatic hydrocarbons (*n*:2, *n*=4,6,8).

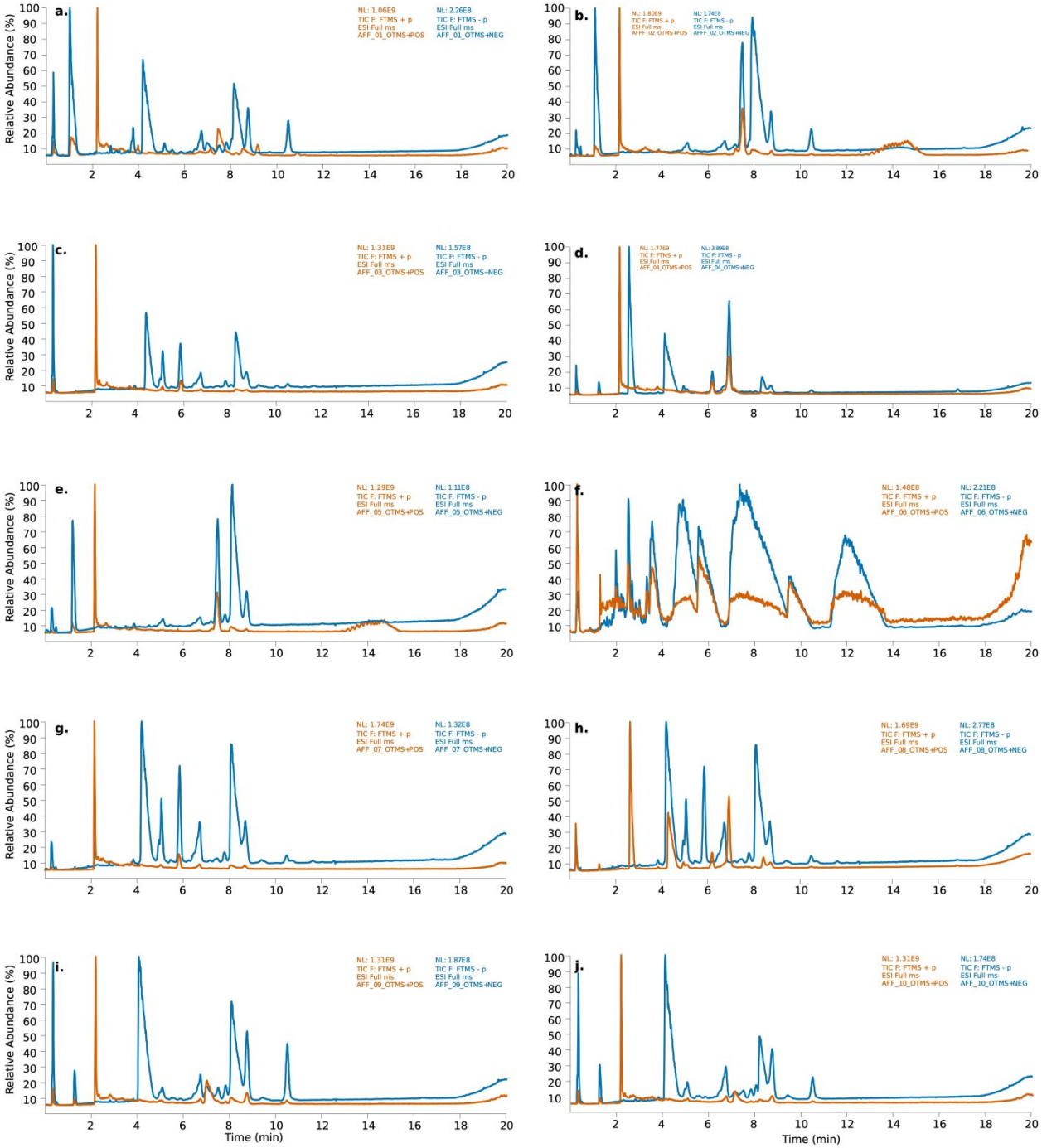

Fig S2. Total Ion Chromatograms in negative (blue) and positive (orange) ionization mode. Panel (a) Contemporary FT 1 Fomtec 3% M. Panel (b) Contemporary FT 2 Chemguard C306-MS-C (c) Contemporary FT 3 Angus Fire Tridol ® M^{C6} 6%. Panel (d) Contemporary FT 4 Solberg Arctic™ U.S. Type 3 (e) Contemporary FT 5 Chemguard C606 MS-C. Panel (f) Class A foam PHOS-CHEK ® WD881. Panel (g) Contemporary FT 6 Angus Fire Tridol® M^{C6} 3%. Panel (h) Contemporary FT 7 Solberg Arctic™ U.S. Type 6. Panel (i) Contemporary FT 8 Fire Service Plus FireAde MIL 3%. Panel (j) Contemporary FT 9 Fire Service Plus FireAde MIL 6%.

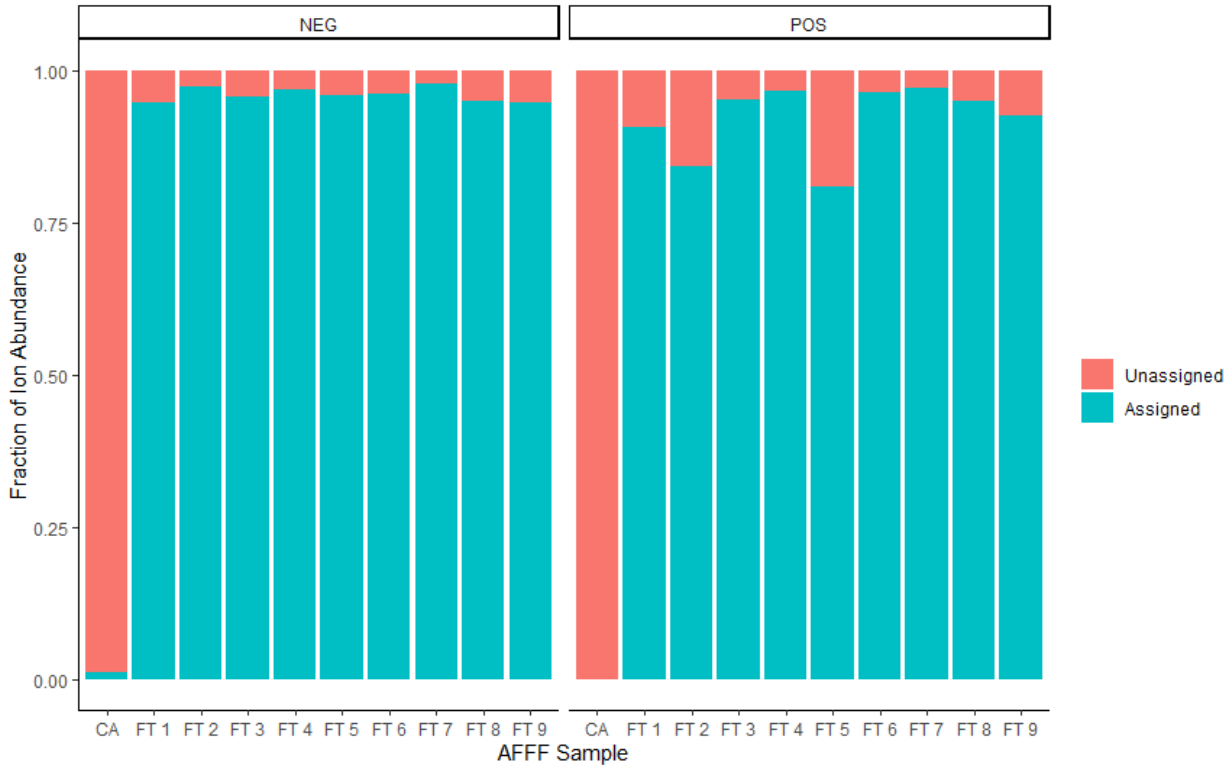

Fig S3. Peak area of most abundant suspect PFAS in positive and negative ionization mode in fluorotelomer (FT)-containing AFFF. AFFF sample designations are noted in Table S1. CA = Class A Foam.

References

(1) Roth, J.; Abusallout, I.; Hill, T.; Holton, C.; Thapa, U.; Hanigan, D. Release of Volatile Per- and Polyfluoroalkyl Substances from Aqueous Film-Forming Foam. *Environ. Sci. Technol. Lett.* **2020**, *7* (3), 164–170. https://doi.org/10.1021/acs.estlett.0c00052.

(2) Koch, A.; Kärrman, A.; Yeung, L. W. Y.; Jonsson, M.; Ahrens, L.; Wang, T. Point Source Characterization of Per- and Polyfluoroalkyl Substances (PFASs) and Extractable Organofluorine (EOF) in Freshwater and Aquatic Invertebrates. *Environ. Sci. Process. Impacts* **2019**, *21* (11), 1887–1898. https://doi.org/10.1039/C9EM00281B.

(3) Hu, X. C.; Tokranov, A. K.; Liddie, J.; Zhang, X.; Grandjean, P.; Hart, J. E.; Laden, F.; Sun, Q.; Yeung, L. W. Y.; Sunderland, E. M. Tap Water Contributions to Plasma Concentrations of Poly- and Perfluoroalkyl Substances (PFAS) in a Nationwide Prospective Cohort of U.S. Women. *Environ. Health Perspect.* **2019**, *127* (6), 067006. https://doi.org/10.1289/EHP4093.

(4) Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. 52.

(5) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.* **2013**, *47* (15), 8187–8195. https://doi.org/10.1021/es4018877.

(6) Houtz, E. F.; Sedlak, D. L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environ. Sci. Technol.* **2012**, *46* (17), 9342–9349. https://doi.org/10.1021/es302274g.

(7) Martin, D.; Munoz, G.; Mejia-Avendaño, S.; Duy, S. V.; Yao, Y.; Volchek, K.; Brown, C. E.; Liu, J.; Sauvé, S. Zwitterionic, Cationic, and Anionic Perfluoroalkyl and Polyfluoroalkyl Substances Integrated into Total Oxidizable Precursor Assay of Contaminated Groundwater. *Talanta* **2019**, *195*, 533–542. https://doi.org/10.1016/j.talanta.2018.11.093.

(8) Janda, J.; Nödler, K.; Scheurer, M.; Happel, O.; Nürenberg, G.; Zwiener, C.; Lange, F. T. Closing the Gap – Inclusion of Ultrashort-Chain Perfluoroalkyl Carboxylic Acids in the Total Oxidizable Precursor (TOP) Assay Protocol. *Environ. Sci. Process. Impacts* **2019**, *21* (11), 1926–1935. https://doi.org/10.1039/C9EM00169G.

(9) Nelson, B. E.; Ford, E. B.; Payne, M. J. RUN DMC: An Efficient, Parallel Code for Analyzing Radial Velocity Observations Using N-Body Integrations and Differential Evolution Markov Chain Monte Carlo. *Astrophys. J. Suppl. Ser.* **2013**, *210* (1), 11. https://doi.org/10.1088/0067-0049/210/1/11.

(10) Foreman-Mackey, D. *Emcee*; 2019.

(11) Weiner, B.; Yeung, L. W. Y.; Marchington, E. B.; D'Agostino, L. A.; Mabury, S. A. Organic Fluorine Content in Aqueous Film Forming Foams (AFFFs) and Biodegradation of the Foam Component 6 : 2 Fluorotelomermercaptoalkylamido Sulfonate (6 : 2 FTSAS). *Environ. Chem.* **2013**, *10* (6), 486. https://doi.org/10.1071/EN13128.

(12) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs)

and AFFF-Impacted Groundwater. *Environ. Sci. Technol.* **2017**, *51* (4), 2047–2057. https://doi.org/10.1021/acs.est.6b05843.

(13) Schymanski, E. L.; Jeon, J.; Gulde, R.; Fenner, K.; Ruff, M.; Singer, H. P.; Hollender, J. Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. *Environ. Sci. Technol.* **2014**, *48* (4), 2097–2098. https://doi.org/10.1021/es5002105.

(14) Darwin, R. *Estimated Quantities of Aqueous Film Forming Foam (AFFF) in the United States,*; Stockholm Convention: Baltimore, MD, 2004.