Supporting Information

Zwiterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foams Formulations and Groundwater from U.S. Military Bases by non-Aqueous Large-Volume Injection HPLC-MS/MS

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Chemicals. A mixture of perfluoroalkyl carboxylates [perfluoro-n-butanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA), perfluoro-n-hexanoic acid (PFHxA), perfluoro-n-heptanoic acid (PFHpA), perfluoro-n-octanoic acid (PFOA), perfluoro-n-nonanoic acid (PFNA), perfluoro-n-decanoic acid (PFDA), perfluoro-n-undecanoic acid (PFUdA)] were purchased from Wellington Laboratories (Guelph, Ontario) in a methanol solvent at concentrations of 2 μg/mL each. A mixture of perfluoroalkyl sulfonates [(perfluoro-1-butanesulfonate (PFBS), perfluoro-1-hexanesulfonate (PFHxS), perfluoro-1-heptanesulfonate (PFHpS), perfluoro-1-octanesulfonate (PFOS), and perfluoro-1-decanesulfonate (PFDS)] were purchased from Wellington Laboratories in a methanol solvent at concentrations from 1.77 μg/mL to 1.93 μg/mL. The perfluoroalkyl carboxylates and sulfonates all have purities of > 98%.The fluorotelomer sulfonates 1H,1H,2H,2H-perfluoro-1-hexanesulfonate (4-2 FtS), 1H,1H,2H,2H-perfluoro-1-octanesulfonate (6-2 FtS), and 1H,1H,2H,2H-perfluoro-1-decanesulfonate (8-2 FtS) were generously donated by Chris Higgins at the Colorado School of Mines as individual solutions in methanol. The internal standards [perfluoro-1-hexane[$^{18}O_2$]sulfonate ([$^{18}O_2$]-PFHxS), perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate ([$^{13}C_4$]-PFOS), perfluoro-n-[$^{13}C_4$]butanoic acid ([$^{13}C_4$]-PFBA) perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid ([$^{13}C_2$]-PFHxA), perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid ([$^{13}C_4$]-PFOA), perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid ([$^{13}C_5$]-PFNA), perfluoro-n-[1,2-$^{13}C_2$]decanoic acid ([$^{13}C_2$]-PFDA), perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid ([$^{13}C_2$]-PFUdA), and perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid ([$^{13}C_2$]-PFDoA)] were purchased from Wellington Laboratories as a mixture in methanol at approximately 2 μg/mL and are 94% to 99% isotopically pure.

Commercial source materials containing 6-2 FtSaB, 6-2 FtSaAm, 6-2 FtTAoS, 6-2 FtTHN$^+$, 5-1-2 FtB, 7-1-2 FtB, 9-1-2 FtB, 5-3 FtB, 7-3 FtB, 9-3 FtB (Table S1) were provided by the Fire Fighting Foam Coalition (FFFC). HPLC grade methanol (> 99%) and ethyl acetate (> 99%), GC grade 2,2,2-trifluoroethanol (> 99%), and ammonium acetate (≅ 98%) were purchased from Sigma-Aldrich (Saint Louis, MO). B&J Brand® reagent water (> 99%) was purchased from VWR (Radnor, PA) and sodium chloride was acquired from Mallinckrodt Chemical (> 99%).

Groundwater Sampling Details for Sites A and B

Site A. Prior to groundwater collection, wells were purged using a peristaltic or bladder pump until water quality parameters (e.g. pH, specific conductivity, temperature, turbidity, oxidation/reduction potential and dissolved oxygen) stabilized. The depth to the groundwater ranged from 0.50 m to 8.8 m. The tubing that came in contact with the sampled groundwater was fluoropolymer free, and new tubing was used for each sample location.

Site B. Groundwater samples were collected from this site following the U.S. EPA's Groundwater Sampling procedures.[30] The depth to the groundwater ranged from 6.7 m to 10 m. Groundwater was collected at each monitoring well using new silicone and polyethylene tubing. The monitoring wells were purged first with a peristaltic pump until stabilization of water quality parameters occurred.

Representative Subsampling. Preliminary data (not shown) revealed that area counts of perfluoroalkyl carboxylates (> C6) and perfluoroalkyl sulfonates (> C4) decreased by 50% to 100% over 6 hr while the analytes were in 3% MeOH/97% reagent water in 6mL glass autosampler vials. This loss was attributed to adsorption onto vials and stratification which indicated that samples that sat for a period of time were no longer homogeneous. As such, the ability of the subsampling protocol in obtaining a representative subsample needed to be determined.

To assess representative subsampling, a volume of 200 mL of blank groundwater in a 250 mL HDPE bottle was spiked to final concentrations of 400 ng/L for each quantitative analyte (**Figure 1 in main text**) and to final concentrations ranging from 84 ng/L to 1,300 ng/L for each semi-quantitative analyte (**Figure 1 in main text**). Representative subsampling was not assessed for qualitative analytes. The 200 mL groundwater sample was allowed to sit overnight to allow the PFCs to stratify,[1] agrigate,[2] adsorb to the container,[3] or any other phenomena that would result in non-representative sub-sampling. The next day right before sub-sampling, the 200 mL sample was repeatedly sonicated in a Model 75HT heated (60 ^{o}C) sonication bath (VWR, Radnor, PA) then gently agitated and inverted. After sonication and agitation a 3 mL subsample was taken from approximately 3.0 cm to 3.5 cm below the meniscus and delivered to a 5 mL micro tube. The subsample was extracted and analyzed as outlined in the main text.

The representativeness of subsampling was defined as the percentage of the analyte concentration in the subsample over that of spiked concentration in the 200mL sample (n=5, ± 95% CI). The representativeness of the subsampling ranged from 76% ± 2.8% (PFDoA) to 106% ± 8.1% (4:2 FtS) for quantitative analytes (Table S7) and from 62% ± 2.5% (6:2 FtTHN^{+}) to 126% ± 12% (5:1:2 FtB) for semi-quantitative analytes (Table S7). Overall, the protocol was deemed acceptable and the analyte concentrations in groundwater were not corrected for subsampling.

Estimating Analyte Concentrations Assuming Equal Molar Response. Estimations of qualitative analyte concentrations are performed by assuming equal molar response to a related analyte. For example, for PFBSaAm, the response of PFBSaAm was ratioed to the response of [$^{13}C_4$]-PFOS (Table S3). Then, the response ratio applyed to PFOS's calibration curve (Table S3) to determine concentration. Finally, the concentration value is multiplied by ratio of the molecular weight of PFBSaAm over the molecular weight of PFOS (385/499) to correct for the difference in the number of molecules per unit weight of each analyte.

Absolute Extraction Efficiency. To determine the absolute efficiency of the extraction procedure, groundwater that gave no detectable analyte signal was ***spiked first*** with analytes to give final concentrations of between 50 and 450 ng/L then extracted (**pre-extraction spikes**). The pre-extraction spikes were compared to groundwater that was ***extracted first*** then spiked with analytes to equivalent concentrations (**post-extraction spikes**). Absolute extraction efficiency was defined as the ratio of pre-extraction spike area counts (n = 5) to post-extraction spike area counts (n = 5) multiplied by 100. The error about each measurement was compounded and reported as ± 95 % CI. Only Ql and Sq analytes were assessed for extraction efficiency. Internal standards were not added before extraction as they correct for incomplete extraction.

The absolute extraction efficiency ranged from 87% ± 8.3% to 99% ± 8.0% for Qn and Sq analytes (Table S4). It is not possible to make comparisons across methods of the extraction efficiencies for the newly-identified PFCs because this is the first method developed for their analysis. Previous methods that report on fluorotelomer sulfonates in groundwater are based on direct-aqueous LVI and extraction efficiency is not reported because the samples were directly injected.[4] However, the absolute extraction efficiencies reported here for perfluoroalkyl sulfonates (from 92% to 98%) and perfluoroalkyl carboxylates (from 91% to 98%) are an improvement over previous LLE-,[5] C18 SPE-,[6] and HLB SPE-[7] based methods and are similar to the WAX SPE-based methods reported by Taniyasu and coworkers[8,9] on which ISO method 25101 is based.[10] The advantage micro-LLE has over SPE is that it requires less sample and generates less liquid and solid waste. For example, the method by Taniyasu and coworkers describe the extraction of 100 mL to 200 mL of sample using 20 mL of solvent.[9]

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Table S1. Descriptive names and acronyms of the newly-identified target analytes.

Compound Name of Newly-Identified Analyte	Acronym
2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-hexyl)thio)propanamido)propane-1-sulfonate	4-2 FtTAoS
2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propanamido)propane-1-sulfonate	6-2 FtTAoS
2-methyl-2-(3-((1H,1H,2H,2H-perfluoro-1-decyl)thio)propanamido)propane-1-sulfonate	8-2 FtTAoS
2-hydroxy-N,N,N-trimethyl-3-((1H,1H,2H,2H-perfluoro-1-octyl)thio)propan-1-aminium	6-2 FtTHN$^+$
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6-2 FtSaB
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-decanesulfonamido)propan-1-aminium	8-2 FtSaB
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-dodecanesulfonamido)propan-1-aminium	10-2 FtSaB
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1- tetradecanesulfonamido)propan-1-aminium	12-2 FtSaB
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-aminium	6-2 FtSaAm
N-(carboxymethyl)-N,N-dimethyl-3-(1H,1H,2H,2H-perfluoro-1-decanesulfonamido)propan-1-aminium	8-2 FtSaAm
N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorooctan-1-aminium	5-1-2 FtB
N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorodecan-1-aminium	7-1-2 FtB
N-(carboxymethyl)-1H,1H,2H,2H,3H -N,N-dimethylperfluorododecan-1-aminium	9-1-2 FtB
N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorooctan-1-aminium	5-3 FtB
N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorodecan-1-aminium	7-3 FtB
N-(carboxymethyl)-1H,1H,2H,2H,3H,3H -N,N-dimethylperfluorododecan-1-aminium	9-3 FtB
N,*N*-dimethyl-3-{[(trideca-perfluorobutyl)sulfonyl]amino}propan-1-aminium	PFBSaAm
N,*N*-dimethyl-3-{[(trideca-perfluoropentyl)sulfonyl]amino}propan-1-aminium	PFPeSaAm
N,*N*-dimethyl-3-{[(trideca-perfluorohexyl)sulfonyl]amino}propan-1-aminium	PFHxSaAm
N,*N*-dimethyl-3-{[(trideca-perfluoroheptyl)sulfonyl]amino}propan-1-aminium	PFHpSaAm
N,*N*-dimethyl-3-{[(trideca-perfluorooctyl)sulfonyl]amino}propan-1-aminium	PFOSaAm
3-(N-(2-carboxyethyl)- trideca-perfluorobutylsulfonamido)-N,N-dimethylpropan-1-aminium	PFBSaAmA
3-(N-(2-carboxyethyl)- trideca-perfluoropentylsulfonamido)-N,N-dimethylpropan-1-aminium	PFPeSaAmA
3-(N-(2-carboxyethyl)- trideca-perfluorohexylsulfonamido)-N,N-dimethylpropan-1-aminium	PFHxSaAmA
3-(N-(2-carboxyethyl)- trideca-perfluoroheptylsulfonamido)-N,N-dimethylpropan-1-aminium	PFHpSaAmA
3-(N-(2-carboxyethyl)- trideca-perfluorooctylsulfonamido)-N,N-dimethylpropan-1-aminium	PFOSaAmA

Table S2. Analyte precursor ions, product ions, and compound-dependant acquisition parameters.

Analyte	Precursor Ion (m/z)	Product Ion (m/z)	CE[a] (V)	CV[a] (V)
Fluorotelomer Thioamido Sulfonates				
4-2 FtTAoS	486	135	38	62
		80	56	
6-2 FtTAoS	586	135	40	64
		80	64	
8-2 FtTAoS	686	135	44	78
		80	68	
Fluorotelomer Thio Hydroxy Ammonium				
6-2 FtTHN$^+$	496	79	44	54
		393	34	
Fluorotelomer Sulfonamido Betaines				
6-2 FtSaB	571	58	38	78
		104	30	
8-2 FtSaB	671	58	40	80
		104	32	
10-2 FtSaB	771	58	44	96
		104	36	
12-2 FtSaB	871	58	48	100
		104	38	
Fluorotelomer Sulfamido Amines				
6-2 FtSaAm	513	58	44	60
		86	34	
8-2 FtSaAm	613	58	48	64
		86	38	
Fluorotelomer Betaines				
5-1-2 FtB	432	58	38	60
		74	40	
7-1-2 FtB	532	58	40	72
		74	44	
9-1-3 FtB	632	58	42	78
		74	52	
5-3 FtB	432	58	38	60
		104	38	
7-3 FtB	514	58	40	72
		104	42	
9-3 FtB	614	58	42	78
		104	50	
Fluorotelomer Sulfonates				
4-2 FtS	327	81	26	42
		307	19	
6-2 FtS	427	81	28	46
		407	22	
8-2 FtS	527	81	32	50
		507	25	

[a] CE (collision energy) and CV (cone voltage)

Table S2 Cont. Analyte precursor ions, product ions, and compound-dependent acquisition parameters.

Analyte	Precursor Ion (m/z)	Product Ion (m/z)	CE[a] (V)	CV[a] (V)
Perfluoroalkyl Sulfonamido Amines				
PFBSaAm	385	85 58	28 44	50
PFPeSaAm	435	85 58	30 44	52
PFHxSaAm	485	85 58	33 44	54
PFHpSaAm	535	85 58	34 45	56
PFOSaAm	585	85 58	35 45	56
Perfluoroalkyl Sulfonamide Amino Carboxylates				
PFBSaAmA	457	85 70	28 50	48
PFPeSaAmA	507	85 70	30 50	52
PFHxSaAmA	557	85 70	33 50	54
PFHxSaAmA	607	85 70	34 52	56
PFOSaAmA	657	85 70	35 52	56

Analyte	Precursor Ion (m/z)	Product Ion (m/z)	CE[a] (V)	CV[a] (V)
Perfluoroalkyl Sulfonates				
PFBS	299	80 99	32 26	50
PFPeS	349	80 99	34 28	56
PFHxS	399	80 99	36 28	58
PFHpS	449	80 99	46 32	64
PFOS	499	80 99	46 34	70
PFNS	549	80 99	50 36	72
PFDS	599	80 99	52 36	76
Perfluoroalkyl Carboxylates				
PFBA	213	169 NA	8 NA	20
PFPeA	263	219 NA	8 NA	20
PFHxA	313	269 119	8 22	20
PFHpA	363	319 169	8 14	20
PFOA	413	369 169	8 18	20
PFNA	463	419 169	8 18	22
PFDA	513	469 269	10 18	22
PFUdA	563	519 169	10 22	22
PFDoA	613	569 169	10 24	22
PFTrDA	663	619 169	12 26	24
PFTeDA	713	669 169	12 26	24

[a] CE (collision energy) and CV (cone voltage)

Table S3. Calibration range, number of points, R^2, and internal standards used for each quantitative (Qn) and semi-quantitative (Sq) analyte and the corresponding calibration curve used for each qualitative (Ql) analyte.

	Calibration Range (ng/L)	Number of Points	R^2	Internal Standard
4:2 FtTAoS	Calculated Using 6:2 FtTAoS Calibration			$[^{13}C_2]$-PFHxA
6:2 FtTAoS	10 to 1,500	5	> 0.99	$[^{13}C_2]$-PFHxA
8:2 FtTAoS	Calculated Using 6:2 FtTAoS Calibration			$[^{13}C_2]$-PFHxA
6:2 FtTHN$^+$	15 to 2,250	5	> 0.99	$[^{13}C_4]$-PFOS
6:2 FtSaB	100 to 15,000	6	> 0.99	$[^{13}C_4]$-PFOS
8:2 FtSaB	Calculated Using 6:2 FtSaB Calibration			$[^{13}C_4]$-PFOS
10:2 FtSaB	Calculated Using 6:2 FtSaB Calibration			$[^{13}C_4]$-PFOS
12:2 FtSaB	Calculated Using 6:2 FtSaB Calibration			$[^{13}C_4]$-PFOS
6:2 FtSaAm	240 to 24,000	5	> 0.98	$[^{13}C_4]$-PFOS
8:2 FtSaAm	Calculated Using 6:2 FtSaAm Calibration			$[^{13}C_4]$-PFOS
5:1:2 FtB	58 to 5,800	5	> 0.98	$[^{13}C_4]$-PFOS
7:1:2 FtB	40 to 6,000	5	> 0.98	$[^{13}C_4]$-PFOS
9:1:2 FtB	32 to 3,200	5	> 0.98	$[^{13}C_4]$-PFOS
5:3 FtB	15 to 1,500	5	> 0.98	$[^{13}C_4]$-PFBA
7:3 FtB	30 to 3,000	5	> 0.98	$[^{13}C_4]$-PFBA
9:3 FtB	27 to 810	4	> 0.98	$[^{13}C_4]$-PFBA
4:2 FtS	5 to 750	5	> 0.99	$[^{18}O_2]$-PFHxS
6:2 FtS	5 to 750	5	> 0.99	$[^{18}O_2]$-PFHxS
8:2 FtS	5 to 750	5	> 0.99	$[^{18}O_2]$-PFHxS

	Calibration Range (ng/L)	Number of Points	R^2	Internal Standard
PFBSaAm	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFPeSaAm	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFHxSaAm	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFHpSaAm	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFOSAm	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFBSaAmA	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFPeSaAmA	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFHxSaAmA	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFHpSaAmA	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFOSAmA	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFBS	5 to 10,000	6	> 0.99	$[^{18}O_2]$-PFHxS
PFPeS	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFHxS	5 to 10,000	6	> 0.99	$[^{18}O_2]$-PFHxS
PFHpS	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFOS
PFOS	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFOS
PFNS	Calculated Using PFOS Calibration			$[^{13}C_4]$-PFOS
PFDS	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFOS
PFBA	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFBA
PFPeA	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFBA
PFHxA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFHxA
PFHpA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFHxA
PFOA	5 to 10,000	6	> 0.99	$[^{13}C_4]$-PFOA
PFNA	5 to 10,000	6	> 0.99	$[^{13}C_5]$-PFNA
PFDA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFDA
PFUdA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFUdA
PFDoA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFDoA
PFTrA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFDoA
PFTeA	5 to 10,000	6	> 0.99	$[^{13}C_2]$-PFDoA

Table S4. Percent absolute extraction efficiency (% AEE) (n = 5, ± 95% CI) for quantitative (Qn) and semi-quantitative (Sq) analytes.[a]

Analyte	% AEE	% 95 CI	Analyte	% AEE	% 95 CI
6:2 FtTAoS (Sq)	99	8.0	PFBS (Qn)	92	3.9
6:2 FtTHN^{+} (Sq)	95	6.8	PFHxS (Qn)	98	8.2
			PFHpS (Qn)	93	4.9
6:2 FtSaB (Sq)	93	7.9	PFOS (Qn)	92	3.4
6:2 FtSaAm (Sq)	97	15	PFDS (Qn)	92	2.5
5:1:2 FtB (Sq)	98	5.8	PFBA (Qn)	93	7.0
7:1:2 FtB (Sq)	90	5.5	PFPeA (Qn)	93	2.4
9:1:2 FtB (Sq)	93	5.7	PFHxA (Qn)	94	5.2
			PFHpA (Qn)	98	11
5:3 FtB (Sq)	97	14	PFOA (Qn)	96	4.5
7:3 FtB (Sq)	88	10	PFNA (Qn)	96	5.1
9:3 FtB (Sq)	87	8.3	PFDA (Qn)	95	5.8
			PFUdA (Qn)	89	3.4
4:2 FtS (Qn)	87	13	PFDoA (Qn)	90	2.9
6:2 FtS (Qn)	97	11	PFTrA (Qn)	91	2.7
8:2 FtS (Qn)	93	7.2	PFTeA (Qn)	93	2.8

[a] Determined at concentrations of between 50 and 450 ng/L

Table S5. Concentrations (mg/L) of newly-identified PFAS and fluorotelomer sulfonates in fluorotelomer-based aqueous film-forming foam formulations from different manufacturers.

	Ansul 2005 mg/L	Chemguard 2010 mg/L	Angus 2002 mg/L	National Foam 2003 mg/L	Buckeye Fire Equipment 2009 mg/L	Fire Service Plus NR[a] mg/L
4:2 FtTAoS[c]	26	ND	25	ND	ND	ND
6:2 FtTAoS	6,100	11,000	4,900	ND	ND	ND
8:2 FtTAoS[c]	1,100	24	170	ND	ND	ND
4:2 FtS	ND	ND	ND	ND	ND	ND
6:2 FtS	ND	ND	ND	42	ND	53
8:2 FtS	ND	ND	ND	19	ND	56
6:2 FtTHN$^+$	ND	ND	2,200	ND	ND	ND
6:2 FtSaB	ND	ND	ND	4,600	ND	4,800
8:2 FtSaB[d]	ND	ND	ND	540	ND	1,800
10:2 FtSaB[d]	ND	ND	ND	450	ND	830
12:2 FtSaB[d]	ND	ND	ND	210	ND	430
6:2 FtSaAm	ND	ND	ND	2,100	ND	3,400
8:2 FtSaAm[e]	ND	ND	ND	450	ND	720
5:1:2 FtB	ND	ND	ND	ND	2,000	ND
7:1:2 FtB	ND	ND	ND	ND	4,700	ND
9:1:2 FtB	ND	ND	ND	ND	1,900	ND
5:3 FtB	ND	ND	ND	ND	530	ND
7:3 FtB	ND	ND	ND	ND	610	ND
9:3 FtB	ND	ND	ND	ND	430	ND

ND- Not Detected (S/N<3) [a] Not recorded (NR). [b] Not Applicable (NA). Calculated assuming equal molar ratios to [c] 6:2 FtTAoS, [d] 6:2 FtSaB, and [e] 6:2 FtSaAm (see main text in SI). Perfluorinated chemicals (e.g. PFOS) were not detected.

Table S6. Concentrations (mg/L) of newly-identified and legacy perfluorinated chemicals in 3M aqueous film forming foam formulations manufactured from 1989-2001.

	1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
PFBSaAm [a]	9	120 ± 2.0	180	140	110
PFPeSaAm [a]	8	140 ± 1.8	180	140	110
PFHxSaAm [a]	189	660 ± 8.1	850	743	690
PFHpSaAm	ND	12 ± 0.40	15	30	24
PFOSaAm	9.9	62 ± 1.1	75	67	37
PFBSaAmA [a]	ND	140 ± 3.1	120	110	150
PFPeSaAmA [a]	4	200 ± 6.3	170	140	130
PFHxSaAmA [a]	ND	930 ± 13	850	850	960
PFHpSaAmA	ND	17 ± 0.16	17	34	44
PFOSaAmA [a]	ND	72 ± 0.81	58	53	65
PFBS	380	220 ± 2.0	160	210	250
PFPeS	210	120 ± 1.5	80	90	120
PFHxS	1700	910 ± 14	760	850	900
PFHpS	410	120 ± 2.0	120	93	140
PFOS	15000	8000	9300	6700	7900
PFNS	160	53 ± 0.97	56	9	27
PFDS	102	51 ± 0.34	52	11	27
PFBA	37	24 ± 0.48	35	31	38
PFPeA	47	36 ± 0.14	52	43	48
PFHxA	170	99 ± 1.1	110	99	170
PFHpA	54	25 ± 0.28	22	26	37
PFOA	150	83 ± 1.3	93	86	170
PFNA	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND
PFTrA	ND	ND	ND	ND	ND
PFTeA	ND	ND	ND	ND	ND
PFS/PFA [b]	39	35	34	28	20
Legacy/Newly-Identified	84	4.1	4.3	3.6	4.2
PFOS/PFHxS	8.8	8.8	12	7.9	8.8

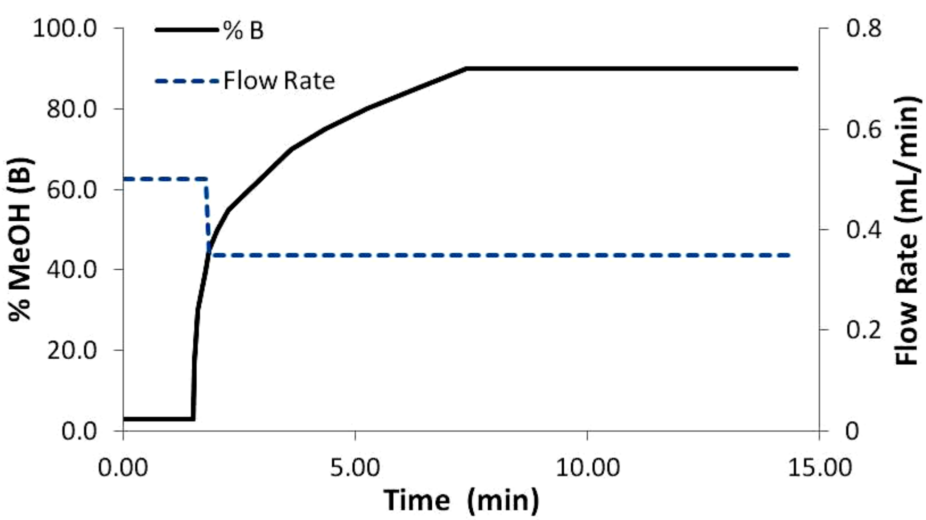
ND = not detected (S/N<3) [a] Calculated assuming equal molar response to PFOS (see main text in SI). [b] Total concentrations of perfluoroalkyl sulfonates (PFS)/ perfluoroalkyl carboxylates (PFA). Telomerization-based perfluorinated chemicals (e.g. 6:2 FtTAoS) were not detected.

Table S7. The percent representativeness of quantitative and semi-quantitative analytes in a subsample (n = 5, ± 95% CI) determined at a spiked concentration (Conc). [a]

Analyte	Representativeness (%)	± 95 CI (%)	Spike Conc (ng/L)
6-2 FtTAoS	69	5	250
6-2 FtTHN^{+}	62	2.5	250
6-2 FtSaB	124	9.6	930
6-2 FtSaAm	82	11	760
5-1-2 FtB	126	12	600
7-1-2 FtB	108	8.2	1250
9-1-2 FtB	88	6.6	340
5-3 FtB	100	7.8	150
7-3 FtB	89	11	314
9-3 FtB	74	7.7	84
4-2 FtS	106	8.1	400
6-2 FtS	102	4.9	400
8-2 FtS	99	8.1	400
PFBS	100	4.1	400
PFHxS	102	2.9	400
PFHpS	97	2.8	400
PFOS	101	1.5	400
PFDS	84	3.4	400
PFBA	96	1.6	400
PFPeA	99	3.4	400
PFHxA	96	1.5	400
PFHpA	95	3.5	400
PFOA	97	1.6	400
PFNA	95	4.7	400
PFDA	94	0.9	400
PFUdA	86	4.3	400
PFDoA	76	2.8	400
PFTrA	78	2.5	400
PFTeA	81	1.6	400

[a] No standards were available for the C5 (PFPeS) and C9 (PFNS) sulfonates so they were excluded.

Figure S1. Gradient conditions used for analyte separation and elution during HPLC.



Time	% B
0.00	3.0
1.50	3.0
1.53	17.0
1.60	30.0
1.76	40.0
1.85	45.0
2.02	50.0
2.26	55.0
3.61	70.0
4.34	75.0
5.24	80.0
6.27	85.0
7.38	90.0
14.5	90.0

Figure S2. Total ion chromatogram indicating lack of retention of C4-10 perfluoroalkyl carboxylates due to breakthrough when the C18 analytical column was used without the Sil and NH_2 guard columns.