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Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

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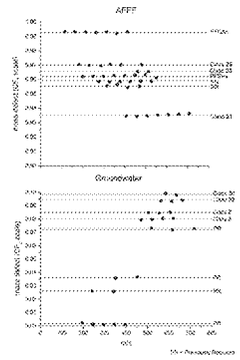
Supporting Information

ABSTRACT: Aqueous film-forming foams (AFFFs), containing per- and polyfluoroalkyl substances (PFASs), are released into the environment during response to fire-related emergencies. Repeated historical applications of AFFF at military sites were a result of fire-fighter training exercises and equipment testing. Recent data on AFFF-impacted groundwater indicates that ~25% of the PFASs remain unidentified. In an attempt to close the mass balance, a systematic evaluation of 3M and fluorotelomer-based AFFFs, commercial products, and AFFF-impacted groundwaters from 15 U.S. military bases was conducted to identify the remaining PFASs. Liquid chromatography quadrupole time-of-flight mass spectrometry was used for compound discovery. Nontarget analysis utilized Kendrick mass defect plots and a "nontarget" R script. Suspect screening compared masses with those of previously reported PFASs. Forty classes of novel anionic, zwitterionic, and cationic PFASs were discovered, and an additional 17 previously reported classes were observed for the first time in AFFF and/or AFFF-impacted groundwater. All 57 classes received an acronym and IUPAC-like name derived from collective author knowledge. Thirty-four of the 40 newly identified PFAS classes derive from electrochemical fluorination (ECF) processes, most of which have the same base structure. Of the newly discovered PFASs found only in AFFF-impacted groundwater, 11 of the 13 classes are ECF-derived, and the remaining two classes are fluorotelomer-derived, which suggests that both ECF- and fluorotelomer-based PFASs are persistent in the environment.



INTRODUCTION

The ubiquity of per- and polyfluoroalkyl substances (PFASs) in the environment,[1−3] wildlife,[4−7] and humans[8,9] is motivating the environmental community to look beyond the occurrence and fate of perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS). Potential links between the use of aqueous film-forming foam (AFFF) at military and civilian sites and drinking water contamination[10] has resulted in attention being focused on the source and extent of AFFF contamination of groundwater.

Measurements of total fluorine in blood,[11−13] water,[14−18] and sludge[19] indicate the presence of additional PFASs beyond classes typically measured, including perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs). However, new analytical methods with the capacity to quantify anionic, zwitterionic, and cationic PFASs in AFFF-impacted groundwater[20] resulted in only infrequent detections of the novel PFASs.[21] Application of the total oxidizable precursor assay on AFFF-impacted groundwater indicates that 25% of PFASs that can be oxidized to PFCAs remain unidentified.[15]

High-resolution mass spectrometry, including quadrupole time-of-flight mass spectrometry (qTOF-MS), provides the high resolving power and mass accuracy[21−24] necessary for discovery of novel PFASs for which no reference standards are available. Nontarget analysis of AFFFs[21,23,25] and firefighter blood[24] led to discoveries of novel homologues and classes of PFASs. Place and Field[21] identified the major classes of PFASs in U.S. Mil-Spec AFFF, and D'Agostino and Mabury[23] reported 22 classes of PFASs in AFFFs and commercial products (CPs).

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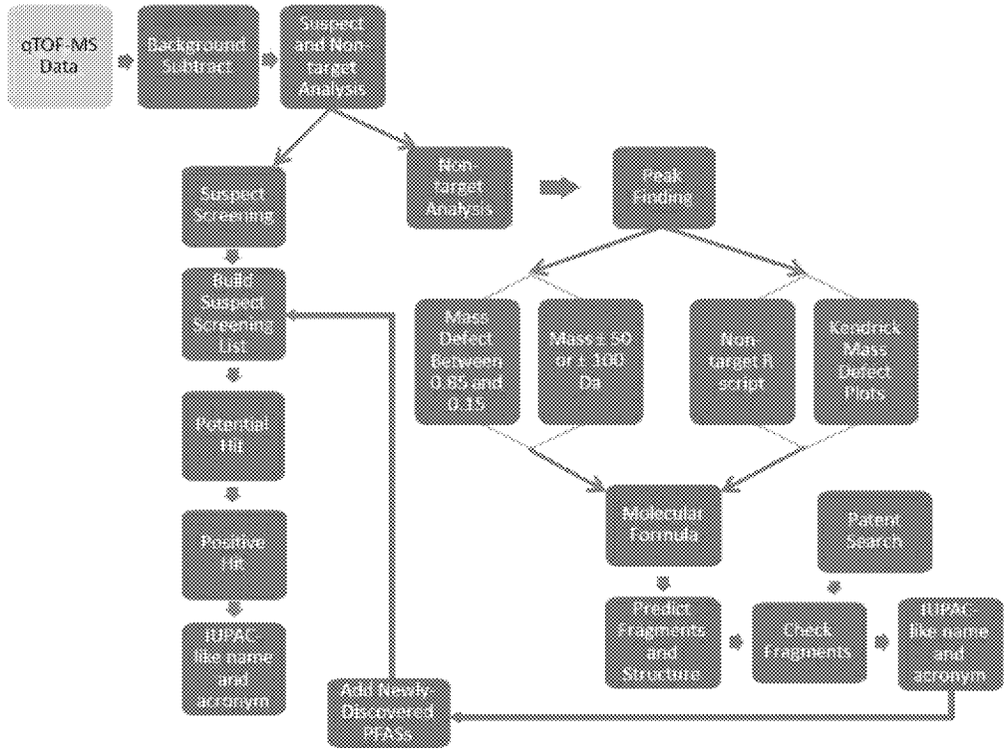

Figure 1. Workflow diagram depicting the steps taken in qTOF-MS data analysis.

While these studies provided advances in our understanding of the composition of AFFF, more systematic approaches have not been undertaken to identify the remaining PFASs in AFFF and AFFF-impacted groundwater. For nontarget analysis of surfactants, Kendrick mass defect (KMD) plots are particularly useful because they aid in identifying homologous series, each characterized by a unique mass defect.[25−27] Once one individual homologue of the series is identified, the remaining homologues are easily identified. Previous studies used KMD plots to identify PFASs in CPs,[22,28,29] and, in our previous work, KMD plots were used to identify only the short-chain (C_2 and C_3) PFSAs.[25]

To the best of our knowledge, KMD plots used in combination with suspect screening has not yet been applied for the systematic identification of the remaining 25% of PFASs in AFFF-impacted groundwater and in AFFFs used by the U.S. military. A set of 3M and fluorotelomer AFFFs, select CPs, and AFFF-impacted groundwater were analyzed by liquid chromatography qTOF-MS. The characteristic differences in the ratio of fluorinated and nonfluorinated carbons in the chain, branching of the fluorinated chain, and the nature of the polar head groups of PFASs manufactured by electrochemical fluorination (ECF) and fluorotelomer-based processes are documented elsewhere.[30−33] The homologous series identified from KMD plots were confirmed using a "nontarget" R script. Structural assignments were confirmed using MS/MS spectra, patents, and in silico fragmentation. A "suspect" list was created and contained all previously reported PFASs identified as degradation products,[22,34−36] metabolites,[34−40] and known PFASs relevant to AFFF.[21,23,24,41] For suspect screening, the suspect list was used to identify additional PFASs in AFFF and AFFF-impacted groundwater. It was beyond the scope of the study to quantify the discovered PFASs or to frame them in the context of total fluorine. However, the investigation resulted in the discovery of 40 novel classes of PFASs and the detection of 17 classes of previously reported PFASs, adding over 240 individual PFASs that can now be associated with AFFF.

■ EXPERIMENTAL SECTION

Chemicals. A description of the reagents and analytical standards used is provided in the Supporting Information (SI).

Sample Collection. *AFFF Formulations.* A 3M AFFF formulation from 1988 plus five previously analyzed 3M AFFFs and five previously analyzed fluorotelomer-based AFFFs,[20,21,25] were analyzed for this study (SI Table S1). The aforementioned AFFFs came from an archive of AFFF samples obtained from U.S. military bases.[21] One AFFF formulation of unknown composition from a reserve tank was donated by California Guardian (Monrovia, CA). Because few records exist to document which AFFFs were used at U.S. military bases, we elected to analyze samples of U.S. Mil-Spec AFFF that were stockpiled for actual use on U.S. military bases.[21,42]

CPs. CPs (SI Table S1) were selected from the Field Laboratory archive of discontinued PFAS-containing products with potential relevance to AFFF. 3M PFOS was acquired from Wellington Laboratories Inc. (Guelph, Ontario, Canada). 3M Fluorad FC-95, FC-100 and FC-129 (3M Company, St. Paul, MN) were received in 1998 in response to a 3M advertisement for free Fluorad kits. Zonyl FSA was purchased from DuPont (Aldrich, Milwaukie, WI) prior to 2012. All products were stored in the dark at room temperature. The Fluorad test kit products were included because they were advertised for use as foaming agents and surface tension reducers. Zonyl FSA was selected as a potential degradation product of fluorotelomer-based PFASs.

Groundwater. Groundwater samples were collected between 2011 and 2015 from firefighter training areas at 13 different U.S. military bases by third parties as previously

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described.[20] No effort was made to collect groundwater samples from the U.S. military sites from which the AFFFs had been collected because there are no records that link AFFF stockpiles to actual use on military bases. A single midconcentration range groundwater sample, based on concentrations of the PFCAs and the PFSAs (unpublished data), was selected as the representative sample for each site. Single groundwater samples from two bases that were archived since 1999[43] were reanalyzed for the present study in a total of 15 groundwater samples from 15 different U.S. military bases. All samples were stored at −4 °C in either polypropylene or HDPE.

Sample Preparation. All AFFFs and CPs were diluted by a factor of 99 000 in 30% methanol (v/v) in water. Undiluted groundwater samples were extracted using a micro liquid−liquid extraction as described previously.[20] A brief description of the extraction is provided in the SI.

Chromatographic Method. Chromatographic separations were conducted using a Shimadzu LC-30AD (Columbia, MO) instrument. A SCIEX TripleTOF 5600+ (Framingham, MA) qTOF-MS with electrospray ionization (ESI) was operated in both positive and negative ionization modes and used to collect qTOF-MS data. Details about the chromatographic method and qTOF-MS data acquisition are provided in the SI. Solvent blanks, consisting of 30% (v/v) methanol in water, were run every 15 AFFF and CP samples, and extraction blanks, consisting of water taken through the extraction process, were run in every batch of groundwater samples to ensure the absence of instrumental contamination or carryover between samples.

qTOF-MS Data Analysis. Data were analyzed using the distinct characteristics of PFASs. Unlike other studies that report low mass defects (−0.1 to 0.15)[21,23,27] of PFASs, which were calculated by subtracting the nominal mass (rounded to the nearest whole number) from the exact mass, we computed the mass defects for PFASs (0.85−0.15)[25,26] using eq 1.[26]

$$\text{mass defect} = \text{exact mass} - \text{nominal mass (rounded down)} \quad (1)$$

Second, PFASs sharing the same polar headgroup but with differing fluorinated carbon chain lengths are almost always observed in AFFF and AFFF-impacted groundwater.[20,21,23,32] Homologous series of PFASs were classified by mass differences of 50 Da ($-CF_2$-) for ECF-based PFASs and by 100 Da ($-CF_2CF_2$-) for fluorotelomer-based PFASs.[20,21,23] The qTOF-MS data were processed with MasterView 2.2 (SCIEX) using nontarget and suspect screening (Figure 1).

Nontarget Screening. Masses detected in the solvent blank (for AFFF or CP) and in the extraction blank (for groundwater) were eliminated from the detected masses in the samples. An exhaustive peak-finding procedure was conducted for all samples. Following the initial selection of peaks (peak criteria in SI), the entire peak list was run through a modified R package "nontarget"[44] (see SI), and first-order KMD plots were created to capture any remaining homologous series, as described previously.[25−27]

Molecular formulas of selected peaks were computed based on the exact mass of the molecular ion ([M]) and the isotope distribution of the [M], [M+1], and [M+2] peaks in the MS spectrum. Parameters and criteria for the molecular formulas are provided in the SI. The MS/MS spectrum of the peak was linked to the formula-finding algorithm in MasterView 2.2 to generate ion formula for each observed product ion based on the molecular formula.

Structures based on the selected molecular formula and fragment ion structures based on the observed exact mass and generated ion formula were reconciled using ChemBioDraw Ultra 14.0 (PerkinElmer, Waltham, MA). Proposed fragment ion structures had mass errors less than 5 mDa and/or 15 ppm relative to the observed exact mass. Confidence levels were assigned to the proposed structure of the molecular ion using established criteria.[45] The proposed fragment structures were checked using the in silico fragmentation software Mass Frontier (see SI; ThermoFisher Scientific, Waltham, MA) and classical mass spectrometry fragmentation theory. However, it should be noted that all fragmentation mechanisms discussed are speculative, and additional mass spectral studies are needed to confirm the proposed mechanisms. Confirmation of each proposed structure was not possible since no commercial standards were available. To increase confidence in the proposed structures, AFFF-related patents were searched. Searchable fragment and CF_2-normalized mass defect databases are included in the SI.

Suspect Screening. Methods used to create the suspect screening list and the criteria used to confirm positive hits are included in the SI.

Naming. All PFASs discovered using the nontarget and suspect screening workflows were given an IUPAC-like name and a corresponding acronym. Acronyms were derived from IUPAC-like names, which were developed based on the authors' collective knowledge of IUPAC nomenclature recommendations.[46] The naming strategy adopted here is not duplicative and is rather synergistic to extend beyond the compound classes included in previous naming efforts.[32] The suggested acronyms were generated by deconstructing the overall compound into recognizable and repeating sections. Whenever possible, acronyms of well-known base structures were incorporated into the acronyms of more complicated compounds as parent names to minimize variability and increase recognizability. In cases where there are no literature precedents, some additional parent acronyms have been suggested (e.g., FASAPS represents perfluoroalkylsulfonamidopropanesulfonate). Common contractions used in acronym generation include: amide or amino = A, dimethylammonio = Am, trimethylammonio = TAm, hydroxy = HO, hydroxymethyl = HOM, hydroxyethyl = HOE, hydroxypropyl = HOP, Carboxymethyl = CM, methyl = Me, ethyl = Et. Acronym rationale and an example are provided in the SI.

RESULTS AND DISCUSSION

Each class associated with AFFFs is classified as either newly discovered or previously reported. Newly discovered PFASs constitute PFASs that have never been observed, to the best of our knowledge. Each newly discovered class was divided into one of the following three groups: novel classes in found in AFFF, derivatives of PFSAs and PFCAs found in AFFFs and CPs, and novel PFAS classes found only in groundwater. It was beyond the scope of the study to differentiate whether the novel PFASs discovered in AFFFs and CPs were present in AFFF-impacted groundwater and is rather part of an ongoing investigation. Previously reported PFASs consist of either additional homologues of a known class or PFASs reported for sources other than AFFF or matrices other than groundwater. Written-out acronyms, IUPAC-like names (SI Table S3), ion formula, exact masses (SI Table S4) and annotated MS/MS spectra (SI Figures S2−S41) for all newly discovered PFASs complement the discussion in the sections below.

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Characteristic Fragments and Neutral Losses of PFASs. Nine fragments were frequently observed in the MS/MS spectra of the newly identified PFASs; four are common in ESI^-, while the remaining five are only seen in ESI^+. For clarity, all fragments and neutral losses are referenced by their respective nominal mass. Fragments m/z 483 in ESI^- and m/z 485 in ESI^+ (SI Table S2) are characteristic of perfluoroalkyl sulfonamido-based compounds[47] and ECF-derived PFASs.[23] Neutral loss of the polar headgroup, either from m/z 483 or the carboxylate/sulfonate in the PFCAs/PFSAs, results in $[C_nF_{2n+1}]^-$ ions (m/z 319, 169, and 119),[47,48] which are indicative of the fluorinated tail. In ESI^+, the appearance of characteristic fragments m/z 440 and 412, corresponding to $C_6F_{13}SO_2NH^+{=}CHCH_2CH_3$ and $C_6F_{13}SO_2NH^+{=}CH_2$, respectively, indicate perfluoroalkyl sulfonamido compounds, as observed by others.[23,49,50] A neutral loss of SO_2 from m/z 412 forms m/z 348, which suggests the presence of a sulfonamide.[49,51] Furthermore, m/z 348 has been observed in the ESI^+ fragmentation of perfluoroalkyl sulfonamido compounds.[23,51] D'Agostino and Mabury identified m/z 104 as a fully protonated betaine,[23] which several novel classes of PFASs contain.

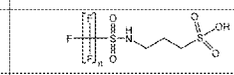
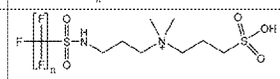
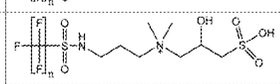
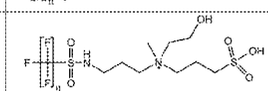
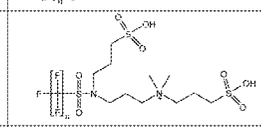
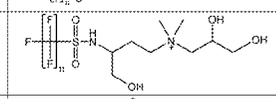
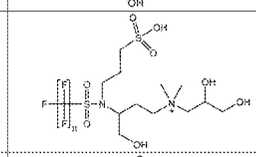
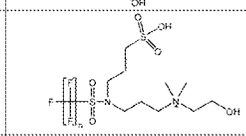
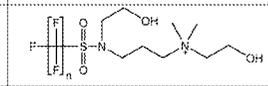
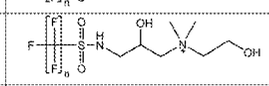
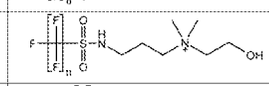
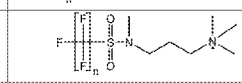
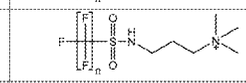
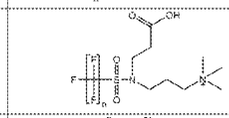
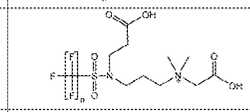
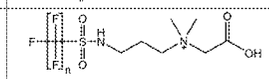
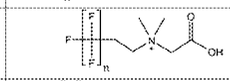
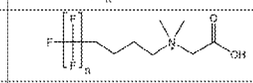
Five common neutral losses were observed (SI Table S2) in MS/MS spectra in both ESI^- and ESI^+. A neutral loss of 122 Da corresponds to a propyl sulfonate moiety, which occurred frequently for the newly discovered PFASs. Loss of a N,N-dimethylamino moiety (45 Da)[52] is characteristic of PFASs containing a tertiary amine.[23] A neutral loss of 80 Da, corresponding to a sulfonate moiety, is observed in PFASs especially when the sulfonate moiety is close to the fluorinated chain.[48] Losses of HF (20 Da), typically in ESI^-, indicates hydrogen substitution within or immediately neighboring the fluorinated chain, and the number of HFs lost corresponds to the number of H substitutions.[31,53] A neutral loss of CO_2 (44 Da) suggests the presence of a carboxylic acid moiety.[54] Any characteristic fragment or neutral loss discussed will not be presented further; rather, unique fragments will be highlighted.

Novel Classes in AFFF. In the AFFFs, 75% of the new PFASs were discovered in 3M AFFFs and CPs produced using ECF, whereas the remaining 25% are fluorotelomer-based PFASs. The wide variety of ECF-derived PFASs discovered, most of which share the same base structure of Class 13, is consistent with ECF synthesis that creates many unintended byproducts in the production of ECF-derived PFASs.[30,33] On the other hand, the limited number of newly discovered fluorotelomer-derived PFASs is evidence telomerization produces few unintentional products.

Novel Classes in 3M AFFF. Sixteen novel classes of PFASs were observed in 3M AFFFs and CPs (Table 1). Homologues within each class vary by 50 Da and contain branched and linear isomers (SI Figure S42–S57), which is indicative of ECF. Confidence levels (Table 1) of each class were assigned based on published criteria.[45] Briefly, no Level 1 were reported since no reference standards are available. Thirty-seven of the 40 novel classes are either Level 2b or 3, depending on whether substituent locations could be determined from the MS/MS spectrum. Only two classes are Level 4, and one class is Level 5, which signify molecular formula and masses of interest, respectively. For brevity, confidence levels will not be discussed for each class. Information on the differences between Levels 2b and 3 and Levels 4 and 5 are outlined in Schymanski et al.[45]

Class 1 contains four homologues (C_3–C_6) as identified by ESI^-. The two observed fragments (SI Figure S2; C_6

Table 1. Newly Discovered PFASs Found in AFFFs and CPs

Class Number	Structure	$n^{a,b}$	Acronym[c]	Confidence Level[d,e]	AFFF/CP Found In
1		3-6	N-SP-FASA	2b	B, C
2		3-8	N-SPAmP-FASA	2b	A, B, C, F
3		3-9	N-SHOPAmP-FASA	3[f]	C, D, E, F, G
4		4-6	N-SPHOEAmP-FASA	3	B, C
5		3-8	N-SPAmP-FASAPS	2b	A, B, C
6		3-6	N-diHOPAmHOB-FASA	3	B, C, O
7		2-6	N-diHOPAmHOB-FASAPS	3	A, B, C
8		2-8	N-HOEAmP-FASAPS	2b	A, B, C
9		2-8	N-HOEAmP-FASE	2b	A, B, C, D, E
10		4-6	N-HOEAmHOP-FASA	3	B, C
11		2-8	N-HOEAmP-FASA	2b	A, B, C, D, E
12		4-8	N-TAmP-N-MeFASA	3	B
13		3-8	N-TAmP-FASA	3	A, B, C, D, E, F, G
14		3-6	N-TAmP-FASAP	3	D, E, F, G
15		4-6	N-CMAmP-FASAP	2b	D, E, F, G
16		3-6	N-CMAmP-FASA	2b	D, E, F, G
17		6, 8, 10	CMAmEt-FA	2b	L
18		4, 6, 8	CMAmB-FA	3	L
19	$C_{n+8}H_{18}O_2SN_2F_{2n+1}$	6, 8, 10	Not applicable	4	I, J
20	$C_{n+10}H_{20}O_7SN_2F_{2n+1}$ or $C_{n+10}H_{18}O_4SN_2F_{2n+1}$	Unknown	Not applicable	5	I, J

[a]Number of CF_2 groups. [b]Homologues were not necessarily detected in a single sample and indicate a detection of each homologue in at least one AFFF. [c]The generic acronym is listed in the table, designated

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Table 1. continued

as **A** (in bold), which can be substituted by the prefix corresponding to the number of CF_2 groups. [d]Defined by Schymanski et al.[45] [e]Confidence level identified for the most abundant homologue in each class. Confidence decreases for higher or lower homologues. [f]Confirmed in CP 3M FC-100 (O, SI Table S1).

homologue) at m/z 78 and 398 are characteristic of the fragment and pseudomolecular ion, respectively, of perfluoroalkyl sulfonamides,[51] which suggests a perfluoroalkyl sulfonamide as a base structure. The relative intensity of the [M+2] isotope peak (~10%) provides additional evidence of two sulfur atoms.

Zwitterionic classes **2**, **3**, **16**, **29**, and **32** were detected in both ESI^- and ESI^+. The ionization mode for which the above classes were identified is discussed within, and the discussion for the complementary ionization mode is discussed in the SI. Class **2** contains six homologues (C_3–C_8) detected by ESI^- and ESI^+ (see SI). In ESI^- (SI Figure S3a; C_6 homologue), a net elimination of $C_6F_{13}SO_2NHCH_2CH{=}CH_2$ from the pseudomolecular ion results in the observance of m/z 166,[55] corresponding to a propyl sulfonate bonded to a tertiary amine. The remaining observed fragments are characteristic of PFASs (SI Table S2). A 3M mist suppression patent confirms the proposed structure of Class **2**.[56]

Classes **3**–**5** are variations of Class **2**, and thus, it is not surprising that Classes **3**–**5** share some fragments with Class **2**. Class **3** has four homologues (C_3–C_6) as identified by both ESI^- and ESI^+ (see SI) as well as a mass difference of 16 Da relative to Class **2**, indicating an additional oxygen atom. In ESI^- (SI Figure S4a; C_6 homologue), net elimination of $C_6F_{13}SO_2NHCH_2CH{=}CH_2$ produces m/z 182 [$C_5H_{12}O_4SN^-$]. The lack of a sulfate ion at m/z 97[57] suggests that m/z 182 contains a 2-hydroxy propyl sulfonate bonded to a tertiary amine, since a sulfite radical anion at m/z 80 is observed. Furthermore, Class **3** was confirmed in a 3M mist suppression patent.[56] For brevity, Classes **4**–**7** are discussed in the SI.

Classes **8**–**11** share the same base structure; however, since Classes **8**–**10** have two hydroxyl groups, Class **11** fragments differently. Class **8** contains seven homologues ranging from C_2 to C_8. In ESI^+ (SI Figure S9; C_6 homologue), the pseudomolecular ion undergoes a net neutral loss of 122 Da from the sulfonamide N to give the base structure (Class **11**) at m/z 529, which then undergoes an O rearrangement[55] and net elimination to produce m/z 456. The migration of the hydroxyl group is consistent with the most common non-H migration of O functionalities.[55,58] From the pseudomolecular ion, the simultaneous cleavage of the S–N bond and a neutral loss of CH_2O forms the base peak m/z 237. A loss of CH_2O is consistent with the loss of primary alcohols as ketones in lignans.[59,60] The structure was further confirmed in a 3M AFFF fire extinguisher patent.[61] Classes **9**–**10** are provided in the SI for brevity.

Class **11** has seven homologues, ranging from C_2 to C_8, identified by ESI^+. A net neutral loss of ethenol (SI Figure S12; C_6 homologue) gives m/z 485. The S–N bond cleavage and an H shift in the pseudomolecular ion forms m/z 145. A subsequent elimination of $HN{=}CHCH{=}CH_2$ with H rearrangement[62] yields the base peak (m/z 90), suggesting a tertiary amine and a primary alcohol. Additional structural confirmation of Class **11** was found in a 3M mist suppression patent.[56]

Classes **12**–**14** share the same propyl trimethylammonium base structure. However, since Classes **12** and **14** have a tertiary sulfonamide N, fragmentation is not always consistent among the three classes. Class **12** contains the C_4–C_8 homologues identified by ESI^+ (SI Figure S13; C_6 homologue). Cleavage of the S–N bond forms an N radical cation (m/z 130).[49,63] Fragmentation of the latter, with an H shift, produces the base peak (m/z 74).[55] Interestingly, Class **12** has the same molecular formula and exact mass as the fluorotelomer sulfonamido amine[21,23] and the fluorotelomer degradation product M4/PT1 identified by Moe et al.[39] A match to the previously reported structures was ruled out since branching (SI Figure S53) and mass differences of 50 Da, corresponding to a single CF_2 group, indicate an ECF-based chemistry rather than a fluorotelomer-based chemistry. Additionally, a neutral loss of 45 Da, was not observed, suggesting the presence of a trimethyl amine rather than a dimethylamine.[52] Several corrosion resistance and aqueous wetting and film-forming patents confirm the structure proposed for Class **12**.[18,64,65]

Class **13** is comprised of the C_3 to C_8 homologues detected by ESI^+ (SI Figure S14; C_6 homologue). Like Class **12**, the S–N bond cleaves to produce m/z 116, an N radical cation,[49,63] with a difference of 14 Da, corresponding to the absence of an additional methylene group on the sulfonamide N. Further fragmentation with a H rearrangement generates the base peak ($\rightarrow$ m/z 60), a common fragment for amine-containing compounds.[55] The exact mass and molecular formula of Class **13** matches the fluorotelomer degradation product M3 identified by Moe et al.,[39] but branching (SI Figure S54) and mass differences of 50 Da suggest an ECF-derived structure rather than the fluorotelomer-based structure M3. Furthermore, the absence of a 45 Da neutral loss suggests a quaternary amine rather than a tertiary amine.[52] Numerous patents support the structure of Class **13** as well as product sheets for 3M Fluorad FC-135.[19,31,56,64,66] For brevity, Classes **14**–**15** are discussed in the SI.

Class **16** contains four homologues (C_3–C_6) as revealed by ESI^- (see SI) and ESI^+. In ESI^+ (SI Figure S17b; C_6 homologue), a H shift produces the base peak at m/z 104. The betaine structure of Class **16** is consistent with a 3M AFFF patent.[56]

Novel Classes in Fluorotelomer AFFFs. Four classes of PFASs were discovered in the fluorotelomer AFFFs (Table 1). Homologues in fluorotelomer AFFFs differ by 100 Da ($-CF_2CF_2-$) and contain only linear isomers (SI Figure S58–S61). Mechanisms for Classes **17**–**20** are in the SI, since these classes are not present in AFFF-impacted groundwater. Although the manufacturing process of fluorotelomer-based PFASs produces fewer unintentional products, the presence of a $-CH_2CH_2-$ spacer increases the complexity of the MS/MS fragmentation.

Derivatives of the PFSAs and PFCAs in AFFFs and CPs. Five classes of PFSA derivatives and one PFCA derivative were discovered in 3M AFFFs and CPs (Table 2). All homologues vary by 50 Da, indicating only ECF-derived chemistries. Isomer peaks are present in chromatograms (SI Figures S62–S67), suggesting alternative placements of double bonds and/or H atoms when present in the depicted structure, although branching cannot be ruled out.

Classes **21**–**22** are discussed in the SI due to no detections in AFFF-impacted groundwater. Class **23** contains homologues

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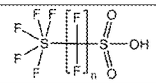
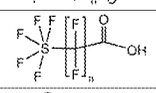
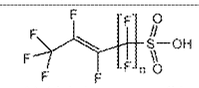
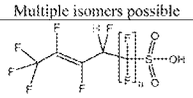
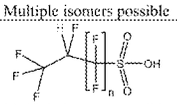
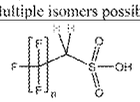
Table 2. Variations on the PFSAs and PFCAs in AFFFs and CPs

Class Number	Structure	$n^{a,b}$	Acronym[c]	Confidence Level[d,e]	AFFF/CP Found In
21		3-9	*n*-F5S-PFAS	2b	A, B, C, D, E, G, M, N
22		6-8	*n+l*-F5S-PFAA[f]	3	M, N
23	 Multiple isomers possible	1-10	UPFAS[g,h]	3	A, B, C, D, E, M, N, P
24	 Multiple isomers possible	1-6	H-UPFAS[g,h]	3	A, B, C, D, E, F, G, M
25	 Multiple isomers possible	0[i]-8	H-PFAS[g,h]	3	A, B, C, D, E, F, G, M, N, P
26	 Multiple isomers possible	5, 7	*m*:1 PFAS[g,h]	3	A, B, C, D, E, F, G, M, N, P

[a]Number of CF_2 groups. [b]Homologues were not necessarily detected in a single sample and indicate a detection of each homologue in at least one AFFF or commercial product. [c]The generic acronym is listed in the table, designated as **A** (in bold), which can be substituted by the prefix corresponding to the number of CF_2 groups. [d]Defined by Schymanski et al.[45] [e]Confidence level identified for the most abundant homologue in each class. Confidence decreases for higher or lower homologues. [f]The generic acronym (**A**) is substituted by the prefix corresponding to the total number of carbon atoms. [g]The generic acronym (**A**) is substituted by the prefix corresponding to the number of carbons bonded to at least 1 fluorine atom. [h]The CP contains a mixture of isomers for each homologue, and the position of the double bond or the hydrogen appears to vary. One isomer was drawn to represent the class. [i]When *n* is 0, the CF_2 group in brackets is not present, and the sulfonic acid group is directly bonded to the carbon with 1H present.

ranging from $n = 1$ to $n = 10$ as indicated by ESI⁻ (SI Figure S24; $n = 5$). Unlike Class **21**, the dominant fragmentation pathway is an initial loss of 80 Da followed by fragmentation of the perfluoroalkyl chain into shorter carbanions.[48,67] The appearance of ions at *m/z* 131, 181, 281, 331, and 381 indicate the presence of a ring or double bond, since fragmentation of PFOS, following loss of 80 Da, yields the same fragments as decarboxylated PFCAs (i.e., *m/z* 119 and 169).[48] Furthermore, the exact mass and molecular formula of Class **23** matches perfluoroethyl cyclohexanesulfonate (PFECHS);[41] however, a comparison of the MS/MS spectrum of a PFECHS standard to Class **23** indicates the absence of *m/z* 80 from the PFECHS spectrum,[41] suggesting that Class **23** is comprised of structural isomers containing a double bond rather than a ring. While Washington et al.[36] tentatively identified Class **23** in sludge-applied soil samples, a low resolution instrument was used and abundance was low;[36] therefore, Class **23** is included in the novel compounds rather than the previously reported PFASs.

Classes **24**-**26** contain at least one H substituted for a F. Due to the presence of an H, fragmentation of these three classes involves a neutral loss of 20 Da. Class **24** contains six homologues, ranging from $n = 1$ to $n = 5$ indicated by ESI⁻ (SI Figure S25; $n = 5$). After the neutral loss of 20 Da, double bond formation (→ *m/z* 423), and sequential loss of 80 Da (→ *m/z* 343), bond cleavage[48] occurs in a similar manner to that observed for Class **23**.

Nine homologues, consisting of $n = 0$ through $n = 8$, comprise Class **25** in ESI⁻ (SI Figure S26; $n = 6$). Following an initial neutral loss of 20 Da (→ *m/z* 461) and subsequent neutral loss of 80 Da (→ *m/z* 381), fragmentation pathways similar to Classes **21** and **23** are observed. Direct homolytic bond cleavage produces *m/z* 411, 381, 331, 281, and 181,[67] while remote charge fragmentation generates the radical anions *m/z* 130 and 230.[48] Similar to Class **23**, *m/z* 119 and *m/z* 169 may be attributed to a positional isomer of the depicted structure.

Class **26** contains two homologues, $n = 5$ and $n = 7$, as indicated by ESI⁻ (SI Figure S27; $n = 7$). Sequential losses of HF (→ *m/z* 443 and → *m/z* 423) from the pseudomolecular ion indicate the presence of two H. The neutral loss of 80 Da (→ *m/z* 343) triggers the bond cleavage[67] observed in Class **24** to produce *m/z* 293, 243, 193, and 143. Although positional isomers may be present, the structure presented for Class **26** was found in a 3M chrome plating patent.[40]

Novel PFAS Classes Found Only in Groundwater. Eleven of the 13 classes (Table 3) found only in groundwater are ECF-derived. The presence of the 11 ECF-derived classes may be attributed to either degradation of PFASs found in 3M AFFF or parent compounds in AFFFs prior to 1988, for which the composition is unknown. The two fluorotelomer classes (Classes **39**−**40**; Table 3) are likely degradation products of a parent compound in fluorotelomer AFFFs, although no biodegradation studies to date have observed these two classes.

ECF-Derived PFASs in AFFF-Impacted Groundwater. Eleven classes of ECF-derived PFASs (Table 3) were found only in AFFF-impacted groundwater. Classes **27**−**38** vary by 50 Da (−CF_2-) and have branched and linear isomers (SI Figure S68−S79), indicating ECF-derived chemistries.

Class **27** contains homologues corresponding to $n = 0$−4 identified by ESI⁻ (SI Figure S28; $n = 3$). Cleavage of the C−O bond and a net neutral loss of 110 Da ($C_2F_2O_3$) yields *m/z* 281,[55] which was observed in Classes **23** and **25**. Subsequent losses of CF_2 produce *m/z* 231, 181, and 131. From the pseudomolecular ion, a neutral loss of CO_2 and an F shift form *m/z* 197, 147, and 135. Rapid F shifts have been observed in fragmentation studies of PFCAs and PFSAs following loss of the polar headgroup.[48]

Class **28** contains C_4, C_5, and C_6 homologues as identified by ESI⁺ (SI Figure S29; C_6 homologue). Class **28** is structurally similar to Class **8**, with a mass difference of 16 Da, indicating the presence of an additional O atom. The net neutral loss of 98 Da (H_2SO_4), forms *m/z* 569.[68] Cleavage of the sulfonamide bond results in C−N double bond formation (*m/z* 185),[69] which is consistent with a sulfonamide. Subsequent neutral loss of ethyne (26 Da) produces the base peak (→ *m/z* 159), suggesting that two methylene groups separate the sulfonate group from the methyl group on the sulfonamide N. An H shift in *m/z* 159 generates *m/z* 116,[55] and a subsequent net neutral loss of 26 Da (C_2H_2) yields *m/z* 90, indicating a quaternary amine bonded to two methylene groups and a primary alcohol. The proposed structure of Class **28** was confirmed in a 3M patent,[61] which suggests that Class **28** may have been in pre-1988 3M AFFFs.

The C_2−C_6 homologues were identified for Class **29** by ESI⁻, while only the C_4−C_6 homologues were detected in ESI⁺ (see SI). This class is structurally similar to Class **5** and differs by 32 Da, consistent with two additional O atoms. In ESI⁻ (SI

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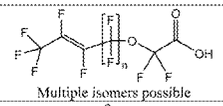
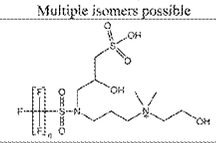
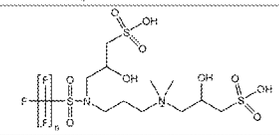
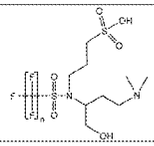
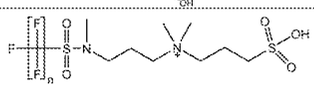
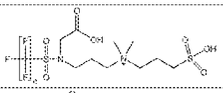
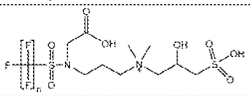
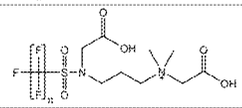
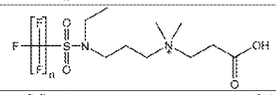
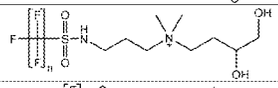
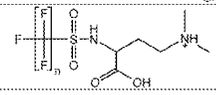
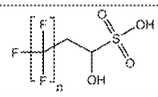
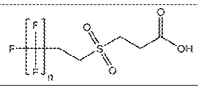
Table 3. Newly Discovered PFASs Found Only in AFFF-Impacted Groundwater

Class Number	Structure	$n^{a,b}$	Acronym[c]	Confidence Level[d,e]
27	 Multiple isomers possible	0[f]-4	O-U-PFAA[g]	3
28		4-6	N-HOEAmP-FASAHOPS	3[h]
29		2-6	N-SHOPAmP-FASAHOPS	3[h]
30		5-6	N-AHOB-FASAPS	3
31		3-6	N-SPAmP-McFASA	2b
32		3-6	N-SPAmP-FASAA	2b
33		3-6	N-SHOPAmP-FASAA	2b
34		3-6	N-CMAmP-FASAA	2b
35		5-6	N-CEAmP-EtFASA	3
36		4-6	N-diHOBAmP-FASA	3
37		4-6	N-AmCP-FASA	3
38	$C_{n+9}H_{22}O_2SN_2F_{2n+1}$	3, 4, 6	Not applicable	4
39		4-8	1HO-*n*:2 FTS	3
40		4, 6, 8	*n*:2 FTSO2PA	2b

[a]Number of CF_2 groups. [b]Homologues were not necessarily detected in a single sample and indicate a detection of each homologue in at least one groundwater sample. [c]The generic acronym is listed in the table, designated as **A** (in bold), which can be substituted by the prefix corresponding to the number of CF_2 groups. [d]Defined by Schymanski et al.[45] [e]Confidence level identified for the most abundant homologue in each class. Confidence decreases for higher or lower homologues. [f]When n is 0, the CF_2 group in brackets is not present, and the atoms on both sides of the brackets are bonded to each other. [g]The generic acronym (**A**) is substituted by the total number of carbons plus the replacement oxygen in the carbon chain (i.e., if $n = 6$, there are seven total carbons plus one oxygen replacement, so "O" should replace "A" in the acronym). [h]Confirmed in CP 3M FC-100 (O, SI Table S1).

Figure S30a; C_6 homologue), the net neutral loss of the 2-hydroxypropyl sulfonate moiety (138 Da, → m/z 621) has been observed in Class **3**. A second neutral loss of 138 Da is observed (→ m/z 483), corresponding to a second 2-hydroxypropyl sulfonate moiety bonded to the quaternary amine. For brevity, Classes **30**−**31** are discussed in the SI.

The C_3−C_6 homologues comprise Class **32** as detected by both ESI^- and ESI^+ (see SI). A net neutral loss of 180 Da (→ m/z 483) in ESI^- (SI Figure S33a; C_6 homologue) suggests the presence of propyl sulfonate and acetic acid.[70] Similar to many previously discussed classes, m/z 166 indicates a propyl sulfonate bonded to a tertiary amine, and a 45 Da neutral loss (→ m/z 438) indicates an N,N-dimethylamino moiety[52] in the fragmentation pathway. For brevity, mechanisms for Classes **33**−**36** are provided in the SI.

Class **37** contains C_4−C_6 homologues detected by ESI^+ (SI Figure S38; C_6 homologue). A net neutral loss of 46 Da (CH_2O_2) gives the base peak m/z 483, indicative of a carboxylate group[71] bonded to the sulfonamide N. The neutral loss of 43 Da (C_2H_5N) to form m/z 440 indicates an N,N-dimethylamino moiety (2 H lost in a previous step).[52] From the pseudomolecular ion, net elimination of $C_8H_7F_{12}NO_2S$ (409 Da) with successive F and a carboxylic acid rearrangements yields m/z 120, which confirms the presence of a tertiary amine and formic acid. Class **38** is discussed in the SI for brevity.

Fluorotelomer PFASs in AFFF-Impacted Groundwater. Two classes of fluorotelomer PFASs were discovered (Table 3). Fluorotelomer-based PFASs have only linear isomers (SI Figure S80−S81) and typically vary by 100 Da (−CF_2CF_2-).

Five homologues (n = 4−8), which vary by 50 Da, comprise Class **39** as indicated by ESI^- (SI Figure S40; n = 6). Loss of water (18 Da) from the pseudomolecular ion (→ m/z 425) indicates a hydroxyl group and an H bonded to the α carbon.[55,72,73] Losses of 80 Da and 2 HF groups[31] from m/z 425 form m/z 293. Subsequent losses of CF_2 produce m/z 243 and m/z 193. An H shift[55] and the resultant neutral loss of the fluorinated tail produces m/z 123, which suggests a CH_2 spacer between the carbon with the hydroxyl group and the fluorinated tail. The absence of branching in all homologues (SI Figure S80) suggests that Class **39** is fluorotelomer-based rather than ECF-derived. Additionally, fluorotelomer PFASs (vary by 100 Da) can degrade to PFASs that vary by 50 Da.[34,35]

Class **40** consists of the C_4, C_6, and C_8 homologues, which vary by 100 Da, as indicated by ESI^- (SI Figure S41; n = 6; m/z 483). Characteristic of fluorotelomer-based chemistries in ESI^-,[31,53] three and four neutral losses of HF produce m/z 287 and 267, respectively, indicating a fluorotelomer product. An H shift[55] generates m/z 137, indicating a sulfone bonded to an ethyl group and a carboxylate. Fragment m/z 137 suggests that Class **40** is a degradation product of DuPont's Zonyl FSA[74] since thioethers are known to oxidize to sulfinyls and sulphones.[23,34,35] Furthermore, the Zonyl FSA product sheet states that the main ingredient, Lithium 3-[2-(perfluoroalkyl)-ethylthio]propionate, is "ultimately biodegradable".[74] Analysis of Zonyl FSA (Q, SI Table S1) indicates the presence of the main ingredient in addition to the sulfinyl and sulphone derivatives, including m/z 383, 483, and 583, suggesting that Class **40** is closely related to 3-[2-(perfluoroalkyl)ethylthio]-propionate.

Previously Reported PFASs. Seventeen classes of previously reported PFASs (SI Tables S5−S6) were found in AFFF and/or AFFF-impacted groundwater. Fragmentation of

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the abundant homologues as well as KMD plots provided confirmation of the previously discovered PFASs. Additional homologues of Cl-PFAS (n = 2−7), O-PFAS (n = 2−9), and K-PFAS (n = 3−8), that were originally discovered in firefighters' blood,[24] were present in AFFFs. Not surprisingly, PFASs rarely occur as single compounds but rather as homologous series.[21,23,25]

H-PFAA (n = 2−8) was found only in groundwater. Previous studies identified H-PFAA as a polymer degradation product in wastewater[22] and sludge-applied soils.[36] A biodegradation study of the 8:2 fluorotelomer alcohol also found H-PFOA as a degradation intermediate.[75] On the other hand, N-OxAmP-FASA (n = 4−6) was originally found in 3M AFFF[23] but also was confirmed in AFFF-impacted groundwater.

Perfluoroalkyl sulfonamides, previously found in fish (n = 4),[76] urban watersheds (n = 8)[77] and AFFF-impacted groundwater (n = 6),[15,16] range from n = 2−8 in AFFF-impacted groundwater. N-EtFASAAs, N-MeFASAAs, and FASAAs, found previously in urban watersheds (n = 8 for all),[77] biosolids (N-EtFOSAA, N-MeFOSAA),[78] and landfill leachate (n = 4−8 for all),[79] have now been detected in a CP (P, SI Table S1; N-EtFASAA n = 2−10) and AFFF-impacted groundwater (n = 3−8 for N-MeFASAAs and n = 4−6 for FASAAs). Additional homologues of the perfluoroalkyl sulfinates, found in harbor seals[80] and the degradation of N-ethyl sulfonamido ethanol (n = 8),[81] were discovered in AFFF-impacted groundwater (n = 4−8).

The observed transformation product n:2 FASO2PA-MePS in aerobic microcosms[34,35] was confirmed in AFFF-impacted groundwater (n = 4, 6, 8). FAPA (n = 3, 5)[34,35,79] and 6:2 FDThP, the main compound in Zonyl FSA,[74] were detected in AFFF-impacted groundwater for the first time. Finally, additional homologues of major PFAS classes were discovered in National Foam AFFF (N-CMAmP-n:2 FASA; n = 14, 16 [14:2 and 16:2 FtSaB], N-AP-n:2 FASA; n = 12 [12:2 FtSaAm], and 10:2, 12:2, and 14:2 FTS; H, Table S1) and Ansul AFFF (n:2 FAThPA-MePS; n = 2 [2:2 FtTAoS]; I, SI Table S1),[21,23] all of which may degrade to long-chained PFCAs.[34,35]

IMPLICATIONS

The discovery of 40 novel classes of PFASs plus additional homologues in 17 previously reported classes of PFASs resulted in the identification of over 240 individual compounds (novel + previously reported) in AFFF and AFFF-contaminated groundwater. The individual PFASs that are now associated with AFFF will aid in fingerprinting and differentiating between AFFF-impacted sites and other sources of PFASs, including PFAS and AFFF manufacturing sites, landfills, and municipal wastewater-impacted systems. However, low-abundance PFASs were not captured if the abundance fell below the threshold set by injection volume, dilution factors, and instrumental settings. Overall, of the newly discovered PFASs, 25% were anionic, 55% were zwitterionic, and 13% were cationic. For complete site characterization with respect to PFASs, zwitterions and cations, whose fate and transport are poorly understood, should be included. Over half of the total classes of PFASs (truly novel + previously reported) were found in AFFF formulations, primarily manufactured by 3M. Interestingly, the unknown reserve tank, 3M's 1988, and 3M's 1989 AFFFs (A-C, SI Table S1) contained the majority of the novel PFASs discovered in AFFF. On the contrary, the 3M AFFFs after 1993 (D-G, SI Table S1) contained fewer new classes and only two classes not found in earlier formulations. Although 3M AFFFs are no longer manufactured and were removed from the U.S. military's Qualified Product List (QPL),[42] the detection of ECF-based PFASs in groundwater is clear evidence of their persistence. Fluorotelomer-based AFFFs, on the other hand, are still stockpiled for use.[82] The 3% U.S. Mil-Spec AFFFs were recently requalified; however, the composition of these new AFFFs currently is unknown.

The limited number of fluorotelomer-based PFASs in AFFFs and groundwater identified in this study suggest that (a) previous AFFF characterization efforts were successful,[21,23] and/or (b) degradation of fluorotelomer-based PFASs to PFCAs may occur more readily than ECF-derived PFASs.[34,35] Published aerobic biodegradation pathways for the fluorotelomer thioether amido sulfonate indicates aerobic degradation to fluorotelomer sulfonates and PFCAs,[34,35] with chain lengths at or below that of the starting material. Anaerobic biodegradation pathways of fluorotelomer-based PFASs are not reported, so the influence of redox conditions on the composition of PFASs is not known. Sorption and transport will also impact the distribution of PFASs observed in groundwater. For example, cationic fluorotelomer-based PFASs in National Foam, which has been listed on the QPL since 1973,[42] sorb strongly to soils and sediments (data not shown). A parallel effort is underway to identify the remaining PFASs in soils and sediments, and this information is needed to fully account for PFASs in groundwater, soil, and sediment at AFFF-contaminated sites. Determination of the mass balance of PFASs in AFFF-impacted groundwater is challenging due to the lack of available analytical standards.

There is some evidence of the degradation of ECF-derived PFASs in AFFF-impacted groundwater, since some hydroxylated PFASs found only in groundwater closely resemble PFASs found in AFFF or may have been compounds in 3M AFFFs prior to 1988. The discovery of N-MeFASAAs, FASAAs, FASAs, and perfluoroalkyl sulfinates in groundwater suggests transformation from more complex ECF-based PFASs, as all four transformation products are known in the degradation pathway from N-EtFOSE and other perfluoroalkyl sulfonamido derivatives to PFOS.[40,78,81,83] Tables 1−3 contain ECF chemistries where n = 8, indicating the possibility that these PFASs could degrade to PFOS. However, frequency of occurrence and relative abundance of the n = 8 ECF-derived homologues need to be taken into consideration, which was outside the scope of this study. The contribution of the remaining ECF-derived homologues to the production of PFSAs is unknown. However, only one aerobic biodegradation study has been published on the polyfluoroalkyl substances in 3M AFFF formulations.[40] The detection of ECF- and fluorotelomer-based PFASs in AFFF-impacted groundwater indicates that 3M- and telomer-based PFASs are persistent in groundwater.[43,84]

Little is known about the newly discovered PFASs with regards to subsurface remediation strategies, transport, and toxicity. The (presumed) wide range of solubilities for the newly discovered PFASs may pose challenges for using ex situ remediation techniques, such as granulated active carbon, because shorter-chained compounds are likely to break through systems designed to capture PFOS and PFOA.[85,86] Shorter-chained anionic and zwitterionic PFASs are expected to migrate downstream of source areas faster than their longer-chained counterparts in a manner analogous to their elution order on analytical C18 columns.[87] To the best of our knowledge, no

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toxicity studies exist for any of the novel PFASs identified. Nonfluorinated cationic surfactants exhibit greater toxicity.[88,89] By analogy, cationic and zwitterionic PFASs, which also have cationic moieties, may be more toxic than the newly discovered anionic PFASs. However, conclusions about potential toxicity regarding the newly discovered PFASs cannot be determined from mere detection.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05843.

Chromatographic Methods, qTOF-MS data acquisition, nontarget and suspect screening criteria, fragmentation mechanisms for Classes **4–7**, **9–10**, **14–15**, **17–22**, **30–31**, **33–36**, **38**, Tables S1–S6, and Figures S1–S81 (PDF)

A searchable fragment and CF_2-normalized mass defect databases for the 57 classes (XLS)

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Notes

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