# Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonagueous Large-Volume Injection HPLC-MS/MS

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Supporting Information

ABSTRACT: A new analytical method was developed to quantify 26 newly-identified and 21 legacy (e.g. perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, and fluorotelomer sulfonates) per and polyfluorinated alkyl substances (PFAS) in groundwater and aqueous film forming foam (AFFF) formulations. Prior to analysis, AFFF formulations were diluted into methanol and PFAS in groundwater were micro liquid-liquid extracted. Methanolic dilutions of AFFF formulations and groundwater extracts were analyzed by largevolume injection (900  $\mu$ L) high-performance liquid chromatography tandem mass spectrometry. Orthogonal chromatography was performed using cation exchange (silica) and anion exchange (propylamine) guard columns connected in series to



a reverse-phase (C18) analytical column. Method detection limits for PFAS in groundwater ranged from 0.71 ng/L to 67 ng/L, and whole-method accuracy ranged from 96% to 106% for analytes for which matched authentic analytical standards were available. For analytes without authentic analytical standards, whole-method accuracy ranged from 78 % to 144 %, and wholemethod precision was less than 15 % relative standard deviation for all analytes. A demonstration of the method on groundwater samples from five military bases revealed eight of the 26 newly-identified PFAS present at concentrations up to 6900 ng/L. The newly-identified PFAS represent a minor fraction of the fluorinated chemicals in groundwater relative to legacy PFAS. The profiles of PFAS in groundwater differ from those found in fluorotelomer- and electrofluorination-based AFFF formulations, which potentially indicates environmental transformation of PFAS.

# INTRODUCTION

Aqueous film forming foam (AFFF) formulations are used to extinguishing hydrocarbon-fuel fires<sup>1,2</sup> and contain per and polyfluorinated alkyl substances (PFAS) to lower the surface tension at the air-AFFF interface.<sup>3</sup> The U.S. military accounts for 75% of all the AFFF formulations used in the United States,<sup>3</sup> and historical fire-training exercises at military bases resulted in the discharge of AFFFs into the environment on a weekly to monthly basis.<sup>3,4</sup> At these and other sites, such as municipal airports, where AFFFs were released elevated concentrations (> 1,000,000 ng/L) of perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, and fluorotelomer sulfonates occur in groundwater and surface water.<sup>3,5-9</sup> Groundwater at sites impacted by AFFF use have the greatest recorded concentrations of PFAS of any aqueous environment.<sup>5,9</sup>

Recently, several classes of zwitterionic, cationic, and anionic PFAS were identified in AFFF formulations used by the U.S. military (Figure 1).<sup>1,9,10</sup> Analytical methods for many of the newly-identified PFAS have not yet been developed but are needed to determine the extent of PFAS contamination in

groundwater. Additionally, comparing the concentration profiles of PFAS in AFFF formulations to those in groundwater provides insights into the environmental fate of those PFAS.

Most of the analytical methods developed to quantify PFAS in aqueous samples employ preconcentration by solid-phase extraction (SPE).<sup>5,11</sup> However, SPE approaches based on C18 and HLB phases poorly retain  $C_4-C_6$  perfluoroalkyl carbox-ylates and sulfonates.<sup>12–15</sup> Methods based on weak anion exchange SPE were developed for anionic PFAS,<sup>15,16</sup> however, they may not be applicable for cationic and zwitterionic PFAS. Furthermore, SPE-based methods generate solid and liquid waste, are laborious, and are prone to positive (e.g., contamination)<sup>12,17</sup> and negative (e.g., analyte loss) artifacts.<sup>18,19</sup> Automated equipment can reduce the labor

Received:	August 28, 2012
Revised:	April 12, 2013
Accepted:	April 16, 2013
Published	April 16 2013

April 16, 2013



**Figure 1.** Target analyte classes, structures, and acronyms. Fluorotelomer PFAS are listed to the left and perfluorinated PFAS are listed on the right. <sup>L</sup>Legacy classes of PFAS. <sup>N</sup>Newly-identified classes of PFAS. Data quality levels include quantitative (Qn), semi-quantitative (Sq), and qualitative (Ql). \*Indicates analytes analyzed for in AFFF only.

associated with SPE; however, such equipment can be economically prohibitive.

Alternatively, large-volume ( $\geq$ 500  $\mu$ L) injection (LVI) of aqueous samples is advantageous because only small sample volumes (<5 mL) and minimal pretreatment (e.g., centrifugation or filtration) are required.<sup>20,21</sup> LVI utilizes a large fraction (> 60 %) of the sample for analyte enrichment at the head of the high-performance liquid chromatography (HPLC) column, in contrast to conventional HPLC in which only a small fraction (1% to 10%) of the sample is analyzed.

Many PFAS are surface active, which cause them to stratify,<sup>22</sup> adsorb to surfaces,<sup>5,11,23</sup> and aggregate,<sup>24</sup> which results in their apparent loss from aqueous samples. These apparent losses are eliminated by liquid–liquid extraction (LLE) because analytes are extracted into an organic solvent. Filtration is not required for LLE so analytes sorbed to suspended particulate matter are potentially coextracted.<sup>25</sup> However, conventional LLE methods typically use sample volumes of up to 1000 mL and up to 120 mL of organic extractant,<sup>25,26</sup> which must be treated further by evaporation and solvent exchange.<sup>25–27</sup>

Although LVI is demonstrated for use with aqueous samples,<sup>20,28,29</sup> LVI of organic extracts has yet to be reported which may be due to incompatibility of large volumes of organic solvent (extract) with reverse-phase HPLC. However,

because PFAS are not prone to loss in organic solvents, new approaches are needed that integrate simple extraction-based techniques with large-volume injection.

The objective of this study was to develop an analytical method for the analysis of the newly-identified and legacy PFAS (Figure 1) in AFFF<sup>1</sup> and groundwater. AFFFs were analyzed by diluting the highly concentrated formulations into methanol. PFAS in groundwater (3 mL) were extracted by micro-LLE, which required a total of 1.7 mL of organic extract per sample. Dilute AFFF formulations and organic extracts of groundwater were analyzed for PFAS by LVI (900  $\mu$ L) with orthogonal HPLC and tandem mass spectrometry. Orthogonal HPLC was accomplished with two guard columns (weak cation exchange, weak anion exchange) that were connected in series with a C18 column for analyte enrichment and separation, respectively. Tandem mass spectrometry (MS/MS) was interfaced with electrospray ionization and operated in positive/negative polarity switching for the detection of the zwitterionic, cationic, and anionic analytes. The final method was demonstrated on 12 AFFF formulations and 19 groundwater samples obtained from five different military bases within the United States.

# EXPERIMENTAL SECTION

**Chemicals.** Chemical and reagent source and purity as well as descriptive scientific names for the target analytes and

analyte	LOD (ng/L)	LOQ (ng/L)	$accuracy^{b}$ (%)	precision <sup>c</sup> (% RSD)	$\operatorname{concn}^d(\operatorname{ng/L})$	internal <sup>e</sup> standard
6-2 FtTAoS	2.6	8.5	$107 \pm 8.7$	9.1	40	[ <sup>13</sup> C <sub>2</sub> ]-PFHxA
6-2 FtTHN <sup>+</sup>	5.0	16	101 ± 6.0	5.6	40	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
6-2 FtSaB	23	76	$131 \pm 13$	11	75	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
6-2 FtSaAm	67	221	$117 \pm 7.7$	8.2	700	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
5-1-2 FtB	3.6	12	144 ± 13	10	35	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
7-1-2 FtB	5.9	19	$128 \pm 12$	11	40	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
9-1-2 FtB	8.7	29	$103 \pm 5.4$	11	170	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
5-3 FtB	4.6	15	$101 \pm 13$	15	75	[ <sup>13</sup> C <sub>4</sub> ]-PFBA
7-3 FtB	7.9	26	96 ± 8.4	10	150	[ <sup>13</sup> C <sub>4</sub> ]-PFBA
9-3 FtB	6.1	20	$78 \pm 8.3$	13	50	[ <sup>13</sup> C <sub>4</sub> ]-PFBA
4-2 FtS	1.6	5.2	$105 \pm 11$	12	40	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS
6-2 FtS	0.84	2.8	99 ± 9.5	11	20	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS
8-2 FtS	1.9	6.3	106 ± 9.1	10	20	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS
PFBS	1.2	4.0	98 ± 9.5	11	40	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS
PFHxS	1.7	5.5	96 ± 4.2	3.7	20	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS
PFHpS	0.88	2.9	$100 \pm 9.1$	11	20	[ <sup>13</sup> C <sub>4</sub> ]-PFOS
PFOS	0.81	2.7	$104 \pm 5.9$	6.3	20	$[^{13}C_4]$ -PFOS
PFDS	0.71	2.4	$103 \pm 2.9$	2.8	20	$[^{13}C_4]$ -PFOS
PFBA	4.1	14	106 ± 8.8	9.4	25	[ <sup>13</sup> C <sub>4</sub> ]-PFBA
PFPeA	1.1	3.7	$102 \pm 6.8$	4.8	35	[ <sup>13</sup> C <sub>4</sub> ]-PFBA
PFHxA	1.4	4.7	$101 \pm 3.8$	4.2	35	[ <sup>13</sup> C <sub>2</sub> ]-PFHxA
PFHpA	1.8	6.0	106 ± 9.8	11	25	[ <sup>13</sup> C <sub>2</sub> ]-PFHxA
PFOA	1.5	5.0	$107 \pm 7.7$	8.5	25	$[^{13}C_4]$ -PFOA
PFNA	1.0	3.3	99 ± 6.4	7.8	25	[ <sup>13</sup> C <sub>5</sub> ]-PFNA
PFDA	0.94	3.1	$105 \pm 7.3$	8.4	25	$[^{13}C_2]$ -PFDA
PFUdA	0.93	3.1	$104 \pm 8.7$	9.1	25	[ <sup>13</sup> C <sub>2</sub> ]-PFUdA
PFDoA	1.0	3.4	$103 \pm 5.9$	6.4	25	[ <sup>13</sup> C <sub>2</sub> ]-PFDoA
PFTrA	1.2	4.1	$103 \pm 6.7$	7.1	25	[ <sup>13</sup> C <sub>2</sub> ]-PFDoA
PFTeA	1.7	5.6	$106 \pm 5.5$	5.9	25	$\begin{bmatrix} {}^{13}C_2 \end{bmatrix}$ -PFDoA

Table 1. Analytical Validation Parameters Limit of Detection (	(LOD), Limit of Quantification (LOQ), Whole-Method Accuracy
and Precision for Quantitative and Semiquantitative Analytes'	s <sup>a</sup>

<sup>*a*</sup>Chemicals not determined included C5 (PFPeS) and C9 (PFNS) sulfonates. <sup>*b*</sup>Determined as the percentage of the ratio of the concentration determined by internal calibration over the concentration determined by standard addition ( $n = 6, \pm 95\%$  CI). <sup>*c*</sup>Precision was calculated as the percent relative standard deviation (% RSD) from the samples used to determine accuracy (n = 6). <sup>*d*</sup>The nominal concentration (concn) at which whole-method accuracy and precision were determined. <sup>*e*</sup>Internal standard used for internal calibration.

internal standards are provided in the Supporting Information (SI) (Table S1). Additionally, for the purpose of brevity individual analytes are referred to by their acronym (Figure 1). Perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, and fluorotelomer sulfonates will be referred to hereafter as legacy PFAS, while the fluorotelomer thioamido sulfonates, fluoro-telomer thiohydroxy ammonium, fluorotelomer sulfonamido betaines, fluorotelomer sulfamido amines, fluorotelomer betaines, perfluoroalkyl sulfonamido amines, and perfluoroalkyl sulfonamide amino carboxylates will be referred to as newly-identified PFAS (Figure 1).

**Sample Collection.** *AFFF Formulations.* AFFF formulations were collected from military bases around the United States as previously described.<sup>1</sup> Briefly, AFFF formulations were subsampled from their original product containers into 60 mL high-density polyethylene (HDPE) bottles and shipped to Oregon State University. The AFFF formulations dated from 1984 to 2011 and are from manufacturers whose AFFF formulations are qualified for use by the U.S. military.

Groundwater. Groundwater was collected from two different U.S. military bases (Sites A and B) for PFAS analysis. Groundwater sampling was conducted by third parties, and detailed sampling protocols are provided in the SI. Groundwater samples were collected in 250 mL solvent-rinsed (methanol and reagent water) HDPE bottles, placed in a cooler filled with ice, and shipped overnight to Oregon State University. In addition, groundwater collected in 1999 from Tyndall Air Force Base (TAFB), Naval Air Station Fallon (NASF), and Wurtsmith Air Force Base (WAFB) and archived at -4 °C in 125 mL HDPE bottles were reanalyzed for this study. The specific details of the archived sample collection are described elsewhere.<sup>4,7</sup>

**Sample Preparation.** *AFFF Formulations.* Six telomerbased AFFF formulations and five electrofluorination-based AFFF formulations were analyzed. Samples of AFFF formulations were prepared by diluting them between 100,000and 10 million-fold in methanol. A single electrofluorinationbased AFFF from 1993(a) was analyzed in triplicate to determine precision. A 1.5 mL aliquot of the dilute AFFF was transferred into a clean polypropylene autosampler vial (MicroSolv, Eatontown, NJ, Part # 9502S-PP-Amber) to which 1.05 ng of each isotopically labeled internal standard was added. Multiple dilutions of each sample were analyzed as needed to achieve area counts for each analyte that fell within the limits of the calibration curves.

Groundwater. To obtain a representative subsample, (see SI) groundwater in HDPE bottles was repeatedly  $(4\times)$  sonicated in a Model 75HT sonication bath (VWR, Radnor, PA) for approximately 20 s then gently mixed and inverted. Next, a 3 mL subsample was taken from approximately 3.0 to

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3.5 cm below the meniscus and delivered to a 5 mL polypropylene microtube (Argos Technologies, Elgin, IL) that contained 0.97 to 1.0 g of sodium chloride. The subsamples were then spiked with 1.05 ng of each isotopically labeled internal standard (Table 1). Then, the samples were acidified with 10  $\mu$ L of 6 N HCl and extracted with 10% (v/v) 2,2,2-trifluoroethanol in ethyl acetate, henceforth referred to as extractant. Ethyl acetate has a similar environment, health, and safety assessment as methanol,<sup>30</sup> and 2,2,2-trifluoroethanol was added to ethyl acetate in a 10% concentration to increase extraction efficiency. Each sample was extracted in triplicate by adding extractant (500  $\mu$ L for the first extraction, 370  $\mu$ L for the second extraction, and 330  $\mu$ L for the third extraction) to the sample, shaking for 45 s, allowing the phases to separate, and then transferring the supernatant to a clean 1.5 mL polypropylene vial. The total volume of extract used per sample was 1.2 mL, and the total volume collected was 1 mL. This collected extract was then brought to 1.5 mL with methanol in the same vial and analyzed without further sample preparation. Methanol was added to the extract to improve chromatography and to increase sample solvent miscibility with the initial mobile phase.

**Orthogonal HPLC MS/MS.** Chromatographic separations were performed by an Agilent 1100 series HPLC (Santa Clara, CA) that was modified to perform 900  $\mu$ L injections (Agilent part # G1363A). Additionally, the HPLC was retrofitted as described previously to eliminate contamination from instrumental sources of PFAS (e.g., solvent delivery lines).<sup>28</sup> Chromatographic separations were achieved using a 4.6 × 12.5 mm × 5  $\mu$ m Zorbax Silica (Sil) guard column that was connected in series to an Agilent 4.6 × 12.5 mm × 5  $\mu$ m Zorbax propylamine (NH<sub>2</sub>) guard column that was connected in series to a Zorbax Eclipse Plus C18 4.6 × 50 mm × 1.8  $\mu$ m analytical column.

The composition of the mobile phases was 10 mM ammonium acetate in HPLC grade water (A) and 10 mM ammonium acetate in HPLC grade methanol (B). Analytes were separated and eluted using a convex gradient program (Figure S1). The autosampler valve was programmed to direct the mobile phase flow past the flow-path of the injection assembly (needle loop + needle + injection valve) at 2.4 min after sample injection to reduce gradient dwell time. By 2.4 min, the sample had been completely transferred from the needle loop and onto the columns. Column eluate was diverted away from the mass spectrometer for the first 7 min after injection in order to wash early eluting matrix components and inorganic salts to waste. This step is analogous to the wash step used for SPE.<sup>19</sup> After 7 min, column eluate was directed to the mass spectrometer.

Analytes were detected by a TQ Detector (Waters Corporation, Milford, MA) triple quadrupole mass spectrometer that was operated in multiple-reaction monitoring (MRM) mode and controlled by MassLynx (Version 4.1). The HPLC-MS/MS system was interfaced with an electrospray ionization source. Two transitions were acquired for each analyte, except for PFBA and PFPeA, (Table S2) and analytes were detected by positive or negative polarity within a single acquisition. Mass spectrometer parameters were as follows: a capillary potential of  $\pm 2800$  V; an extractor potential of  $\pm 2$  V; a source and desolvation temperature of 150 and 450 °C, respectively; and a desolvation gas and cone gas flow of 1100 L/h and 75 L/h, respectively.

Compound-dependent acquisition parameters (e.g., cone voltage and collision energy) (Table S2) were optimized by infusing analytical standards or reference materials (see below) diluted in methanol to yield analyte concentrations between 0.1 and 1 mg/L. For analytes without analytical standards or reference materials, compound-dependent mass spectrometer parameters were optimized by infusing dilute (10–20,000-fold in methanol) AFFF formulations that contained those analytes<sup>1</sup> (Table S2).

Analyte Identification and Quantification. Due to the differences in the availability and the purity of standards, analytes and the confidence about analyte concentrations in samples were classified into three groups. Analytes for which authentic analytical standards were commercially available (perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, and fluorotelomer sulfonates) and their data were classified as quantitative (Qn) (Figure 1). Semiquantitative (Sq) data were generated for analytes that were donated to Oregon State University (see the SI) as reference materials and these included 6:2 FtTAoS, 6:2 FtTHN<sup>+</sup>, 6:2 FtSaB, 6:2 FtSaAm, and the fluorotelomer betaines (Figure 1). The concentrations of Sq analytes in reference materials were determined from manufacturer MSDS<sup>31-33</sup> and patent data. The analytes C4 and C8 fluorotelomer thioamido sulfonates (FtTAoS), C8, C10, and C12 fluorotelomer sulfonamide betaines (FtSaB), C8 fluorotelomer sulfonamide amine (8:2 FtSaAm), C4-C8 perfluoroalkyl sulfonamide amines (PFSaAm), C4-C8 perfluoroalkyl sulfonamide amino carboxylates (PFSaAmA), C5 and C9 perfluoroalkyl sulfonates (Figure 1) and their data were classified as qualitative (Ql) because neither authentic analytical standards nor reference materials were available for these analytes.

Calibration standards were prepared by first extracting reagent water (B&J Brand, Morristown, NJ), as described above for groundwater, to generate a blank extract. Calibration standards for Qn and Sq analytes were then prepared in 1 mL of blank extract diluted with 500  $\mu$ L of methanol with 1.05 ng of each internal standard. Analytes were quantified using 1/xweighted internal-standard calibration. The range, number of points, and coefficient of determination  $(R^2)$ , for each calibration curve is presented in the SI (Table S3). Concentrations of Ql analytes were estimated by assuming equal molar response to a related Qn or Sq analyte (Table S3); see the SI for an example. Analyte concentrations in AFFFcontaminated groundwater can span up to 6 orders of magnitude so, when necessary, dilutions were needed so that analyte area counts fell within those of calibration curves, which spanned only 2-3 orders of magnitude (Table S3). Therefore, samples that produced analytical signals above that of the highest calibration standard were reanalyzed by subsampling 15–60  $\mu$ L of the original groundwater, diluting the subsample to 3 mL with reagent water (a 50-200-fold dilution, respectively), and then extracting the diluted subsample as described above.

For positive identification, Qn and Sq analytes were required to have retention times that varied less than  $\pm 0.25$  min of those in calibration standards. However, because calibration standards were not available for Ql analytes, Ql analytes in groundwater extracts were required to have retention times that varied less than  $\pm 0.25$  min when compared to the retention times for those analytes in dilute AFFF formulations. Additionally, the ratio of the two product ions (transitions) for each analyte (not applicable for PFBA and PFPeA) (Table S2) in groundwater extracts were required to be within 20% of those in calibration standards or in dilute AFFF formulations.

**Method Limits of Detection and Quantification.** To determine the method limits of detection (LOD), calibration standards (n = 6 to 12) for Qn and Sq analytes were prepared in blank groundwater around their estimated LODs (from preliminary experiments) and then extracted as outlined above. LODs were calculated by multiplying the 1/x-weighted regression-residual standard deviation ( $\sigma_{x/y}$ ) by 3.3, subtracting the *y*-intercept, and then dividing by the slope. This approach for determining LODs is similar to that recommended by Vial and Jardy<sup>34</sup> and is approved by the International Conference on Harmonization (ICH) for the validation of analytical procedures.<sup>35</sup> The limit of quantification (LOQ) was then defined as 3.3 times the LOD.

Whole-Method Accuracy, Precision, and Absolute Extraction Efficiency. To determine whole-method accuracy, concentrations determined by internal standard calibration were compared to those obtained by standard addition. First, replicate (n = 11) aliquots (3 mL) of groundwater with no detectable analyte signal were spiked with analytes (Ql and Sq) to give final concentrations that were within 10-fold of their LOQs (Table 1) along with 1.05 ng of each internal standard. Six of the spiked aliquots were then extracted as described above, and analytes were quantified by internal standard calibration. Within-run precision (repeatability) was calculated by taking the percent relative standard deviation (% RSD) of the six replicates. Next, the remaining five aliquots were spiked to give 0.5-, 0.75-, 1.0-, 1.5-, and 2.0-fold additions above the concentration of the first six aliquots, and standard-addition analysis was performed using the 11 aliquoted samples (6 data points at the Y intercept).

Accuracy (%) was defined as the analyte concentration in spiked groundwater as determined by internal-standard calibration divided by the analyte concentration determined by standard addition, multiplied by 100. For analytes without well-matched isotopically labeled internal standards, an internal standard that yielded computed concentrations closest to those obtained by standard addition was selected for use in all subsequent experiments (Table 1). The uncertainty about the whole-method accuracy was compounded from each measurement and reported as  $\pm 95\%$  CI. In addition, the absolute extraction efficiency was determined using procedure outlined in the SI.

## RESULTS AND DISCUSSION

**Micro LLE and Orthogonal HPLC.** The extraction method required only 3 mL of groundwater per sample and a total of 1.7 mL of organic solvent for extraction (1.2 mL extractant + 0.5 mL methanol). The solid waste generated (two polypropylene vials and pipet tips) and the organic solvent used for extraction was less than that required by other SPEand LLE-based HPLC-MS/MS methods.<sup>12,25,36–39</sup> Additionally, the direct analysis of dilute AFFF formulations and groundwater extracts eliminated the need for sample blow down and solvent exchange.

The HPLC method outlined above resulted in well-resolved and reproducible chromatography for zwitterionic, cationic, and anionic analytes (Figure 2). Analytes were concentrated by cation and anion exchange onto the Sil and  $NH_2$  guard columns, respectively, during sample loading. Without the use of the Sil and  $NH_2$  guard columns, analytes eluted at the front of the chromatogram (Figure S2) and were poorly resolved



Figure 2. Typical chromatograms of zwitterionic, cationic, and anionic analytes detected in groundwater (unspiked) from military bases.

because the injected sample is highly elutropic on a C18 analytical column. Perfluorooctanesulfonamide (FOSA), which was un-ionized in the groundwater extract, was not retained by the chromatographic system. However, FOSA was not found in AFFF formulations<sup>1</sup> so it was not included in the analyte list nor was the method optimized for its analysis. However, ongoing research indicates that un-ionized PFAS species can be determined by orthogonal chromatography through minor modifications of the chromatographic system.

Elution of analytes from the Si and NH<sub>2</sub> phases was facilitated by ammonium acetate (10 mM) because methanol and water alone did not elute the analytes. Analytes were eluted from the Si and NH<sub>2</sub> guard columns under high aqueous mobile phase conditions (< 25%B) and were refocused at the head of the C18 analytical column before they were subsequently separated by reverse-phased mechanisms. No extra equipment (e.g., extra switching valves or stand-alone high-pressure pumps) was needed to perform the orthogonal HPLC described.

Applications describing the use of orthogonal HPLC with columns placed in series are limited to a few bioanalytical analyses<sup>40-43</sup> and for determining naturally occurring carboxylic acids in plants.<sup>44</sup> To the authors' best knowledge, coupling of large volume injection of organic extracts with orthogonal HPLC has not been previously described.

Limit of Detection and Quantification. The LOD for Qn and Sq analytes was between 0.71 ng/L and 67 ng/L with a median LOD of 1.7 ng/L (Table 1). Because this is the first method validation for newly-identified PFAS a comparison to existing LODs could not be made. However, the LODs presented here are similar to those reported elsewhere for the SPE-based analyses for legacy PFAS in groundwater<sup>39,45</sup> and lower than those of aqueous LVI-based methods.<sup>9,36</sup> Jin et al. were able to achieve detection limits for PFOA and PFOS in groundwater of 0.03 ng/L and 0.05 ng/L, respectively, but the SPE-based approach required 1000 mL of groundwater and 16.5 mL of solvent.<sup>38</sup> A LLE-based method gave an average of

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3-fold lower LODs for PFAS in wastewater; however, it required the use of 900 mL of sample, 120 mL of organic solvent, and evaporation and solvent exchange steps.<sup>25</sup>

Whole-Method Accuracy, Precision, and Absolute Extraction Efficiency. Whole-method accuracy ranged between 96% and 106% for Qn analytes and between 78% and 144% for Sq analytes (Table 1). For Qn analytes, whole-method precision as indicated by % RSD ranged between 2.8% and 12%, while precision ranged between 5.6% and 15% for Sq analytes (Table 1). While comparisons cannot be made for the newly-identified PFAS, the accuracy and precision of the legacy PFAS reported here is similar<sup>9,38</sup> to or improved<sup>36</sup> compared to other methods for PFAS analysis in groundwater. Finally, the absolute extraction efficiency of the micro-LLE procedure was between 87% and 99% for Qn and Sq analytes (Table S4). A comparison of absolute extraction efficiencies to other methods is presented in the SI.

Method Demonstration: AFFF Formulations and Groundwater from Military Sites. Fluorotelomer PFAS. Fluorotelomer thioamidosulfonates (4:2, 6:2, and 8:2) were found in three (Ansul, Chemguard, Angus) of the six fluorotelomer-based AFFF formulations that are approved for military use (Table S5). Of the three homologues, the 6:2 FtTAoS was the dominant form present in AFFF formulations (Table S5). Ansul was the only provider of fluorotelomer-based AFFF formulations qualified for military use during the time the fire-training areas reported in this study were in operation (1940-early 1990s) (Tables 2-4).<sup>1</sup> Fluorotelomer sulfonates were detected at low levels only in AFFF formulations that contained fluorotelomer sulfonamido betaines (e.g., National Foam and Fire Service Plus) (Table S5). No perfluoroalkyl sulfonates or carboxylates were found in fluorotelomer-based AFFF formulations (Table S5).

At three out of five military sites (Site A, Site B, and Tyndall AFB) fluorotelomer thioamidosulfonates were found in groundwater at concentrations lower than those of fluorotelomer sulfonates and other legacy PFAS (Tables 2 and 3). 6:2 FtTAoS was present at concentrations up to 6900 ng/L at Site A (Table 2). Although Schultz et al. analyzed for 6:2 FtTAoS in the samples from TAFB, it was not detected.<sup>9</sup> However, the detection limits for the present study are 2 orders of magnitude lower than those by Schultz et al for legacy PFAS.<sup>9</sup>

Ratios of the 4:2, 6:2, and 8:2 FtTAoS homologues in groundwater varied between sites (Tables 2–4) and differed from those of the Ansul AFFF formulation tested (Table S5). Ansul AFFF formulations that predate 2005 may have had FtTAoS homologue ratios that vary from the one tested. Additionally, partitioning to aquifer sediments may impact relative groundwater concentrations; however, no partitioning data are yet available for the FtTAoS class of PFAS.

In contrast, fluorotelomer sulfonate concentrations in groundwater were high compared to those of the fluorotelomer thioamidosulfonates; 6:2 FtS occurred at concentrations up 220,000 ng/L at Site A (Table 2). Previously, Schultz reported 6:2 FtS at 14,600,000 ng/L in TAFB.<sup>9</sup> Previous analysis of groundwater samples from NASF did not reveal any fluorotelomer sulfonate contamination,<sup>9</sup> which is consistent with the absence of other newly-identified telomer-based PFAS in groundwater at this site (Table 4). Because the fluorotelomers sulfonates are not found in Ansul AFFF (Table S5), it is hypothesized that they form as products of fluorotelomer thioamidosulfonate degredation in groundwater. Laboratory studies are underway to test this hypothesis and to

Table 2. Concentrations of the Per and Polyfluorinated Alkyl Substances Detected in Groundwater at Site A  $(1942-1990)^a$ 

	Sample 1 (ng/L)	Sample 2 (ng/L)	Sample 3 (ng/L)	Sample 4 (ng/L)
4:2 FtTAoS <sup>b</sup>	<lod< td=""><td><lod< td=""><td>210</td><td>490</td></lod<></td></lod<>	<lod< td=""><td>210</td><td>490</td></lod<>	210	490
6:2 FtTAoS	<lod< td=""><td><lod< td=""><td>6900</td><td>86</td></lod<></td></lod<>	<lod< td=""><td>6900</td><td>86</td></lod<>	6900	86
8:2 FtTAoS	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
4:2 FtS	370	6500	7500	11,000
6:2 FtS	8900	36,000	220,000	93,000
8:2 FtS	120	58	370	180
PFBSaAm <sup>c</sup>	$2.8^{d}$	54	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFPeSaAm <sup>c</sup>	$4.4^{d}$	8.7	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFHxSaAm <sup>c</sup>	45	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFFOSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFBSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFPeSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFHxSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFFOSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFBS	7100	24,000	43,000	150,000
PFHxS	36,000	100,000	240,000	360,000
PFHpS	1100	3700	11,000	3700
PFOS	19,000	15,000	78,000	19,000
PFDS	7	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFBA	3400	12,000	24,000	57,000
PFPeA	12,000	21,000	69,000	120,000
PFHxA	19,000	63,000	130,000	350,000
PFHpA	3300	11,000	15,000	45,000
PFOA	12,000	35,000	51,000	220,000
PFNA	130	40	220	390
PFDA	17	<lod< td=""><td>&lt;3.1</td><td>6.5</td></lod<>	<3.1	6.5
PFUdA	<lod< td=""><td><lod< td=""><td>&lt;3.1</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>&lt;3.1</td><td><lod< td=""></lod<></td></lod<>	<3.1	<lod< td=""></lod<>
PFDoA	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFTrA	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFTeA	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

<sup>*a*</sup>Of the remaining newly-identified PFAS found in fluorotelomerbased AFFF formulations (Table S5), no 6:2 FtTHN<sup>+</sup>, fluorotelomer sulfonamido betaines, fluorotelomer sulfonamido amines, nor fluorotelomer betaines were detected, and the C5 (PFPeS) and C9 (PFNS) sulfonates and C7 (PFHpSaAm and PFHpSaAmA) were not included. <sup>*b*</sup>Calculated assuming equal molar response to 6:2 FtTAoS (see main text). <sup>*c*</sup>Calculated assuming equal molar response to PFOS (see main text). <sup>*d*</sup>Concentration above LOQ but below the lowest calibration standard.

identify other potentially persistent degradation intermediates and the conditions under which they form.

Of the remaining newly-identified PFAS found in fluorotelomer-based AFFF formulations (Table S5), no fluorotelomer thiohydroxy ammonium, fluorotelomer sulfonamido betaines, fluorotelomer sulfonamido amines, nor fluorotelomer betaines were detected in the groundwater samples analyzed for this demonstration of the analytical method (Tables 2-4). These classes of fluorotelomer-based PFAS were not in AFFF formulations approved for U.S. military use during the time that the fire-training areas at these field sites were in operation, with the exception of fluorotelomer sulfonamido betaines. Moe et al. detected fluorotelomer sulfonamido betaines, which are found in National Foam AFFF formulations, and their degradation products in soils near a European airport firetraining facility.<sup>10</sup> The potential for detecting newly-identified PFAS is likely controlled by the AFFF products used and their time of application. The study by Moe et al.<sup>10</sup> indicates the

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Table 3. Concentrations of the Per and Pe	lyfluorinated Alk	yl Substances Detected in	Groundwater at Site B (	$(1950 - 1993)^a$
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	Sample 1 (ng/L)	Sample 2 (ng/L)	Sample 3 (ng/L)	Sample 4 (ng/L)	Sample 5 (ng/L)	Sample 6 (ng/L)	Sample 7 (ng/L)	Sample 8 (ng/L)
4:2 FtTAoS <sup>b</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
6:2 FtTAoS	<lod< td=""><td><lod< td=""><td><lod< td=""><td>68</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>68</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>68</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	68	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
8:2 FtTAoS	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
4:2 FtS	<lod< td=""><td>5.2</td><td><lod< td=""><td>44</td><td><lod< td=""><td>100</td><td>160</td><td>99</td></lod<></td></lod<></td></lod<>	5.2	<lod< td=""><td>44</td><td><lod< td=""><td>100</td><td>160</td><td>99</td></lod<></td></lod<>	44	<lod< td=""><td>100</td><td>160</td><td>99</td></lod<>	100	160	99
6:2 FtS	<lod< td=""><td>1400</td><td>210</td><td>860</td><td>3500</td><td>15,000</td><td>3900</td><td>37,000</td></lod<>	1400	210	860	3500	15,000	3900	37,000
8:2 FtS	<lod< td=""><td>660</td><td>660</td><td>66</td><td>1200</td><td>2300</td><td>620</td><td>1400</td></lod<>	660	660	66	1200	2300	620	1400
PFBSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFPeSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFHxSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFFOSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFBSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><math>4.1^{d}</math></td><td><lod< td=""></lod<></td></lod<>	$4.1^{d}$	<lod< td=""></lod<>
PFPeSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
$PFHxSaAmA^{c}$	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>8.0</td><td><lod< td=""></lod<></td></lod<>	8.0	<lod< td=""></lod<>
PFFOSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFBS	12	1500	640	7300	2900	2800	17,000	24,000
PFHxS	81	11,000	10,000	9800	18,000	17,000	74,000	170,000
PFHpS	<lod< td=""><td>580</td><td>410</td><td>120</td><td>920</td><td>490</td><td>1700</td><td>4100</td></lod<>	580	410	120	920	490	1700	4100
PFOS	88	15,000	23,000	4000	29,000	20,000	44,000	65,000
PFDS	<lod< td=""><td>33</td><td><lod< td=""><td><lod< td=""><td>16</td><td><lod< td=""><td><lod< td=""><td>26</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	33	<lod< td=""><td><lod< td=""><td>16</td><td><lod< td=""><td><lod< td=""><td>26</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>16</td><td><lod< td=""><td><lod< td=""><td>26</td></lod<></td></lod<></td></lod<>	16	<lod< td=""><td><lod< td=""><td>26</td></lod<></td></lod<>	<lod< td=""><td>26</td></lod<>	26
PFBA	8.5	1100	980	3000	2000	1700	5900	13,000
PFPeA	$4.9^{d}$	2000	1800	8100	3300	6000	15,000	35,000
PFHxA	<4.7	5400	2400	12,000	11,000	7700	29,000	99,000
PFHpA	<6.0	480	1600	860	670	1200	1300	7200
PFOA	8.6	890	2500	840	1700	3700	3000	57,000
PFNA	<lod< td=""><td>56</td><td>680</td><td>15</td><td>110</td><td>110</td><td>130</td><td>400</td></lod<>	56	680	15	110	110	130	400
PFDA	<3.1	8	19	<3.1	12	10	7.6	17
PFUdA	<lod< td=""><td><math>3.7^{d}</math></td><td>5.2</td><td>&lt;3.1</td><td><math>4.2^{d}</math></td><td>&lt;3.1</td><td>&lt;3.1</td><td><math>4.9^{d}</math></td></lod<>	$3.7^{d}$	5.2	<3.1	$4.2^{d}$	<3.1	<3.1	$4.9^{d}$
PFDoA	<lod< td=""><td>&lt;3.4</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>&lt;3.4</td><td><lod< td=""><td>&lt;3.4</td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<3.4	<lod< td=""><td><lod< td=""><td><lod< td=""><td>&lt;3.4</td><td><lod< td=""><td>&lt;3.4</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>&lt;3.4</td><td><lod< td=""><td>&lt;3.4</td></lod<></td></lod<></td></lod<>	<lod< td=""><td>&lt;3.4</td><td><lod< td=""><td>&lt;3.4</td></lod<></td></lod<>	<3.4	<lod< td=""><td>&lt;3.4</td></lod<>	<3.4
PFTrA	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>PFTrA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>PFTrA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>PFTrA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>PFTrA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	PFTrA	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
PFTeA	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>PFTeA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>PFTeA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>PFTeA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>PFTeA</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	PFTeA	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>

<sup>a</sup>Of the remaining newly-identified PFAS found in fluorotelomer-based AFFF formulations (Table S5), no 6:2 FtTHN<sup>+</sup>, fluorotelomer sulfonamido betaines, fluorotelomer sulfonamido amines, nor fluorotelomer betaines were detected, and the C5 (PFPeS) and C9 (PFNS) sulfonates and C7 (PFHpSaAm and PFHpSaAmA) were not included. <sup>b</sup>Calculated assuming equal molar response to 6:2 FtTAOS (see main text). <sup>c</sup>Calculated assuming equal molar response to PFOS (see main text). <sup>d</sup>Concentration above LOQ but below the lowest calibration standard.

# Table 4. Concentrations of the Newly-Identified Perfluorinated Chemicals Detected in Archived Samples Taken from Wurtsmith Air Force Base (WAFB), Naval Air Station Fallon (NASF), and Tyndall Air Force Base (TAFB)<sup>*a*,*e*</sup>

	years of operation							
		1980-1	1992	1950	1952-1993			
	TAFB TY22FtA (ng/L)	TAFB T 11-2 (ng/L)	TAFB PW-7 (ng/L)	TAFB PW-10 (ng/L)	NASF MW 16 (ng/L)	NASF MW 51-U (ng/L)	WAFB FT-3 (ng/L)	
4:2 FtTAoS <sup>b</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
6:2 FtTAoS	<lod< td=""><td><lod< td=""><td><lod< td=""><td>8.8</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>8.8</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>8.8</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	8.8	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
8:2 FtTAoS	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
PFBSaAm <sup>c</sup>	$4.1^{d}$	11	<lod< td=""><td>720</td><td><lod< td=""><td>550</td><td>26</td></lod<></td></lod<>	720	<lod< td=""><td>550</td><td>26</td></lod<>	550	26	
PFPeSaAm <sup>c</sup>	$2.8^d$	7.8	5.1	190	<lod< td=""><td>61</td><td>79</td></lod<>	61	79	
PFHxSaAm <sup>c</sup>	5.7	8.3	6.3	260	<lod< td=""><td>260</td><td>36</td></lod<>	260	36	
PFFOSaAm <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
PFBSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td>62</td><td>660</td><td><lod< td=""><td>9.7</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>62</td><td>660</td><td><lod< td=""><td>9.7</td><td><lod< td=""></lod<></td></lod<></td></lod<>	62	660	<lod< td=""><td>9.7</td><td><lod< td=""></lod<></td></lod<>	9.7	<lod< td=""></lod<>	
PFPeSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td>7.9</td><td>610</td><td><lod< td=""><td>5.8</td><td>&lt;2.7</td></lod<></td></lod<></td></lod<>	<lod< td=""><td>7.9</td><td>610</td><td><lod< td=""><td>5.8</td><td>&lt;2.7</td></lod<></td></lod<>	7.9	610	<lod< td=""><td>5.8</td><td>&lt;2.7</td></lod<>	5.8	<2.7	
PFHxSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td>10</td><td>590</td><td><lod< td=""><td>38</td><td>&lt;2.7</td></lod<></td></lod<></td></lod<>	<lod< td=""><td>10</td><td>590</td><td><lod< td=""><td>38</td><td>&lt;2.7</td></lod<></td></lod<>	10	590	<lod< td=""><td>38</td><td>&lt;2.7</td></lod<>	38	<2.7	
PFFOSaAmA <sup>c</sup>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	

<sup>*a*</sup>Of the remaining newly-identified PFAS found in fluorotelomer-based AFFF formulations (Table S5), no 6:2 FtTHN<sup>+</sup>, fluorotelomer sulfonamido betaines, fluorotelomer sulfonamido amines, nor fluorotelomer betaines were detected and the C5 (PFPeS) and C9 (PFNS) sulfonates and C7 (PFHpSaAm and PFHpSaAmA) were not included; <sup>*b*</sup>Calculated assuming equal molar response to 6:2 FtTAOS (see main text); <sup>*c*</sup>Calculated assuming equal molar response to PFOS (see main text); <sup>*d*</sup>Concentration above LOQ but below the lowest calibration standard <sup>*c*</sup>See Schultz et al. for sample descriptions (e.g. FT-3) and data on fluorotelomer sulfonates, perfluoroalkyl sulfonates, and perfluoroalkyl carboxylates.<sup>4</sup>

potential for detecting a wider array of the newly-identified PFAS at civilian (e.g., airports and refineries) and military sites inside and outside the US.

Prefluorinated PFAS. Only 3M only sold AFFF formulations to the military that were formulated with electrofluorinationderived PFAS. The only newly-identified PFAS found in 3M AFFFs were cationic perfluoroalkyl sulfonamidoamines ( $C_4-C_8$ PFSaAm) and zwitterionic perfluorosulfonamide amino carboxylate ( $C_4-C_8$  PFSaAmA). These classes of PFAS are in greater abundance in the AFFF formulations manufactured in and after 1993 than in the one manufactured in 1989 (Table S6); no 3M AFFF formulations manufactured before 1988 were available for analysis at the time of this study. Within the perfluoroalkyl sulfonamidoamine and sulfonamide amino carboxylate classes,  $C_6$  is the most abundant homologue in AFFF (Table S6).

PFOS was present at higher levels than any other PFAS in electrofluorination-based AFFF formulations and occurred at levels 8–12 times greater than that of PFHxS (Table S6). Lower quantities of perfluoroalkyl carboxylates were found relative to the perfluoroalkyl sulfonates in the electro-fluorination-based AFFF formulations.

Cationic perfluoroalkyl sulfonamidoamines  $(C_4-C_6$  PFSaAm) were present in groundwater at low concentrations (<LOD to 720 ng/L) at Site A, TAFB, NASF, and WAFB (Tables 2 and 4). Zwitterionic perfluoroalkyl sulfonamide amino carboxylates were not detected at Site A (Table 2) and occurred only at trace levels at Site B, TAFB, NASF, and WAFB (Tables 3 and 4). The low concentrations or absence of these PFASs in groundwater may be due to their degradation and/or interactions with sediment. To date, no data are available on the partitioning behavior or degradation of these cationic and zwitterionic PFAS.

By comparison, the legacy PFAS including perfluoroalkyl sulfonates and perfluoroalkyl carboxylates occur at much higher concentrations in groundwater compared to the newlyidentified PFAS (Tables 2 and 3). Data are not shown for these legacy PFAS for the TAFB, NASF, and WAFB sites because they were found at concentrations similar to those that appear in Schultz et al.<sup>9</sup> There are no apparent patterns in the ratios of perfluoroalkyl sulfonates to carboxylates (Tables 2 and 3) for the limited number of samples analyzed, and this may reflect variations between sites as well as variations in the actual composition of the 3M AFFF formulations sold to the military over time.

In groundwater, PFHxS occurs at concentrations greater than (Site A) or similar to (Site B) those of PFOS, while in all 3M AFFF formulations tested, the abundance of of PFHxS is lower than PFOS (Table S6). The relative abundance of PFHxS observed in groundwater may arise from the degradation of the newly-identified telomer- and electrofluorination-based PFAS for which the  $C_6$  is the most abundant homolog (Table S5 and S6).

# ENVIRONMENTAL IMPLICATIONS

The current analytical method is useful for determining a wide range of zwitterionic, cationic, and anionic PFASs that exist in AFFF formulations and in AFFF-contaminated groundwaters. The same analytical methodology may potentially be used for the analysis of soil and sediment in field and laboratory studies to determine the occurrence, fate, and transport of the newlyidentified PFAS as well as their response to treatment strategies. The concentrations of PFOS and PFOA found in groundwater by this study are orders of magnitude greater than the U.S. Environmental Protection Agency provisional health advisory levels for PFOS (200 ng/L) and PFOA (400 ng/ L).<sup>46</sup> The profiles of the PFAS detected in groundwater differ from those in AFFF formulations, which may indicate the potential transformation to persistent perfluoroalkyl sulfonates, perfluoroalkyl carboxylates, and fluorotelomer sulfonates. Of the newly-identified PFAS, only the fluorotelomer thioamidosulfonates and the newly-identified 3M classes were found in groundwater, which may be related to the limited number of AFFF formulations approved for use (3M, Ansul, National Foam) during the time that fire-training activities occurred at the sites tested.

### ASSOCIATED CONTENT

### Supporting Information

Text, Tables S1–S7, and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors would like to thank all of the people who provided samples and site history; this publication would not have been possible without their assistance. We acknowledge our collaborators Christopher Higgins, Jennifer Sepulvado, Kaneen Christensen, and Charles Schaefer for a collection of samples from Site A as part of their AFCEE Project 689 and information provided at that site. Additionally, we would like to thank David Sedlak, Erika Houtz, Susan Baez-Cazull, and Jeffery Dale. Thank you to the Fire-Fighting Foam Coalition (FFFC) who generously donated standards. We are grateful to Mindy Berger for her editorial assistance. We would like to acknowledge Monica Best for her help in processing samples. Finally, we would like to recognize our funding source, the Strategic Environmental Research and Development Program (SERDP) project 548 ER-2128.

### REFERENCES

(1) Place, B. J.; Field, J. A. Identification of novel fluorochemicals in aqueous film-forming foams (afff) used by the US military. *Environ. Sci. Technol.* **2012**, *46*, 7120–7127.

(2) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2005**, *40*, 32–44.

(3) Moody, C. A.; Field, J. A. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environ. Sci. Technol.* **2000**, *34*, 3864–3870.

(4) Moody, C. A.; Field, J. A. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.* **1999**, 33, 2800–2806.

(5) Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* **2011**, *13*, 20–31.

(6) Kärrman, A.; Elgh-Dalgren, K.; Lafossas, C.; Møskeland, T. Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (afff) contamination. *Environ. Chem.* 2011, *8*, 372–380.

(7) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at wurtsmith air force base, michigan, USA. J. Environ. Monit. 2003, 5, 341-345.

(8) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Determination of perfluorinated surfactants in surface water samples by two independent analytical techniques: liquid chromatography/tandem mass spectrometry and 19f nmr. Anal. Chem. 2001, 73, 2200-2206.

(9) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/ MS. Environ. Sci. Technol. 2004, 38, 1828-1835.

(10) Moe, M. K.; Huber, S.; Svenson, J.; Hagenaars, A.; Pabon, M.; Trümper, M.; Berger, U.; Knapen, D.; Herzke, D. The structure of the fire fighting foam surfactant forafac1157 and its biological and photolytic transformation products. Chemosphere 2012, 89, 869-875.

(11) de Voogt, P.; Sáez, M. Analytical chemistry of perfluoroalkylated substances. TrAC, Trends Anal. Chem. 2006, 25, 326-342.

(12) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. Analysis of perfluorinated acids at parts-perquadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. Environ. Sci. Technol. 2004, 38, 5522-5528.

(13) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environ. Sci. Technol. 2005, 39, 3946-3956.

(14) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. A. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into etobicoke creek. Environ. Sci. Technol. 2001, 36, 545-551.

(15) Taniyasu, S.; Kannan, K.; So, M. K.; Gulkowska, A.; Sinclair, E.; Okazawa, T.; Yamashita, N. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. J. Chromatogr., A 2005, 1093, 89-97.

(16) Taniyasu, S.; Kannan, K.; Yeung, L. W. Y.; Kwok, K. Y.; Lam, P. K. S.; Yamashita, N. Analysis of trifluoroacetic acid and other shortchain perfluorinated acids (c2-c4) in precipitation by liquid chromatography-tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (c5-c18). Anal. Chim. Acta 2008, 619, 221-230.

(17) Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorochemicals in municipal landfill leachates. Chemosphere 2011, 82, 1380-1386.

(18) Poole, C. F.; Gunatilleka, A. D.; Sethuraman, R. Contributions of theory to method development in solid-phase extraction. J. Chromatogr., A 2000, 885, 17-39.

(19) Busetti, F.; Backe, W. J.; Bendixen, N.; Maier, U.; Place, B.; Giger, W.; Field, J. A. Trace analysis of environmental matrices by large-volume injection and liquid chromatography-mass spectrometry. Anal. Bioanal. Chem. 2012, 402, 175-186.

(20) Backe, W. J.; Ort, C.; Brewer, A. J.; Field, J. A. Analysis of androgenic steroids in environmental waters by large-volume injection liquid chromatography tandem mass spectrometry. Anal. Chem. 2011, 83, 2622-2630.

(21) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry - characterization of municipal wastewaters. Environ. Sci. Technol. 2006, 40, 289-295.

(22) Ju, X.; Jin, Y.; Sasaki, K.; Saito, N. Perfluorinated surfactants in surface, subsurface water and microlayer from dalian coastal waters in china. Environ. Sci. Technol. 2008, 42, 3538-3542.

(23) Holm, A.; Wilson, S. R.; Molander, P.; Lundanes, E.; Greibrokk, T. Determination of perfluorooctane sulfonate and perfluorooctanoic acid in human plasma by large volume injection capillary column switching liquid chromatography coupled to electrospray ionization mass spectrometry. J. Sep. Sci. 2004, 27, 1071-1079.

(24) López-Fontán, J. L.; Sarmiento, F.; Schulz, P. C. The aggregation of sodium perfluorooctanoate in water. Colloid Polym. Sci. 2005, 283, 862-871.

(25) González-Barreiro, C.; Martínez-Carballo, E.; Sitka, A.; Scharf, S.; Gans, O. Method optimization for determination of selected perfluorinated alkylated substances in water samples. Anal. Bioanal. Chem. 2006, 386, 2123-2132.

(26) Chiron, S.; Fernandez Alba, A.; Barcelo, D. Comparison of online solid-phase disk extraction to liquid-liquid extraction for monitoring selected pesticides in environmental waters. Environ. Sci. Technol. 1993, 27, 2352-2359.

(27) Haller, M. Y.; Müller, S. R.; McArdell, C. S.; Alder, A. C.; Suter, M. J. F. Quantification of veterinary antibiotics (sulfonamides and trimethoprim) in animal manure by liquid chromatography-mass spectrometry. J. Chromatogr., A 2002, 952, 111-120.

(28) Backe, W. J.; Field, J. A. Is spe necessary for environmental analysis? A quantitative comparison of matrix effects from largevolume injection and solid-phase extraction based methods. Environ. Sci. Technol. 2012, 46, 6750-6758.

(29) Chiaia, A. C.; Banta-Green, C.; Field, J. Eliminating solid phase extraction with large-volume injection LC/MS/MS: Analysis of illicit and legal drugs and human urine indicators in us wastewaters. Environ. Sci. Technol. 2008, 42, 8841-8848.

(30) Capello, C.; Fischer, U.; Hungerbuhler, K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. Green Chem. 2007, 9, 927-934.

(31) DuPont Capstone 1157: Material safty data sheet 2012.

(32) Chemguard Inc Chemguard s-106a: Material saftey data sheet 2011.

(33) Chemguard Inc Chemguard s-103a: Material safty data sheet. 2011.

(34) Vial, J.; Jardy, A. Experimental comparison of the different approaches to estimate lod and loq of an HPLC method. Anal. Chem. 1999, 71, 2672-2677.

(35) International Conference On Harmonisation Validation of analytical procedures: Text and methodology q2(r1). 2005.

(36) Plumlee, M. H.; Larabee, J.; Reinhard, M. Perfluorochemicals in water reuse. Chemosphere 2008, 72, 1541-1547.

(37) Ma, R.; Shih, K. Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong. Environ. Pollut. 2010, 158, 1354-1362

(38) Jin, Y. H.; Liu, W.; Sato, I.; Nakayama, S. F.; Sasaki, K.; Saito, N.; Tsuda, S. Pfos and pfoa in environmental and tap water in china. Chemosphere 2009, 77, 605-611.

(39) Murakami, M.; Kuroda, K.; Sato, N.; Fukushi, T.; Takizawa, S.; Takada, H. Groundwater pollution by perfluorinated surfactants in tokyo. Environ. Sci. Technol. 2009, 43, 3480-3486.

(40) Benjamin, E. J.; Firestone, B. A.; Schneider, J. A. A dual-column HPLC method for the simultaneous determination of dhpg (9-[(1,3dihydroxy-2-propoxy)methyl]guanine) and its mono and diesters in biological samples. J. Chromatogr. Sci. 1985, 23, 168-170.

(41) Buchanan, D. N.; Thoene, J. G. Dual-column high-performance liquid chromatographic urinary organic acid profiling. Anal. Biochem. 1982, 124, 108-116.

(42) Herbert, B. H.; Drake, S.; Nelson, J. A. A dual-column HPLC method for the simultaneous measurement of 6-thioguanine and adenine in rna or DNA. J. Liq. Chromatogr. 1982, 5, 2095-2110.

(43) Link, A. J.; Eng, J.; Schieltz, D. M.; Carmack, E.; Mize, G. J.; Morris, D. R.; Garvik, B. M.; Yates, J. R. Direct analysis of protein complexes using mass spectrometry. Nat. Biotechnol. 1999, 17, 676-682.

(44) Touraine, B.; Astruc, S. Purification and dual-column HPLC determination of carboxylic acids in tissues, phloem and xylem saps of soybean plants. Chromatographia 1990, 30, 388-392.

(45) Enevoldsen, R.; Juhler, R. Perfluorinated compounds (pfcs) in groundwater and aqueous soil extracts: Using inline spe-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 2010, 398, 1161-1172.

(46) U.S. Environmental Protection Agency Emerging contaminants -perfluorooctane sulfonate (pfos) and perfluorooctanoic acid (pfoa) fact sheet; Washington, DC, May, 2012; p 6.

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