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Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS

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Aqueous film-forming foams (AFFF) are complex mixtures containing fluorocarbon- and hydrocarbon-based surfactants that are used to fight hydrocarbon-fueled fires. The military is the largest consumer of AFFF in the United States, and fire-training activities conducted at military bases have led to groundwater contamination by unspent fuels and AFFF chemicals. A direct-injection, liquid-chromatography tandem mass spectrometry (LC MS/MS) method was developed to quantify a suite of fluorotelomer sulfonate surfactants in groundwater collected from military bases where fire-training activities were conducted. The 4:2, 6:2, and 8:2 fluorotelomer sulfonates were detected and quantified in groundwater from two of the three military bases. The total fluorotelomer sulfonate concentrations observed at Wurtsmith AFB, MI, and Tyndall AFB, FL, ranged respectively from below quantitation (≤0.60) to 182 μg/L and from 1100 to 14 600 μg/L. Analyses of a fluorotelomer-based AFFF concentrate by negative ion fast atom bombardment/mass spectrometry and LC MS/MS analyses indicate that the AFFF concentrate contains only a small amount of fluorotelomer sulfonates and that fluoroalkylthioamido sulfonates are the main anionic fluorosurfactant in the mixtures. More research is needed to determine the fate of fluoroalkylthioamido sulfonates in the environment.

Introduction

Environmental concern over fluorinated alkyl surfactants is emerging due to their occurrence in humans and wildlife and their bioaccumulative, nondegradative, and toxic properties (*1*−*4*). Fluorinated alkyl surfactants as well as hydrocarbon surfactants are used as "active ingredients" in aqueous film-forming foams (AFFFs), which are used to fight hydrocarbon-fueled fires. The fluorinated alkyl substances present in AFFF lower the surface tension (15−20 dyn/cm), thus smothering the flames, preventing air from reaching flammable materials, and therefore, suppressing re-ignition of the fire (*5*). Formulations of AFFF contain mixtures of fluorosurfactants produced by either electrochemical fluorination or fluorotelomerization as well as hydrocarbon surfactants, cosolvents, and solvents (*6*). Although AFFFs compose only a small percent of the total fluorosurfactant production, repeated applications of AFFF during fire-training activities conducted at military bases has led to groundwater contamination by AFFF chemicals, unspent fuels, and solvents. AFFFs have been commercially available for fire-fighting applications since their development by the United States Navy and 3M Company in the mid-1960s**.** Up to 1982, the 3M Company, an electrochemical fluorinated-based AFFF manufacturer, was the sole supplier of AFFF to the U.S. military. From 1983 to 1988, both Ansul Incorporated and 3M were awarded military AFFF contracts. Ansul Incorporated purchased their fluorochemicals, which were fluorotelomer-based, from the former Ciba-Geigy Corporation. From 1989 to 2001, the contract was again held solely by 3M, and since 2002, the contract has gone to Kidde National Foam (*7*).

The fluorotelomerization process yields products characterized by homologous fluoroalkyl chains that are linear and contain only even numbers of fluorinated carbons. By contrast, electrochemical fluorination produces mixtures of linear and branched chains with both odd and even numbers of fluorinated carbons (*8*, *9*). In addition, the fluorotelomerization synthesis process inserts an ethyl group between the fluoroalkyl chain and the end-group that determines the compounds functionality; this ethyl moiety distinguishes fluorotelomer-based chemicals from those produced by electrochemical fluorination. In referring to fluorotelomer sulfonates, the numbers of fluorocarbons (X) and hydrocarbons (Y) are designated in a ratio X:Y. For example, the compound $F(CF_2CF_2)_3CH_2CH_2SO_3^-NH_4^+$ (1-octanesulfonic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-, ammonium salt) is referred to as 6:2 fluorotelomer sulfonate (6:2 FtS) since it has six fluorinated carbons and two hydrocarbons in the fluoroalkyl chain.

Liquid chromatography (LC) in conjunction with tandem mass spectrometry (MS/MS) was employed in various investigations to analyze perfluoroalkyl carboxylates and sulfonates in human sera (*10*), in animal tissues (*11*−*15*), and in surface water (*16*, *17*). LC MS/MS was the approach of choice for analyzing fluorosurfactants in these studies because it is sensitive and selective. To date, fluorotelomer-based surfactants have received little attention. In at least one previous study, 6:2 FtS was indicated as an internal standard (*10*). However, careful reading of this paper suggests that it was not used as an internal standard since "quantitation of the analytes was based on comparison of a single product ion peak area to the response of two standard curves" (*10*). Initial attempts to use the 6:2 FtS as an internal standard in the authors' laboratory produced confounding results because it was detected in unspiked groundwater samples (*7*, *18*−*20*).

In this paper, the development and application of a quantitative, direct-injection LC MS/MS method for identifying fluorotelomer sulfonates in groundwater is reported. To the best of our knowledge, this is the first instance in which fluorotelomer sulfonates have been observed in groundwater and the first description of a methodology for their quantitative analyses. This methodology was applied to groundwater collected from Naval Air Station (NAS) Fallon, NV; Tyndall Air Force Base (AFB), FL; and Wurtsmith AFB, MI. The concentrations of perfluoroalkyl carboxylates at NAS Fallon, Tyndall AFB, and Wurtsmith AFB were determined in previous studies (*21*, *22*). Data for perfluoroalkyl sulfonates, however, had only been obtained in these earlier investigations for Wurtsmith AFB (*22*). Therefore, to complete the data sets for all three classes of fluorosurfactants, the same method described in this paper for the fluorotelomer

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sulfonates was used to quantify the perfluoroalkyl sulfonates in samples obtained from NAS Fallon and Tyndall AFB. The concentrations of the three classes of fluorosurfactants were compared. Finally, high-resolution fast atom bombardment mass spectrometry (FAB MS) was used to examine AFFF formulations in an attempt to identify possible sources of fluorotelomer sulfonates in groundwater.

Experimental Section

Standards and Reagents. A standard of 6:2 FtS (98%) was purchased from Apollo Scientific Limited (Derbyshire, U.K.). Potassium perfluorobutane sulfonate (PFBS), potassium perfluorohexane sulfonate (PFHxS), and potassium perfluorooctane sulfonate (PFOS) standards were provided by the 3M Company (St. Paul, MN). It was determined by LC MS/MS analysis that this mixture of salts did not contain any major impurities (≤3%). The minor impurities present (of perfluorosulfonate homologues) were accounted for in the overall determination of each perfluorosulfonate concentration. The internal standard, hexafluoroglutaric acid (97%), was obtained from Acros Organics (New Jersey). Zonyl TBS was provided by the DuPont Company and was used as a reference material known to contain a mixture of fluorotelomer sulfonates; it is important to point out that Zonyl TBS is not used in AFFF formulations (*23*).

The solvents used for the LC separations were Milli-Q water (Bedford, MA) and optima grade methanol (Fisher Scientific, Pittsburgh, PA), and both were filtered with anion-exchange cartridges (BioBasix Ax cartridges, Thermo Hypersil-Keystone, Bellefonte, PA) prior to use. The aqueous phase was 2 mM ammonium acetate (98%) (Aldrich Chemical, Milwaukee, WI) buffer. The LC column rinse consisted of 10% (v/v) formic acid (97%) (Sigma-Aldrich, St. Louis, MO) in optima grade 2-propanol (Fisher Scientific, Pittsburgh, PA).

Field Sites and Sample Collection. Samples for this study were collected in 1999 from sites associated with fire-training activities at Wurtsmith AFB, Tyndall AFB, and NAS Fallon. Although the exact history of fire-training activities at each site is not known, it is known that AFFF was used at each site. The bases were in operation as follows: NAS Fallon (1950s−1993), Tyndall AFB (1980−1992), and Wurtsmith AFB (1952−1993). Unfortunately, the specific history of AFFF usage (years, formulation type, etc.) is unknown. The physical characteristics of each site and methods by which samples were collected have been detailed in previous publications describing the studies performed at these locations (*21, 22*). The groundwater samples were stored in high-density polyethylene brown bottles at 4 °C. Formalin was not used to preserve samples because it suppresses analyte signals (unpublished data); however, visual inspection did not reveal any bacterial growth in the vessels. A total of 18 groundwater samples were obtained from wells surrounding the FTA-02 fire pad at Wurtsmith AFB (Figure 1). One set of four groundwater samples, all from within 50 m of the fire-training pit, were each collected from Tyndall AFB and NAS Fallon (*21*).

Spike and Recovery. Spike and recovery experiments were performed to determine the precision and accuracy of the direct injection LC MS/MS method for fluorotelomer sulfonates and perfluoroalkyl sulfonates. Water drawn from Wurtsmith AFB background well (FT-D2 MW 2), in which no fluorotelomer sulfonates were detected, was used as blank groundwater for spike and recovery experiments (*22*). A single aliquot of blank groundwater was spiked with the 6:2 FtS standard to a final concentration of 5.0 μg/L and analyzed five times. Another aliquot of blank groundwater was spiked with authentic standards of PFBS, PFHxS, and PFOS to final concentrations each of 3.5 μg/L and then analyzed five times.

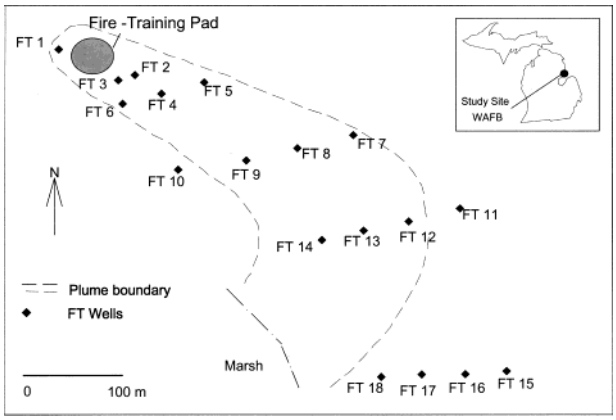

FIGURE 1. Map showing the FTA-02 groundwater plume at Wurtsmith AFB, MI.

Standard addition experiments also were performed on two different well samples from each site (Wurtsmith AFB well FT-13, Wurtsmith AFB well FT-2, Tyndall AFB well TY22FTA, and Tyndall AFB well PW-10). The levels (above the linear range) of fluorotelomer sulfonates observed in Wurtsmith AFB well FT-2 (total concentration = 88 μg/L), Tyndall AFB well TY22FTA (total concentration = 1100 μg/L), and Tyndall AFB well PW-10 (total concentration = 14 600 μg/L) were all beyond the upper limit of the linear range of calibration. Consequently, the groundwaters from these wells were diluted by factors of 10, 180, and 2250, respectively. The diluted groundwater samples were spiked to final concentration of 17.7, 12.2, and 13.0 μg/L, respectively. The undiluted Wurtsmith AFB well FT-13 was spiked to contain a final concentration of 31.7 μg/L. One standard addition experiment was performed with perfluoroalkyl sulfonates on a sample from Tyndall AFB well TY22FTA; after diluting this sample by a factor of 100, PFBS, PFHxS, and PFOS standards were spiked to achieve final concentrations of 3.6, 4.6, and 5.0 μg/L, respectively.

The method detection limit was determined as outlined by Grant et al. (*24*) where a blank groundwater sample was spiked to a concentration 1−5 times the estimated detection limit (approximately 1.00 μg/L); seven replicate aliquots of this sample were then analyzed. The method detection limit was calculated by multiplying the standard deviation of the replicate analyses by the one-sided *t*-value corresponding to 6 df and a 99% confidence level. The quantitation limit was defined as the concentration needed to produce a signal-to-noise of 10:1 within the groundwater matrix.

Liquid Chromatography/Mass Spectrometry. All separations were performed on a Waters 2690 liquid chromatograph (LC) (Milford, MA) equipped with a reverse-phase Betasil C-18 150 mm × 2 mm column (Thermo Hypersil-Keystone, Bellefonte, PA) that was heated to 35 °C. The gradient consisted of increasing methanol from 30 to 90% over 5 min followed by a 5-min hold at 90% methanol and 5 min of equilibration at 30% methanol. All accessible poly(tetrafluoroethylene) (PTFE) lines were replaced with polyetheretherketone (PEEK) tubing (Upchurch Scientific, Oak Harbor, WA). The LC was directly interfaced to the electrospray ionization (ESI) source of a Micromass Quattro Micro triple quadrupole mass spectrometer (Beverly, MA). The triple quadrupole was operated in the negative ESI mode, and multiple reaction monitoring was used for quantitation. The capillary voltage was 3.05 kV, and the cone potential was set at a value between 20 and 65 V depending on the compound of interest. The temperatures of the source block and desolvation capillary were 125 and 250 °C, respectively. The flow rates of the nebulizer and desolvation gases were 80 and 575 L/h, respectively. Argon was used as the collision gas, and the

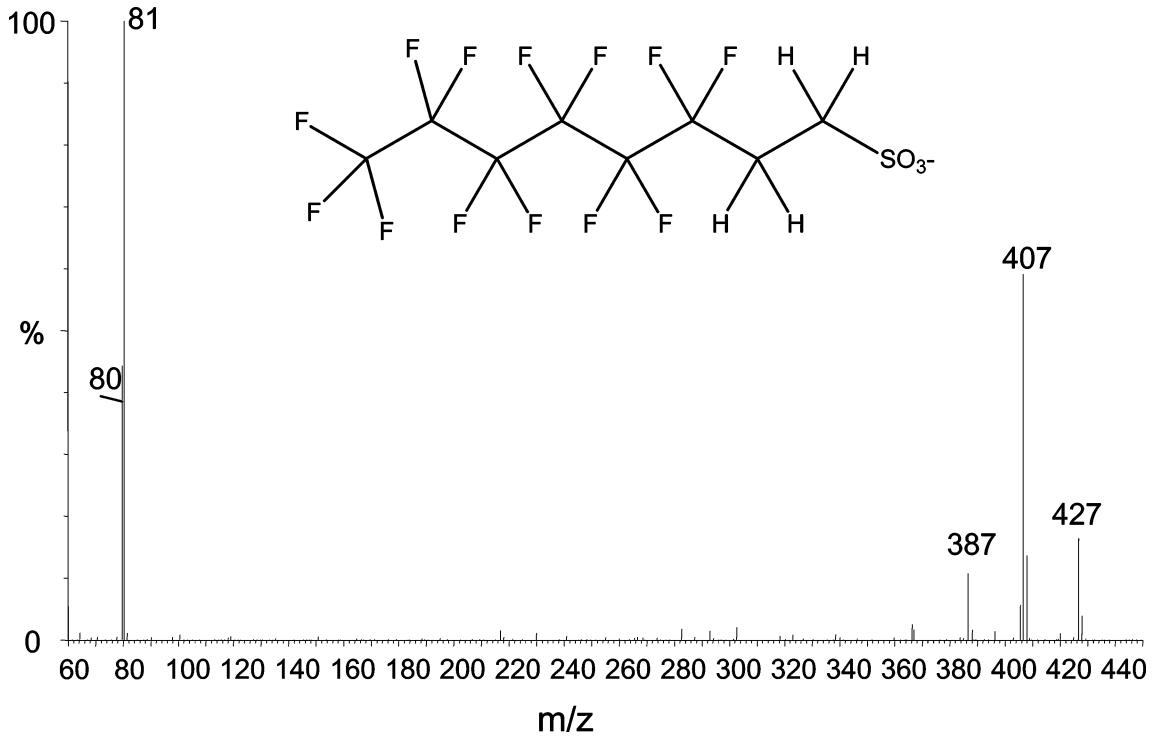

FIGURE 2. Negative ESI MS/MS mass spectrum of 6:2 FtS.

collision energy was set at a value between 15 and 40 eV depending on the compound being analyzed.

To obtain ions suitable for quantitation, standards and Zonyl TBS were first infused with a syringe pump into the Micromass Quattro Micro triple quadrupole mass spectrometer (Beverly, MA) at a flow rate of 30 μL/min, and the mass spectrometer was tuned to optimum. Quantitation of the fluorotelomer sulfonates was based on the loss of HSO_3^- from the fluorotelomer sulfonate precursor ($[M]^- \rightarrow [M-81] + HSO_3^-$), which is characterized by the appearance of a signal in the precursor's product ion spectrum at m/z 81 (HSO_3^-). The transition monitored for the internal standard, hexafluoroglutaric acid, was m/z 239 → m/z 131, which corresponds to the loss of $C_3F_5^-$ from the precursor $[M-1]^-$. Hexafluoroglutaric acid was chosen as the internal standard for the quantification of the fluorotelomer sulfonates because to the best of our knowledge it has no industrial uses, and it was not observed in the NAS Fallon, Tyndall AFB, or Wurtsmith AFB groundwater samples. Quantitation was based on the ratio of the peak area of the analyte to that of the internal standard. 6 point calibration curves (not including the origin) were constructed for 6:2 FtS between the limits of 0.60 and 30.9 μg/L. All calibration curves were plotted using linear regression, weighted $1/X$, and $r^2 > 0.99$. Authentic standards of 4:2 and 8:2 FtS were commercially unavailable. Therefore, for the quantification of these compounds, response factors were assumed equal to that of an equimolar amount of 6:2 FtS.

The transitions monitored for the perfluoroalkyl sulfonates were based on the loss of the sulfonate ion ($[M]^- \rightarrow [M-80] + SO_3^-$), which is characterized by the appearance of a signal at m/z 80 (SO_3^-) in the product ion spectrum. Calibration curves of PFBS, PFHxS, and PFOS were produced between the limits of 0.58 and 31.3 μg/L, 0.47 and 31.8 μg/L, and 0.62 and 31.5 μg/L, respectively. Because authentic standards of perfluoropentane sulfonate (PFPS) and perfluoroheptane sulfonate (PFHpS) were not commercially available, their response factors were assumed equal to that of an equimolar amount of PFHxS.

The greatest reduction in background was achieved by replacing the accessible PTFE tubing in the Waters LC system with PEEK lines. Despite this extreme measure, persistently high backgrounds were still observed occasionally, especially after the analysis of highly concentrated samples. In such cases, the entire LC, including the column, was rinsed with 10% formic acid in IPA. This procedure would be performed as necessary overnight or for a few hours depending on the strength of observed background. After a formic/IPA rinse, the column was reequilibrated, a procedure that takes up to a couple of hours.

Fast Atom Bombardment/Mass Spectrometry. Fast atom bombardment mass spectrometry (FAB MS) experiments were performed on a Kratos MS-50TC (Manchester, U.K.) double-focusing instrument. The analyte of interest was mixed on the probe tip with a 3-nitrobenzyl alcohol (98%, Sigma-Aldrich) matrix. Xenon gas was used to generate the primary ionizing beam from an Ion-Tech gun operated at 7−8 kV. For high mass accuracy measurements, a mixture of poly(ethylene glycol)s (PEGs) was used as the reference compound; the mixture consisted of three PEGs with masses of 600, 800, and 1000 Da in the ratio 4:2:1, respectively.

Results and Discussion

Liquid Chromatography/Mass Spectrometry. The negative ESI mass spectrum (Figure 2) of the 6:2 FtS (m/z 427) exhibits peaks corresponding to the neutral losses of HF (m/z 407) and 2 HF (m/z 387), the loss of SO_3^- (m/z 80), and the loss of HSO_3^- (m/z 81), which produces the most abundant peak. No evidence for spectral or background interferences in the m/z 427 → m/z 81 transition was found; therefore, this highly favored reaction was used for quantitation of the 6:2 FtS. For the quantitation of the perfluoroalkyl sulfonates, the $[M]^- \rightarrow m/z$ 80 transition was monitored, where M equals the mass of the perfluoroalkyl sulfonate Although other investigators have reported interferences for the m/z 499 (PFOS) → m/z 80 transition in biological matrixes (*10*), this interference was not observed for the AFFF-contaminated groundwater analyzed in the present study. The split chromatographic peaks shown in Figure 3 indicate the presence of both branched and linear isomers of the electrochemically fluorinated PFOS and PFHxS. Quantitations of PFOS and PFHxS

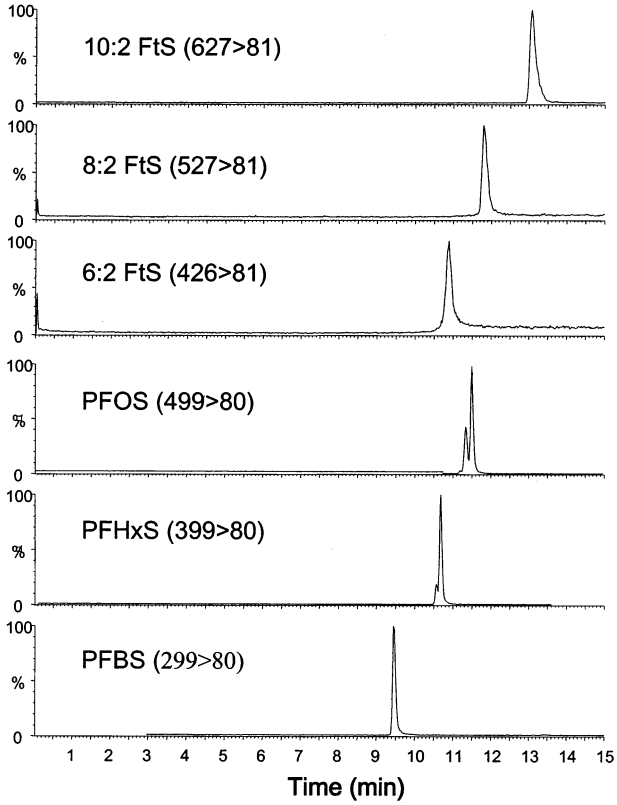

FIGURE 3. LC MS/MS chromatograms of 6:2 FtS, 8:2 FtS, and 10:2 FtS (in Zonyl TBS) and authentic standards of PFBS, PFHxS, and PFOS. The product ion transition used for quantitation is indicated in each chromatogram.

were based on the integration of both peaks. Chromatograms of the 6:2−10:2 FtS in Zonyl TBS and of authentic standards of PFBS, PFHxS, and PFOS indicated the following overall elution order: PFBS < 4:2 FtS (not shown) < PFHxS < 6:2 FtS < PFOS < 8:2 FtS < 10:2 FtS (Figure 3).

The Zonyl TBS was analyzed to establish that homologous fluorotelomer sulfonates could be detected without interference. This test was necessary because only a single authentic standard of a fluorotelomer sulfonate, 6:2 FtS, could be obtained. Higher chained fluorotelomer sulfonates (12:2−16:2) were detected in the Zonyl TBS but are not shown. The Zonyl TBS mixture contained less than 1% 4:2 FtS. Due to complications in carryover when analyzing the Zonyl TBS, the mixture was not used for calibration.

Accuracy, Precision, and Detection Limits for LC MS/MS. The average percent recovery of the 6:2 FtS spiked into background well groundwater was 104%, and the precision associated with this recovery, as indicated by the relative standard error (RSE), was 3% (Table 1). No fluorotelomer sulfonates were detected at NAS Fallon, and no blank groundwater was available from Tyndall AFB. Thus, no spike and recovery experiments were performed for the fluorotelomer sulfonates on samples from these two bases.

To validate the LC MS/MS method for quantification of perfluoroalkyl sulfonates, spike recoveries were performed with groundwater drawn from NAS Fallon well MW 50U, which was previously found not to contain perfluoroalkyl sulfonates. The average percent recoveries (and RSEs) for PFBS, PFHxS, and PFOS were 111 (±1%), 117 (±2%), and 89 (±3%) (Table 1), respectively.

Standard addition experiments were performed with groundwater samples out of two wells from Wurtsmith AFB and two wells from Tyndall AFB, from all of which fluorotelomer sulfonates were detected. No standard additions were performed with samples from NAS Fallon since no

TABLE 1. Recoveries of 6:2 FtS, PFBS, PFHxS, and PFOS Spiked into Groundwater Samples from Wurtsmith Air Force Base and Tyndall Air Force Base[a]

compd added	sample well	*n*	initial concn (μg/L)	final measd concn (μg/L)	% recovery
6:2 FtS	WAFB FT-D2 MW 2 (background well)	5	nd	5.0	104 ± (3)
6:2 FtS	WAFB FT-13	2	16	31.7	108 ± (5)
6:2 FtS	WAFB FT-2	2	8.8[b]	17.7	95 ± (4)
6:2 FtS	TAFB TY22FTA	2	6.0[c]	12.2	96 ± (2)
6:2 FtS	TAFB PW-10	2	6.5[d]	13.0	101 ± (8)
PFBS	NASF MW 50U	5	nd	3.5	111 ± (1)
PFBS	TAFB TY22FTA	4	0.10[e]	3.6	82 ± (2)
PFHxS	NASF MW 50U	5	≤LOQ	3.5	117 ± (2)
PFHxS	TAFB TY22FTA	5	1.1[e]	4.6	120 ± (3)
PFOS	NASF MW 50U	5	≤LOQ	3.5	89 ± (3)
PFOS	TAFB TY22FTA	5	1.5[e]	5.0	93 ± (2)

[a] % RSEs are given in parentheses. nd, not detected; ≤LOQ, less than or equal to the quantitation limit. [b] Diluted by a factor of 10. [c] Diluted by a factor of 180. [d] Diluted by a factor of 2250. [e] Diluted by a factor of 100.

fluorotelomer sulfonates were detected in them. The percent recoveries ranged from 96−101 at Tyndall AFB and 95−108 at Wurtsmith AFB (Table 1). The percents of PFBS, PFHxS, and PFOS recovered from aliquots of groundwater drawn out of Tyndall AFB well TY22FTA ranged from 82 (±2%) to 120 (±3%) (Table 1).

The precision of the direct injection LC MS/MS method was estimated by calculating the relative standard error of five replicate analyses of unspiked groundwater samples collected from Wurtsmith AFB and Tyndall AFB. Since a wide range of fluorotelomer sulfonate concentrations were observed at Wurtsmith AFB, estimates of analytical precision were obtained from a set of five replicate analyses performed on groundwater from well FT-2 and a similar set from well FT-13. The RSEs calculated for unspiked groundwater from the FT-2 and FT-13 wells were 7% and 3%, respectively (Table 2). The sample taken from Tyndall AFB well T11-2 was also analyzed five times; the RSE from this set of measurements was estimated to be 8% (Table 2).

The method detection limit, defined as the minimum concentration of an analyte that can be reported with 99% confidence to be greater than zero, was 0.33 μg/L for the 6:2 FtS (Table 3). The quantitation limit, defined as the concentration required to produce a signal-to-noise of 10:1, was 0.60 μg/L for the 6:2 FtS (Table 3). For LC MS/MS quantitation of perfluoroalkyl sulfonates taken from NAS Fallon and Tyndall AFB, the method detection limits and quantitation limits were 0.32 and 0.58 μg/L for PFBS, 0.15 and 0.47 μg/L for PFHxS, and 0.36 and 0.62 μg/L for PFOS (Table 3). The method detection limits and quantitation limits estimated in a previous study by direct injection mass spectrometry (no LC) for the perfluoroalkyl sulfonates at Wurtsmith AFB were 3 and 5 μg/L, respectively (Table 3) (*22*); these values are an order of magnitude higher than those estimated in the present study from the NAS Fallon and Tyndall AFB samples (Table 3). The perfluorinated carboxylate method detection limits and quantitation limits were determined by GC/MS in previous studies to be 18 and 36 μg/L (*21*), respectively, for samples collected from sites at NAS Fallon and Tyndall AFB and 3 and 13 μg/L (*22*), respectively, for samples from Wurtsmith AFB (Table 3).

Application to Groundwater Samples. The LC MS/MS method was applied to groundwater samples from NAS Fallon, Tyndall AFB, and Wurtmsith AFB to quantitatively determine the levels of 4:2−12:2 fluorotelomer sulfonates. The 4:2 FtS, 6:2 FtS, and 8:2 FtS were all present in varying

TABLE 2. Concentrations of Fluorotelomer Sulfonates, Perfluoroalkyl Sulfonates, and Perfluoroalkyl Carboxylates in Groundwater Samples from NAS Fallon (NASF), Tyndall AFB (TAFB), and Wurtsmith AFB (WAFB) (μg/L)[a]

sample	4:2 FtS	6:2 FtS	8:2 FtS	PFBS	PFPS	PFHxS	PFHpS	PFOS	PFHxA	PFHpA[b]	PFOA
NASF MW 51U	nd	nd	nd	210	216	876	nd	380	372 ± (1)[c]	149 ± (2)[c]	6570 ± (1)[c]
NASF MW 16	nd	nd	nd	54	38	115	nd	≤LOQ	57 ± (6)[c]	18 ± (5)[c]	460 ± (2)[c]
NASF MW 50U	nd	nd	nd	nd	nd	≤LOQ	nd	≤LOQ	nd[c]	nd[c]	nd[c]
NASF MW 17	nd	nd	nd	≤LOQ	≤LOQ	≤LOQ	nd	≤LOQ	nd[c]	nd[c]	nd[c]
TAFB PW-10	7.3	14 600	3.3	144	134	920	nd	2300	144[c]	38[c]	116[c]
TAFB PW-07	5.7	7100	0.70	82	73	540	nd	270	73[c]	22[c]	64[c]
TAFB T11−2	4.2	4630 ± (8)	≤LOQ	58	70	360	nd	210	64 ± (3)[c]	19 ± (2)[c]	42 ± (2)[c]
TAFB TY22FTA	1.1	1080	17	10	8.3	107	nd	147	nd[c]	nd[c]	nd[c]
WAFB FT 1	nd	2.9	1.5	na[d]	na[d]	36[d]	na[d]	8[d]	5[d]	na[d]	5[d]
WAFB FT 2	nd	88 ± (7)	≤LOQ	na[d]	na[d]	120[d]	na[d]	14[d]	5[d]	na[d]	98[d]
WAFB FT 3	nd	95	0.78	na[d]	na[d]	104[d]	na[d]	110[d]	5[d]	na[d]	105[d]
WAFB FT 4	nd	2.0	nd	na[d]	na[d]	5[d]	na[d]	9[d]	nd[d]	na[d]	nd[d]
WAFB FT 6	nd	nd	nd	na[d]	na[d]	5[d]	na[d]	9[d]	nd[d]	na[d]	nd[d]
WAFB FT 5	nd	42	nd	na[d]	na[d]	18[d]	na[d]	16[d]	nd[d]	na[d]	3[d]
WAFB FT 10	nd	≤LOQ	≤LOQ	na[d]	na[d]	9[d]	na[d]	7[d]	nd[d]	na[d]	nd[d]
WAFB FT 7	nd	≤LOQ	nd	na[d]	na[d]	na[d]	na[d]	na[d]	nd[d]	na[d]	nd[d]
WAFB FT 8	nd	53	2.7	na[d]	na[d]	30[d]	na[d]	8[d]	nd[d]	na[d]	20[d]
WAFB FT 9	nd	66	3.7	na[d]	na[d]	46[d]	na[d]	40[d]	nd[d]	na[d]	19[d]
WAFB FT 11	nd	7.2	≤LOQ	na[d]	na[d]	na[d]	na[d]	na[d]	nd[d]	na[d]	nd[d]
WAFB FT 12	1.24	27	1.3	na[d]	na[d]	23[d]	na[d]	6[d]	8[d]	na[d]	15[d]
WAFB FT 13	nd	16 ± (3)	6.5	na[d]	na[d]	26[d]	na[d]	30[d]	nd[d]	na[d]	24[d]
WAFB FT 14	nd	173	8.7	na[d]	na[d]	27[d]	na[d]	16[d]	nd[d]	na[d]	8[d]
WAFB FT 18	nd	139	1.6	na[d]	na[d]	33[d]	na[d]	20[d]	nd[d]	na[d]	10[d]
WAFB FT 17	nd	8.7	1.1	na[d]	na[d]	9[d]	na[d]	4[d]	nd[d]	na[d]	nd[d]
WAFB FT 15	nd	0.98	nd	na[d]	na[d]	na[d]	na[d]	na[d]	nd[d]	na[d]	nd[d]
WAFB FT 16	nd	0.90	nd	na[d]	na[d]	na[d]	na[d]	na[d]	nd[d]	na[d]	nd[d]

[a] % RSEs is given in parentheses. In data shown by Moody and Field (*21*), % RSDs were converted to % RSEs by dividing by $n^{1/2}$. nd, not detected above the detection limit; na, sample well not analyzed. [b] PFHpA, perfluoroheptanoic acid. [c] Determined by Moody and Field (*21*). [d] Determined by Moody et al. (*22*).

TABLE 3. Limits of Detection (LOD) and Limits of Quantitation (LOQ) for Fluorotelomer Sulfonates, Perfluoroalkyl Sulfonates, and Perfluoroalkyl Carboxylates[a]

		6:2 FtS	PFBS	PFHxS	PFOS	PFOA
NAS Fallon	LOD	0.33	0.32	0.15	0.36	18[b]
	LOQ	0.60	0.58	0.47	0.62	36[b]
Tyndall AFB	LOD	0.33	0.32	0.15	0.36	18[b]
	LOQ	0.60	0.58	0.47	0.62	36[b]
Wurtsmith AFB	LOD	0.33	nd[c]	nd[c]	3[c]	3[c]
	LOQ	0.60	nd[c]	nd[c]	5[c]	13[c]

[a] All concentrations are reported as μg/L. [b] Determined by Moody and Field (*21*). [c] Quantification of PFBS and PFHxS was based on the assumption that response factors were equal to an equimolar amount of PFOS (*22*).

concentrations at Wurtsmith AFB and Tyndall AFB. No fluorotelomer sulfonates were detected (detection limit 0.33 μg/L) at NAS Fallon. Odd-numbered (e.g., 5:2 or 7:2) fluorotelomer sulfonates were not detected, this being consistent with the fluorotelomerization process for which only even-numbered homologues are produced (*8*, *9*).

Naval Air Station Fallon, Nevada. At this site, the total micromolar distribution of fluorosurfactants was 0% fluorotelomer sulfonates, 25% perfluoroalkyl sulfonates, and 75% perlfuoroalkyl carboxylates (Table 4, Figure 4a). No fluorotelomer sulfonates were observed above the detection limit at NAS Fallon. Although, NAS Fallon was in operation from the 1950s through 1988, it appears that no fluorotelomer-based AFFF was used at this site. However, relatively high concentrations of PFBS, PFPS, PFHxS, and PFOS were detected in the NAS Fallon wells MW 51U and MW 16; the total perfluorinated sulfonate concentrations in these two wells were 1680 and 206 μg/L (Table 4), respectively. No perfluorinated sulfonates were observed above the quantitation limit in wells MW 50U and MW 17. These findings for the perfluoroalkyl sulfonates mimic the levels of perfluorinated carboxylates at NAS Fallon obtained from a previous study (*21*) (Table 4).

TABLE 4. Total Concentrations of Fluorotelomer Sulfonates (FtS), Perfluoroalkyl Sulfonates (PFS), and Perfluoroalkyl Carboxylates (PFC) in Groundwater Samples from NAS Fallon (NASF), Tyndall AFB (TAFB), and Wurtsmith AFB (WAFB) (μg/L)

sample	total [FtS]	total [PFS]	total [PFC]
NASF MW 51U	0	1680	7090[a]
NASF MW 16	0	206	535[a]
NASF MW 50U	0	0	0[a]
NASF MW MW 17	0	0	0[a]
TAFB PW-10	14 600	3500	298[a]
TAFB PW-07	7100	960	159[a]
TAFB T11−2	4600	700	125[a]
TAFB TY22FTA	1100	273	0[a]
WAFB FT 1	4.4	44[b]	10[b]
WAFB FT 2	88	134[b]	103[b]
WAFB FT 3	96	213[b]	110[b]
WAFB FT 4	2.1	14[b]	0[b]
WAFB FT 6	0	14[b]	0[b]
WAFB FT 5	42	34[b]	3[b]
WAFB FT 10	0	16[b]	0[b]
WAFB FT 7	0	na[b]	0[b]
WAFB FT 8	56	38[b]	20[b]
WAFB FT 9	70	86[b]	19[b]
WAFB FT 11	7.2	na[b]	0[b]
WAFB FT 12	29.7	29[b]	23[b]
WAFB FT 13	22.4	56[b]	24[b]
WAFB FT 14	182	43[b]	8[b]
WAFB FT 18	141	53[b]	10[b]
WAFB FT 17	9.8	13[b]	0[b]
WAFB FT 15	0.98	na[b]	0[b]
WAFB FT 16	0.90	na[b]	0[b]

[a] Determined by Moody and Field (*21*). [b] Determined by Moody et al. (*22*). na, sample well not analyzed.

Tyndall Air Force Base, Florida. The total micromolar distribution of fluorosurfactants quantified at Tyndall AFB

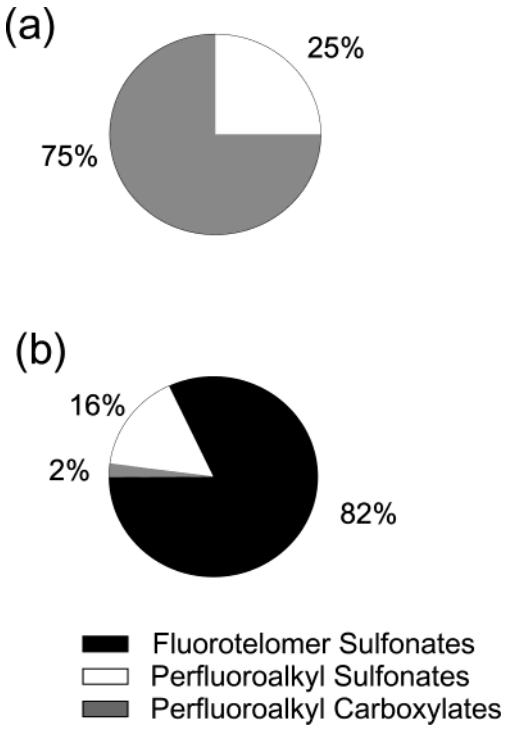

FIGURE 4. Distribution of fluorosurfactants on a μM basis (a) at NAS Fallon and (b) at Tyndall AFB.

is represented in a pie graph (Figure 4b). The fluorotelomer sulfonates were the most abundant (82%) fluorosurfactant observed at this site. The highest fluorotelomer sulfonate concentrations measured in this study were in samples collected from Tyndall AFB; total FtS concentrations ranged from 1100 to 14 600 μg/L (Table 4). The predominant fluorotelomer sulfonate was the 6:2 FtS, which accounted for 99% of fluorotelomer sulfonate present (Table 2). The second most abundant fluorotelomer sulfonate, 4:2 FtS, was present in all four wells, ranging in concentration from 1 to 8 μg/L (Table 2). The 8:2 FtS was quantified in three out of the four wells, ranging in concentration from 0.7 to 17 μg/L (Table 2). The highest total concentrations of fluorotelomers were observed for wells within 15 m of the fire-training pad, PW-10 (14,600 μg/L) and PW-7 (7,100 μg/L), and the lowest concentrations were detected 30 m down gradient from the pad, T11-2 (4600 μg/L), and 40 m north of the pad, TY22FTA (1100 μg/L).

The total perfluoroalkyl sulfonate concentrations, which ranged from 273 to 3500 μg/L (Table 4), accounted for 16% of the total content of fluorosurfactants observed at Tyndall AFB (Figure 4b). The perfluoroalkyl carboxylates, whose total concentrations ranged from below detection to 298 μg/L (Table 4), accounted for only 2% of the total fluorosurfactants detected at this site (Figure 4b).

The presence of fluorotelomer sulfonates, perfluoroalkyl carboxylates, and perfluoroalkyl sulfonates in the groundwater collected from this site is consistent with the facts that military contracts for both fluorotelomer-based and electrochemical fluorinated-based AFFF formulations had been issued during the period 1983−1988 and that these years fall in the middle of the time (1980−1992) during which Tyndall AFB had been in operation. The composition of fluorotelomer sulfonates observed at Tyndall suggests that the fluorotelomer products supplied to the U.S. military from 1983 to 1988 through Ansul Incorporated, contained predominantly 6:2 FtS as the feedstock or other fluorotelomer chemicals that degraded primarily to 6:2 FtS.

Wurtsmith Air Force Base, Michigan. Fluorotelomer sulfonates, perfluoroalkyl sulfonates, and perfluoroalkyl carboxylates were all observed at Wurtsmith AFB**.** The total concentrations ranged from below detection (0.33 μg/L) to 182 μg/L for fluorotelomer sulfonates, from 13 to 213 μg/L for perfluoroalkyl sulfonates (not all wells were analyzed), and below detection (3 μg/L) to 105 μg/L for perfluoroalkyl carboxylates (Table 4).

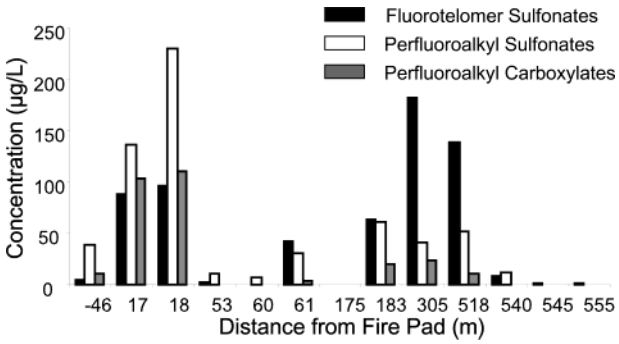

FIGURE 5. Distance vs concentration plot for fluorosurfactants at Wurtsmith AFB.

The 6:2 FtS concentrations were the highest among the fluorotelomer sulfonates, ranging from 0.90 to 173 μg/L (Table 2). The second most abundant fluorotelomer sulfonate was the 8:2 FtS, ranging in concentration from 0.78 to 8.66 μg/L (Table 2); the 4:2 FtS was only found in the FT-12 well at a concentration of 1.24 μg/L. The composition of these three homologues at Wurtsmith AFB contrasts with that observed at Tyndall AFB, where the 4:2 FtS was the second most abundant fluorotelomer after the 6:2 FtS. For purposes of comparison, total perfluoroalkyl sulfonate concentrations (PFOS and PFHxS) detected in Wurtsmith AFB groundwater ranged from 13 (FT-17) to 213 μg/L (FT-3) (*22*), while total perfluorocarboxylate concentrations, perfluorooctanoic acid (PFOA), and perfluorohexanoic acid (PFHxA) were from below the detection limit (3 μg/L) to 110 μg/L (FT-3) (*21*).

The spatial distribution of concentrations among the different classes of chemicals differed (Figure 5). High concentrations of 6:2 FtS were observed in wells close in proximity to the fire-training pad; wells FT-2 (17 m) and FT-3 (18 m) contained 6:2 FtS concentrations of 88 and 95 μg/L, respectively. However, the highest 6:2 FtS concentrations measured in the plume were in wells FT-14 (173 μg/L) and FT-18 (139 μg/L) located downgradient of the fire pad at 305 and 518 m, respectively (Figure 5). By contrast, the concentrations of perfluoroalkyl sulfonates and carboxylates were highest near the fire-training pad and lower in wells downgradient of the training pad (Figure 5).

It is conceivable that the peak in fluorotelomer sulfonate concentration that occurred downstream in 1999 (Figure 5), the year the samples were collected from this site might be the result, in part, of conservative chemical transport in the plume illustrated in Figure 1. Wurtsmith AFB's long period of operation (1952−1993) spans the years (1983−1988) during which AFFF formulations were based on chemicals produced by both electrochemical fluorination and fluorotelomerization. Thus, chemicals released between 1983 and 1988, transported at a flow rate on the order of 0.1 m/day (*25*−*27*), could by the year 1999 very likely have become distributed in the vicinity of wells FT-14 and FT-18 (approximately 300−500 m) downstream, respectively. Simplistic reasoning of this sort cannot, however, account for the relatively high concentrations of fluorotelomer sulfonates near the fire-training pad nor the uneven distribution of the electrochemically based perfluoroalkyl sulfonates and perfluoroalkyl carboxylates, which were used in AFFF throughout the entire period Wurtsmith AFB was in operation.

AFFF and Fluorotelomer Sulfonates. In an effort to gain knowledge of the composition of an AFFF mixture based on

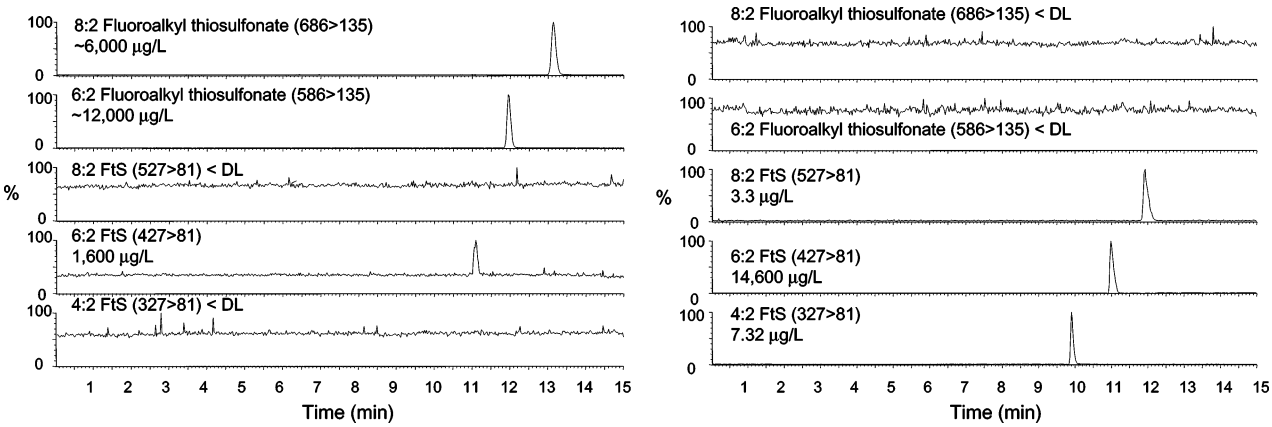

FIGURE 6. A comparative LC MS/MS analysis of (a) fluorotelomer-based AFFF and (b) Tyndall AFB well PW-10 with fluoroalkylthioamido sulfonates and fluorotelomer sulfonates indicated. < DL indicates below detection.

fluorotelomer chemicals, negative ion FAB MS as well as the LC MS/MS method described in this paper were used to analyze a single fluorotelomer-based AFFF. The identities of the fluorosurfactants used in fluorotelomer-based AFFF formulations are proprietary and, therefore, not listed in a material safety data sheet. The AFFF product was provided by Tyndall AFB and was presumably sold by Ansul Incorporated to the military on contract sometime during the years of 1983−1988. AFFF is transported and stored as a concentrate; prior to application, it is diluted to 3 or 6% (by volume) with freshwater, saltwater, or hard water. Thus, the AFFF from Tyndall AFB was far more concentrated than what would have been applied in the field. For this reason, it was diluted approximately 200 000-fold prior to LC MS/MS analysis. The 6:2 FtS was detected in the AFFF concentrate, but the 4:2 FtS and 8:2 FtS were not. A standard of the 6:2 FtS yielded a signal at *m/z* 427 by negative ion FAB MS (*28*); however, no fluorotelomer sulfonates were detected by FAB MS in the AFFF concentrate. Instead three higher molecular weight molecules were observed at masses *m/z* 486, 586, and 686 (*28*). The mass difference of 100 corresponds to a $[CF_2CF_2]$ group, which is consistent with the chemicals produced by fluorotelomerization where the fluoroalkyl group is $F(CF_2CF_2)_nCH_2CH_2-R$. FAB MS measurements performed at high mass accuracy and ESI MS/MS analyses of the product ion fragmentation patterns of the three higher molecular weight precursors identified the latter as fluoroalkylthioamido sulfonates with a structural formula that is consistent with $R_f-SCH_2CH_2CONHC(CH_3)_2CH_2SO_3^-$, where $R_f = F(CF_2CF_2)_nCH_2CH_2^-$ and $n = 2$ (*m/z* 486), 3 (*m/z* 586), or 4 (*m/z* 686).

Given the presence of fluoroalkylthioamido sulfonates in the AFFF concentrate, those groundwater samples containing the highest concentrations of fluorotelomer sulfonates were reanalyzed semiquantitatively for the fluoroalkylthioamido sulfonates by LC MS/MS (Figure 6). The transition $[M]^- \rightarrow [M - 135] + C(CH_3)_2CHSO_3^-$ (*m/z* 135) was used for the semiquantitation. Analysis of the AFFF concentrate supplied to Tyndall AFB yielded an estimate of 1600 μg/L for the concentration of 6:2 FtS (Figure 6a). Lack of an authentic standard precluded rigorous quantitation of the fluoroalkylthioamido sulfonates; however, assuming response factors equal to those of equimolar amounts of 6:2 FtS, the concentrations of the 6:2 and 8:2 fluoroalkylthioamido sulfonates in the AFFF concentrate were estimated to be 12 000 and 6000 μg/L, respectively (Figure 6a). Provided that the preceding assumption is valid, the fluoroalkylthioamido sulfonates are much more abundant in the AFFF concentrate than the fluorotelomer sulfonates.

None of the fluoroalkylthioamido sulfonates were observed in any of the groundwater samples, including the Tyndall AFB well PW-10 that contained such exceptionally high fluorotelomer sulfonates concentrations (Figure 6b). This raises interesting questions about the fate of the fluoroalkylthioamido sulfonates in groundwater. Based on the concentration of 6:2 FtS in the AFFF concentrate at hand (1600 μg/L), the concentration of 6:2 FtS in an AFFF formulation (i.e., after dilution of the concentrate to 3 vol %) used in fire-training activities would only be ~50 μg/L. Since the concentrations of 6:2 FtS in the four wells at Tyndall AFB all exceeded 1000 μg/L, it is difficult to imagine how they arose strictly in terms of a direct application of AFFF containing something on the order of 50 μg/L of 6:2 FtS. Therefore, it seems plausible that degradation of the fluoroalkylthioamido sulfonates (and cationic and nonionic fluorosurfactants also present in the AFFF products) into fluorotelomer sulfonates could have occurred.

The present study emphasizes how little is known concerning the fate and transport of fluorotelomer sulfonates in groundwater. Previous studies have shown that the 6:2 FtS is susceptible to biodegradation under sulfur-limiting and aerobic conditions (*29*); however, it is certainly not known if these transformations could have occurred under the conditions that existed at Tyndall AFB or Wurtsmith AFB. Studies are needed to better understand the transport and biodegradation of fluorotelomer sulfonates, fluoroalkylthioamido sulfonates, other AFFF fluorochemicals (e.g., cationic and nonionic), and their precursors under various aerobic and anaerobic conditions.

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