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Concentrations, Distribution, and Persistence of Fluorotelomer Alcohols in Sludge-Applied Soils near Decatur, Alabama, USA

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Soil samples were collected for fluorotelomer alcohol (FTOH) analyses from six fields to which sludge had been applied and one "background" field that had not received sludge. Ten analytes in soil extracts were quantified using GC/MS. Sludge-applied fields had surface soil FTOH concentrations exceeding levels found in the background field. For 8:2nFTOH, which can degrade to perfluorooctanoic acid, impacted surface-soils ranged from 5 to 73 ng/g dry weight, clearly exceeding the background field in which 8:2nFTOH was not detected. The highest [FTOH] generally was 10:2nFTOH, which had concentrations of <5.6 to 166 ng/g. For the first time, we document the persistence of straight-chained primary FTOHs (n-FTOHs) and branch-chained secondary FTOHs (sec-FTOHs), which are transformation products of n-FTOHs, in field soils for at least five years after sludge application. Ratios of sec-FTOHs to n-FTOHs were highest for 7:2sFTOH/8:2nFTOH (~50%) and decreased with increasing chain length to a minimum for the longest-chained analytes, 13:2sFTOH/14:2nFTOH (~10%). Disappearance half-lives for FTOHs, calculated with these data, ranged from 0.85 to 1.8 years. These analytical results show that the practice of sludge application to land is a pathway for the introduction of FTOHs and, accordingly, their transformation products, perfluorocarboxylic acids, into the environment.

Introduction

Over the past decade, global concerns regarding the effects of potentially persistent, bioaccumulative, and toxic perfluorocarboxylic acids (PFCAs) on environmental health have inspired a variety of research efforts to address potential sources to the environment (*1–4*). Fluorotelomer alcohols (FTOHs) stand prominently among possible sources of PFCAs

due to their (1) intensive usage in diverse applications such as clothing, upholstery, carpeting, and fast-food packaging (*5*); (2) their volatile nature; and (3) their propensity to degrade to PFCAs and related compounds (*6, 7*). Additionally, fluorotelomer-based polymers, which commonly are composed chiefly of 8:2nFTOHs linked to long polymeric backbones, recently have been determined to undergo degradation to form FTOHs (*7, 8*). Several studies have analyzed a range of consumer products to confirm the presence of unbound FTOHs in a wide variety of commercially and industrially available fluorinated materials (*9, 10*); residual FTOHs and structurally similar volatile polyfluorinated sulfonamides have been reported in the range of 0.04–3.8% (dry-mass basis) for tested materials (*9*).

Given the potential for consumer products to act as sources of FTOHs, and their physical–chemical properties favoring a high atmospheric mobility, e.g., low water solubility and high vapor pressure (*11*), several studies have been undertaken to determine the extent to which FTOHs have been distributed in the environment. Field monitoring confirmed the presence of FTOHs in the air of Europe (181–288 pg ΣFTOH/m^3) and North America (11–165 pg ΣFTOH/m^3), with the greatest abundance in urban areas (*12, 13*). Recently, trace levels of FTOHs in surface water and effluents from wastewater treatment plants were reported with a range of <0.13–10 ng ΣFTOH/L (*14*). Unlike these numerous studies on FTOHs in air and water, however, peer-reviewed publications on the distribution and fate of FTOHs in soils and sediments are relatively sparse (*15*).

Finally, several laboratory experiments looking for 8:2nFTOH biodegradation have shown that telomer acids and perfluorooctanoic acid (PFOA) are produced by incubating 8:2nFTOH in pure-culture–, sludge–, and soil–microbial systems, or by dosing animals for designated periods (*6, 16–18*). These experimental systems generally share similar biotic degradation pathways from 8:2nFTOH to PFOA, including a volatile secondary FTOH (specifically 7:2sFTOH, $CF_3(CF_2)_6CH(CH_3)OH$; generically sec-FTOH for 8:2nFTOH homologues) which is a direct precursor to PFOA (*6*). Also, microcosm studies have identified the generation of FTOHs and PFCAs from aged fluorotelomer polymers in soil settings (*7*). Taken altogether, the above studies establish that microbes exposed to fluorotelomer products are capable of transforming them to intermediate fluorinated metabolites, thence to PFCAs in soil environments.

Study Background. For several years, Decatur Utilities, in Decatur, AL, has been permitted to apply sewage sludge on local agricultural land. For part of this time, including as late as 2006, the Decatur sludge has been found to have PFOA and PFOA precursors at about 10- to a 100-fold greater concentrations than other municipal sludges reported in the peer-reviewed literature (*19*). Given these anomalous values, in late 2007 the U.S. Environmental Protection Agency (USEPA) collected and analyzed a small number of samples of surface soils and sludges from this operation, and the results of these analyses documented elevated levels of several FTOHs and PFCAs (*15, 20*). Based upon these results, the USEPA revisited the Decatur area in March 2009 and collected surface soils in expanded number from six impacted fields and one background field. To evaluate potential transport into the deeper soils, subsurface soils were collected from two depths at selected sites as well. Analytical results for perfluoroalkylates in these samples are reported in an accompanying paper (*19*).

In this paper, we report analytical methods and results for FTOHs in selected fields from near Decatur, Alabama to

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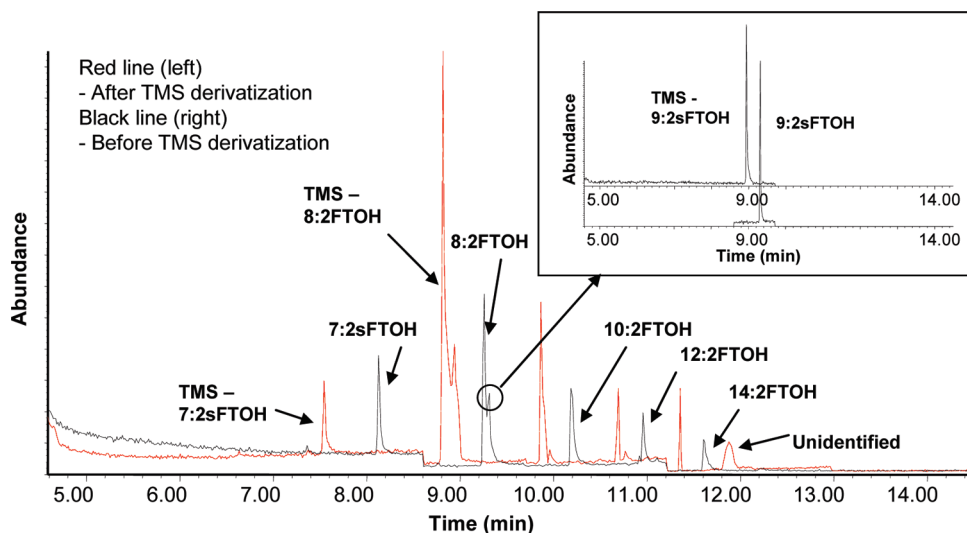[⊥] Region IV, Environmental Protection Agency.

FIGURE 1. PCI-mode mass chromatograms of an extract of a Decatur soil before and after TMSI derivatization. Only the largest peaks are identified for the purpose of clarity. Retention times of all target analytes decreased with derivatization.

which sludge from Decatur Utilities has been applied. Changes in the levels of soil FTOHs with increasing time intervals since sludge application are discussed. In addition, we identify and quantify relationships between several *sec*-FTOHs and their precursors, the primary FTOHs (*n*-FTOHs). The transformation of FTOHs in soil settings is discussed in view of their role as continuing sources of PFCAs in the environment as well.

Experimental Section

Sample Collection. Samples were collected by USEPA regional personnel on March 23–25, 2009. Sample collection procedures are detailed, and sample locations are depicted, in our online Supporting Information (SI; Figure SI1) as well as our accompanying paper (*19*).

Chemicals. All chemicals used in this study were of the highest purity offered by suppliers and they are identified in the Supporting Information.

Soil Sample Extraction. In the laboratory, field samples were homogenized by repeatedly passing them through 2-mm, stainless-steel sieves, coning and quartering until the sample was reduced to four approximately 1-g aliquots. In addition, aliquots were removed from all samples to measure moisture content, which was used to calculate the concentrations reported herein on a dry-weight (dw) basis from the extractions which were performed on moist soils. Our extraction protocol for FTOHs from sludge-treated soils was developed and validated in our previous efforts (*15*). Briefly, 3 mL of mass-labeled 8:2*n*FTOH (70 ng/mL) was spiked into each extraction tube, prepared with 1 g of soil, as an extraction internal standard to evaluate overall extraction efficiency, and then vortexed. Next, 5 mL of HLB-cartridge-polished water was added, followed by 4 mL of MTBE as an extracting solvent. The prepared soil–water–MTBE mixture was rotated overnight on a Labquake rotisserie. After centrifugation at 10 000*g* for 30 min in a Sorvall RCSC centrifuge, the MTBE fraction was separated with a 1000-μL Hamilton syringe and transferred to a preweighed 12-mL glass vial. For these sludge-applied soils, this extraction step was repeated twice more, and the resulting MTBE extracts (~12 mL) were combined and stored at −20 °C immediately until analysis. For the analysis, the extract vial was removed from the freezer and 1 mL of extract, from which water had exsolved by freezing at the vial bottom, was transferred into a GC vial and 20 μL of mass-labeled 10:2*n*FTOH (50 ng/mL) was added as the matrix internal standard prior to GC/MS injection.

GC/MS Analytical Methods, Quantitation, and Data Analysis. We analyzed MTBE extracts of soil samples on an Agilent Technologies (Palo Alto, CA) 6890N GC system equipped with a 5975N mass-selective detector (MSD) operating in positive chemical-ionization (PCI) mode with CH_4 reagent gas for quantitation of the compounds listed in Table SI2. We have reported details of our analytical, quantitation, and data-analysis procedures in our previous paper (*15*) and we summarize them again in the Supporting Information.

Results

Data-Quality Metrics. In the Supporting Information, we report quality data reflecting on field aspects of this study including (1) blanks and reference soil taken to the fields; (2) background-field samples; and (3) duplicate samples collected in the field. Conventional quality data reflecting laboratory aspects of this study include (1) standard-curve back prediction; and (2) recovery internal standards. All of these metrics indicate that the data in this study are of high quality (SI).

Confirmation of the Analyte Identity. Analytical methods have been reported for the detection and quantitation of FTOHs in air samples (*12, 21*) and tissues of FTOH-dosed animals (*22*). Whereas single-quadrupole GC/MS analysis in these matrices enjoys the benefit of relatively simple matrices of air or predictable matrix effects for common tissues among test animals, the complex matrix effects that potentially are unique to every soil sample offer special challenges to analyte confirmation (*15*). Because single-quadrupole mass spectrometer analyses do not include the mass transitions observed in MS/MS analyses, analytes often are identified solely using fragment ions and comparison with retention times of standards (Figure SI2). However, in our experience, confirmation of FTOH identity in soil matrices using these criteria alone can be ambiguous. Consequently, our method for analysis and confirmation of FTOHs in soils employs four criteria: (1) a protonated quantifying ion ($[M + H]^+$); (2) a qualifying-fragmentation ion (loss of HF + H_2O from a $[M + H]^+$); (3) elution time; and (4) an elution shift after derivatization of extracts with trimethylsilylimidazole to form trimethylsilyl (TMS) derivatives. Derivatization of analytes shifts their elution to earlier times with a concurrent loss of underivitized-analyte peaks, but does not affect elution of most interfering compounds (Figure 1). As an example of the qualifying-ion fragment, 14:2*n*FTOH is presented for identification of the FTOH for which an authentic standard

TABLE 1. Mean FTOH Concentrations in Surface Soils from Decatur, AL (ng/g dry soil) Grouped by Field

field ID	sample ID	depth (cm)	summary statistic	6:2nFTOH (ng/g)	7:2sFTOH (ng/g)	8:2nFTOH (ng/g)	9:2sFTOH (ng/g)	10:2nFTOH (ng/g)	11:2sFTOH (ng/g)	12:2nFTOH (ng/g)	13:2sFTOH (ng/g)	14:2nFTOH (ng/g)	8:2FTAcr (ng/g)	M8:2nFTOH (% Rec.)
09D	1	0−10	mean	2	19	33	15	45	6	18	2	16	<0.9	113.1
			SD	-	0.8	5.7	2.7	5.9	1.4	4.7	0.1	4.2	-	9.8
09D	2	0−10	mean	<0.9	9	30	8	42	6	23	3	19	<0.9	111
			SD	-	2.1	1.7	1.1	0.1	0.3	0.5	0.4	0.2	-	5.3
09D	3	0−10	mean	<0.9	15	34	10	31	8	15	3	19	<0.9	107.6
			SD	-	1.3	1.7	0.1	0.9	1.6	1.7	0.0	0.9	-	3.2
09D	4	0−10	mean	<0.9	22	54	14	77	13	48	6	51	<0.9	111.4
			SD	-	0.3	3.6	1.2	7.2	2.2	2.6	0.8	4.6	-	2.7
09D	5	0−10	mean	1.2	20	35	13	42	7	16	3	18	n.d.	105.9
			SD	-	8.7	8.8	4.3	12.7	3.0	6.4	<2.5	9.3	-	4.4
09E	1	0−10	mean	<0.9	5	11	3	17	3	9	0.9	6.2	n.d.	106.6
			SD	-	1.3	3.1	0.6	4.0	0.5	2.1	-	0.9	-	4.9
09E	2	0−10	mean	<0.9	8	21	6	23	4	15	<0.5	9	<0.9	109.2
			SD	-	2.4	6.4	0.8	6.3	0.1	1.7	<2.4	1.2	<0.9	6.9
09E	3	0−10	mean	<0.9	7	18	3	20	2	7	1.3	4	n.d.	115
			SD	-	2.0	8.4	1.4	9.6	-	2.4	-	1.0	-	0.0
09E	4	0−10	mean	2	17	36	15	65	10	54	1	24	<0.9	113
			SD	-	0.6	3.3	8.1	15.1	3.2	13.3	-	3.0	-	4.2
09E	5	0−10	mean	<0.9	19	63	24	166	14	133	1	52	<0.9	111.7
			SD	-	2.2	9.9	0.7	12.7	1.0	29.3	-	13.7	-	3.3
09F	1	0−10	mean	<0.9[a]	36	65	21	76	17	41	6	42	<0.9	111.1
			SD	-	8.4	6.2	2.6	5.8	1.7	6.0	0.1	2.9	-	2.5
09F	2	0−10	mean	n.d.[b]	16	22	8	25	8	17	4	21	<0.9	112.6
			SD	-	2.3	3.5	0.9	3.7	1.0	3.4	0.1	4.6	-	4.9
09F	3	0−10	mean	n.d.	37	73	16	70	10	35	2	23	<0.9	114
			SD	-	2.1	5.9	0.6	8.9	0.1	3.8	-	3.0	-	3.3
09F	4	0−10	mean	n.d.	11	20	7	21	5	11	2	12	n.d.	112.8
			SD	-	0.4	0.2	0.1	1.6	0.3	0.3	-	0.3	-	8.2
09F	5	0−10	mean	n.d.	20	45	13	39	9	19	3	21	<0.9	120
			SD	-	0.3	2.1	1.4	4.4	0.2	0.4	0.3	2.4	-	0.7
09C	1−1	0−10	mean	n.d.	7	11	5	11	5	7	1	10	n.d.	97.7
			SD	-	0.2	0.2	0.4	0.3	0.2	0.1	0.1	1.1	-	0.7
09B	2−1	0−10	mean	<0.9	5	11	4	7	9	7	2	11	n.d.	101.3
			SD	-	0.29	0.66	0.3	1.2	0.25	0.6	-	1.0	-	1.5
09B	3−1	0−10	mean	4	7	17	7	16	5	9	4	13	<0.9	109
			SD	-	-	2.80	0.47	4.5	-	0.9	-	1.8	-	2.2
09G	1	0−10	mean	<0.9	5	15	6	14	8	9	3	13	<0.9	111.2
			SD	-	0.3	0.1	0.8	0.8	0.6	0.3	0.2	1.0	-	2.1
09G	2	0−10	mean	<0.9	13	21	9	26	7	14	4	16	<0.9	108.8
			SD	-	2.0	3.9	2.4	9.0	0.6	3.6	0.5	1.8	-	0.7
09G	3	0−10	mean	n.d.	2	5	2	<5.6	4	4	1	5	n.d.	107.2
			SD	-	-	0.7	0.5	1.0	0.1	0.7	-	0.6	<0.10	9.3
09G	4	0−10	mean	<0.9	6	13	7	12	9	10	4	15	<0.9	93.7
			SD	-	0.1	1.5	0.3	1.1	0.1	0.7	0.2	0.8	-	24.4
09G	5	0−10	mean	1.5	2	5	2	<5.6	2	2	<0.5	3	<0.9	117.8
			SD	-	-	0.3	0.1	0.7	-	-	-	0.1	-	12.5

[a] Concentrations above the MDLs but less than LOQs were reported as less than the analyte's respective LOQ. [b] n.d. (non-detection) represents a value less than MDL.

was not available (Figure SI3). We matched the retention times of six analytes with genuine standards (Figure SI2A) and confirmed them by monitoring two ions in PCI-mode (e.g., 14:2nFTOH, Figure SI3).

Concentrations of FTOHs in Study Soils. Samples from the background field, 09Bgd, which never received biosolids, and trip blanks contained no quantifiable FTOHs (Table SI4 and Figure SI4). Excepting samples from field 09H, which received only a single sludge application in the distant past (Table SI4), all target analytes from 7:2sFTOH to 14:2nFTOH were detected in most soil samples from sludge-treated fields (Table 1). For 8:2nFTOH, which can degrade to PFOA, sludge-impacted surface-soil [8:2nFTOH] ranged from 5 to 73 ng/g. The most enriched FTOHs in soils were 10:2nFTOH and 12:2nFTOH. Sludge-impacted surface soil [10:2nFTOH] ranged from <5.6 to 166 ng/g and [12:2nFTOH] ranged from 2 to 134 ng/g. Overall, fields 09D and 09F were the most contaminated with total [FTOHs] of 169 and 163 ng/g on dry-mass bases, respectively (Figure 2). In contrast, fields 09B, 09C and 09G had about 2−3 fold lower total [FTOHs].

The 6:2nFTOH and 8:2FT-acrylate (F(CF$_2$)$_8$CH$_2$−CH$_2$−OC(O)CH=CH$_2$) were quantifiable only in a few of the investigated soils, and then only at low levels (Table 1). The coincident observation of unquantifiable 6:2nFTOH but significant 12:2nFTOH in the soils is notable in that significant amounts of 6:2nFTOH commonly are measured in commercial/industrial products, while 12:2nFTOH residual in fluorinated materials often is not among the highest concentrations (9, 10). Possible causes for these contrasting observations include their chemical properties such as water solubility, octanol−air partitioning, and evaporative potential. For example, relatively short-chain 6:2nFTOH possesses high solubility (18.8 mg/L) and low sorption potential to soils (K_d = 2−17 L/kg for 0.52−8.18 soil organic carbon %) (23). These properties could facilitate the dissolved-phase transport or wash-off from the impacted soils. Evaporative potentials of low-molecular-weight FTOHs also might exceed those of heavier homologues. Another possible cause for low 6:2nFTOH contamination might be rapid transformation of short-length FTOHs, such as 4:2nFTOH and 6:2nFTOH, in a water−soil setting (23).
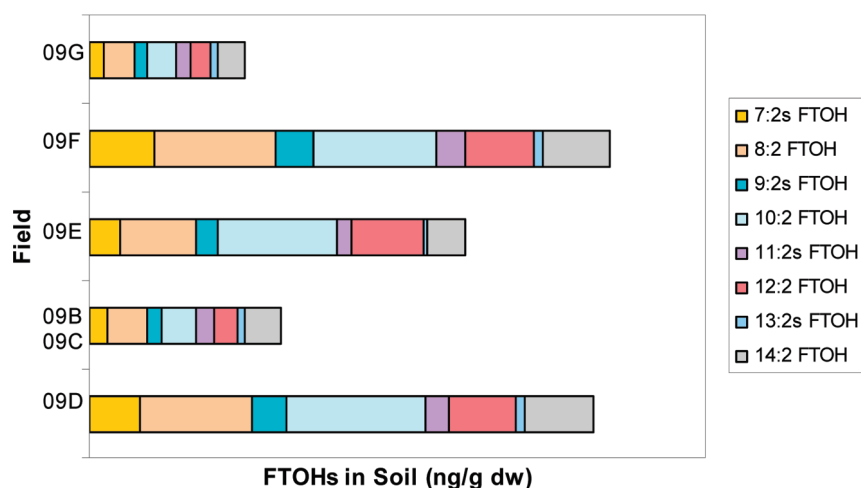
FIGURE 2. Geometric mean FTOH concentrations in investigated fields (ng/g dry soil). Each field had 5 sampling sites except contiguous fields 09B and 09C, which had similar sludge application histories and only 3 samples between them.

TABLE 2. First-Order Disappearance Constants and Half-Lives from Surface Soil Field Data (n = 31 Samples)

| | FTOH F stats[a] | | disappearance rate constant, half life | | | |
| | | | supported[b] | | unsupported[c] | |
FTOH Species	sludge app. rate	time since app.	k (yr^{-1})	$T_{1/2}$(yr)	k (yr^{-1})	$T_{1/2}$(yr)
7:2s	**13.33**	**36.38**	0.73 ± 0.08	0.99	1.90 ± 0.25	0.37
8:2n	2.28	**22.98**	0.65 ± 0.07	1.09		
9:2s	3.20	**19.03**	0.53 ± 0.06	1.34	2.62 ± 0.30	0.27
10:2n	0.84	**23.55**	0.84 ± 0.10	0.85		
11:2s	0.68	1.73			1.41 ± 0.25	0.50
12:2n	0.09	**14.17**	0.65 ± 0.08	1.11		
13:2s	3.92	0.37				
14:2n	1.50	**8.73**	0.39 ± 0.02	1.79		
Crit F (0.01)	**7.82**	**7.68**				

[a] F statistics test whether variation among sludge-application rates or a linear model of FTOH variation among classes through time explains a significant component of variation relative to among samples sharing a common sludge-application rate or time since sludge application. Bolded values are significant at $P = 0.01$. See text for details. [b] n-FTOH values are tabulated as "supported" based on their long disappearance $T_{1/2}$ value relative to literature degradation $T_{1/2}$ value, but whether they actually are supported by degradation of precursor remains uncertain; see text for details. [c] Unsupported model does not account for effect of n-FTOH precursors: data are from field 09C and field 09G where sludge application had elapsed 4 and 5 years, respectively, values equating to or exceeding about three estimated half-lives for the product compounds. See text for significance of this fact.

Discussion

Impacts of Sludge Application Cessation on FTOH Disappearance. The 2009 survey results that we report herein are compared with those of the 2007 reconnaissance survey (15) in Figure SI5. Though the data are few for the 2007 survey, $n = 5$ for September 2007 campaign versus $n = 23$ for March 2009, there appears to be a clear overall decrease in [FTOH] between the two sampling efforts (Figure SI5). For example, summing geometric means for n-FTOHs and their sec-FTOH transformation products, $\Sigma 8{:}2n$FTOH (i.e., [7:2sFTOH] + [8:2nFTOH]), was 210 ng/g in September 2007, but was about 5-fold lower in March 2009, only 42 ng/g. Similarly, differences between 2007 and 2009 for $\Sigma 10{:}2n$FTOH, $\Sigma 12{:}2n$FTOH, and $\Sigma 14{:}2n$FTOH were about 7-, 4-, and 2-fold, respectively. This decrease is evident in the only field that was sampled in both surveys as well, field 09B, however, there were only two independent surface samples drawn in each survey (Figure SI6).

Numerous factors potentially contribute to the heterogeneity of our soil FTOH results including variation in sludge FTOH concentrations, variation in sludge-application rates among fields, and time interval between application of sludge and soil sampling. Based on the best records available, all of the fields reported upon in this study received sludge applications during the period when Decatur sludges con-

tained the highest concentrations of fluorinated compounds, 2002–2006 (19). The potential effects of "variation in sludge-application rates among fields for 2002–2006", and the "time interval between last high-concentration sludge application (2006) and soil sampling" on the variability of our data can be evaluated independently because these variables are not correlated (19). Log-transformed soil [FTOH]s are plotted as a function of each of these variables in Figure SI7. These data are not bivariate-normally distributed so we assessed the significance of potential relationships plotted in Figure SI7 using an analysis of variance for unequal repeated measures (24), the results of which are tabulated in Table 2. These statistical results indicate that only 7:2sFTOH is significantly related ($p = 0.01$) to the sludge application rate for the years 2002–2006 when Decatur sludges were particularly high in fluorinated compounds. In contrast, the shorter-chain FTOHs, 7:2sFTOH through 10:2nFTOH, and the longer primary FTOHs, 12:2nFTOH and 14:2nFTOH, all are significantly related ($p = 0.01$) to time interval from the last sludge application in 2006 or earlier (Table SI1) and soil sampling (Table 2; Figure SI7).

Degradation of n-FTOHs to sec-FTOHs. To the best of our knowledge, along with the few exploratory data reported in Ellington et al. (15), the data we depict in Table 1 constitute the first detections of sec-FTOHs in environmental settings,
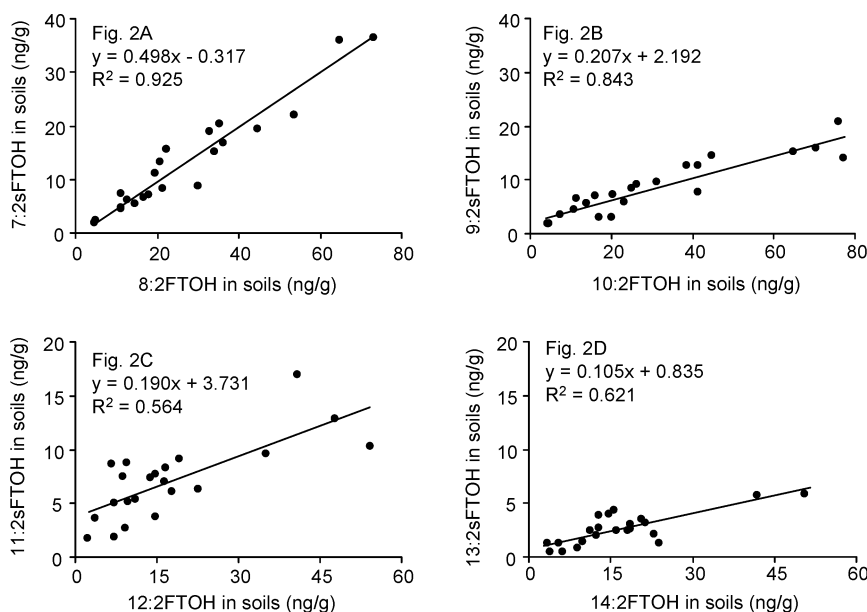
FIGURE 3. Relationship between *n*-FTOH and its *sec*-FTOH transformation product in sludge-applied surface soils ($n = 23$). All correlations were significant (Pearson, $p < 0.001$).

i.e., nonlaboratory. Of these compounds, the 7:2*s*FTOH first was identified by Wang et al. (*6*) as a volatile intermediate in a biodegradation sequence starting with the primary 8:2*n*FTOH and leading to recalcitrant products including PFOA. In this scheme, 8:2*n*FTOH is oxidized to the 8:2-telomer acid (8:2-FTA) which is subject to β-oxidation to form the 8:2-unsaturated acid (8:2-FTUA), which degrades to 7:2*s*F-TOH, the direct precursor to PFOA (*6*). Guided by this laboratory study of the 8:2*n*FTOH degradation sequence, Ellington et al. (*15*) performed exploratory analyses of a few sludge-treated soils for homologous *n*- and *sec*-FTOH pairs. With the larger number of sludge-treated soil samples of our present study, we explored the relationships between the *sec*-FTOHs and their *n*-FTOH precursors, finding a statistically significant relationship for each of the four FTOH pairs we examined (Figure 3). These observations support the idea that *n*-FTOHs are degrading to form *sec*-FTOHs in these sludge-applied soils. The ratio of 7:2*s*/8:2*n*, the shortest homologous pair we detected, was the highest at 0.50, and the longest homologous pair yielded the lowest ratio, 13:2*s*/14:2*n* = 0.10. Two intermediate-length homologous pairs exhibited similar ratios: 0.21 and 0.19 for 9:2*s*/10:2*n* and 11:2*s*/12:2*n*, respectively. This pattern suggests that the susceptibility to degradation of *sec*-FTOHs, relative to their *n*-FTOH precursors increases with increasing chain length.

Depth Profiles. Potential transport of surface-retained FTOHs was studied with subsurface soils from three sites in fields 09B and 09C (Table SI7). No analytes were evident at either of two sampled depths, except for the recovery internal standard which indicated satisfactory recoveries (Table SI7). If the alcohols do leach to deeper soil, evidently they remain in solution and pass through the soil column. Although these data are limited in terms of sample number and depths, they suggest that subsurface soil solids do not constitute a major reservoir for FTOHs in the environment.

Disappearance Half-Lives. Following the logic of our accompanying paper (*19*), we calculated the field disappearance half-lives ($T_{1/2}$) of *n*-FTOHs using the simplest first-order disappearance model (*19*) in which the first-order disappearance constant, k (yr^{-1}), is given by the slope of the least-squares line in ln[FTOH] vs time (yr) space. All modeled parameters, generated using data for all seven fields, are summarized in Table 2. Field-determined disappearance half-lives (Table 2) are comparable for 7:2*s*FTOH (0.99 yr),

8:2*n*FTOH (1.09 yr), 9:2*s*FTOH (1.34 yr), 10:2*n*FTOH (0.85 yr), and 12:2*n*FTOH (1.11 yr), but 14:2*n*FTOH was a little longer (1.79 yr).

Our calculated disappearance half-life for 8:2*n*FTOH in field soils, ~1 yr, greatly exceeds the range of degradation half-lives reported for 8:2*n*FTOH in laboratory soil microcosms of about 7−28 days (*6, 25, 26*). One possible cause for this discrepancy is that the concentration of *n*-FTOHs might be *supported* by degradation of precursor compounds by a pathway leading to *n*-FTOHs. We have no data on the presence or absence of *n*-FTOH precursor compounds in our samples, but polyfluoroalkyl-phosphoric acids (PAPs) (*27, 28*) and fluorotelomer-based polymers (*7*) both are potential sludge constituents that have been shown to degrade to *n*-FTOHs.

The support of precursor compounds apparently complicates characterization of the persistence of the *sec*-FTOHs; for example, the least-squares line in ln[13:2*s*FTOH] vs time actually has a positive slope, albeit for a nonsignificant relationship (data not shown). Increasing concentration through time would suggest that a product compound is being made by precursor degradation faster than it is being lost by degradation and other processes. For *sec*-FTOHs, we can partially overcome obfuscating effects from precursor degradation by assuming the degradation series of *n*-FTOH to *sec*-FTOH approximates *transient equilibrium*, i.e., when the $T_{1/2}$ of the precursor compound exceeds that of the product, after about three product half-lives, the precursor and product approximate a constant ratio defined by (*29*)

$$\frac{[n\text{-FTOH}]}{[sec\text{-FTOH}]} = \frac{(k_s^u - k_n^u)}{k_n^u} \tag{1}$$

where k^u designates the *unsupported* first-order rate constant for the compound identified in the subscript. Modeling results for unsupported *sec*-FTOHs also are summarized in Table 2. Whereas the supported disappearance half-lives for *n*-FTOHs ranged from 0.8 to 1.8 years, the estimated unsupported half-lives were much shorter, 0.3−0.5 years (Table 2). Caution is merited in the interpretation of these unsupported modeling estimates because the disappearance-rate constants we input to eq 1 for *n*-FTOHs might be supported values as we discussed above. To the extent that the k_n values we input to

eq 1 are supported values, the estimated unsupported $T_{1/2}$ values we calculate for *sec*-FTOHs should be regarded as upper limits.

Perspective. We detected elevated levels of numerous *n*- and *sec*-FTOHs in soils that had last received sludge applications as much as five years earlier. Comparison of the general FTOH concentrations we report herein with the PFCA concentrations we report in these same soils (*19*), shows that the [FTOH]s commonly are about 1/4 those of the [PFCA]s within the first year after sludge application in the soils we studied. Considering that the disappearance half-lives we calculate for FTOHs brackets about a year (Table 2), these data suggest that FTOHs, or their precursors, had significant concentrations in the sludge that was applied to the fields. To the extent the sludge applied is not atypical in the ratio [FTOH]/[PFC], these data suggest that characterization of sludges for PFC loading should include analysis of FTOHs and perhaps other precursor compounds, as well.

Acknowledgments

Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.

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