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Degradability of an Acrylate-Linked, Fluorotelomer Polymer in Soil

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Fluorotelomer polymers are used in a broad array of products in modern societies worldwide and, if they degrade at significant rates, potentially are a significant source of perfluorooctanoic acid (PFOA) and related compounds to the environment. To evaluate this possibility, we incubated an acrylate-linked fluorotelomer polymer in soil microcosms and monitored the microcosms for possible fluorotelomer (FT) and perfluorinated-compound (PFC) degradation products using GC/MS and LC/MS/MS. This polymer scavenged FTs and PFCs aggressively necessitating development of a multistep extraction using two solvents. Aged microcosms accumulated more FTs and PFCs than were present in the fresh polymer indicating polymer degradation with a half-life of about 870−1400 years for our coarse-grained test polymer. Modeling indicates that more-finely grained polymers in soils might have half-lives of about 10−17 years assuming degradation is surface-mediated. In our polymer-soil microcosms, PFOA evidently was lost with a half-life as short as 130 days, possibly by polymer-catalyzed degradation. These results suggest that fluorotelomer-polymer degradation is a significant source of PFOA and other fluorinated compounds to the environment.

Introduction

Fluorotelomers (FTs) and fluorotelomer polymers (FTPs) are marvels of convenience enjoyed in modern society. Imparting antiwetting and antistaining properties to a wide cross-section of modern products—clothing, upholstery, carpeting, fast-food containers—FTs and FTPs are highly valued by consumers. Now, following decades of sales and use, FTs and FTPs are widely dispersed throughout technologically advanced economies, and they have been estimated to have direct and indirect financial impacts in excess of $1.7 billion dollars per year (*1*), a value exceeding the 2007 gross domestic product of more than thirty nations (*2*).

At the same time, recent research has identified byproducts of this industry, including perfluorooctanoic acid (PFOA; C_8), other perfluorocarboxylic acids (PFCAs), and related perfluorinated compounds (PFCs), as being globally distributed in humans (*3*−*6*), ecosystem media (*7*−*10*), and wildlife (*11*−*14*). And still other studies have indicated that PFOA has multiple modes of toxicity in mammalian systems (*15, 16*). Taken together, these factors have focused considerable attention on PFOA and related compounds in the environmental-science community and popular media, as well as attracting close scrutiny by the environmental agencies of several countries, including the United States Environmental Protection Agency (USEPA).

There are several recognized sources of PFOA-related compounds to the environment, e.g., releases from manufacturing facilities and sewage-treatment plants, as well as leaching of trace levels of residual PFCs from FTPs (*17, 18*), but it remains unclear whether these recognized sources can account for the magnitude or pattern of PFOA distribution documented in these and other studies. A key uncertainty is whether the FTPs can degrade to form PFCAs. The prominence of this FTP-degradability issue lies in how it might impact the source term for PFCAs. If PFCAs can be generated from FTPs by polymeric degradation, the source term of PFCAs to the environment could be much greater than that of presently recognized sources. If the source term of PFCAs to the environment is bolstered by FTP degradation, future environmental loads of PFCAs, including PFOA, could be much larger than presently anticipated.

To address this uncertainty regarding whether FTPs might degrade, and in support of the USEPA mission, we performed a 546-day incubation of an acrylate-linked FTP (AFTP; Figure 1) mixed into soil microcosms to determine whether the AFTP degraded to form FTs and PFCs using gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem-mass spectroscopy (LC/MS/MS).

Background

FTPs often are composed dominantly of 8-carbon perfluorinated chains that are linked, along with lesser quantities of nonfluorinated moieties, to long polymeric backbones by one of a few functionalities, among these, the acrylate linkage of our test material (*19*) (Figure 1). Given this variable composition, as well as the large molecular mass and solid physical state, FTPs cannot be analyzed directly to inspect for and quantify molecular-scale degradation. Instead, degradation of aged FTPs can be evaluated by whether concentrations of inferred degradation products have increased over those of new FTPs. The mere presence of possible degradation products in samples does not indicate degradation, however, because low levels of these compounds are present in new FTPs as "residuals" and "impurities" from manufacturing.

Potential pathways for AFTP degradation include cleavage of the carbon backbone to form the 8-2 fluorotelomer acrylate (8-2FTAc), or hydrolysis of the ester linkage between the perfluorinated chain and the carbon backbone to form the 8-2 fluorotelomer alcohol (8-2FTOH; Figure 1) (*20*). If 8-2FTAc is formed, it likely is subject to degradation to form 8-2FTOH. Further degradation of 8-2FTOH has been shown via oxidation to 8-2 fluorotelomer carboxylic acid (8-2FTCA) and then to 8-2 fluorotelomer unsaturated carboxylic acid (8-2FTUCA) (*21*). β-oxidation of 8-2FTUCA is known to occur through a series of transitory intermediates to form PFOA, the conventionally inferred terminal compound identified for this oxidative degradation sequence (Figure 1) (*21*). Degradation of 8-2FTUCA also can yield the 7-3 fluorotelomer unsaturated carboxylic acid (7-3FTUCA) and then the 7-3 fluorotelomer carboxylic acid (7-3FTCA) which possibly can undergo β oxidation to PFOA (*21*).

Fluorotelomers and PFCs exhibit both hydrophobic and lipophobic properties in most settings. As a consequence,

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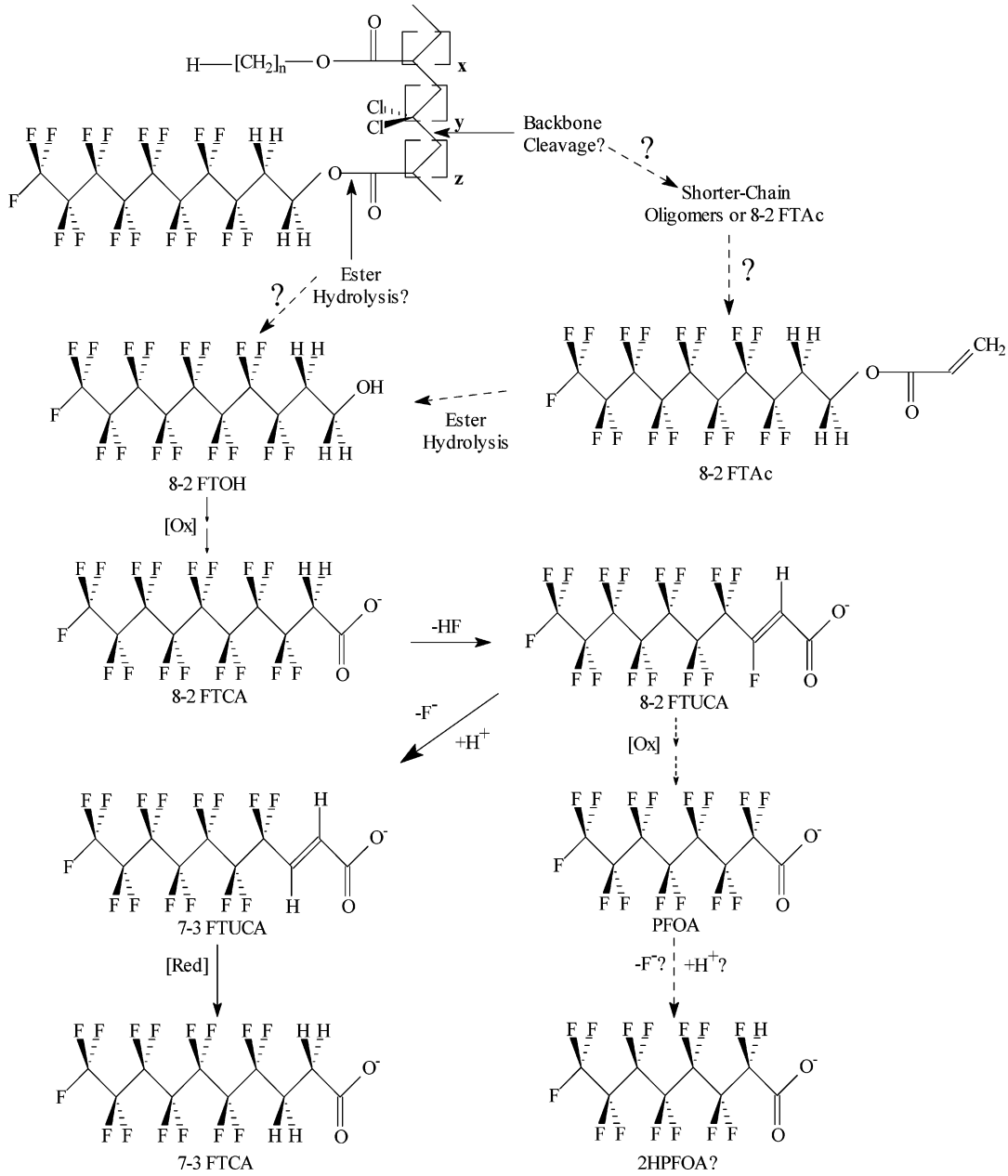

FIGURE 1. Conceptual model for degradation of AFTP through intermediary products to PFOA and a possible product of PFOA, or other PFC, degradation. See text for explanation. The depicted AFTP is after Russell et al. (*19*).

the tendency of FTs and PFCs is to coattract each other to the exclusion of unfluorinated chemicals, consistent with their design intent. However, this coassociative habit hinders the efficacy of nonfluorinated solvents to extract FTs and PFCs from FTPs in two ways:

(1) The equilibrated distribution of FTs and PFCs between FTPs and nonfluorinated solvents favors the FTP phase; in a methods-development experiment, we extracted, with 60/40 acetonitrile (ACN)/H_2O (v/v), $^{13}C_5$-perfluorononanoic acid ($^{13}C_5$PFNA) that was spiked onto our test AFTP, Supporting Information, Section 4 (SI:4). Recovery was incomplete and the calculated distribution coefficient (K_d) was 23 ([solid]/[solution]); and

(2) The cohesive forces between fluorinated organic molecules, including FTs, PFCs, and FTPs, exceed those of adhesive forces with most common nonfluorinated solvents (*22*). Consequently, in nonfluorinated solvents the FTPs remain intact physically shielding FTs and PFCs in the FTP interior from equilibrating with the solvent altogether (Figure 2). The magnitude of this second effect is reflected in the $^{13}C_5$PFNA-sorption experiment (SI:4) in that, when the test polymer structure was "opened up" by dissolution in one of the more effective solvents, methyl tert-butyl ether (MTBE), before spiking with $^{13}C_5$PFNA, the subsequent extraction recovery fell precipitously: $K_d = 170$ compared to $K_d = 23$ for the polymer that was not treated with MTBE, reflecting exposure of interior sorption sites by the MTBE treatment (SI:4).

In an effort to address these challenges, Larsen et al. (*23*) conducted an exhaustive method-development effort for the characterization of FTs and PFCs in FTPs, and argued that the polymeric phase must be dissolved completely to characterize the FT and PFC content. This necessity to completely dissolve the FTP polymeric phase to determine FT and PFC content confounds interpretability of the only two previous literature studies reporting conclusions on the biodegradability of AFTPs (*19, 20*). Both studies reported finding no FTs or PFCs beyond those that could be accounted for in the fresh polymer; however, the AFTP microcosms of these studies were extracted with ACN (*20*) and isopropanol

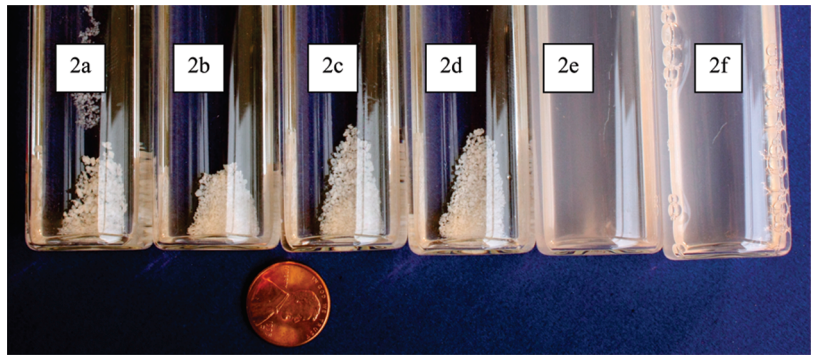

FIGURE 2. Our test acrylate-linked fluorotelomer polymer (AFTP) in candidate extraction solvents. The persistence of granular AFTP in water (a), methanol (MeOH;2b), 60% acetonitrile/40% water (ACN/H_2O;2c), and 93% ACN/7% 200 mM NaOH (d) indicates that the surface tension of the liquids exceeds that of the AFTP phase so that the solid particles are stable. In contrast, methyl tert-butyl ether (MTBE;2e) and tetrahydrofuran (THF;2f) have sufficiently low surface tensions to "dissolve" the solid AFTP. Solvents in which the solid AFTP is stable cannot wet the AFTP (*22*), leaving AFTP particle interiors and associated perfluorinated molecules effectively shielded from solvent extractions. The ACN/NaOH solvent shown above, with the solid AFTP particles remaining undissolved, (d) is the same solvent used by Russell et al. (*20*) to extract their soil/AFTP microcosms. The MTBE (e) and ACN/H_2O (c) were the primary and secondary solvents used in our extraction. The appearance of the MTBE, apparently clouded by AFTP micelles, compares closely with that of the THF (f) which Larsen et al. (*23*) identified as effective for extracting fluorotelomer chemicals.

(*19*). Assuming the AFTPs used in these earlier studies had solubilities similar to the AFTP we tested (Figure 2), these two studies failed to achieve the complete FTP dissolution determined to be necessary to characterize FTs and PFCs in FTPs by Larsen et al. (*23*).

This fluorophilicity also renders one of the most common methods used to evaluate efficacy of extraction, recovery of spiked internal recovery standards, ineffective for use with soil−FTP microcosms. This is true because, if FTPs do degrade, their perfluorinated products will tend to remain entrained within and sorbed to the source polymer as described above (SI:4). In contrast, internal recovery standards spiked into soil−FTP microcosms will be exposed mostly to the spatially dominating soil matrix of the microcosm as opposed to the relatively trace FTP.

Experimental Design and Methods

Our test AFTP was prepared by an FTP manufacturer with the intent of minimizing residual-FT and PFC content (SI: 2.3) to maximize our ability to resolve small concentration increases during the course of the experimental incubation, should there be any. The test soil was a sandy loam with 8.7% organic matter and a cation-exchange capacity of 8.2 meq/100 g that is sold commercially by a company from Sugar Hill, GA (SI:2.2), upon which we had performed much of our methods development (*24, 25*). Treatment microcosms were prepared by placing about 10 mg of the AFTP, 5 g of soil, and sufficient 18-MΩ water to saturate soil pores, about 2 g, into 16-mL centrifuge tubes, sealing the tubes with oversized caps (SI:3) and storing in an incubator maintained at 25 °C (SI:1 and 3). For these specifications, the microcosms consisted of about 3- to 4-cm-deep saturated soil plugs; the intent of this design was to assure: 1) wetting of the AFTP surface; and 2) moist soil conditions over protracted incubation periods with a mix of aerobic and anaerobic environments assuming typical gas-diffusion rates through short path-lengths of water-saturated soil pores (*26, 27*). With the objective of overcoming potentially long enzyme-induction lag periods, a second set of treatment microcosms was prepared identically to those described above, but augmented by inoculation with a consortium of nonengineered microbes that is sold commercially to enhance soil productivity (SI: 2.4).

We prepared for this research by developing methods for extraction/analysis of FTs and PFCs from soils (*24, 25, 28*) and by reviewing methods summarized for us by researchers conducting similar studies that were ongoing at the time. With this preparation, we designed this study to have several sampling rounds consisting of treatments including (1) soil, endogenous microbes, AFTP, and (2) soil, inoculated microbes, AFTP; and controls including (1) incubated, aged soil, inoculated microbes, (2) incubated, aged water, (3) freshly prepared sand blank, (4) freshly prepared solvent blank, (5) freshly prepared soil blank, endogenous microbes, (6) freshly prepared sand, AFTP, and (7) freshly prepared AFTP alone. However, with each early extraction effort, we discovered unacceptable artifacts and, consequently, we consumed several rounds trying to master extractions and analyses that would generate unflawed and interpretable data. Achieving this objective was made exceedingly difficult by (1) the number of analytes with widely varying properties requiring sequential extraction procedures for analysis on two instruments, (2) the mix of two complex matrices, soil and polymer, each having needs exclusive of the other for effective extraction, and (3) temporally changing complications with each new extraction attempt deriving from target-analyte degradation during incubation from dominantly one family of analytes, fluorotelomers, to dominantly another family, perfluorinated acids (SI:5.2.1). Following more than a year of efforts to develop artifact-free extraction and analysis procedures for all the target analytes, we arrived at the methods, and results for two sampling rounds, reported herein. To accommodate loss of the early sampling rounds, for each new sampling round, we would (1) prepare three new treatment microcosms identically to those originally prepared for this study to represent time zero and to allow us to compare directly all results within each sampling round using internally consistent extraction and analytical methods; and (2) extract three replicate microcosms of each treatment and control for all analytes. In summary, treatments, controls, and the AFTP alone were extracted in MTBE three times based on methods developed by Ellington et al. (*28*) followed by ACN:H_2O based on methods developed by Washington et al. (*24, 25*) (SI:5.2).

GC/MS in positive-chemical-ionization (PCI) mode was used to analyze 8-2FTAc, 8-2FTOH, and homologues with mass-labeled recovery and matrix internal standards (SI:6.1). We used LC/MS/MS in negative electrospray-ionization ((−)ESI) mode to analyze PFOA and its homologues, C_6 (perfluorohexanoic acid-PFHxA) through C_{12} (perfluoro-

dodecanoic acid-PFDoA), as well as internal recovery and matrix internal standards (SI:6.2).

Discussion

Mass Balance. All analytical results are reported in Tables S3 and S4. These data support the conclusion that multiple extraction rounds were needed to deplete the AFTP and AFTP-containing microcosms of FTs and PFCs. For example, the first MTBE extraction typically recovered between 3 and 70% of the total recovered in all four sequential extractions with the fraction varying between chemical species and period of incubation (Table S5). Efficacy of later extraction steps also varied as a function of these variables; however, summing the molar contributions for the series 8-2FTAc → 8-2FTOH → 8-2FTUCA → PFOA indicates that the four-step extraction did effectively deplete the fresh AFTP and time-zero microcosms of FTs and PFCs in that the last two extraction rounds summed to yield only about 6% of the total extractions (Table S5). In contrast, the aged microcosms yielded 10−50% of their total analytes in extraction rounds 3 and 4 (Table S5); consequently, the aged microcosms might have yielded significantly more analytes with additional extraction rounds. As such, these data likely represent essentially all of the FTs and PFCs in the unaged AFTP, but potentially could *understate* the PFC content of the aged soil−AFTP microcosms. This observation is important because, if the aged microcosms have an excess of FTs and PFCs over the fresh AFTP, this difference is not an artifact of an ineffective extraction of the AFTP or the time-zero microcosms.

This recalcitrance of the AFTP to yield all of its FTs and PFCs to extraction does not negate AFTPs as potential sources of PFCs to the environment; rather, it reflects that the *rate* of contribution to the environment likely will be limited by partitioning of the PFCs to water encountering the AFTPs in the environment. If AFTPs do not degrade, then their role as a source of PFCs to the environment will end when the AFTPs are depleted of their residual FTs and PFCs by partitioning to by-flowing waters. In contrast, if AFTPs do degrade, they will continue to yield low PFC concentrations into by-flowing water after their residuals are depleted until the AFTPs no longer generate FTs and PFCs.

Based on the structure of AFTPs and the FTOH studies of Wang et al. (*29*), Russell et al. (*20*) developed a conceptual model for 8-2FTs wherein AFTP degradation proceeds according to 8-2FTAc → 8-2FTOH → 8-2FTCA → 8-2FTUCA → 7-2sFTOH → PFOA; following this logic, microcosms having molar sums of these analytes exceeding that of the fresh AFTP would be accepted as evidence of polymeric degradation. We analyzed all of these compounds except the particularly unstable 8-2FTCA and 7-2sFTOH. In addition, we analyzed compounds potentially leading to PFOA homologues, e.g., perfluorohexanoic acid (PFHxA) through perfluorododecanoic acid (PFDoA), thus allowing for the quantification of homologously related possible-degradation sequences as was done by Russell et al. (*20*) (Figure 3). Inspection of Figure 3 reveals numerous incidences in which one or more potential degradation sequences exceeded that of the fresh polymer indicating that the AFTP degraded. Sequences in the aged triplicate microcosms that had statistically greater quantities (SI:9) than the triplicate extractions of the fresh AFTP include (Figure 3, Table S7) the following: (1) C_6 in the 497-d endogenous microcosms ($P < 0.01$); (2) C_8 in the 497-d inoculated microcosms ($P < 0.01$); (3) C_{10} in the 546-d endogenous microcosms ($P < 0.05$); (4) C_{10} in the 497-d inoculated microcosms ($P < 0.01$); (5) C_{10} in the 546-d inoculated microcosms ($P < 0.05$); (6) C_{12} in the 546-d endogenous microcosms ($P < 0.01$); and (7) C_{12} in the 546-d inoculated microcosms ($P < 0.01$).

Inspection of Figure 3 also reveals numerous occurrences in which the triplicate 546-d microcosms had molar summations of less than the triplicate 497-d microcosms. Evidently, one or more compounds in each degradation sequence degraded to one or more undetermined products. Based on the results of multiple studies, this loss likely is due in part to the conversion of FTOHs to products other than PFOA, with conversion efficiency from 8-2FTOH to PFOA and other identified products commonly summing to less than about 60% (*21, 29−31*). In one of these studies, an alternative degradation pathway giving rise to a specific product was identified, i.e., 7-3FTCA (*29*). In another study, a possible alternative product was identified, i.e., PFHxA, but the transformation pathway remained undetermined (*21*). To account for these undetermined compounds, Russell et al. (*20*) invoked the research of Wang et al. (*29*) to justify modeling the degradation of 8-2FTOH to PFOA as having a PFOA-yield efficiency of 28%, effectively modeling the product imbalance as equal to [PFOA]/0.28. Following Russell et al.'s lead, we modeled the 8-perfluorinated-C sequence as 8-2FTAc → 8-2FTOH → PFOA(1 + 1/0.28) and depicted this "Russell-model" in Figure 3 as well. All four triplicate-microcosm treatments, endogenous and inoculated, 497-d and 546-d, subjected to the Russell model, are calculated to have more PFC equivalents than the fresh AFTP, indicating polymer degradation in every case (Figure 3), further supporting our conclusion based on experimental data that the AFTP degraded.

Among the compounds that decreased between the 497-d and 546-d microcosms were the C_6 through C_8 PFCAs in the endogenous microcosms (Table 1; SI:10). Whereas PFCAs commonly are considered recalcitrant, terminal degradation products, at least one other incubation study depicted a possible loss of PFOA as well (*30*). Application of the Student's *t* test to our data indicate that the decreases were statistically significant (SI:10). Moreover, the magnitude of these changes

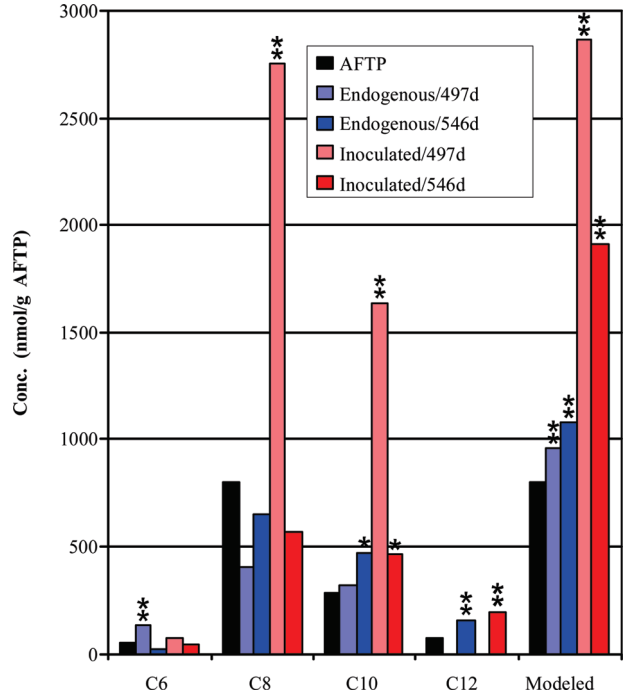

FIGURE 3. Molar recoveries from test AFTP and aged microcosms of selected analytes. For C_6, the summed sequence is 6-2FTAc → 6-2FTOH → PFHxA; for C_8, 8-2FTAc → 8-2FTOH → 8-2FTUCA → PFOA; for C_{10}, 10-2FTAc → 10-2FTOH → PFDA; for C_{12}, 12-2FTAc → 12-2FTOH → PFDoA; and for modeled C8, we used the assumption of Russell et al. (*20*) that the yield efficiency for PFOA was 28% (see text for details). Asterisks indicate microcosms have significantly more selected PFC equivalents than does the AFTP at the 95% level (*) or the 99% level (**) (SI:9).

TABLE 1. PFCAs in Endogenous Microcosms (nmol/g)

treatment & time	PFHxA		PFHpA[a]		PFOA		PFNA		PFDA	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
497 days	158.7	5.4	110.7	28.0	184.3	23.7	2.5	1.3	8.6	4.2
546 days	19.0	5.5	44.1	14.0	141.9	17.1	2.9	1.1	11.4	3.6
change	–139.8	7.7	–66.6	31.3	–42.4	29.2	0.4	1.7	2.8	5.6

[a] Perfluoroheptanoic acid - PFHpA, C_7.

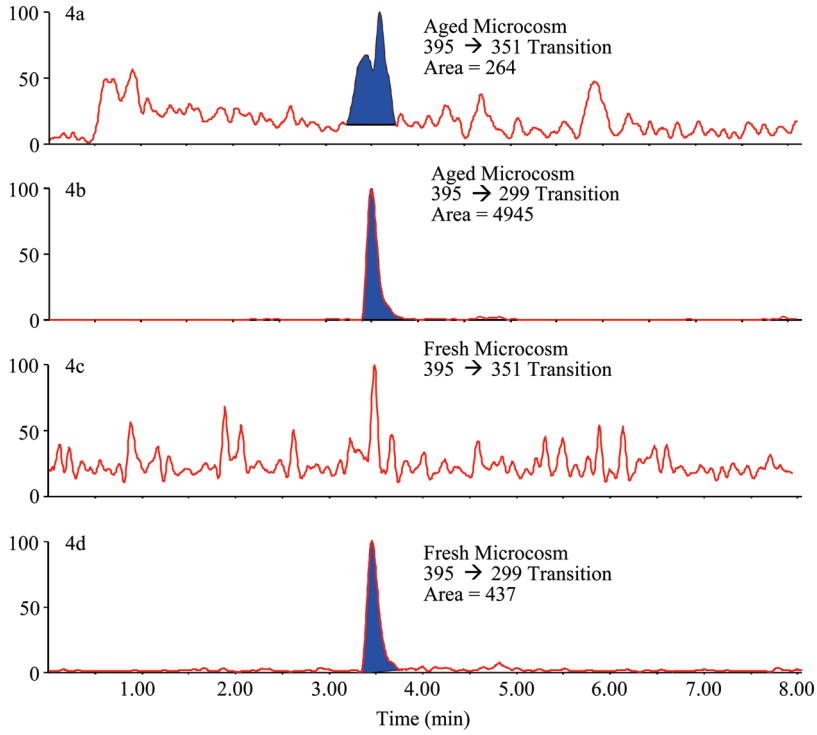

FIGURE 4. LC/MS/MS chromatograms for two transitions of a possible product of PFOA degradation, 2HPFOA. The signals were about 10-fold larger in aged microcosms (a and b) than in fresh polymer (c and d). See text for details.

in PFCAs follows a homologous pattern, i.e., the decreases were greatest for C_6 series, followed by C_7, then C_8. In contrast, C_9 and C_{10} did not change significantly (Table 1; SI:10).

The temporal decreases of PFCAs observed in our study suggested that one or more products of PFCA degradation might be present in the 546-d microcosm extracts as well. Using LC/MS/MS to select candidate masses in the first quadrupole and by scanning fragments in the third quadrupole, we have identified a possible product of PFOA degradation that had a strong MS/MS signal in the aged, inoculated microcosms, but little to no signal for extracts of the AFTP, test soil, and unaged microcosms (Figure 4; SI:10). For the possible PFOA degradation product, 2HPFOA (Figure 1), the identified peak (Figure 4) was $m/z = 395$, corresponding to loss from PFOA of F and gain of H. For this peak, we identified two transitions, 395 → 351 and 395 → 299, corresponding to loss of CO_2 to form $F_3C(CF_2)_5CHF^-$ and loss of H+5F to form $F_3C(CF_2)_2(CF)=(CF)C\equiv CCOO^-$, respectively. This hypothetical PFOA degradation product, 2HPFOA, might help account for the loss of PFOA depicted in Dingleson et al. (*30*) as well as be an intermediary in the unidentified path leading from 8-2FTOH to PFHxA for which Wang et al. (*21*) argued.

We modeled the loss of C_6 through C_8 in the endogenous microcosms as first-order in [PFCA] (SI:10) to calculate a half-life ($t_{1/2}$) for C_6 of 16 days, for C_7 of 37 days, and for C_8 of 130 days. We stress that these calculated half-lives are for soil−*AFTP* microcosms, in which the source of the PFCAs ultimately is the AFTP, whether from residuals and/or degradation products. This is important because our experiment with sorption of $^{13}C_5$PFNA on our test AFTP (SI:4) showed that PFCAs sorb strongly to AFTPs when AFTPs are present. Among other possible effects, strong sorption of the perfluorinated chain of PFCAs on AFTPs may destabilize bonds on distal, relatively hydrophilic carboxyl moieties so that the AFTP surface might act to catalyze PFCA degradation at rates substantially faster than in soil without AFTPs. Regardless, our experiment offers no justification to extrapolate these apparent PFCA-loss half-lives in soil−*AFTP* microcosms to soil alone.

Modeling Degradation Rates of Test AFTP and Commercial AFTPs. A pseudo-first-order degradation rate for the AFTP in the microcosms can be modeled conservatively by (1) assuming the AFTP was composed entirely of the ester-linked fluorotelomers (Figure 1); (2) treating the reaction as first-order in the total moles of polymer-bound fluorotelomers whether exposed to the aqueous environment or isolated deep in the AFTP interior, consistent with the approach of Russell et al. (*20*); (3) attributing the molar excesses that we observed in the aged microcosms, relative to the fresh AFTP (Figure 3; Tables S6 & S7), to ingrowth from AFTP degradation (SI:11); (4) assuming that PFCA precursors all degrade to one of our analytes, which likely is incorrect and thus overly conservative; and (5) assuming that PFCAs were stable over the course of the incubation, which evidently is overly conservative as well. Applying this rough model to our data, we arrived at apparent half-lives for our test AFTP of about 870−25 000 y (Table S9).

Whereas the above AFTP-degradation modeling does not require knowledge regarding the degradation rate of any degradation products, the AFTP half-life estimate generated from this effort potentially is subject to overestimation if there are degradation products for which we did not analyze; the apparent losses of PFOA and shorter-chain PFCAs (Table 1) are suggestive that some unknown fraction remains unaccounted for in our analyte list. Another estimate of AFTP halflife, that is unaffected by the existence of unknown degradation products, can be generated if the half-life of a degradation product is known. Koch et al. (*32, 33*) recently reported the half-life of 8-2FTOH in soil to be 28 days. Using this 28-day FTOH half-life value, our 546-day FTOH data and a two-component first-order model (SI:11.2), we estimate a half-life for our test AFTP of 290−1400 years which overlaps the independently derived estimate above. While this second half-life estimation is not subject to overestimation due to the presence of unaccounted-for degradation products, it is subject to underestimation because it assumes that all the FTOH is subject to degradation when, in fact, FTOH located deep within AFTP particles might be sheltered by the surrounding polymeric structure. Based on these considerations, we consider the best estimate for the test AFTP half-life to be the range enveloped by both estimates, i.e., 870−1400 y.

This estimated half-life for our test AFTP overlaps the estimate of Russell et al. (*20*) of 1200−1700 years. However, there are substantive differences between these estimates in the experimental and modeling methodologies they are built upon that preclude a substantive comparison of the results of these studies (SI:12): Russell et al. extracted their fresh polymer, which served as the benchmark to which aged microcosms were compared, with tetrahydrofuran which is an effective AFTP solvent (Figure 2), but extracted the aged microcosms with ACN which is an ineffective AFTP solvent (Figure 2); in contrast, all our extractions were performed with MTBE, an effective AFTP solvent (Figure 2), followed by ACN. Given the inconsistent extraction procedures between the fresh polymer and aged microcosms used by Russell et al., their experimental results are not a conservative database for inference regarding polymer degradation; in contrast, we subjected our polymer and aged microcosms to the same aggressive extraction procedure, so our results are a conservative database for inference regarding polymer degradation (SI:12).

Nonperfluorinated materials in aqueous solutions cannot lower the surface tension of water below the critical surface tension of fluorotelomer moieties (*22*), hence, AFTP particles cannot be wetted on their fluorotelomer interiors. In the absence of water, environmental microbes and enzymes are unable to migrate to the anhydrous interior of AFTPs so the degradation that we observed in our experiment likely took place at the AFTP surface. For systems in which a solid surface is subject to chemical attack from aqueous surroundings, and when the surface area is limited, the difference in degradation rates between systems often is proportional to the difference in specific surface area (SI:12). Based on particle-size analysis, the specific area of our test AFTP was about 0.05 m^2/g AFTP. In contrast, the specific area of a typical commercial AFTP can be calculated to be about 14 m^2/g AFTP (SI:12) or about 300-times that of our test AFTP.

Given the differences in specific area between our test AFTP and typical commercial AFTPs, and using the half-lives we arrived at experimentally for our test AFTP, our best estimate of a typical, acclimated half-life for a commercial AFTP in soil is about 10−17 yrs (SI:12.1−12.4).

Perspective. Our estimate of commercial AFTP stability contrasts diametrically with those of Russell et al. (*20*), the only other AFTP degradation study published in peer-reviewed literature. While these studies examined the same category of polymer, AFTPs, they had prominent differences as well: (1) we used a multistep extraction to exhaust the AFTP of residual FTs and PFCs for analysis whereas Russell et al. used a one-step extraction with ACN-NaOH, an ineffective solvent for AFTPs, so the FTs and PFCs actually present in their aged microcosms remain an unknown quantity; (2) Russell et al. used an AFTP with much smaller particle size, and higher surface area, than us; and (3) we modeled the degradation rate as first-order in surface area whereas Russell et al. modeled it as first order in mass. Russell et al.'s extractions almost certainly did not recover all the FTs and PFCs in their microcosms for the following reasons: (1) Russell et al.'s ACN-based extracting solvent did not dissolve our test AFTP (Figure 2), which is structurally similar to the AFTP used by Russell et al. and related research has shown that thorough extraction of FTs and PFCs from FTPs *requires* dissolution of the polymer (*23*); and (2) our experiments with extraction of a ^{13}C-labeled PFCA from the AFTP using an ACN solvent similar to that of Russell et al. showed that much of the PFCA did not dissolve in the solvent, instead remaining sorbed to the AFTP (SI:4). Consequently, the reported half-lives of Russell et al. (*20*) most likely do not characterize AFTP degradation rates. On the other hand, after AFTP-degradation has progressed appreciably, reaction rates might deviate from strictly first-order in surface area (SI:12); though our modeled half-lives for typical commercial AFTPs of 10−17 yrs account for this factor, our model-input assumptions could be flawed. If our modeling is flawed, half-lives of typical AFTPs might be as long as those we observed experimentally for our test AFTP, i.e., 870−1400 yrs. Both studies must be viewed within these limitations. While these uncertainties call for further study, such work is not without complications (SI:13). Regardless, our research demonstrates that AFTPs can degrade in soils through attack on the carbon backbone and/or the ester linkage connecting the polymer backbone to the fluoroalkyl side chains. Since the carbon backbone and ester linkages are characteristic of all AFTPs, we believe that all AFTPs are susceptible to this type of degradation, albeit at rates that are sensitive to factors such as interfacial surface area, hydrophilicity/phobicity, the presence of biodegradable moieties, and the presence of groups that bind to AFTP surfaces, reducing bioavailability. Given our findings and modeling, as well as the remaining uncertainties, prudence dictates inclusion of AFTP biodegradation as a source of PFOA and PFCAs to the environment.

Epitaph. We dedicate this paper to our friend and coauthor Dr. John Evans who passed away shortly before completion of the manuscript. John was an insightful scientist, generous collaborator, patient teacher and beloved family man, and we are better for having known him.

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Supporting Information Available

Text detailing study design, materials used, a supporting side experiment, extraction and procedures, assimilation of analytical results, statistical analyses, and modeling; exhaustive tables of analytical results. Supporting text is divided into sections by subject and referenced in this paper by relevant section. This information is available free of charge via the Internet at http://pubs.acs.org.

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