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Decades-Scale Degradation of Commercial, Side-Chain, Fluorotelomer-Based Polymers in Soils and Water

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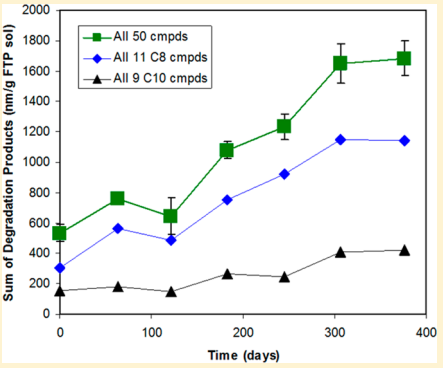
Supporting Information

ABSTRACT: Fluorotelomer-based polymers (FTPs) are the primary product of the fluorotelomer industry. Here we report on a 376-day study of the degradability of two commercial acrylate-linked FTPs in four saturated soils and in water. Using an exhaustive serial extraction, we report GC/MS and LC/MS/MS results for 50 species including fluorotelomer alcohols and acids, and perfluorocarboxylates. Modeling of seven sampling rounds, each consisting of ≥5 replicate microcosm treatments, for one commercial FTP in one soil yielded half-life estimates of 65−112 years and, when the other commercial FTP and soils were evaluated, the estimated half-lives ranged from 33 to 112 years. Experimental controls, consisting of commercial FTP in water, degraded roughly at the same rate as in soil. A follow-up experiment, with commercial FTP in pH 10 water, degraded roughly 10-fold faster than the circum-neutral control suggesting that commercial FTPs can undergo OH^--mediated hydrolysis. 8:2Fluorotelomer alcohol generated from FTP degradation in soil was more stable than without FTP present suggesting a clathrate guest−host association with the FTP. To our knowledge, these are the only degradability-test results for commercial FTPs that have been generated using exhaustive extraction procedures. They unambiguously show that commercial FTPs, the primary product of the fluorotelomer industry, are a source of fluorotelomer and perfluorinated compounds to the environment.



INTRODUCTION

Comprising roughly 80% of the fluorotelomer-industry product line,[1] side-chain fluorotelomer-based polymers (FTPs; Supporting Information (SI) Figure S1) are used in a variety of consumer products to impart antiwetting and antisoiling properties to product surfaces. While FTP manufacturing has been shown to be a source of perfluoroalkylates to the environment,[2] there remains a pressing need to elucidate the long-term role commercial FTPs play as sources, both while they are in use and following disposal. At the same time, the very trait that FTPs were designed to impart, a disinclination to interact with all other materials, thwarts simple efforts to characterize FTP fate in environmental settings.

The first peer-reviewed effort to determine the degradability of FTPs under environmental conditions reported that no degradation was detectable at rates equating to half-lives of about a millennium.[3] We subsequently disputed this conclusion, with arguments including that the extraction used on the aged FTP was grossly inadequate to exhaust the FTP of all compounds that were used to infer degradation, among numerous other concerns.[4,5] In support of our position, we countered with results of a study conducted with an industry-synthesized test FTP, containing much lower residual monomer compounds to facilitate effective FTP-degradation testing, but which also was more coarsely grained than commercial FTPs so that estimated specific surface area of the test FTP was about 300-fold less than commercial FTPs. We reported test FTP degradation rates on the order of a thousand years, when rates were normalized to a test FTP-mass basis, but argued the coarsely grained FTP particle interiors did not participate as part of the chemical system. Based on this logic, we argued that the FTP surfaces were the only part of the FTP effectively participating in the test system, just as is common in many heterogeneous reactions involving solids,[6,7] but particularly so considering that FTPs repel water by design. With this logic as justification, we normalized the rate to an estimated surface area and reported half-life estimates for commercial FTPs of 10−17 years. Because the effect of this modeling effort on predicted half-lives for commercial FTPs was so large and our modeling was unconfirmed experimentally, many considered the issue to be unresolved.[5,8]

In the years since, little has been published in peer-reviewed literature specifically addressing this intractable problem. The only exceptions we know of are (i) a paper reporting our extensive efforts at methods development for testing the degradability of commercial FTPs;[9] and (ii) Rankin et al. tested a noncommercial FTP using matrix-assisted laser desorption/

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ionization time-of-flight mass spectrometry (MALDI-TOF).[10] Here we report upon experimental efforts we carried out on two commercial FTPs, trying the methods described in both these papers.

EXPERIMENTAL SECTION

Commercial Polymers. Two commercial acrylate-linked FTPs, manufactured by DuPont, were tested for degradability.[11,12] FTPs consist of fluorinated telomers bound to a carbon backbone (SI Figure S1); the FTPs tested here contain ∼50% C8 telomers and ∼30% C10 telomers (SI Tables S1 and S2). Immediately before experimental efforts, the commercial FTP sol stocks were rotated on a roller mill overnight to ensure homogeneity, after which ∼80 mL aliquots were transferred to new, methanol-washed 125 mL high-density polyethylene containers. All subsequent samples were prepared from these aliquots which were hand shaken before each use.

Test Soils. Four surface soils were used to test the degradability of the commercial FTPs: two ultisols, an alfisol and a commercial topsoil (SI Table S3). The soils were prepared by passing them through a methanol-washed 2 mm stainless-steel sieve, and thoroughly mixing in the sieve pan to homogenize.

Analytical. In an effort to identify all major *residual* fluorotelomer species in our test commercial FTPs, we surveyed patents and literature. With our test commercial FTPs dissolved in methyl *tert*-butyl ether (MTBE), we injected them on an Agilent 6890N gas chromatograph equipped with an Agilent 5975 mass spectrometer (GC/MS) running in positive chemical-ionization (PCI) mode. We searched for each compound identified in our survey, focusing the quadrupole on the protonated molecular ion ($[M + H]^+$) in selected-ion mode; this exercise was performed on all homologues of each species ranging from C6 to C20.

With the objective of confirming the chemical identity of each peak detected in our GC/MS analytical survey of the test commercial FTPs, we attempted to obtain authentic standards. When standards were unavailable, we tentatively identified the species by a combination of efforts including: (i) adding silylation reagent to the extract and observing loss of the $[M + H]^+$ peaks offset by the appearance of peaks for the $[M + H]^+$ trimethylsilyl-derivative ions;[13] (ii) checking for sequential elution by chain length when multiple inferred homologues were detected; (iii) looking for expected fragments in negative chemical-ionization mode; and/or (iv) observing relative retention times for similar chemical species the identity of which had been confirmed.

Using a similar approach for *impurity* species and potential degradation products (SI Figure S1, which identifies chemicals and acronyms), we surveyed the literature and performed an analytical reconnaissance survey, using a Waters Acquity ultraperformance liquid chromatograph interfaced with a Waters Quattro Premier XE tandem mass spectrometer (LC/MS/MS) operated in negative electrospray-ionization mode, on extracts from (i) the commercial FTPs of this study; (ii) an earlier investigation we performed on an experimental test FTP;[4] and (iii) an investigation of fluorotelomer and perfluorinated compounds in biosolids and biosolids-applied agricultural soils.[14,15]

Based on all these efforts, we identified 71 analytes (GC/MS-26 total, 8 confirmed with standards; and LC/MS/MS-45 total, 16 confirmed with standards) to monitor, excluding internal and recovery standards (SI Tables S4 and S5). While this literature/analytical survey does not guarantee identification of all compounds, all major fluorinated species in new FTPs should be identified in patents, and our analyte list includes all species in the patents. Consequently, if compounds remain unidentified in our survey, they are degradation products in aged microcosms and such omissions would result in underestimation of FTP degradation rate.

Quantitation was performed with authentic standards when available, and compounds were semiquantitated as similar compounds when standards were not available. All quantitations were performed using internal standards, $^{13}C_2$-6:2nFTOH for GC/MS and 9 ^{13}C-labeled species for LC/MS/MS. Sources of all chemicals are summarized in SI Discussion S1, and all analytes, detection and quantitation parameters are summarized in SI Tables S4 and S5.

Also, we attempted to characterize our commercial FTPs using MALDI-TOF according to recently reported methods,[10,16] but these efforts were unsuccessful (SI Discussion S2).

FTP Preparation. Commercial FTP sols are synthesized with up to percent-level concentrations of fluorotelomer monomers, on a mass-per-mass of dry-FTP basis.[9] These high concentrations obfuscate detection of FTP degradation in experiments because FTP degradation is inferred from changes in fluorotelomer monomer and perfluorinated degradation products during FTP incubation.[3,4,17] Analytical uncertainty among replicates containing the high levels of residuals typical in commercial FTP sols is likely to exceed changes in experimental analytes during FTP incubation for anticipated FTP half-lives, rendering experiments using these commercial FTP sols insensitive for detecting degradation.[9] Also, because the design intent of FTPs is to repel interaction with other molecules, attack of the FTP bonds most susceptible to cleavage might well proceed from a direction other than that of the fluorotelomer chains. Given this, appropriate selection of a biodegradable substrate, that is consistent with the FTP's intended use, is critical.

Based on these considerations, we settled on applying the commercial FTP sols to cotton tufts by (i) drawing 10 μL of commercial FTP sol by autopipette; (ii) depositing it on preweighed ∼0.013 g compact tufts of cotton, that had been determined to bear no detectable concentrations of any study analyte, and reweighing to determine FTP sol mass on the cotton; and (iii) drying the FTP tufts at 127 °C. Cotton was identified as an intended substrate and 127 °C temperature was used to dry the FTP sol according to one of the test commercial FTP patents,[11] so our experimental design was consistent with intended use. We determined that drying the commercial FTP for 20 min resulted in time-invariant analyte concentrations that were between 2 and 3 orders of magnitude lower than that of the initial FTP sol, a concentration range that should allow detection of analyte accumulation for realistic FTP half-lives.[9] This FTP application technique was determined to be reproducible for: (i) FTP sol mass; (ii) FTP solids mass remaining after drying; and (iii) FTP residuals concentrations. Finally, the cotton cellulose base was biodegradable so that FTP degradation might proceed through the substrate.

Extraction. Based upon extensive method development,[9] extractions were performed with four serial MTBE extractions for GC/MS and LC/MS/MS analytes followed by four serial extractions with 90%/10% acetonitrile/water (ACN/H_2O) (volume/volume) for LC/MS/MS analytes. Prior to LC/MS/MS analysis, ACN/H_2O extracts were subjected to four MTBE-tetrabutylammonium hydrogen sulfate liquid−liquid cleanups.

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Table 1. Experimental Design Summary[a]

Sample, Control and Blank Names	Experimental-Unit Composition						Extraction Schedule and Experimental-Unit Count (days after initiation and no. units/ sampling round)							
	Soil	Microbes	Substrate	Moisture	FTP	Dry T (C)	Aging	0	63	121	183	245	306	376
Seven-Round Detailed-Rate Experimental Units														
Rate-Constant Treatment	Appling	endogenous	cotton	saturation	4	127	yes	5	9	7	7	7	7	7
Cell-Viability Control	Appling	endogenous	cotton	saturation	4	127	yes	2	2	2	2	2	2	2
FTP In-use Control	none	none	cotton	dry	4	127	yes	0	3	3	3	3	3	3
Time Control	Appling	endogenous	cotton	saturation	4	127	note	1	0	0	2	2	2	2
FTP Preparation Control	none	none	cotton	saturation	4	127	no	0	0	0	0	5	5	0
Process Blank	none	none	none	dry	none	none	no	0	1	1	1	1	1	1
Three-Round Range-Finding Experimental Units														
Pontypool Soil Treatment	Pontypool	endogenous	cotton	saturation	4	127	yes	5	0	0	5	0	0	5
Cowart Soil Treatment	Cowart	amended	cotton	saturation	4	127	yes	5	0	0	5	0	0	5
Pacolet Soil Treatment	Pacolet	endogenous	cotton	saturation	4	127	yes	5	0	0	5	0	0	5
FTP3 Treatment	Appling	endogenous	cotton	saturation	3	127	yes	5	0	0	5	0	0	5
Unheated FTP Control	Appling	endogenous	cotton	saturation	4	22	yes	0	0	0	5	0	0	5
Moisture Control	Appling	endogenous	cotton	moist only	4	127	yes	0	0	0	5	0	0	5
Wet FTP Control	none	none	cotton	saturation	4	127	yes	0	0	0	5	0	0	5
Soil Blank	Appling	endogenous	cotton	saturation	none	none	yes	5	0	0	0	0	0	0

[a]Note: Time Control FTP was dried at time zero and stored in tube, above unwetted soil until extraction when the tube contents were wetted and extracted. When we observed that 7:2s FTOH increased through time, we added FTP Preparation Controls which were prepared immediately before extraction and which yielded results closely similar to time zero Time Controls and time zero Rate-Constant Treatments as expected.

Recovery internal standards were added to microcosms prior to extraction for both GC/MS (10:1 FTOH) and LC/MS/MS ($^{13}C_8$–PFOA). The extraction procedure is summarized in SI Figure S5. This is the only peer-reviewed extraction procedure that has been shown to exhaust commercial FTPs (prepared as described above) of all known major polyfluorinated residuals and impurities, whether the FTP is alone (on cotton) in the extraction vessel or mixed into a soil microcosm, or whether the FTP is newly prepared or has been subjected to simulated aging by spiking with perfluorocarboxylates (PFCAs).[9]

This approach of exhausting a commercial FTP of all analytes, for all anticipated conditions (alone or in soil, new or aged) avoids pitfalls of earlier efforts including: (i) setting an experimental benchmark for defining FTP degradation by characterizing initial FTP analytes with an aggressive tetrahydrofuran dissolution of the FTP but extracting aged-FTP/soil microcosms for all analytes one time with a considerably weaker ACN/H_2O effort;[3] (ii) performing an experiment on a custom-prepared test FTP having larger particle size than commercial FTPs then modeling commercial FTP reaction rates from these results as first-order in FTP surface area;[4] and (iii) performing an experiment on a custom-prepared FTP having a lower average molecular weight than commercial FTPs and finding the lower molecular weight FTP chains may degrade more rapidly than higher molecular weights.[10]

Microcosm Design. All treatments, controls and blanks were prepared in Nalgene 16 mL polypropylene copolymer centrifuge tubes with caps. For treatments, ∼3 g of moist soil was placed in the tube, then the FTP-bearing cotton tuft was added, suspended above the soil by its perimeter fibers. Then ∼4 g of deionized water was added to all tubes unless design for the tube specified otherwise, and the tube was vortexed until the cotton was intimately contacted with the soil slurry. This mass of water was chosen to saturate the soil-cotton-FTP mass to (i) promote wetting of the hydrophobic FTP surface under positive hydrostatic head; (ii) minimize loss of volatile analytes by fostering equilibrium sorption to FTP, cotton and soil surfaces; (iii) minimize loss of volatiles by decreasing diffusion rates; and (iv) to ensure wetted microcosm conditions over a protracted one-year incubation period (SI Discussion S3).

Experimental Design. The constitution, replicate number and schedule for all experimental units are summarized in Table 1. To accommodate the labor-intensive extraction and analytical procedures, we opted to perform a *Detailed-Rate Experiment* on one test commercial FTP (FTP4; SI Tables S1 and S2) in one soil (Appling Sandy Loam; SI Table S3) consisting of seven sampling rounds over roughly one year.

Expecting that FTP degradation rates vary among soils and FTPs, we conducted *Range-Finding Experiments* with three other soils (SI Table S3) and one other commercial FTP (FTP3; SI Tables S1 and S2) which entailed three sampling rounds over one year.

Informed by the results of these experiments, we conducted *Follow-Up Experiments* to address ambiguities arising during the course of the experiments.

Detailed-Rate Experiment. Five or more Rate-Constant Treatment tubes were analyzed in each sampling round for use in modeling FTP degradation rate (Table 1). To check whether microcosms remained biologically active, two tubes per round were used as Cell-Viability Controls (CVCs); on extraction day, CVC caps were removed so the headspace equilibrated with lab air then replaced. The next day headspace was removed by syringe and needle, injected on GC, and analyzed for CO_2, CH_4 and N_2O,[18] using overnight changes in headspace composition as an inference metric for bioactivity. FTP in-use controls, consisting of FTP dried on cotton at time zero and stored in a tube, were analyzed with the intent to determine FTP stability when exposed to air and analytical reproducibility over the course of the experiment. For the time controls, the FTP-bearing cotton tuft was suspended above air-dry soil until extraction day at which time water was added, the microcosm homogenized by vortexing and extracted; the intent of these controls was to check that extraction of FTP that had not been

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exposed directly to soil would yield similar results to time zero over the course of the experiment. Based on results for the FTP Controls and the Time Controls explained below, we added preparation controls for several rounds late in the experiment for which we dried FTP sol on cotton immediately before extraction. We included a process blank in each sampling round to demonstrate analyte concentrations were low in the absence of FTP.

Range-Finding Experiments. These experimental treatments (Table 1) were prepared to test (i) FTP degradation variation among soils by incubating FTP4 in three other soils (Pontypool, Pacolet, Cowart Treatments); and (ii) FTP degradation variation between commercial FTPs by incubating commercial FTP3 in Appling Soil (FTP3 Treatment). We added a microbial amendment, that we used in our first FTP study, to the Cowart Treatments.[4] Controls included (i) Unheated-FTP Controls testing the effect of drying FTP4 at room temperature rather than 127 C, leaving much higher and more variable residuals, on detecting degradation; (ii) Moisture Controls testing the effect of incubating in moist soil, with ample air-filled pore space that might allow FTOH-volatilization losses, on detecting degradation; and (iii) Wet-FTP Controls that incubate FTP-bearing cotton in deionized water to determine the FTP stability in water. Soil Blanks were run in round one to confirm earlier analyses of all test soils showing low to nondetectable concentrations of all analytes in the absence of FTP.

Follow-Up Experiments. FTP hydrolysis experiment: based on unexpected results (explained below) for the Wet FTP Control, an 11-day scoping FTP hydrolysis experiment was conducted with extra FTP4-bearing cotton tufts that had been prepared as contingencies with the original experimental units. Treatments for each sample round in this follow-up experiment included two tubes buffered at pH 3 (citrate buffer) and two tubes buffered at pH 10 (boric-acid buffer).[19] Sample rounds also included a control tube consisting of the FTP-bearing cotton in an otherwise air-filled tube. To the extent allowed by remaining stock, FTP-bearing cotton tufts were incubated for chosen periods, extracted for GC/MS analytes and analyzed.

8:2FTOH degradation experiment: the half-life of 8:2FTOH in aerobic soil has been reported to range from about one to 4 weeks.[20,21] Considering this finding, and assuming FTP half-lives are on the scale of decades or longer, unless other factors are at play, in a one-year FTP experiment FTOHs should in-grow in the first 2−6 months to low concentrations and plateau at this low range for the balance of the experiment. As we report below, these expectations contrast with our findings in that FTOHs increased throughout the one-year incubation period, rising to be a dominant product by experiment's end, without any clear concentration plateau.

To investigate this discrepancy, we performed an incubation experiment with 8:2FTOH, identical in microcosm design to the FTP experiment (cotton, soil, saturated moisture status in a capped centrifuge tube), but lacking the FTP. To minimize volatilization losses, 8:2FTOH in methanol was added to saturated soil/cotton via a syringe with a long stainless-steel needle inserted nearly to the bottom of the soil plug. These microcosms were monitored for loss of 8:2FTOH and production of degradation products.

Data Manipulation. Analytical results for the three extract fractions (MTBE-GC/MS, MTBE-LC/MS/MS, ACN/H_2O-LC/MS/MS; SI Figure S5) were normalized to mass of FTP sol added to the microcosm and summed together using SI Equations S3−S5.

RESULTS AND DISCUSSION

Quality Metrics. Analytical results for the detailed-rate and range-finding experiments are tabulated in SI Tables S7−S19. Recoveries of $^{13}C_8$−PFOA averaged 100.2% for all treatments and controls (range = 74−118%), indicating excellent recoveries for ACN/H_2O extractions. Recoveries of 10:1 FTOH averaged 96.0% for sample round one (range = 86−105%) indicating good recovery for MTBE extractions; 10:1 FTOH recoveries decreased in later rounds likely due to volatilization of the 10:1 FTOH stock solution, nonetheless, the integrity of the MTBE extractions are demonstrated with the round-one data (SI Discussion S4). Process Blanks (SI Table S18) and Soil Blanks (SI Table S19) returned low analyte concentrations relative to treatments indicating no problems with laboratory contamination. Cell-Viability Controls evolved biogenic gases in every sampling round confirming microcosm viability (SI Table S20).

Looking at the dominant residuals in commercial FTP4, the FTP In-use Controls (FTP dried on cotton and aged in a capped tube) roughly tripled in 8:2 and 10:2nFTOHs during the experiment (SI Table S16). For the Time Control (SI Table S15; same as In-use Control but FTP suspended above air-dried soil until extraction), 8:2nFTOH remained relatively low, but 7:2sFTOH increased to slightly higher levels than did 8:2nFTOH in the In-Use Controls. The Wet FTP Control (SI Table S12; same as In-Use Control, but incubated in deionized water) also increased in nFTOHs, albeit much more markedly than the In-Use or Time Controls (SI Tables S11 vs S15 or S14). Given these unexpected control results, during the experiment we instituted preparation controls in late experimental rounds (Table 1), for which we dried FTP on cotton immediately before extraction. By comparing these late-round Preparation Controls (SI Table S17) to early round Time Controls (SI Table S15), we confirmed that our extraction and analytical practices yielded effectively identical results throughout the experiment when the FTP was not aged so these control changes were not an analytical artifact. It is noteworthy that these Preparation Controls (without soil; SI Table S17) also compare very similarly to time-zero rate-constant treatments (with soil; SI Table S7) demonstrating that microbial enzymes or other soil components, mixed with extraction solvents, cannot account for changes observed in this present FTP experiment. Similar comparisons of extraction efficacy, with and without soil, and with and without aging, were included in our first FTP experiment[4] so soil-enzyme artifacts were shown by experimental design to be irrelevant for our first FTP experiment as well as for this experiment.

Taken as a whole, based on (i) quality metrics in spike recoveries, controls, and blanks; (ii) reproducibility of results through time; and (iii) closely similar results with soil (all time zero treatments) or without soil present (Preparation Controls), variation in analytical results observed over the course of this experiment are due solely to degradation of the commercial FTPs.

Confirmation of Commercial FTP Degradation. Of the 71 analytes we monitored (SI Tables S4 and S5), we detected 50 analytes at least once in our experimental systems. Of the 50 detected compounds, a large majority on a molar basis were analytes confirmed by authentic standards; 91% in the last sampling round, for example. Expressing all 50 detected

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analytes on a moles-per-mass-FTP-sol (where the 8:8 and 8:10 ethers are doubled to account for both fluorinated chains in this and all subsequent summations as appropriate), and summing the total moles, every treatment in our experiment—all four soils and both commercial FTPs—had highly statistically greater total moles of degradation products at the end of the experiment than the beginning (SI Tables S21–S22). These results are conclusive evidence that commercial FTPs can degrade under environmental conditions at levels that are detectable in a single year when the FTP is judiciously prepared for testing, extraction is exhaustive and the target-analyte list thorough.

Detailed-Rate Modeling. Following a lag period in the first 120 days, possibly associated with diffusion to reaction centers, cotton-substrate degradation and/or enzyme induction, degradation products for commercial FTP4 in saturated Appling Soil show clear upward trends (Figure 1). Inspecting

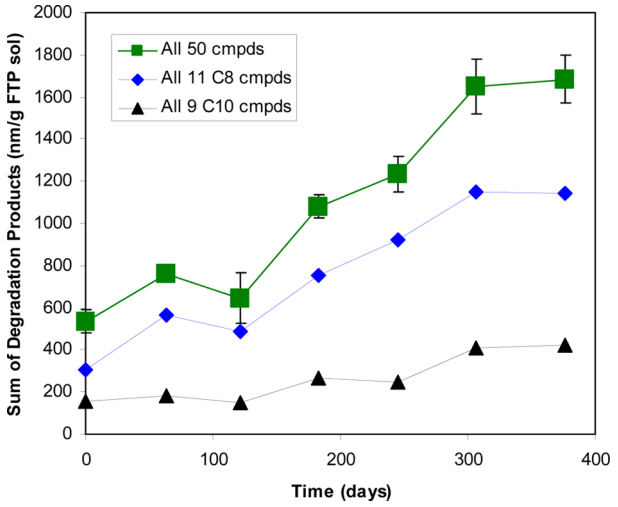

Figure 1. Sums of molar concentrations (of FTP residuals and degradation products) vs time for Rate-Constant Treatments. Error bars (1 SD) are plotted only for "all 50 compounds" for clarity. Taken together, the C8 and C10 compounds shown here comprise about 80% of the original commercial FTP (FTP4 in SI Table S2). The average of at least five replicate microcosms (Table 1), each of the seven data points for the "all 50 compounds" is the composite result of at least 60 extractions and 500 mass-spectral analyses.

the upward trends for all 50 analytes, the 11 C8 analytes, and the 9 C10 analytes (Figure 1), the visual slopes decrease in the order 'all analytes > C8s > C10s.' This variation in slopes might simply reflect decreasing proportions of the FTP being represented in each fraction (SI Table S2) or it might also reflect decreasing rates of degradation with increasing chain length, in which case the FTP would degrade at numerous rates as opposed to one, perhaps varying through time as loss of vicinal telomers varies through time. If various FTP fractions were to degrade at different rates, due to varying degrees of hydrophobicity among chain lengths for example, then the fractional distribution of homologues detected at the end of the experiment should differ systematically from that of the original FTP. In fact, the fractional distribution of the fluorotelomer monomers reported in the original patent[11] and this same fraction for the sum of the nFTOHs plus PFCAs in the last round of the experiment compare reasonably well (SI Table S23). Small differences that are present could be due to a combination of differences in recoveries among chain lengths including unconfirmed degradation products, and between the commercial FTP batch used in this experiment and the patent. Based on these data, it is reasonable to model FTP degradation as proceeding independently of telomer chain length.

Considering that the 50 analytes we report result from a comprehensive effort to represent all residual fractions, that 11 of these analytes are C8 chain lengths, and that C8 telomers comprise roughly 50% (mass basis) of all telomers in the original FTP (SI Table S2), we opted to model using the (i) sum of all 50 analytes; and (ii) sum of 11 C8 analytes. Using a simple first-order degradation model, in which moles of product are treated in aggregate with a simple summation (SI Discussion S5), and assuming we extract and account for 100% of all FTP degradation products, we estimate a half-life for commercial FTP4 in saturated Appling Soil of 94 (C8) to 112 (all analytes) years (SI Discussion S5).

An appealing aspect of the above approach is its simplicity, one reactant (FTP) degrading at a rate proportional to its remaining amount at any specific time to a conceptually single stable product. However, much information is left untapped by treating the reaction products in aggregate. Instead of a single aggregate data point at any given time, in reality there are data for each of numerous products, instead of a single equation there are first-order equations for production and loss of each product—constraints offering the potential of tighter model resolution.

Presented with the then-newly recognized phenomenon of radio-decay chains, wherein A → B → C···, Bateman[22] solved the system of first-order differential equations governing the decay process.[23] In recent years, a more general solution of this system of equations, allowing for advective loss from the system and equilibrium distribution between sorbed and dissolved phases, has been derived and applied with success to first-order degradation of a series of chemical degradation products under environmental conditions.[24] Following this precedent, we also modeled our data using the Bateman eqs (SI Discussion S5). The best fit to all data that we achieved was with a commercial FTP $T_{1/2}$ of 81 years, again assuming 100% recovery of all degradation products (Figure 2 and SI Figure S11; Table S25).

A noteworthy result of this modeling is that the best-fit calculated half-life for 8:2FTOH is ~1200 days (SI Table S24), much in excess of the half-life of 8:2FTOH reported for aerobic soils, <28 days.[20,21] This discrepancy was the impetus for the follow-up experiment we report below.

Addressing recoveries, in extended fluorotelomer-degradation experiments, Wang and coinvestigators have reported some of the most advanced efforts, achieving molar balances as high as 72–95%.[21] These experiments were run with ^{14}C-labeled compounds and, for the best molar balances, 20–40% was accounted for by soil combustion and ^{14}C analysis, or not accounted for at all. Assuming we roughly equaled Wang et al.'s best recovery efforts excluding his ashed-^{14}C fraction, of ~100% - 20% = 80%, the half-life for commercial FTP4 in saturated Appling Soil falls in the range of 65–90 years. Combining the 80% (best Wang balance) and 100% (better than Wang) recoveries, our best estimated half-life for commercial FTP4 in saturated Appling Soil encompasses the range of 65–112 years (SI Discussion S5). This range of estimates are conservatively high because several of Wang's experiments resulted in lower molar balances than 80%,[21] and because our experiment was longer than Wang's, involved more analytes and included a challenging FTP phase.

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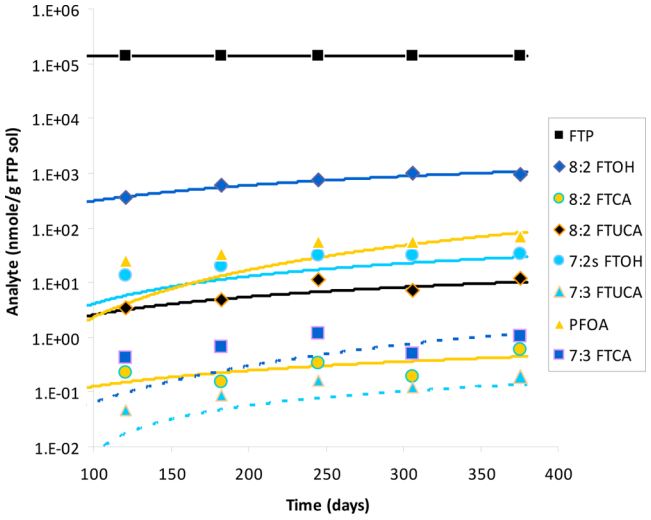

Figure 2. Commercial FTP4 and degradation products vs time. Symbols are experimental data points. Lines are best-fit modeled values using an analytical solution for a degradation series that is first-order in reactant, assuming 100% recovery of all degradation products, and with an FTP half-life of 81 years. See SI Discussion S5 for assumed degradation scheme, and best-fit degradation constants and half-lives.

Range-Finding Modeling. We modeled these data semiquantitatively by comparing half-lives to the detailed-rate data based on the half-year and year data for all 50 analytes and all 11 C8 analytes (SI Discussion S5). All three range-finding soils and the range-finding commercial FTP (FTP3) returned shorter half-lives than the detailed-rate experiment (commercial FTP4, saturated Appling Soil; SI Discussion S5), with half-lives falling between ~50% and 80% of the detailed-rate experiment (Table 2). Incorporating the lower end of this range, our final best estimated range of half-lives for these two commercial FTPs in four saturated soils, conservatively assuming 80−100% recovery of all degradation products over the one-year experiment with FTP and soil both present, is 33−112 years.

Addressing controls, both the moisture controls and the unheated-FTP controls returned longer half-lives than any treatment (Table 2) supporting our hypothesis that volatilization losses through air-filled pores (or poor FTP wetting with low moisture) and high residuals in air-dried FTPs yield ineffectual experimental designs.

As noted above, the Wet FTP Control, containing the commercial FTP4 dried on cotton in deionized water, returned unexpected results, yielding a half-life falling at about 50% that of the detailed-rate treatments (Table 2). The data for this control differ from all treatments in that nFTOHs accumulated to high concentrations, but all other analytes remained low (SI Table S12). These results suggest the possibility of abiotic hydrolytic scission at the ester linkage to form the FTOHs.

Follow-Up FTP-Hydrolysis Experiment. Results for this experiment were limited by the number of contingency FTP/cotton tufts we had prepared with the rest of the experimental units. Nevertheless, the results clearly showed an FTOH increase in the pH 10 treatments, almost doubling over the 11-day experiment, while FTOH in the pH 3 treatments and dry controls remained constant (Figure 3). These results suggest

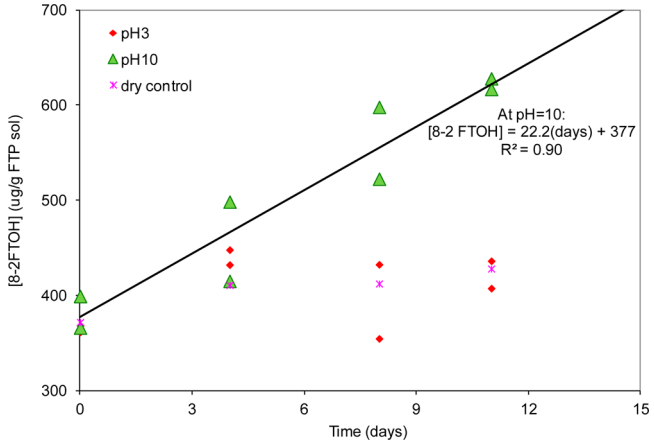

Figure 3. 8:2FTOH vs time for commercial FTP4 in deionized water buffered to pH 3 and pH 10. Correlation of the pH 10 data with the line of least squared error is significant at $P = 0.003$, and the modeled pseudo-first-order half-life is 5.5 years, although this half-life is a qualitative estimate provided solely for perspective. See text for details.

Table 2. Range-Finding Half Lives for Commercial FTP Degradation, Expressed Relative to Detailed-Rate Treatment Half Life of 66−112 Years[a]

Treatments and Controls: Salient Features	Commercial FTP Drying Temperature (° C)	Soil Moisture Status	Soil Microbial Consortia	Half Life Relative to Detailed Rate Experiment for All Data (AD) and C8 Data (AD%)	(C8%)
Teatment Microcosms: Tested to Characterize Variability among Soils and Commerical FTPs					
FTP4/Appling Soil Treatment: Detailed-Rate Experiment as **benchmark**	127	saturated	endogenous	100	100
FTP4/**Pacolet Soil Treatment**: different soil	127	saturated	endogenous	47	45
FTP4/**Pontypool Soil Treatment**: different soil	127	saturated	endogenous	68	78
FTP4/**Cowart Soil Treatment**: different soil, microbe amended	127	saturated	amended	54	58
FTP3 Treatment/Appling Soil: different commercial polymer	127	saturated	endogenous	59	64
Control Microcosms: Tested for Presence of Possible Experimental Artifacts					
wet FTP4 Control/no soil: **hydrolysis check**	127	saturated	none	54	63
FTP4/Moisture Control (Appling): **volatilization loss**	127	moist	endogenous	126	175
Unheated FTP4 Control/Appling Soil: **air-dried FTP**, high residuals	~22	saturated	endogenous	122	112

[a]Note: AD designates all data (50 analytes) and C8 designates the 11 C8 analytes.

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that the ester linkage of commercial FTP4 undergoes base-mediated nucleophilic acyl substitution reaction ($B_{AC}2$).[25] Due to the paucity and scatter of data in this scoping experiment, modeling of reaction rate is only qualitative. Conceding this limitation, we estimate a pseudo-first-order $T_{1/2}$ for hydrolysis at pH 10 of 5.5 years. It is noteworthy that this pseudo-first half-life (5.5 years) is only ~1/10 that of our year-long experiment (63 years) at uncontrolled pH in deionized water. In contrast, the pH of the unbuffered Wet-FTP Controls fell in the range of 5 < pH < 6, four to 5 orders of magnitude lower in $[OH^-]$ than the pH 10 hydrolysis experiment. Taken altogether, the ester linkage of FTP4, and the results of these two experiments suggest base mediated hydrolysis being dominant at pH = 10, and some other reaction mechanism dominating at lower pHs.

These results are of practical importance because: (i) variability associated with biologically mediated reactions are absent with hydrolysis; (ii) potentially, commercial FTPs could be breaking down when consumer products are wetted during use, exposing consumers to PFCA precursors; (iii) in light of these hydrolysis results, the smaller FTOH increases exhibited by the in-use controls and preparation controls, which were incubated in air-dry state, might reflect much slower hydrolytic degradation of "dry" FTP from water sorbed from the air, although this hypothesis is tenuous for these experimental data; and (iv) because the product of this reaction is volatile and landfills are not airtight, landfilled materials treated with these FTPs could be a repository of ongoing contributions of volatile fluorotelomers to the environment. Considering all this, these preliminary hydrolysis results merit further research.

Follow-Up 8:2FTOH Degradation Experiment. A follow-up experiment was performed to determine whether the saturated state (and inferred limited O_2) of our experimental system might explain the apparent longevity of nFTOHs in the year-long FTP experiment relative to 8:2FTOH half-lives in aerobic soil of <28 days.[20,21] For this follow-up experiment (microcosms spiked with 8:2FTOH but not with FTP) 8:2FTOH in saturated Appling Soil had a half-life of roughly 210 days (SI Discussion S6), longer than literature values for aerobic soils, but insufficiently long to explain nFTOH stability in the FTP degradation experiment. Instead of plateauing at low concentrations at the half-year mark as one would expect for literature values of half-life, for our experiment, nFTOHs increased throughout the course of the one-year experiment to be dominant products (SI Table S7) with an 8:2FTOH apparent half-life of 1200 days (SI Table S24). Because the only design difference between our follow-up experiment (8:2FTOH $T_{1/2}$ = 210 days) and the year-long experiment (8:2FTOH $T_{1/2}$ = 1200 days) is the presence of the FTP, this suggests additional stability is imparted to FTOH in intimate association with, or being generated within, an FTP matrix.

The phenomenon of clathrate formation, in which a hydrophobic guest molecule finds harbor in host-lattice cavities, simultaneously imparting thermodynamic solvency stabilization to the guest and lattice stabilization to the host, is well-known in polymer chemistry.[26] Molecular host−guest associations commonly are classified by host conformation; when encasing host appendages are bound at one terminus, but otherwise free, the resulting host−guest complex has been termed "molecular clips."[27] Considering that fluorotelomers are repelled by most other molecules, but have a strong tendency to coassociate, FTPs and FTP-generated FTOHs might maintain a classic molecular-clip clathrate host−guest type relationship wherein both the FTP and the FTOH maintain their lowest energetic position by maintaining the original geometric conformation of the FTP after hydrolytic cleavage at the ester bond. For this scenario, as FTPs proceed to degrade, accumulating polymer-structure imperfections and guest monomers, the stability of the FTP clathrate-guest lattice complex would decrease, and the dissolution-reaction activation energy barrier ultimately would as well (SI Figure S14). An outcome of such a scenario is the sudden release of FTOHs as the solvation energy dissipates relative to the free energy of the FTP clathrate host−guest complex. Consequently, FTP-treated materials might retain apparent stability for protracted periods, apparently generating few fluorotelomer compounds, followed by a sudden release when a critical point is achieved in the FTP-hydrolysis reaction coordinate (SI Figure S14). So it could be that fluorotelomer-generation rate in landfills, for example, is not a smooth function through time, but sporadic as critical dispersion points are achieved in disposed materials (SI Figure S14).

General Discussion. While we show here, for the first time, compelling evidence of the degradation of two commercial, acrylate-linked fluorotelomer-based polymers, with decades-scale half-lives, this work does not stand alone. Instead it comports with a number of previous studies showing degradation of FTPs. In addition to our previous study with a test FTP synthesized for us by industry,[4] Rankin et al. reported degradation of a lab-synthesized FTP, arriving at an estimated half-life of 8−111 years.[10] In another example, Hatfield and Hakes studied the photolytic degradation of an acrylate polymer containing a perfluorobutane sulfonamide functional group; these researchers observed polymer degradation with calculated half-lives of about a decade and less.[28] Finally, Russell et al. reported a half-life for a urethane FTP of as short as 28 years, albeit using an extraction method that we have argued to be flawed.[17] Taken altogether, our present study of two commercial FTPs in four soils, as well as these independent studies, report half-lives ranging from 8 to 112 years, a wide range, but one that is realistic considering variation in environmental conditions (e.g., moisture status, bioactivity, redox, pH, and temperature) as well as chemical/structural variation among FTPs. Also, our present study of two commercial FTPs, taken as a group with these previous studies, are strongly mutually supportive that commercial FTPs degrade under environmental conditions at scales that are one to 2 orders of magnitude shorter than millennium scale.

Summarizing some limitations, and retrospective and prospective implications of this present work:

1. Our half-lives for commercial FTPs in saturated soils of 33 to 112 years might exceed that of aerobic soils substantially because: (i) water saturation likely limited O_2 diffusion and thereby aerobic reactions (this is supported by our long 8:2FTOH half-life in saturated soil relative to literature-reported aerobic half-lives); and (ii) our assumed recoveries of 80−100% might be overly optimistic for a year-long incubation in a complex soil/FTP matrix with many volatile reaction products.
2. In our 2009 FTP study,[4] we noted a loss of recovered PFCAs and speculated that one possible cause of this loss might be degradation of PFCAs in the presence of FTPs. We saw no such loss in this study, instead observing PFOA increases throughout the study (SI Table S7). Based on our extensive method development,[9] our

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suspicion is that our previous losses were due to incomplete recovery of PFCAs from degraded FTPs using 60/40 ACN/H_2O as opposed to the 90/10 we used in this current effort.

3. In our 2009 FTP study,[4] we reported possible detection of HPFOA (PFOA-F+H). We were unable to rule out this possible detection in the current FTP study, with observation of the same MS/MS transition over the entire course of the experiment (SI Discussion S7).
4. Our methods development[9] and this present study definitively confirm that comparing a single-step ACN extraction of soil/FTP microcosms to tetrahydrofuran FTP dissolution as a basis for inferring commercial FTP degradation yields grossly misleading conclusions as we argued in our earlier paper.[4,5]
5. The general consistency of our new half-life estimates for commercial FTPs of 33−112 years and the other studies mentioned above with our earlier modeled value of ∼10 to 17 years supports our modeling of coarsely grained experimental FTP as being roughly first order in FTP surface area rather than FTP mass.[4]
6. Given the consistent decades-scale half-lives reported for several FTPs in peer-reviewed literature (including the two commercial FTPs we report here),[4,10,17] it is a useless distraction to study fluorotelomer monomers with the objective of determining the degradation rate of polymers.
7. Because this study shows that dominant products of commercial FTP degradation include volatile FTOHs, and because landfills are not airtight, commercial FTPs potentially might be a source of fluorotelomers to the environment even after disposal. This potentially constitutes a large long-term environmental load for PFOA and longer homologues, and merits further research.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as cited in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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