**Supporting Information for:**

**“Abiotic hydrolysis of fluorotelomer-based polymers as a source of perfluorocarboxylates at the global scale”**

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**Supporting Methods**

**Commercial Polymer.** A commercial acrylate FTP, manufactured by DuPont, was tested for hydrolytic degradability. Registered in the United States under Patent #5674961 on October 7, 1997, the inventor of record was John J. Fitzgerald and the patent is owned by E.I. Du Pont de Nemours and Company.[1](#_ENREF_1) The FTP tested here contained ~50% C8 telomers and ~30% C10 telomers (Table S1), and a drawing of the general structure is shown in Figure 1 of the paper.

**Table S1: Physical properties of tested commercial fluorotelomer-based polymer**



Immediately before experimental efforts, the commercial FTP sol stock was rotated on a roller mill overnight to assure 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.

**Water.** Municipal water from Athens, GA public water supply was deionized in the EPA, Athens laboratory building central deionizing unit, then deionized a second time at the bench in the laboratory to 18 MΩ/cm resistance.

**Chemicals.** Chemicals used in this study were of the highest purity offered by the suppliers, uniformly ≥97% purity. Telomer alcohols, 8:2 nFTOH, 10:2 nFTOH and 13C2-6:2 FTOH, were purchased as certified standards from Wellington Laboratories through TerraChem (Shawnee Mission, KS, USA).

Methyl tert-butyl ether (MTBE) was purchased from Fisher Scientific (Fairlawn, NJ, USA). Cotton balls, from Fisher Healthcare (Pittsburgh, PA, USA), were used without pretreatment or cleanup because GC/MS analyses of extracts of the cotton indicated no contamination with analytes planned for this experiment.

Chemicals for buffer preparation included sodium hydroxide, purchased from J.T. Baker (Phillipsburg, NJ, USA), boric acid, potassium chloride and sodium citrate purchased from Fisher Scientific (Fairlawn, NJ, USA), potassium phosphate from Aldrich Chemical (Milwaukee, WI, USA) and sodium phosphate purchased from Fox Scientific, Inc. (Alvarado, TX). Buffers were prepared as shown in Table S2.

**Table S2: pH Buffer Composition**



1. Sodium citrate

**Mounting of FTP on Cotton.** The commercial FTP sol was applied to cotton tufts by: i) drawing 10 uL of commercial FTP sol by autopipette; ii) depositing it on ~0.013 g compact tufts of cotton, that had been determined to bear no detectable concentrations of any study analyte; and iii) drying the FTP tufts at 127 oC, consistent with the patent example.[1](#_ENREF_1) This procedure minimizes residual FTOHs in the FTP product that can obfuscate determination of FTOHs arising from degradation. The thought process leading to this design is described in our earlier paper.[2](#_ENREF_2)

**Data Quality Inspection.** We quantitated these data using 13C2-6:2 FTOH as a matrix internal standard, so all standards, treatments, controls and process blanks had the same concentration of 13C2-6:2 FTOH (100 ng/mL). While variation in instrument sensitivity should be mostly compensated by use of an internal standard large systematic changes might affect the slope calculations we report here. To check for this effect, we plotted the mean 13C2-6:2 FTOH peak area for each data set that generated a rate constant, with the data plotted in order of the sample-run sequence. This is shown as Figure S1. While there is a general downward trend in 13C2-6:2 FTOH peak area, replicate 1 stands out from all other replicate runs, especially for pHs 5 through 8. As a consequence of analytical difficulties we had in initial efforts with these samples, immediately before the analytical runs we report here, we had maintained the GC/MS with actions including: i) replacing the gooseneck inlet line and gold seal; ii) trimmed the front of the analytical column; and iii) cleaned the ionizing source and replaced the filament.

Evidently, injection of the earliest samples on the freshly maintained instrument affected instrument sensitivity more so than later sample runs when the instrument was closer to steady-state. Given this observation, and considering that our quality-assurance metrics all were based on single-sample results (check standards, process blanks) but our experimental interpretation focused on the composite slope of nine-sample sequences, we repeated our analyses of Replicate 1 with instrument sensitivity more closely consistent with all other runs (see Rep 1r in Figure S1). We report the repeated measures of Replicate 1, i.e., Rep 1r, and used these data in all calculations reported herein.

Values of pH over most of the course of the experiment are reported in Table S3. Consistent with the hydrolysis mechanism not consuming OH- (Figure 1 of paper) the buffered pH values showed no evidence of trending over the course of the experiment.

 

*Figure S1: Mean 13C2-6:2 FTOH peak area plotted as a function of analytical sequence. The 13C2-6:2 FTOH peak areas for pHs 5-8 of Rep 1 grossly exceeded subsequent samples, presumably because the GC/MS had been maintained immediately before this sample run. Out of an abundance of caution we repeated analyses of Rep1, reported above as Rep 1r.*

**Table S3: Measured pH in microcosms over the course of the experiment**



**Table S4: FTOH in controls (FTOH added to cotton tuft in water at time 0)**



**Table S5: Missing and Expunged Data**



**Supporting Data**

**Table S6: pH 5 Raw Data and kobs**



**Table S7: pH 6 Raw Data and kobs**



**Table S8: pH 7 Raw Data and kobs**



**Table S9: pH 8 Raw Data and kobs**



**Table S10: pH 9 Raw Data and kobs**



**Table S11: pH 10 Raw Data and kobs**



**Table S12: pH 11 Raw Data and kobs**



**Table S13: pH 12 Raw Data and kobs**



**Supporting Discussion**

Experimental and modeled kinetic values are tabulated below.

**Table S14: Summary of Experimental and Modeled Kinetic Variables**



**Table S15: Modeled Kinetic Constants**



 The T1/2 for 10:2 FTOH falls in a range a little longer than for 8:2 FTOH for pH 5 and 6 (Table S14). To help elucidate whether this discrepancy reflects different rates of hydrolytic attack for the 8:2 vs. 10:2 fluorotelomer, or simply an extraction/analytical artifact, in Figure S3 we compared the molar ratio of 8:2 FTOH to 10:2 FTOH to that reported in the original patent (Table S1). Figure S3 suggests that hydrolysis rate is independent of fluorotelomer chain length and that the discrepancy is due to extraction/analytical artifact for two reasons: i) after time 0, the ratio at any given pH varies very little over time (were hydrolysis a function of fluorotelomer chain length, this ratio should change through time); and ii) for pH 7 through 12, the molar ratio falls close to that reported in the patent for this polymer[1](#_ENREF_1) as reported in Table S1 (as would be expected if hydrolysis rate was equal among each fluorotelomer length).



*Figure S2: [8:2 FTOH]/[10:2 FTOH] molar ratio vs time. After a high degree of variation in molar ratio at time 0, the molar ratio fell to nearly constant values that are close to that reported for the FTP in the patent description.*

 A noteworthy feature of the data is that pH 5 experimental T1/2s are longer than higher pH values (Figure 4, Figure S2, Table S14). Given the simplicity of the experimental system (FTP on cotton, in buffered water), the only experimental trait that is unique to the pH 5 treatments is choice of buffer. Sodium citrate was used to buffer pH 5 only; other buffers were employed for all other experimental pHs (Table S2). Citrate has been shown to modify cellulose, acting as a plasticizing agent.[3](#_ENREF_3), [4](#_ENREF_4) Modification of the cotton cellulose substrate for the FTP in our experiment might have affected contact of the water with our FTP.

**Model Derivation & Application of Equation 4**

At time t0, start manufacturing commercial acrylate fluorotelomer polymer FTP at constant rate Φ in units of tons/year (t/yr). At time t0, FTP0 tons of FTP exist. At any time t, FTP degrades at a rate directly proportional to the mass of FTP that is present. For these conditions, production of FTP is given by:

 (S1)

And degradation is given by:

 (S2)

where kobs is a constant having units yr-1 for this model. Overall, changes in FTP are given by:

 (S3)

Integrating Equation S3:

 (S4)

where c is an integration constant. Constant c can be solved for by noting the initial boundary condition that at t = t0, FTP = FTP0 and:

 (S5)

Because ln(1) = 0, Equation S5 reduces to 0 + c = 0. Therefore c = 0, and:

 (S6)

Rearranging Equation S6 to solve for FTP and kobs:

 (S7)

 (S8)

Equation S8 is identical to Equation 4 of the paper.

 The commercial production rate of FTPs, Φ in Equations 4 and S8, was reported by (Zhanyun) Wang et al.[5](#_ENREF_5) The average yield of PFCAs from FTOHs was reported by (Ning) Wang et al. to be 25%.[6](#_ENREF_6) We used the values reported in these two references, the fractions of 8:2 FTOH and 10:2 FTOH moieties in our commercial test FTP (Table S1), and our estimated hydrolysis half-lives of 55 years to 89 years, to estimate the potential future impact of FTPs already produced on global PFCA loads. This effort is tabulated in Table S16 and depicted in Figure 6.

 This model obviously is a simplification. In particular, the timing of when hydrolysis initiates relative to when the FTP was produced is not accounted for. The central effect of varying this timing would be to shift the arc of the curves in Figure 6 as opposed to the asymptote of mass that the curves approach. The only way in which the maximum loads might be shifted downward is to assure that some fraction of the FTPs already produced are never hydrolyzed or the hydrolysis products are completely contained in perpetuity. Even if one could assure one of these conditions, an off-setting effect is that FTPs are continuing to be manufactured today, in contrast to our conservative modeling assumption that commercial FTP production ended in 2014 (Table S16). In fact Wang et al.[5](#_ENREF_5) assumed the fluorotelomer component of commercial FTPs would continue to be manufactured through the year 2030.



**Supplemental References:**

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