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] 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

Backbone Linkage	Telomer Linkage	Patent Location	Mass % of Fluorotelomer	Mass % of Fluorotelomer Component						
				6	8	10	12	14	16	18
acrylate	ester	Detailed Description	79 to 85	smaller	50	29	11	smaller	smaller	smaller
		Example 1	83	3	50	31	10	3	2	1

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 $^{13}C_2$-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

Nominal pH (SU)	NaOH (g)	$Na_3C_6H_5O_7 \cdot 2H_2O$ (1) (g)	KH_2PO_4 (g)	$B(OH)_3$ (g)	Na_2HPO_4 (g)	KCl (g)	Final Volume (mL)	Measured pH (SU)
5	1.878	11.5					1000	4.99
6	0.228		6.804				1000	5.93
7	2.37		13.608				2000	6.94
8	1.872		6.804				1000	7.98
9	0.852			3.092		3.728	1000	8.82
10	1.756			3.092		3.728	1000	9.91
11	0.303				6.56		1000	10.92
12	1.548					6.012	1000	12.32

(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 ^{o}C, consistent with the patent example.[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]

Data Quality Inspection. We quantitated these data using $^{13}C_2$-6:2 FTOH as a matrix internal standard, so all standards, treatments, controls and process blanks had the same concentration of $^{13}C_2$-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 $^{13}C_2$-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 $^{13}C_2$-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.

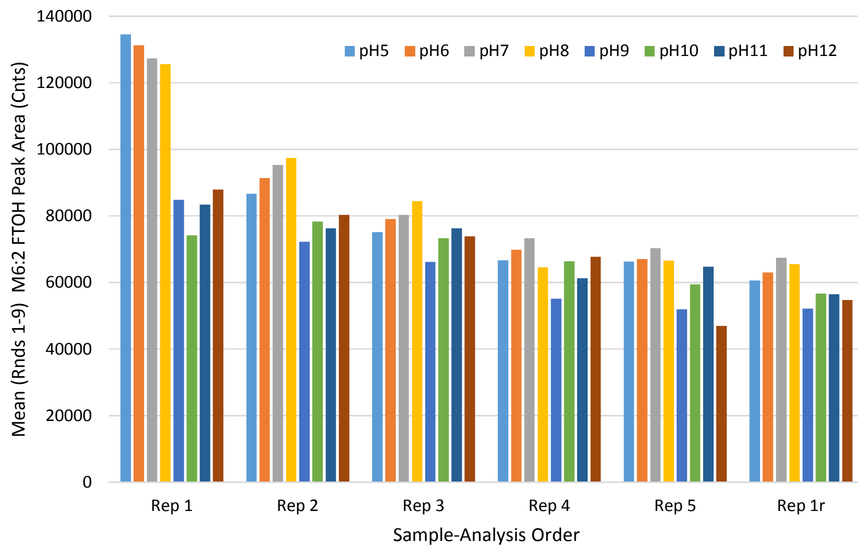

Figure S1: Mean $^{13}C_2$-6:2 FTOH peak area plotted as a function of analytical sequence. The $^{13}C_2$-6:2 FTOH peak areas for pHs 5-8 of Rep 1 grossly exceeded subsequent samples, presumably because the GC/MS had been maintained immediately before this sample run. Out of an abundance of caution we repeated analyses of Rep1, reported above as Rep 1r.

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

Extraction Day #	Nominal pH values							
	5	6	7	8	9	10	11	12
0	4.99	5.93	6.94	7.98	8.82	9.91	10.92	12.32
7	4.94	5.85	6.82	7.90	8.84	9.85	10.86	12.26
14	4.95	5.92	6.91	7.96	8.90	9.93	10.90	12.32
21	4.97	5.86	6.81	7.91	8.80	9.82	10.83	12.24
28	4.99	5.85	6.80	7.90	8.81	9.80	10.80	12.25
35	4.99	5.91	6.85	7.85	8.80	9.78	10.81	12.23
42	4.98	5.92	6.90	7.93	8.83	9.80	10.77	12.28
49	4.96	5.87	6.81	7.88	8.82	9.82	10.84	12.30
56	4.98	5.91	6.91	7.85	8.86	9.83	10.84	12.31
Mean	4.97	5.89	6.86	7.91	8.83	9.84	10.84	12.28
St. Dev.	0.019	0.033	0.054	0.045	0.032	0.051	0.047	0.035

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

Time (days)	[8:2 FTOH] (ng/mL extract)				
	Rep1	Rep2	Rep3	Rep4	Rep5
0	92.11	86.93	85.69	86.11	86.37
7	24.77	24.79	22.78	21.48	23.68
14	26.67	26.74	24.34	24.72	23.93
21	12.01	12.15	11.50	11.92	11.55
28	9.15	10.19	8.97	9.55	11.91
35	9.34	9.41	10.25		10.25
49	5.17	5.33	5.85		
63	4.90	4.86	4.93	4.50	
77	3.90	3.72		3.83	4.12

Table S5: Missing and Expunged Data

pH	Day #	Replicate	Analyte	Reason
8	1	3	10:2	mishandled
8	7	4	8:2 & 10:2	mishandled
8	63	4	8:2 & 10:2	outlier
9	1	3	8:2 & 10:2	mishandled
9	7	5	10:2	outlier
9	49	5	8:2 & 10:2	mishandled
9	63	2, 5	8:2 & 10:2	mishandled
10	49	5	8:2 & 10:2	mishandled
12	14	2	10:2	outlier
12	21	5	10:2	outlier
12	35	2	8:2 & 10:2	outlier

Supporting Data

Table S6: pH 5 Raw Data and k_{obs}

Time (days)	pH 5 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	186.74	185.04	267.48	235.34	231.99	221.32	35.19	0.159
7	343.05	299.45	382.05	416.12	371.92	362.52	43.87	0.121
14	525.89	446.92	586.96	559.80	551.34	534.18	53.43	0.100
21	784.62	590.23	711.46	703.69	904.22	738.84	115.67	0.157
28	813.34	694.14	1020.77	968.25	779.80	855.26	135.62	0.159
35	1202.37	1064.53	1504.01	1381.18	1393.44	1309.10	174.29	0.133
49	996.74	1270.65	1436.24	1070.00	1270.48	1208.82	175.78	0.145
63	1428.08	1461.70	1962.96	1860.99	1698.26	1682.40	236.77	0.141
77	1440.37	1873.67	2491.37	2100.97	2341.89	2049.65	413.93	0.202
k (1/d)	1.86E-05	2.49E-05	3.25E-05	2.71E-05	2.90E-05	2.64E-05	5.18E-06	0.196
r^2	0.89	0.99	0.97	0.93	0.94			

Time (days)	pH 5 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	40.16	26.34	59.01	35.04	58.37	43.79	14.48	0.331
7	88.70	91.41	112.64	110.87	119.21	104.57	13.64	0.130
14	148.50	127.40	149.83	136.53	126.81	137.81	11.07	0.080
21	211.22	176.72	222.60	198.84	234.73	208.82	22.34	0.107
28	258.24	203.19	253.85	280.58	249.18	249.01	28.31	0.114
35	345.04	307.82	413.01	336.28	320.26	344.48	40.91	0.119
49	306.82	418.73	289.55	282.21	322.21	323.91	55.24	0.171
63	500.73	466.68	735.14	556.08	497.30	551.18	107.77	0.196
77	412.67	529.49	775.94	585.52	573.45	575.41	131.25	0.228
k (1/d)	1.72E-05	1.56E-05	2.34E-05	1.71E-05	1.55E-05	1.78E-05	3.23E-06	0.182
r^2	0.99	0.98	0.98	0.98	0.99			

Table S7: pH 6 Raw Data and k_{obs}

Time (days)	pH 6 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	195.24	194.44	206.15	232.83	181.05	201.94	19.43	0.096
7	646.91	585.68	687.93	585.86	667.92	634.86	47.10	0.074
14	956.84	970.39	1075.61	1062.12	1012.11	1015.41	53.09	0.052
21	1160.46	1213.83	1537.66	1380.66	1580.13	1374.55	187.46	0.136
28	1538.07	1731.28	2046.05	1727.85	1851.02	1778.85	186.71	0.105
35	1600.54	1679.22	2264.41	2144.51	2253.33	1988.40	322.79	0.162
49	2324.29	1939.00	2611.85	2787.12	2579.40	2448.33	329.20	0.134
63	2747.31	2859.26	3263.05	3013.83	3059.95	2988.68	197.48	0.066
77	2881.34	3036.59	3308.84	3409.53	3892.83	3305.83	389.88	0.118
k (1/d)	4.02E-05	4.11E-05	4.66E-05	4.77E-05	5.13E-05	4.54E-05	4.67E-06	0.103
r^2	0.97	0.96	0.95	0.97	0.98			

Time (days)	pH 6 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	12.51	16.89	22.36	30.84	28.36	22.19	7.66	0.345
7	173.95	190.92	178.80	129.32	166.31	167.86	23.33	0.139
14	196.94	211.55	281.77	296.23	254.98	248.30	43.16	0.174
21	301.85	325.68	402.87	347.61	332.06	342.01	37.79	0.111
28	487.26	546.59	478.17	427.45	502.49	488.39	43.03	0.088
35	454.74	481.37	488.23	567.84	603.94	519.22	63.43	0.122
49	683.24	579.12	653.72	717.02	713.13	669.25	56.49	0.084
63	973.29	844.75	840.61	791.13	818.62	853.68	70.18	0.082
77	929.21	876.51	1012.62	1044.72	1073.58	987.33	82.21	0.083
k (1/d)	2.92E-05	2.53E-05	2.76E-05	2.87E-05	2.95E-05	2.81E-05	1.73E-06	0.062
r^2	0.96	0.94	0.98	0.98	0.98			

Table S8: pH 7 Raw Data and k_{obs}

Time (days)	pH 7 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	186.33	191.33	294.11	224.14	286.04	236.39	51.19	0.217
7	514.49	524.39	595.13	591.44	587.06	562.50	39.57	0.070
14	703.51	754.46	755.88	780.79	832.34	765.40	46.79	0.061
21	843.49	1022.36	1158.10	1136.69	1214.19	1074.97	147.01	0.137
28	994.73	1215.00	1355.38	1328.16	1323.53	1243.36	148.99	0.120
35	1388.04	1627.85	1885.83	1608.78	1808.33	1663.77	194.01	0.117
49	1360.84	1834.90	2182.01	2013.78	2215.55	1921.42	348.10	0.181
63	1966.08	2168.16	2537.24	2640.59	2694.53	2401.32	318.39	0.133
77	2421.61	2784.60	3100.73	2995.60	3037.80	2868.07	276.36	0.096
k (1/d)	3.06E-05	3.61E-05	4.12E-05	4.06E-05	4.13E-05	3.80E-05	4.64E-06	0.122
r^2	0.97	0.99	0.99	1.00	0.99			

Time (days)	pH 7 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	37.93	46.43	100.83	84.14	104.24	74.71	30.80	0.412
7	223.44	184.77	266.61	204.11	220.00	219.79	30.32	0.138
14	272.63	272.23	336.10	302.82	343.68	305.49	33.87	0.111
21	371.44	426.54	389.14	377.43	494.14	411.74	50.79	0.123
28	485.34	526.08	564.88	549.64	580.11	541.21	37.07	0.068
35	654.65	692.96	719.38	650.56	680.21	679.55	28.40	0.042
49	578.29	735.63	776.56	761.15	850.90	740.51	100.31	0.135
63	969.74	963.07	1023.38	1028.19	1008.23	998.52	30.32	0.030
77	1273.31	1344.86	1330.43	1150.72	1212.50	1262.36	81.41	0.064
k (1/d)	3.33E-05	3.57E-05	3.44E-05	3.22E-05	3.23E-05	3.36E-05	1.48E-06	0.044
r^2	0.95	0.98	0.98	0.99	0.99			

Table S9: pH 8 Raw Data and k_{obs}

Time (days)	pH 8 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	164.92	208.80	228.80	248.84	227.66	215.80	31.78	0.147
7	374.30	482.94	469.60		450.00	444.21	48.53	0.109
14	560.72	660.02	626.16	609.62	648.26	620.95	38.91	0.063
21	750.06	866.15	944.26	873.41	936.80	874.14	77.95	0.089
28	809.29	1026.32	1033.55	1077.36	1121.17	1013.54	120.35	0.119
35	1124.54	1360.45	1372.74	1343.81	1329.52	1306.21	102.87	0.079
49	1647.07	1831.26	1866.68	1775.48	1734.38	1770.98	85.89	0.048
63	1859.29	2003.39	2131.83		2315.05	2077.39	193.64	0.093
77	2232.22	2527.04	2592.20	2568.62	2221.23	2428.26	185.49	0.076
k (1/d)	3.09E-05	3.35E-05	3.50E-05	3.48E-05	3.21E-05	3.33E-05	1.76E-06	0.053
r^2	0.99	0.99	0.99	1.00	0.97			

Time (days)	pH 8 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	35.09	38.36		104.32	106.53	71.07	39.70	0.559
7	192.54	220.09	223.24		176.57	203.11	22.43	0.110
14	279.99	356.28	332.05	342.66	348.79	331.95	30.37	0.092
21	427.48	512.11	458.68	521.58	511.32	486.24	41.11	0.085
28	511.98	608.00	613.13	564.97	624.46	584.51	46.39	0.079
35	630.32	744.43	699.15	756.51	752.50	716.58	53.40	0.075
49	862.65	1022.45	998.12	1029.69	1048.02	992.18	74.59	0.075
63	956.45	1256.73	1127.80		1218.30	1139.82	133.66	0.117
77	1229.79	1474.83	1421.92	1402.80	1170.90	1340.05	131.88	0.098
k (1/d)	3.42E-05	4.24E-05	4.05E-05	3.94E-05	3.59E-05	3.85E-05	3.35E-06	0.087
r^2	0.99	1.00	0.99	0.99	0.95			

Table S10: pH 9 Raw Data and k_{obs}

Time (days)	pH 9 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	251.32	274.94		302.12	82.25	227.66	99.13	0.435
7	489.64	623.67	604.41	587.15	332.57	527.49	120.58	0.229
14	712.91	855.21	1003.11	938.82	528.13	807.64	190.25	0.236
21	901.03	1200.33	1330.01	1329.37	975.20	1147.19	199.76	0.174
28	1332.96	1542.88	1659.49	1555.21	1515.79	1521.27	118.55	0.078
35	1483.86	1848.98	1846.79	1744.85	1538.41	1692.58	171.98	0.102
49	1755.57	2214.55	2258.67	2196.87		2106.41	235.33	0.112
63	2844.27		2678.22	2596.84		2706.44	126.11	0.047
77	2576.50	3356.57	3149.50	3230.02	2710.23	3004.56	341.18	0.114
k (1/d)	3.82E-05	4.49E-05	3.93E-05	4.14E-05	3.94E-05	4.06E-05	2.65E-06	0.065
r^2	0.95	1.00	0.99	0.99	0.96			

Time (days)	pH 9 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	39.35	31.91		73.52	65.52	52.57	20.07	0.382
7	159.57	178.13	149.63	202.48		172.45	23.24	0.135
14	218.37	290.39	290.96	352.70	199.47	270.38	61.91	0.229
21	342.41	431.73	438.56	495.54	302.52	402.15	78.13	0.194
28	529.03	597.82	764.04	622.00	611.59	624.90	85.84	0.137
35	550.21	817.93	868.31	818.43	616.05	734.19	141.34	0.193
49	803.81	1002.95	1103.01	1082.95		998.18	136.60	0.137
63	1255.30		1297.85	1358.04		1303.73	51.62	0.040
77	1239.19	1628.56	1457.34	1671.38	1224.30	1444.15	209.86	0.145
k (1/d)	3.90E-05	4.77E-05	4.44E-05	4.77E-05	3.68E-05	4.32E-05	5.02E-06	0.116
r^2	0.97	1.00	0.97	1.00	0.97			

Table S11: pH 10 Raw Data and k_{obs}

Time (days)	pH 10 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	188.58	222.19	236.99	186.74	188.38	204.58	23.44	0.115
7	666.14	773.38	676.04	671.57	684.29	694.28	44.71	0.064
14	1007.60	1466.45	1384.86	1377.62	1412.36	1329.78	183.45	0.138
21	1587.91	1859.37	1950.09	1750.75	2045.08	1838.64	177.53	0.097
28	2335.23	2780.96	2827.10	2939.72	2538.06	2684.21	244.03	0.091
35	3100.12	3658.46	3607.75	3480.47	3401.77	3449.71	220.23	0.064
49	3819.56	4544.99	4659.18	3736.97		4190.17	479.10	0.114
63	4998.40	6629.57	6104.02	6114.13	6091.11	5987.45	598.10	0.100
77	6187.71	7300.66	7321.62	6122.16	7315.70	6849.57	634.58	0.093
k (1/d)	8.94E-05	1.09E-04	1.07E-04	9.33E-05	1.07E-04	1.01E-04	9.17E-06	0.091
r^2	1.00	0.99	1.00	0.96	1.00			

Time (days)	pH 10 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	0.00	0.00	47.92	15.37	27.06	18.07	20.20	1.118
7	177.72	218.39	186.86	187.76	289.82	212.11	46.07	0.217
14	368.36	647.85	556.52	555.31	516.51	528.91	101.90	0.193
21	817.79	969.37	1023.54	827.15	869.35	901.44	90.93	0.101
28	1066.80	1200.01	1192.57	1079.96	1064.24	1120.71	69.30	0.062
35	1481.31	1844.73	1793.41	1614.13	1917.17	1730.15	178.53	0.103
49	1845.05	2505.55	2513.30	1931.35		2198.81	360.40	0.164
63	2208.51	3043.16	3027.85	2920.14	2999.28	2839.79	356.07	0.125
77	2824.22	3708.59	3584.80	3393.65	3671.53	3436.56	363.32	0.106
k (1/d)	8.53E-05	1.14E-04	1.12E-04	1.04E-04	1.12E-04	1.06E-04	1.20E-05	0.113
r^2	0.99	0.99	0.99	0.99	0.99			

Table S12: pH 11 Raw Data and k_{obs}

Time (days)	pH 11 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	623.55	1069.52	663.98	636.65	810.54	760.85	188.02	0.247
7	3212.28	3962.59	3369.42	3670.59	4904.68	3823.91	669.23	0.175
14	4522.96	6757.79	7221.34	6244.20	7363.18	6421.89	1148.42	0.179
21	7858.85	10926.38	11302.53	10252.99	10720.80	10212.31	1369.08	0.134
28	9328.30	12895.12	12726.13	10422.28	12132.97	11500.96	1559.50	0.136
35	11753.68	16585.60	15722.00	15635.80	15473.90	15034.20	1883.94	0.125
49	15348.83	22185.07	17690.98	19093.49	18030.53	18469.78	2486.57	0.135
63	17262.74	21098.14	20339.81	18560.06	19366.60	19325.47	1501.13	0.078
77	26289.04	27605.05	22497.58	30061.86	23602.46	26011.20	3048.48	0.117
k (1/d)	3.50E-04	3.87E-04	3.21E-04	3.94E-04	3.18E-04	3.54E-04	3.57E-05	0.101
r^2	0.97	0.96	0.93	0.95	0.95			

Time (days)	pH 11 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
7	925.74	1205.01	1040.31	1207.82	1380.46	1151.87	174.49	0.151
14	1702.20	2902.63	2968.67	2474.23	2844.57	2578.46	526.04	0.204
21	3690.49	5268.57	4837.87	4265.17	4676.42	4547.70	598.97	0.132
28	3842.05	5715.61	5905.80	4899.56	5376.31	5147.87	823.99	0.160
35	5753.85	7889.02	7209.59	7508.75	7555.06	7183.26	834.59	0.116
49	8260.45	10626.99	8047.36	8998.79	9245.42	9035.80	1019.24	0.113
63	9227.91	11098.49	10422.78	8780.28	8702.69	9646.43	1063.86	0.110
77	14003.74	13523.43	11163.46	12872.95	11761.97	12665.11	1187.69	0.094
k (1/d)	4.03E-04	4.13E-04	3.42E-04	3.68E-04	3.39E-04	3.73E-04	3.39E-05	0.091
r^2	0.98	0.97	0.96	0.96	0.94			

Table S13: pH 12 Raw Data and k_{obs}

Time (days)	pH 12 Nanomoles of 8:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	8280.24	4938.92	9478.22	6216.44	5628.88	6908.54	1902.68	0.275
7	52798.65	66256.29	61765.90	52775.96	38018.10	54322.98	10820.89	0.199
14	69163.25	91692.87	73871.38	69908.75	54672.51	71861.75	13265.35	0.185
21	105462.71	125496.71	115331.63	91648.66	73065.70	102201.08	20530.22	0.201
28	114398.57	119616.55	128208.63	102631.24	85688.89	110108.77	16497.34	0.150
35	130523.68		149167.72	116358.01	99660.34	123927.44	21029.90	0.170
49	178782.68	181428.56	162503.68	137991.34	122245.01	156590.25	25835.68	0.165
63	165473.44	177212.93	172769.95	158641.73	128695.29	160558.67	19167.58	0.119
77	178184.89	226880.59	166662.21	181707.80	143536.42	179394.38	30453.48	0.170
k (1/d)	2.75E-03	3.23E-03	2.49E-03	2.62E-03	2.10E-03	2.64E-03	4.09E-04	0.155
r^2	0.88	0.92	0.81	0.96	0.94			

Time (days)	pH 12 Nanomoles of 10:2 FTOH Recovered per g FTP Solids							
	Rep 1-2	Rep 2	Rep 3	Rep 4	Rep 5	Mean	St Dev	COV
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
7	15526.16	28864.76	27709.08	16349.33	16005.94	20891.05	6770.14	0.324
14	29856.74		32128.98	26043.28	19644.00	26918.25	5460.98	0.203
21	53835.58	62329.03	51880.00	30350.89		49598.87	13609.98	0.274
28	62226.41	63048.18	57924.97	35274.42	32764.20	50247.63	14967.92	0.298
35	73472.85		73954.33	49428.10	42532.85	59847.03	16258.47	0.272
49	96014.21	89853.85	77233.47	67138.60	60840.44	78216.11	14813.85	0.189
63	91092.80	86481.33	93806.37	84380.83	58815.63	82915.39	13974.49	0.169
77	100413.29	115441.53	90810.92	91208.34	62358.39	92046.50	19371.01	0.210
k (1/d)	3.47E-03	3.33E-03	2.98E-03	3.07E-03	2.18E-03	3.01E-03	5.02E-04	0.167
r^2	0.89	0.91	0.89	0.99	0.83			

Supporting Discussion

Experimental and modeled kinetic values are tabulated below.

Table S14: Summary of Experimental and Modeled Kinetic Variables

pH	Nominal Measured	5 4.97	6 5.89	7 6.86	8 7.91	9 8.83	10 9.84	11 10.84	12 12.28
8:2 FTOH	Experimental k_{obs} (1/yr)	2.64E-05	4.54E-05	3.80E-05	3.33E-05	4.06E-05	1.01E-04	3.54E-04	2.64E-03
	Modeled k_{obs} (1/yr)	3.44E-05	3.46E-05	3.57E-05	4.04E-05	5.62E-05	1.22E-04	3.83E-04	2.55E-03
	Experimental $T_{1/2}$ (yr)	71.9	41.8	49.9	57.0	46.7	18.8	5.4	0.72
	Modeled $T_{1/2}$ (yr)	55.2	54.8	53.1	47.0	33.8	15.6	5.0	0.74
10:2 FTOH	Experimental k_{obs} (1/yr)	1.78E-05	2.81E-05	3.36E-05	3.85E-05	4.32E-05	1.06E-04	3.73E-04	3.01E-03
	Modeled k_{obs} (1/yr)	2.12E-05	2.14E-05	2.24E-05	2.68E-05	4.23E-05	1.10E-04	3.88E-04	2.84E-03
	Experimental $T_{1/2}$ (yr)	106.6	67.5	56.5	49.3	43.9	17.9	5.1	0.63
	Modeled $T_{1/2}$ (yr)	89.5	88.5	84.7	70.7	44.8	17.3	4.9	0.67

Table S15: Modeled Kinetic Constants

Parameter	8:2 FTOH	10:2 FTOH
K_{H2O}	3.43E-05	2.11E-05
k_{OH-}	2.68E-02	3.24E-02
m	0.597	0.616

The $T_{1/2}$ 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] as reported in Table S1 (as would be expected if hydrolysis rate was equal among each fluorotelomer length).

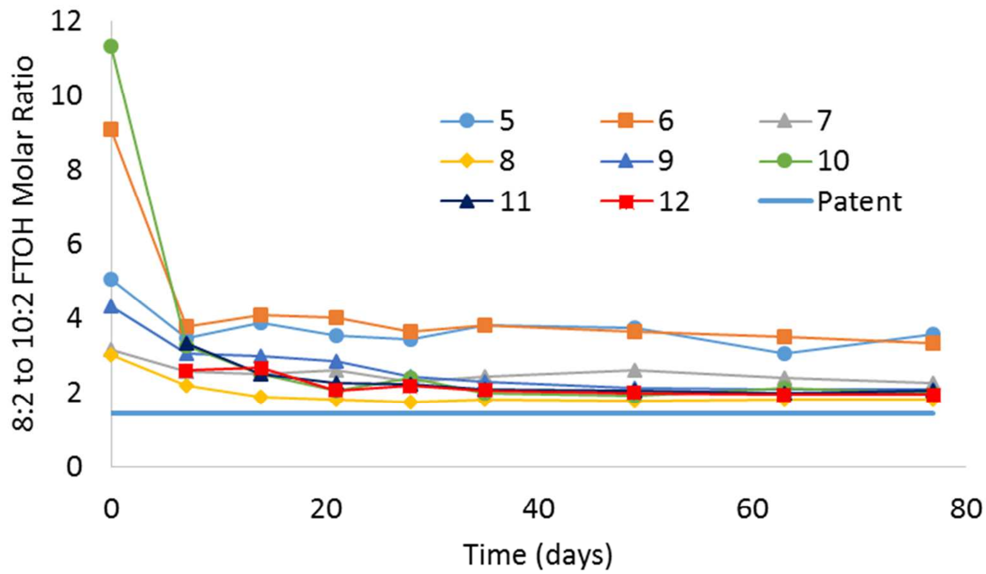

Figure S2: [8:2 FTOH]/[10:2 FTOH] molar ratio vs time. After a high degree of variation in molar ratio at time 0, the molar ratio fell to nearly constant values that are close to that reported for the FTP in the patent description.

A noteworthy feature of the data is that pH 5 experimental $T_{1/2}$s 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, 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 t_0, start manufacturing commercial acrylate fluorotelomer polymer FTP at constant rate Φ in units of tons/year (t/yr). At time t_0, FTP_0 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:

$$\frac{d[FTP]}{dt} = \Phi \qquad \text{(S1)}$$

And degradation is given by:

$$\frac{d[FTP]}{dt} = -k_{obs}[FTP] \qquad \text{(S2)}$$

where k_{obs} is a constant having units yr^{-1} for this model. Overall, changes in FTP are given by:

$$\frac{d[FTP]}{dt} = \Phi - k_{obs}[FTP] \qquad \text{(S3)}$$

Integrating Equation S3:

$$\int \frac{d[FTP]}{\Phi - k_{obs}[FTP]} = \int dt = -\frac{1}{k_{obs}} ln\left(\frac{\Phi - k_{obs}[FTP]}{\Phi - k_{obs}[FTP]_0}\right) + c = t - t_0 \qquad \text{(S4)}$$

where c is an integration constant. Constant c can be solved for by noting the initial boundary condition that at $t = t_0$, FTP = FTP_0 and:

$$-\frac{1}{k_{obs}} ln\left(\frac{\Phi - k_{obs}M[FTP]_0}{\Phi - k_{obs}[FTP]_0}\right) + c = t - t_0 \qquad \text{(S5)}$$

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

$$-\frac{1}{k_{obs}} ln\left(\frac{\Phi - k_{obs}M[FTP]_0}{\Phi - k_{obs}[FTP]_0}\right) = \Delta t \qquad \text{(S6)}$$

Rearranging Equation S6 to solve for FTP and k_{obs}:

$$\Phi - k_{obs}M = (\Phi - k_{obs}[FTP]_0)e^{-k_{obs}\Delta t} \qquad \text{(S7)}$$

$$k_{obs}[FTP] = \Phi - (\Phi - k_{obs}[FTP]_0)e^{-k_{obs}\Delta t}$$

$$[FTP] = \frac{\Phi - (\Phi - k_{obs}[FTP]_0)e^{-k_{obs}\Delta t}}{k_{obs}} \qquad \text{(S8)}$$

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] The average yield of PFCAs from FTOHs was reported by (Ning) Wang et al. to be 25%.[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] assumed the fluorotelomer component of commercial FTPs would continue to be manufactured through the year 2030.

Table S16: Values Generated by Application of Equation 4 as Depicted In Figure 6

Time Increment		Annual FTP Production (1)	Accumulated Production (1)	55 Year Half Life								89 Year Half Life							
				FTP Remaining		FTP Moieties Liberated		PFCAs Generated (3)		Post-2015 PFCA Gen'd		FTP Remaining		FTP Moieties Liberated		PFCAs Generated (3)		Post-2015 PFCA Gen'd	
				Initial Mass	Ending Mass	8:2 FTOH Mass (2)	10:2 FTOH Mass (2)	PFOA Mass	PFDA Mass	PFOA Mass	PFDA Mass	Initial Mass	Ending Mass	8:2 FTOH Mass	10:2 FTOH Mass	PFOA Mass	PFDA Mass	PFOA Mass	PFDA Mass
(years)		(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)	(tons)
1960	**1960**	0	0	0	0	0	0	0	0			0	0	0	0	0	0		
1961	**1979**	500	9500	0	8448	525.9	315.54	131	79			0	8831	335	201	84	50		
1980	**1994**	1500	32000	8448	27494	2252.9	1351.74	563	338			8831	29092	1454	872	363	218		
1995	**2004**	4000	72000	27494	61821	5089.6	3053.76	1272	763			29092	65395	3303	1982	826	495		
2005	**2014**	9000	162000	61821	139060	11469.8	6881.88	2867	1720			65395	147079	7460	4476	1865	1119		
2015	**2015**	0	162000	139060	137319	12340.6	7404.36	3085	1851	0	0	147079	145938	8031	4818	2008	1205	0	0
	2020	0	162000	137319	128933	16533.55	9920.1299	4133	2480	1048	629	145938	140365	10818	6491	2704	1623	697	418
	2025	0	162000	128933	121059	20470.457	12282.274	5118	3071	2032	1219	140365	135004	13498	8099	3375	2025	1367	820
	2030	0	162000	121059	113666	24166.941	14500.165	6042	3625	2957	1774	135004	129848	16076	9646	4019	2411	2011	1207
	2035	0	162000	113666	106725	27637.684	16582.611	6909	4146	3824	2295	129848	124888	18556	11133	4639	2783	2631	1579
	2040	0	162000	106725	100207	30896.472	18537.883	7724	4634	4639	2783	124888	120119	20941	12564	5235	3141	3227	1936
	2045	0	162000	100207	94088	33956.249	20373.75	8489	5093	5404	3242	120119	115531	23234	13941	5809	3485	3801	2281
	2050	0	162000	94088	88342	36829.168	22097.501	9207	5524	6122	3673	115531	111119	25441	15264	6360	3816	4352	2611
	2055	0	162000	88342	82947	39526.641	23715.984	9882	5929	6797	4078	111119	106875	27563	16538	6891	4134	4883	2930
	2060	0	162000	82947	77881	42059.381	25235.629	10515	6309	7430	4458	106875	102793	29604	17762	7401	4441	5393	3236
	2065	0	162000	77881	73125	44437.449	26662.47	11109	6666	8024	4815	102793	98867	31566	18940	7892	4735	5884	3530
	2070	0	162000	73125	68659	46670.291	28002.175	11668	7001	8582	5149	98867	95091	33454	20073	8364	5018	6356	3814
	2075	0	162000	68659	64466	48766.775	29260.065	12192	7315	9107	5464	95091	91459	35270	21162	8818	5291	6810	4086
	2080	0	162000	64466	60530	50735.229	30441.137	12684	7610	9599	5759	91459	87966	37017	22210	9254	5553	7247	4348
	2085	0	162000	60530	56833	52583.471	31550.082	13146	7888	10061	6036	87966	84607	38697	23218	9674	5805	7666	4600
	2090	0	162000	56833	53362	54318.842	32591.305	13580	8148	10495	6297	84607	81375	40312	24187	10078	6047	8070	4842
	2095	0	162000	53362	50104	55948.236	33568.942	13987	8392	10902	6541	81375	78267	41866	25120	10467	6280	8459	5075
	2100	0	162000	50104	47044	57478.125	34486.875	14370	8622	11284	6771	78267	75278	43361	26017	10840	6504	8833	5300
	2150	0	162000	47044	25052	68474.118	41084.471	17119	10271	14033	8420	75278	50998	55501	33301	13875	8325	11868	7121
	2200	0	162000	25052	13341	74329.711	44597.826	18582	11149	15497	9298	50998	34549	63726	38235	15931	9559	13924	8354
	2250	0	162000	13341	7104	77447.934	46468.76	19362	11617	16277	9766	34549	23405	69297	41578	17324	10395	15317	9190
	2300	0	162000	7104	3783	79108.452	47465.071	19777	11866	16692	10015	23405	15856	73072	43843	18268	10961	16260	9756

(1) FTP production as estimated in Wang et al. 2014. Environment International. 70. p. 62-75. All masses reported in metric tons.

(2) FTOHs generated assumed to be 50% FTP mass for 8:2 FTOH and 30% FTP mass for 10:2 FTOH, consistent with the FTP tested in this study (Methods Table 1).

(3) PFCA yield from FTOHs is assumed to be 25%, consistent with Wang et al. 2009. Chemosphere. 75. p. 1089-1096.

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