Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
This journal is © The Royal Society of Chemistry 2023

Supplementary Information for

Electrochemical Degradation of a C6-Perfluoroalkyl Substance (PFAS) using a Simple Activated Carbon Cathode

Diana Ackerman Grunfeld[a], Adele M. Jones[a], Jun Sun[b], Song Thao Le[a], Russell Pickford[c], Qingguo Huang[d], Michael Manefield[a], Naresh Kumar[b], Matthew Lee[a] and Denis M. O'Carroll[a*]

[a] School of Civil and Environmental Engineering, Water Research Centre, The University of New South Wales, Sydney, NSW 2052, Australia.

[b] School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia.

[c] Bioanalytical Mass Spectrometry Facility, Mark Wainwright Analytical Centre, The University of New South Wales, Sydney, NSW 2052, Australia.

[d] College of Agricultural and Environmental Sciences Crop and Soil Sciences, The University of Georgia, Griffin, GA 30223, USA.

* Corresponding Author. Email: d.ocarroll@unsw.edu.au

† Electronic Supplementary Information (ESI) available.

Table of Figures

Table of Tables

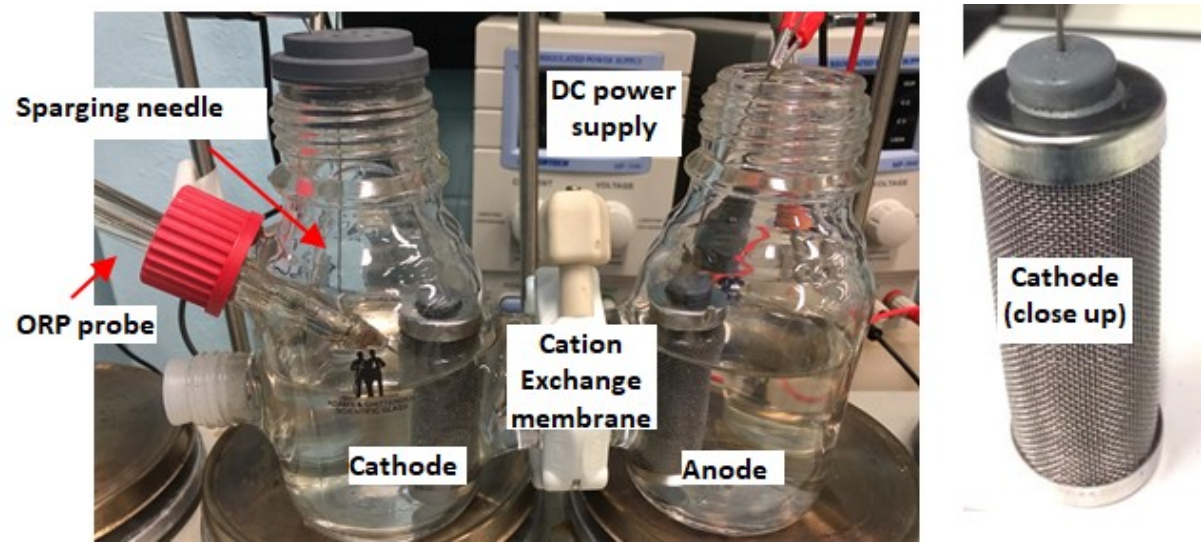


Fig. S1. Picture of the H-cell setup employed (left) and a close up of the packed GAC-stainless steel mesh electrodes used (right).

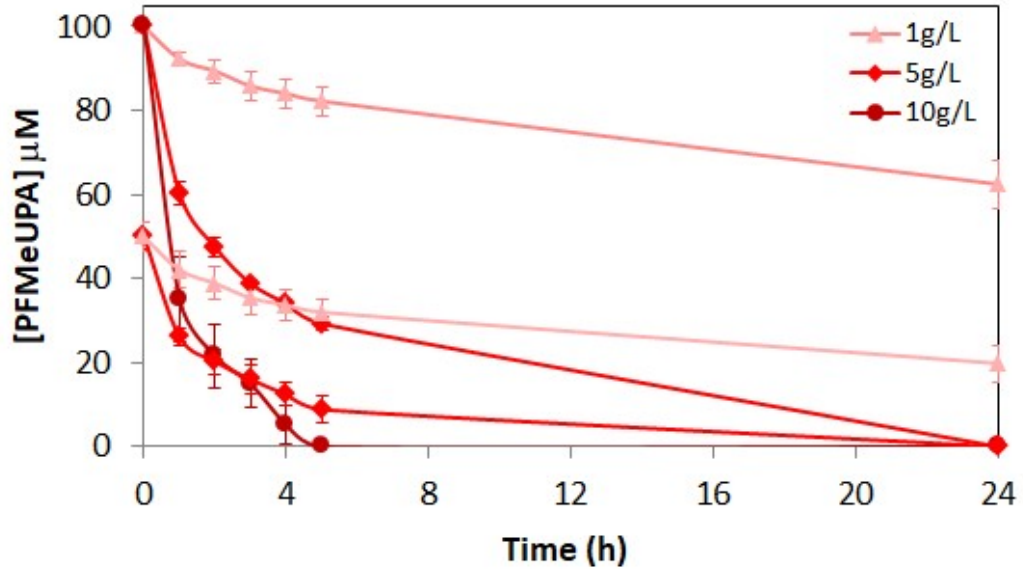


Fig. S2. Sorption of 50 or 100 µM PFMeUPA to 1, 5 and 10 g/L of GAC over 24 hours. (error bars represent one standard deviation from the mean (n = 3)

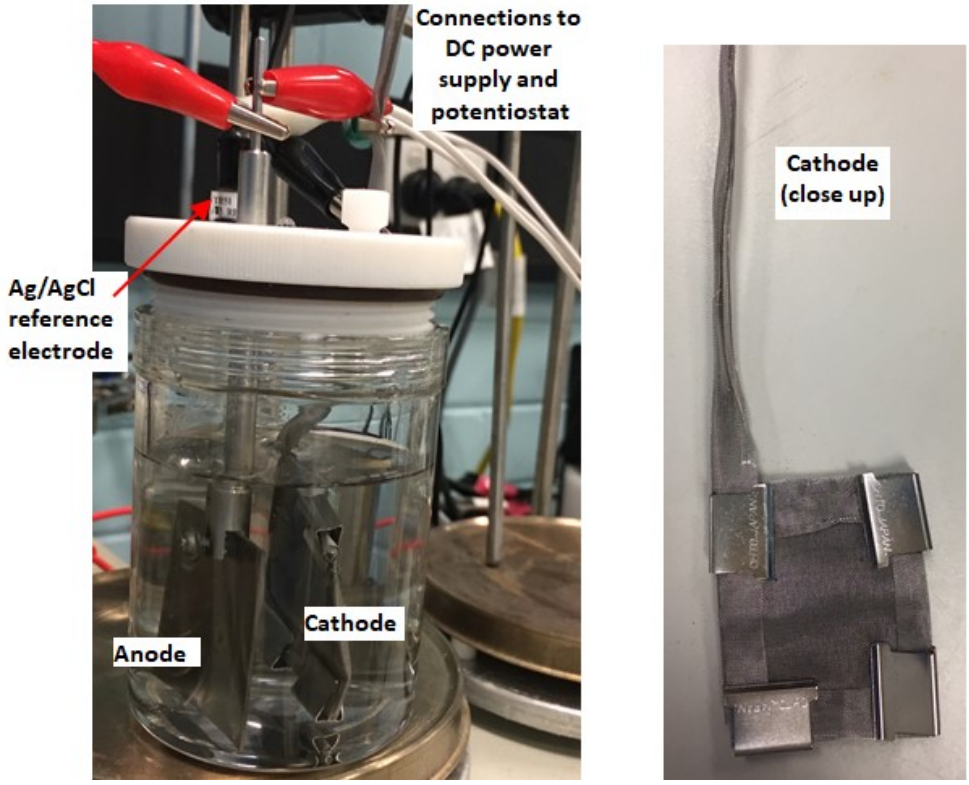


Fig. S3. Picture of the single cell setup (left) and a close-up of the GAC packed square mesh cathode employed (right).

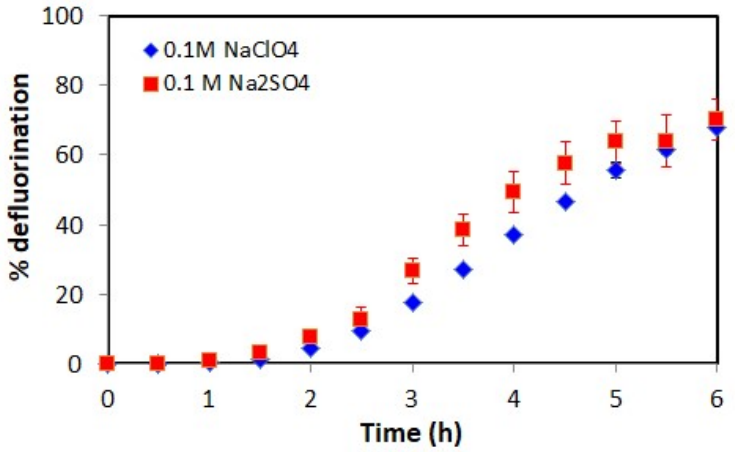


Fig. S4. The impact of unbuffered 0.1 M $NaClO_4$ or 0.1 M Na_2SO_4 as the electrolyte in the reductive defluorination of PFMeUPA. Data points are the average of duplicate measurements and errors represent the range. First order rates were measured between 2 and 5 hours, with rate constants determined to be 9.15±1.32 x 10^{-5} s^{-1} in 0.1 M Na_2SO_4 and 7.54±0.33 x 10^{-5} s^{-1} in 0.1 M $NaClO_4$.

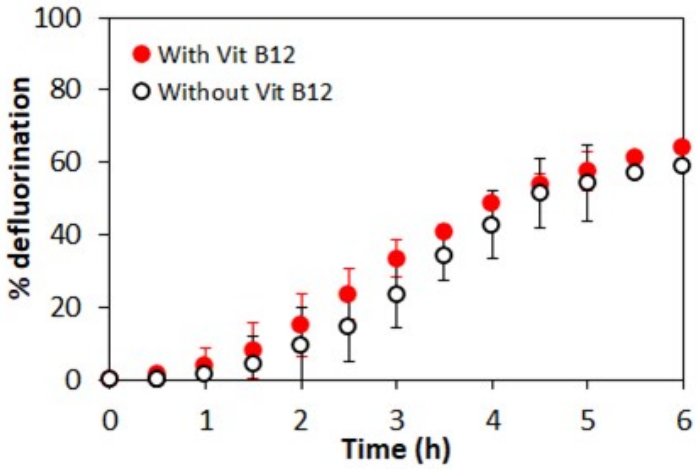


Fig. S5. Percentage defluorination of PFMeUPA following the application of 10 V at 70°C in a pH 6.8 buffered solution in the presence or absence vitamin B_{12} (100 µM). Data points represent the average of duplicate measurements and error bars represent the range.

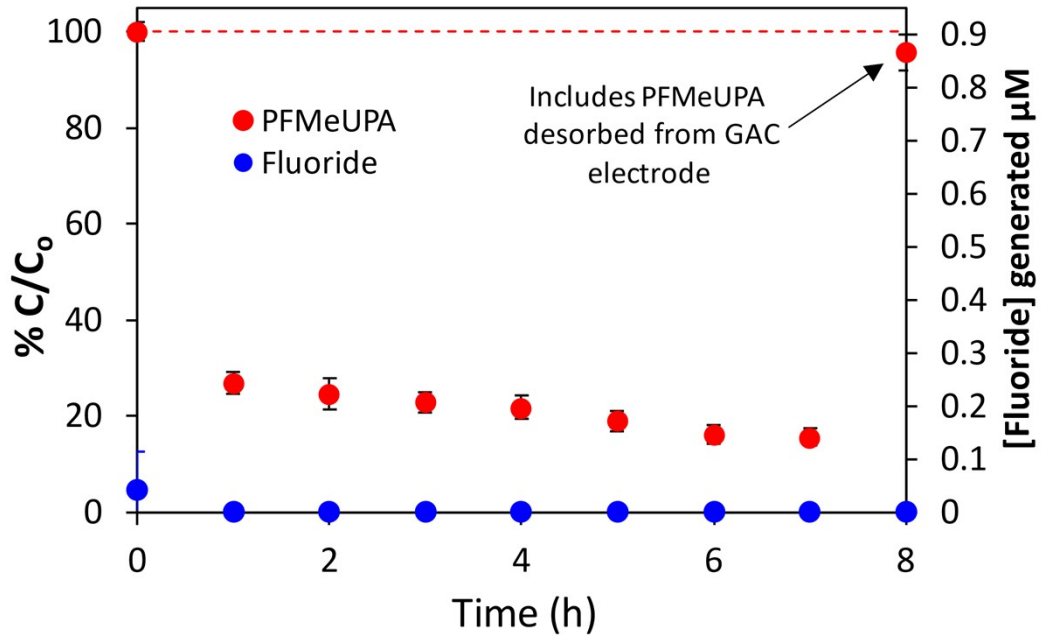


Fig. S6. Control experiments indicating no loss of PFMeUPA or generation of fluoride after reaction of PFMeUPA in the H-cell with nitrogen gas purging over 85 °C in the absence of an applied volage of 10 V. The red dashed line represents 100% C/C_o (i.e. no loss of PFMeUPA) and the maximum concentration of fluroide able to be generated which is 0.9 µM. Data points are the average of duplicate measurements, and error bars represent the range about the average.

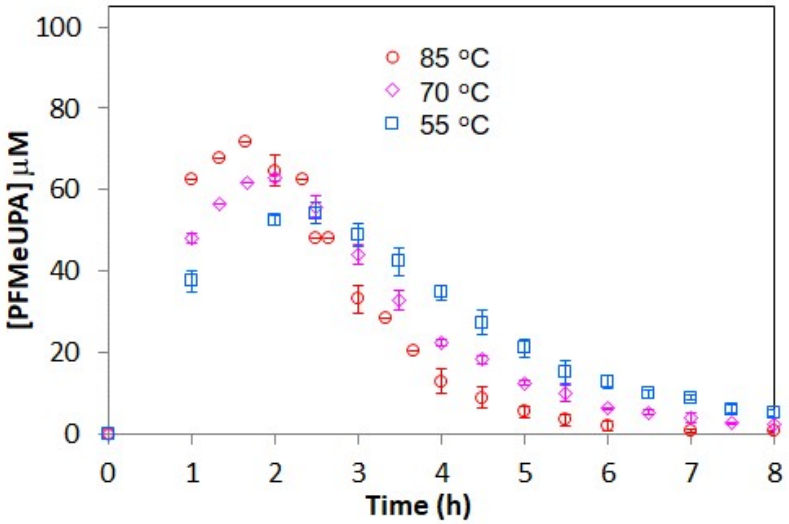


Fig. S7. Concentration of PFMeUPA measured in the aqueous collected from experiments conducted in the H-cell at an applied cell voltage of 10 V at 55, 70 and 85°C. Data points represent the average of duplicate measurements and error bars represent the range. Note that the time zero measurement represented here is that measured after 12 h of adsorption.

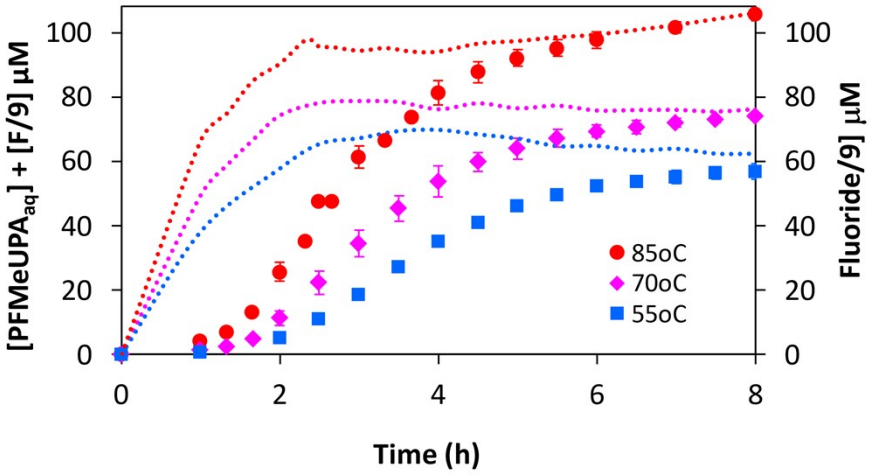
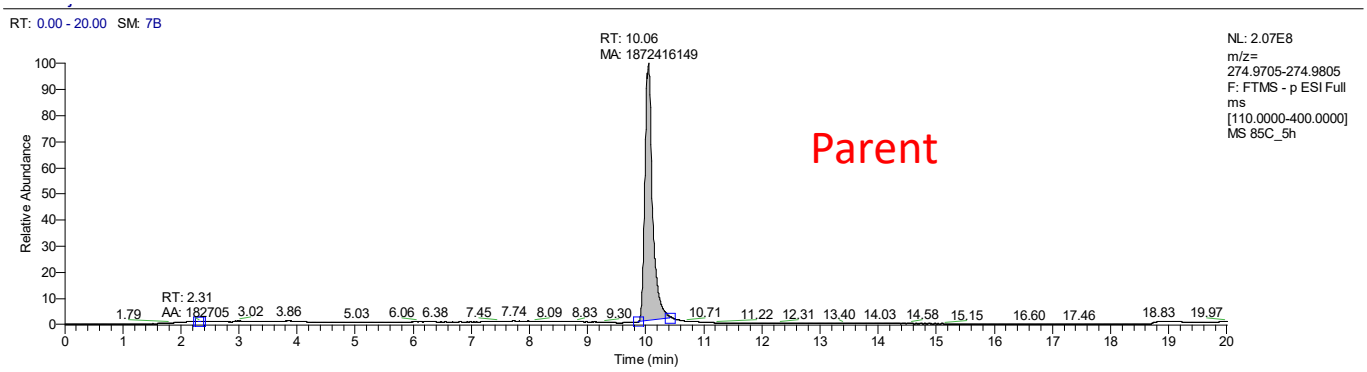
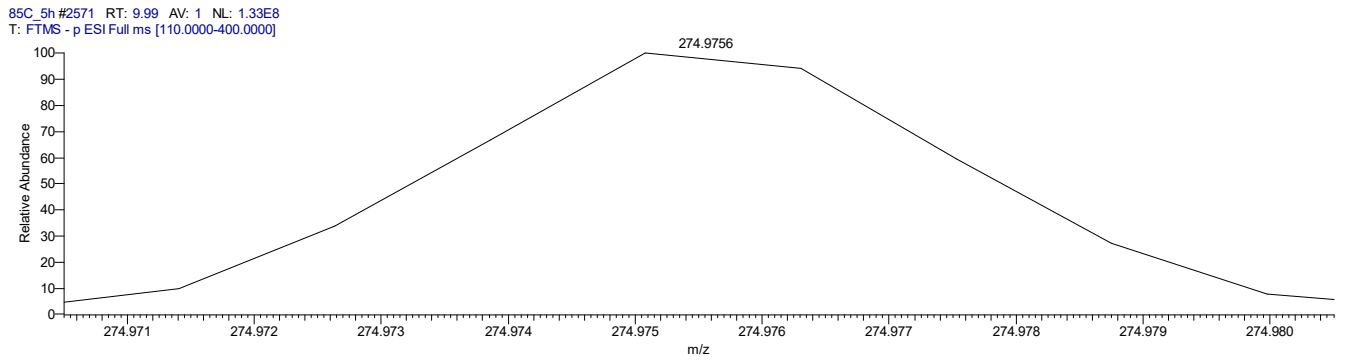
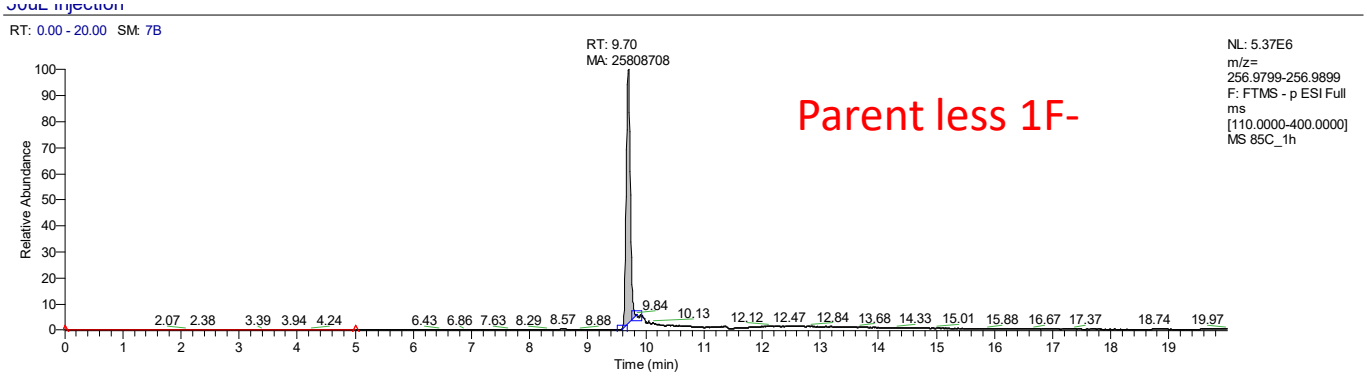
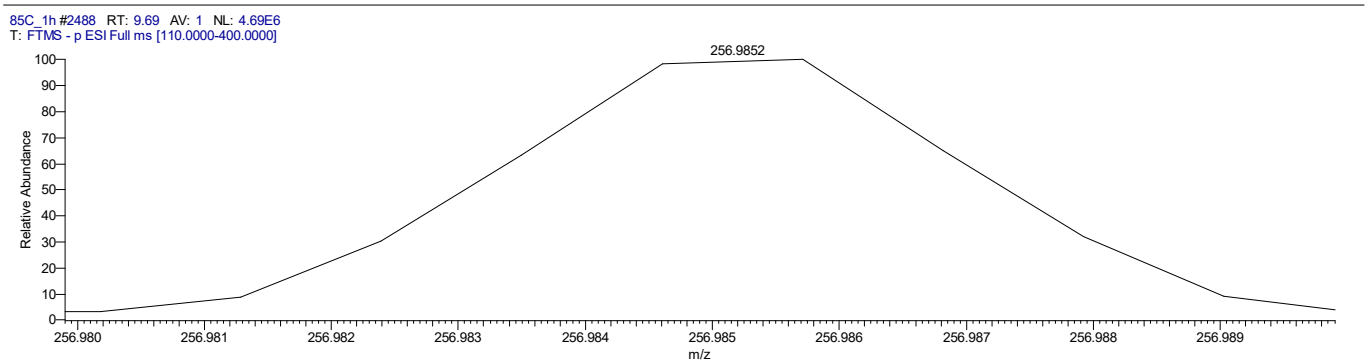


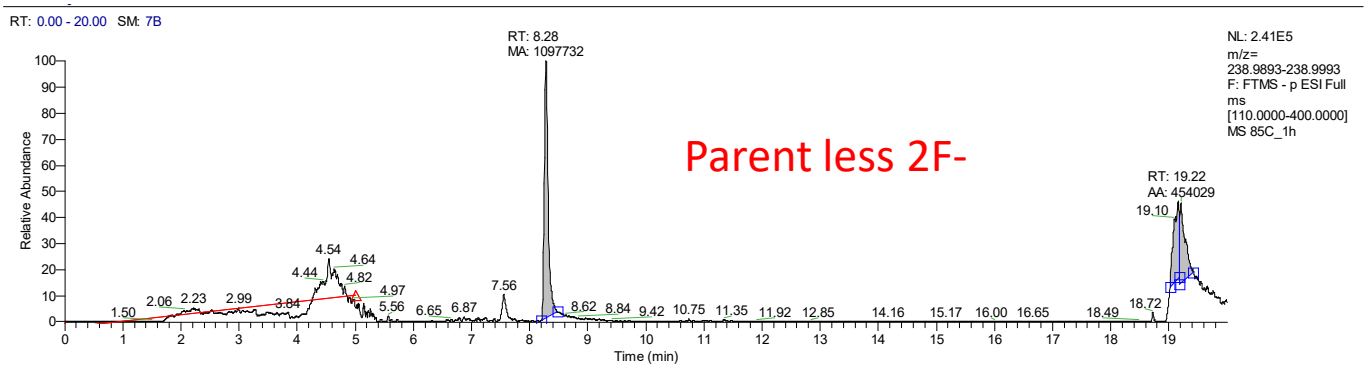
Fig. S8. Defluorination of PFMeUPA with an applied cell voltage of 10 V at 55, 70 and 85°C. Dashed lines show the mass balance of dissolved PFMeUPA and fluoride at each timepoint (left axis). Data points represent the average of duplicate fluoride measurements and error bars represent the range about the average (right axis).

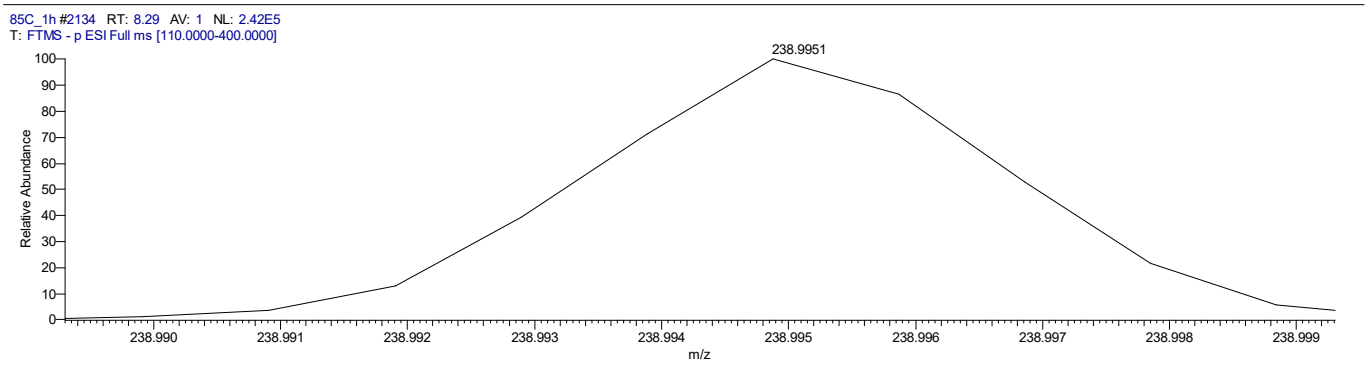

RT: 0.00 - 20.00 SM: 7B
RT: 10.06
MA: 1872416149
NL: 2.07E8
m/z=
274.9705-274.9805
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_5h
Parent
Relative Abundance
RT: 2.31
AA: 182705
Time (min)

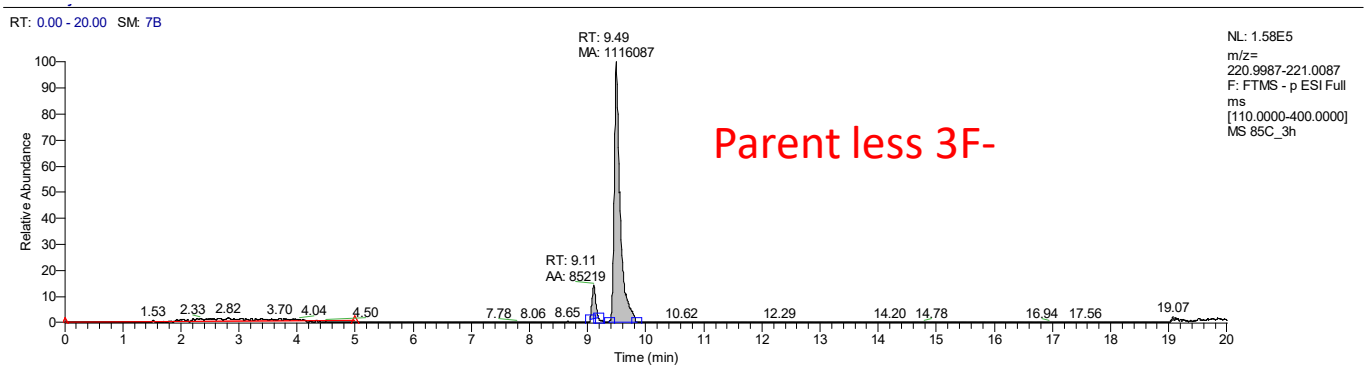

85C_5h #2571 RT: 9.99 AV: 1 NL: 1.33E8
T: FTMS - p ESI Full ms [110.0000-400.0000]
274.9756
Relative Abundance
m/z

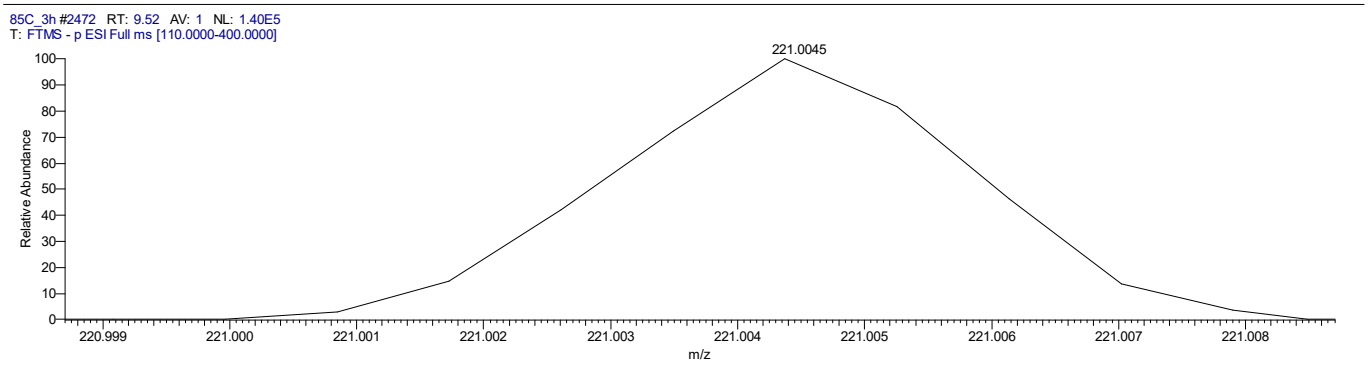

RT: 0.00 - 20.00 SM: 7B
RT: 9.70
MA: 25808708
NL: 5.37E6
m/z=
256.9799-256.9899
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_1h
Parent less 1F-
Relative Abundance
Time (min)

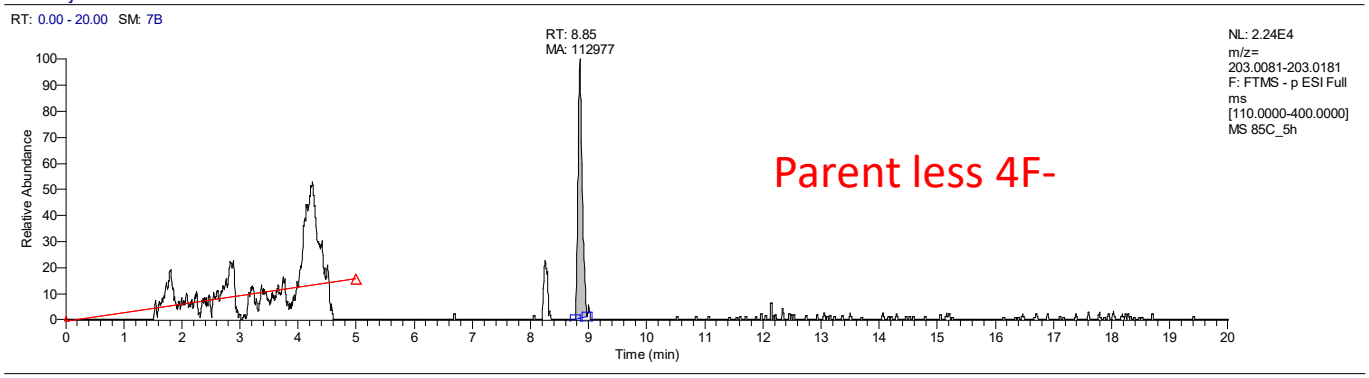

85C_1h #2488 RT: 9.69 AV: 1 NL: 4.69E6
T: FTMS - p ESI Full ms [110.0000-400.0000]
256.9852
Relative Abundance
m/z

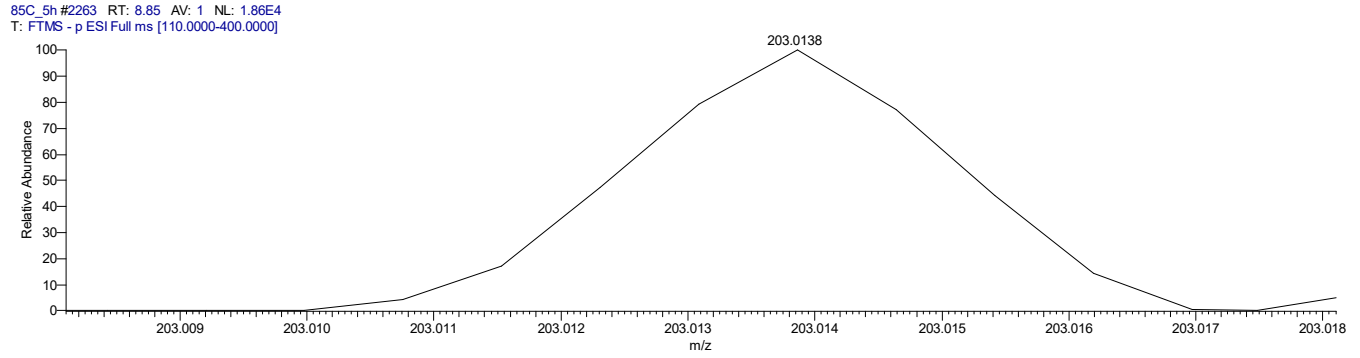

RT: 0.00 - 20.00 SM: 7B
RT: 8.28
MA: 1097732
NL: 2.41E5
m/z=
238.9893-238.9993
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_1h
Parent less 2F-
RT: 19.22
AA: 454029
Relative Abundance
Time (min)

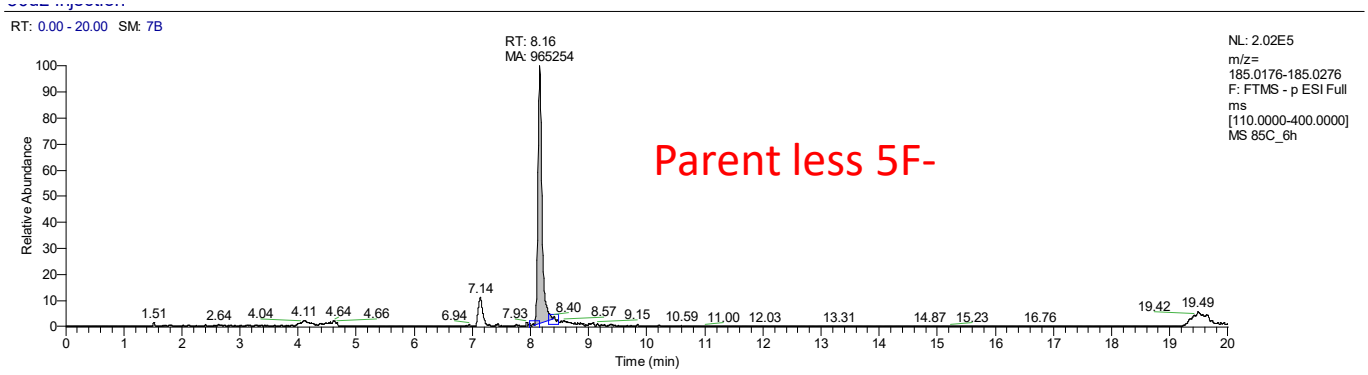

85C_1h #2134 RT: 8.29 AV: 1 NL: 2.42E5
T: FTMS - p ESI Full ms [110.0000-400.0000]
238.9951
Relative Abundance
m/z

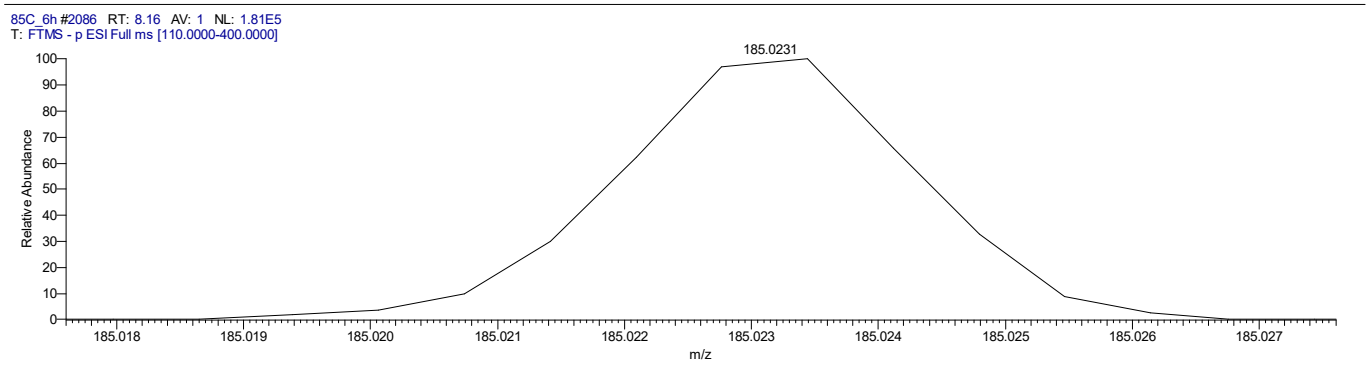

RT: 0.00 - 20.00 SM: 7B
RT: 9.49
MA: 1116087
NL: 1.58E5
m/z=
220.9987-221.0087
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_3h
Parent less 3F-
RT: 9.11
AA: 85219
Relative Abundance
Time (min)


85C_3h #2472 RT: 9.52 AV: 1 NL: 1.40E5
T: FTMS - p ESI Full ms [110.0000-400.0000]
221.0045
Relative Abundance
m/z


RT: 0.00 - 20.00 SM: 7B
RT: 8.85
MA: 112977
NL: 2.24E4
m/z=
203.0081-203.0181
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_5h
Parent less 4F-
Relative Abundance
Time (min)


85C_5h #2263 RT: 8.85 AV: 1 NL: 1.86E4
T: FTMS - p ESI Full ms [110.0000-400.0000]
203.0138
Relative Abundance
m/z


RT: 0.00 - 20.00 SM: 7B
RT: 8.16
MA: 965254
NL: 2.02E5
m/z=
185.0176-185.0276
F: FTMS - p ESI Full
ms
[110.0000-400.0000]
MS 85C_6h
Parent less 5F-
Relative Abundance
Time (min)


85C_6h #2086 RT: 8.16 AV: 1 NL: 1.81E5
T: FTMS - p ESI Full ms [110.0000-400.0000]
185.0231
Relative Abundance
m/z

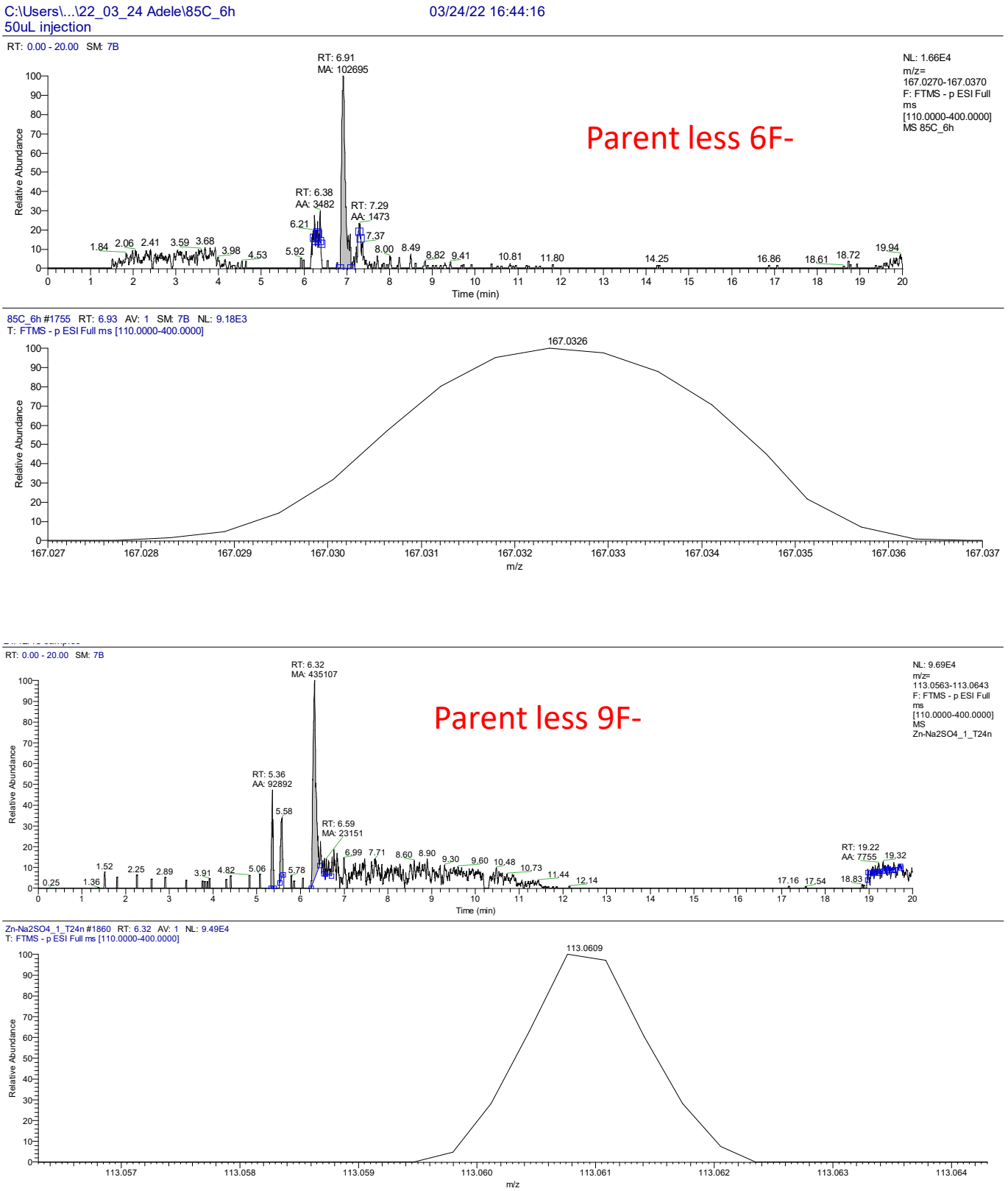
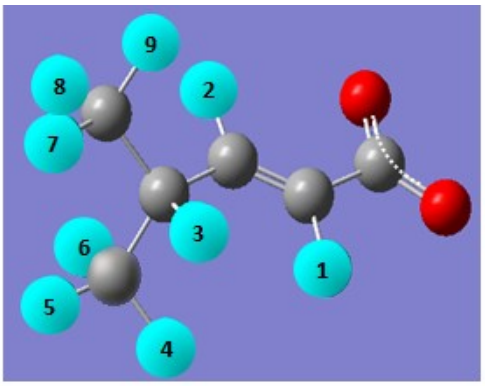


Fig. S9. Screenshots of HRMS data for all of the degradation products identified.



Numbering Scheme for Hydrodefluorination Products and Associated BDEs in the Table Below

Position → / Product ↓	1	2	3	4	5	6	7	8	9
PFMeUPA	475.71	472.56	350.86	492.91	495.87	494.57	494.39	492.23	497.82
PFMeUPA -1F	487.22	487.54		502.68	499.51	501.90	499.51	502.14	502.68
PFMeUPA -2F		500.01		502.52	499.11	501.04	499.75	502.27	502.61
PFMeUPA -3F		500.69		486.83		487.39	504.39	504.77	507.57
PFMeUPA -4F		501.00				463.85	507.72	506.37	510.11
PFMeUPA -5F		503.99					510.16	510.90	513.57
PFMeUPA -6F							512.21	513.57	515.04
PFMeUPA -7F								498.10	502.00
PFMeUPA -8F									475.78

Fig. S10. Bond dissociation energies (BDEs) in kJ.mol^{-1} determined for the reduction pathway identified from the HRMS data. Lowest energy values are highlighted in yellow. Those values which are within 1 kJ.mol^{-1} of the lowest value are highlighted in orange.

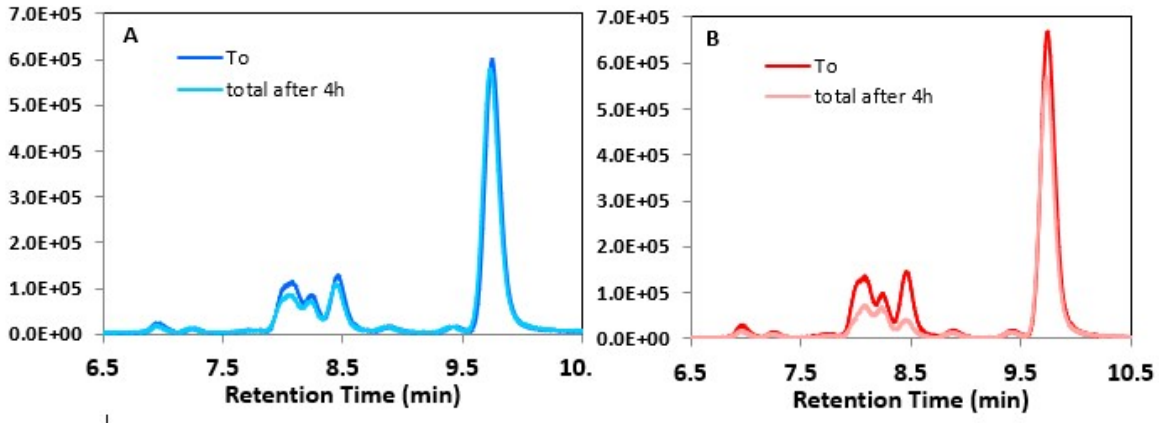


Fig. S11. LCMS spectra at time 0 (To) and after 4 hours without (A) and with (B) the addition of vitamin B12 as the catalyst. Total ater 4 hours represent the sum of aqueous and sorbed PFOS concentration after 4 hours.

Table S1. Parameters summary for the detection of PFOS and its isomers.

ISOMER	L-PFOS	6-PFOS	5- AND 3-PFOS	4-PFOS	3,5-PFOS	1- AND 2-PFOS
Precursor m/z	499	499	499	499	499	499
Product m/z	80	169	280	330	280	99
Dwell time (msec)	3	5	5	5	5	5
Collision energy	41	35	35	35	35	40

Table S2. Table of possible breakdown products that were analysed for using the Thermo LTQ Orbitrap XL ultra-high resolution mass spectrophotometer, where M refers to the molecular mass of the breakdown product, and MH- refers to the mass of the product in negative ion mode. Those products observed in the electrochemical cell or zinc reactions are noted. Note that no saturated products were observed.

Identifier	Formula	MH-	Observed	observed MH-	abs Diff exp-obs (in mmu)	accuracy in ppm	C	F	H	O	M
Parent	$C_6F_9HO_2$	274.9755	Yes	274.9755	0.041	0.15	6	9	1	2	275.9833
Parent less an F	$C_6F_8H_2O_2$	256.9849	Yes	256.9852	0.320	1.24	6	8	2	2	257.9927
Parent less 2 F-	$C_6F_7H_3O_2$	238.9943	Yes	238.9948	0.498	2.09	6	7	3	2	240.0021
Parent less 3 F-	$C_6F_6H_4O_2$	221.0037	Yes	221.0045	0.777	3.52	6	6	4	2	222.0115
Parent less 4 F-	$C_6F_5H_5O_2$	203.0131	Yes	203.0138	0.656	3.23	6	5	5	2	204.0210
Parent less 5 F-	$C_6F_4H_6O_2$	185.0226	Yes	185.0231	0.534	2.89	6	4	6	2	186.0304
Parent less 6 F-	$C_6F_3H_7O_2$	167.0320	Yes	167.0326	0.613	3.67	6	3	7	2	168.0398
Parent less 7 F-	$C_6F_2H_8O_2$	149.0414	No				6	2	8	2	150.0492
Parent less 8 F-	$C_6FH_9O_2$	131.0508	No				6	1	9	2	132.0587
Parent less 9 F-	$C_6H_{10}O_2$	113.0603	Yes	113.0609	0.649	5.74	6	0	10	2	114.0681
saturated less 3 F-	$C_6F_6H_6O_2$	223.0194	No				6	6	6	2	224.0272
saturated less 4 F-	$C_6F_5H_7O_2$	205.0288	No				6	5	7	2	206.0366
saturated less 5F-	$C_6F_4H_8O_2$	187.0382	No				6	4	8	2	188.0460
saturated less 6 F-	$C_6F_3H_9O_2$	169.0476	No				6	3	9	2	170.0555
saturated less 7 F-	$C_6F_2H_{10}O_2$	151.0571	No				6	2	10	2	152.0649
saturated less 8 F-	$C_6FH_{11}O_2$	133.0665	No				6	1	11	2	134.0743
saturated less 9 F-	$C_6H_{12}O_2$	115.0759	No				6	0	12	2	116.0837

Table S3. Averaged integration areas and retention times of degradation products identified from the HRMS data in the 85°C electrochemical experiment samples (top) and 70°C zinc experiment samples (bottom).

Averaged 85°C electrochemical data

Time (h) →	Retention	0	1	2	2.5	3	3.5	4	5	6	7	8	0.1M Na_2SO_4 Blank
Product Identifier ↓	Time (min)												
Parent	9.95	2.52E+10	1.78E+10	1.63E+10	1.20E+10	8.83E+09	6.49E+09	4.48E+09	1.87E+09	1.19E+09	5.42E+08	3.23E+08	7.45E+04
Parent less 1 F-	9.70	2.59E+06	2.58E+07	3.22E+06	1.46E+06	7.99E+05	5.74E+05	4.99E+05	5.30E+05	5.82E+05	3.01E+05	2.78E+05	0.00E+00
Parent less 2 F-	8.28	0.00E+00	1.10E+06	4.85E+06	5.99E+06	4.86E+06	3.52E+06	2.85E+06	1.35E+06	6.91E+05	3.35E+05	1.58E+05	0.00E+00
Parent less 3 F-	9.49	0.00E+00	0.00E+00	1.29E+06	1.50E+06	1.12E+06	1.34E+05	2.69E+04	4.31E+05	1.27E+05	9.22E+04	4.15E+04	0.00E+00
Parent less 4 F-	8.85	0.00E+00	1.45E+05	3.15E+05	1.89E+05	2.79E+05	2.50E+05	2.48E+05	1.13E+05	5.88E+04	3.14E+04	1.81E+04	0.00E+00
Parent less 5 F-	8.16	0.00E+00	1.70E+04	2.59E+05	3.68E+05	5.45E+05	7.16E+05	8.18E+05	9.09E+05	9.96E+05	8.99E+05	8.57E+05	0.00E+00
Parent less 6 F-	6.91	0.00E+00	0.00E+00	0.00E+00	1.91E+04	3.19E+04	4.88E+04	5.97E+04	8.39E+04	8.22E+04	9.42E+04	5.94E+04	0.00E+00

Averaged 70°C zinc data

Time (h) →	Retention	0	1	2	3	4	5	6	7	8	24	0.1M Na_2SO_4 Blank
Product Identifier ↓	Time (min)											
Parent	10.47	7.42E+10	5.88E+10	4.27E+10	3.55E+10	2.78E+10	1.79E+10	9.36E+09	5.39E+09	3.73E+09	9.35E+07	3.46E+03
Parent less 1 F-	10.27	5.04E+08	2.15E+09	2.76E+09	2.74E+09	2.28E+09	1.74E+09	1.07E+09	6.66E+08	4.80E+08	2.30E+08	0.00E+00
Parent less 2 F-	10.15	8.18E+06	2.02E+08	4.83E+08	6.67E+08	8.56E+08	1.11E+09	1.33E+09	1.47E+09	1.58E+09	1.60E+09	0.00E+00
Parent less 3 F-	8.00	7.77E+04	4.47E+06	8.74E+06	1.11E+07	9.59E+06	1.18E+07	1.11E+07	1.13E+07	1.10E+07	5.75E+06	0.00E+00
Parent less 4 F-	7.47	4.47E+05	1.11E+07	2.33E+07	3.06E+07	3.41E+07	3.78E+07	4.08E+07	4.22E+07	4.35E+07	4.08E+07	0.00E+00
Parent less 5 F-	7.20	0.00E+00	1.64E+07	3.48E+07	4.35E+07	5.23E+07	6.46E+07	7.21E+07	7.62E+07	7.92E+07	8.20E+07	0.00E+00
Parent less 6 F-	7.08	1.40E+06	8.62E+07	1.82E+08	2.22E+08	2.70E+08	3.37E+08	3.74E+08	3.77E+08	3.81E+08	3.67E+08	0.00E+00
Parent less 9 F-	6.29	0.00E+00	4.44E+04	1.80E+05	2.02E+05	2.82E+05	3.71E+05	3.97E+05	4.31E+05	4.47E+05	4.35E+05	4.45E+03