Supporting Information for:

Identification of novel perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass spectrometry (TOFMS)

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This document includes one table, and 12 SI figures, on 13 pages.

Table S1. Water samples description and GPS coordinates.

Sample ID	Description	Latitude	Longitude
CFR 001	Cape Fear river Tar Heel, NC	34.74525	-78.78574
CFR 002	Cape Fear river below Huske lock and dam #3	34.83026	-78.82246
CFR 003	unnamed tributary	34.83179	-78.82375
CFR 004	Cape Fear river above Huske lock and dam #3	34.83544	-78.82347
CFR 005	Cape Fear river below Rockfish creek	34.96820	-78.81579
CFR 006	Rockfish Creek	34.95610	-78.84424
CFR 007	Rockfish Creek WWTP effluent	34.96834	-78.82765
CFR 008	Cape Fear River at Fayetteville boat ramp access	34.99669	-78.85076
CFR 009	Regional drinking water sample	34.94199	-78.92422

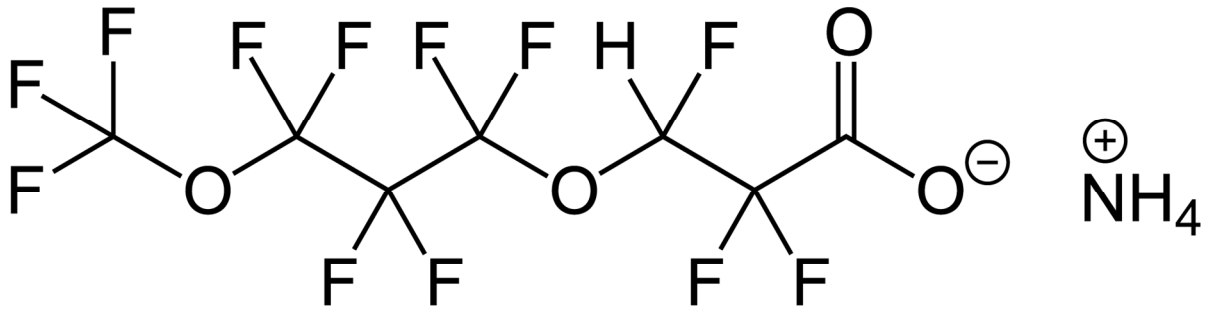


Figure S1. The structure of ADONA (4,8-dioxa-3H-perfluorononanoate) a polyfluorinated compounds used to replace classic perfluorinated compounds such as APFO.

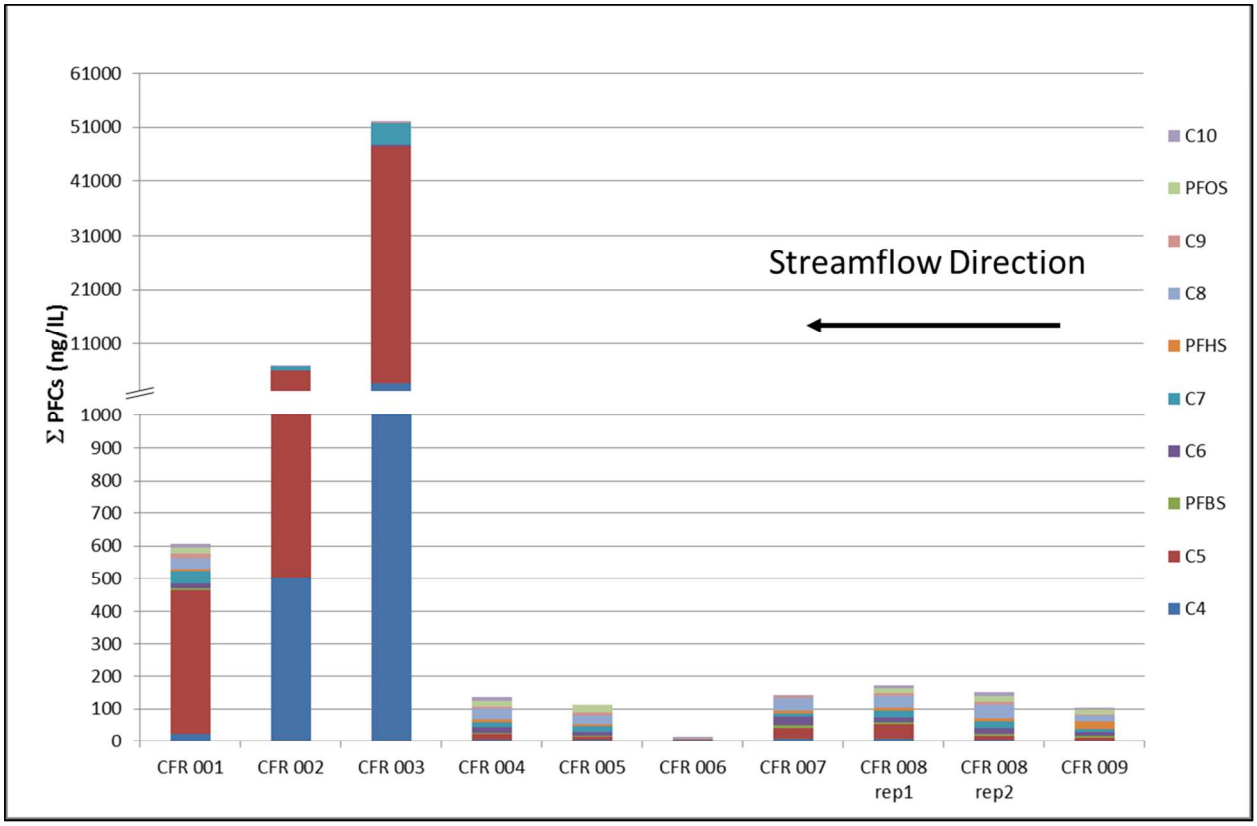


Figure S2. PFAAs found in water samples from the Cape Fear River. Note the y-axis is a split scale.

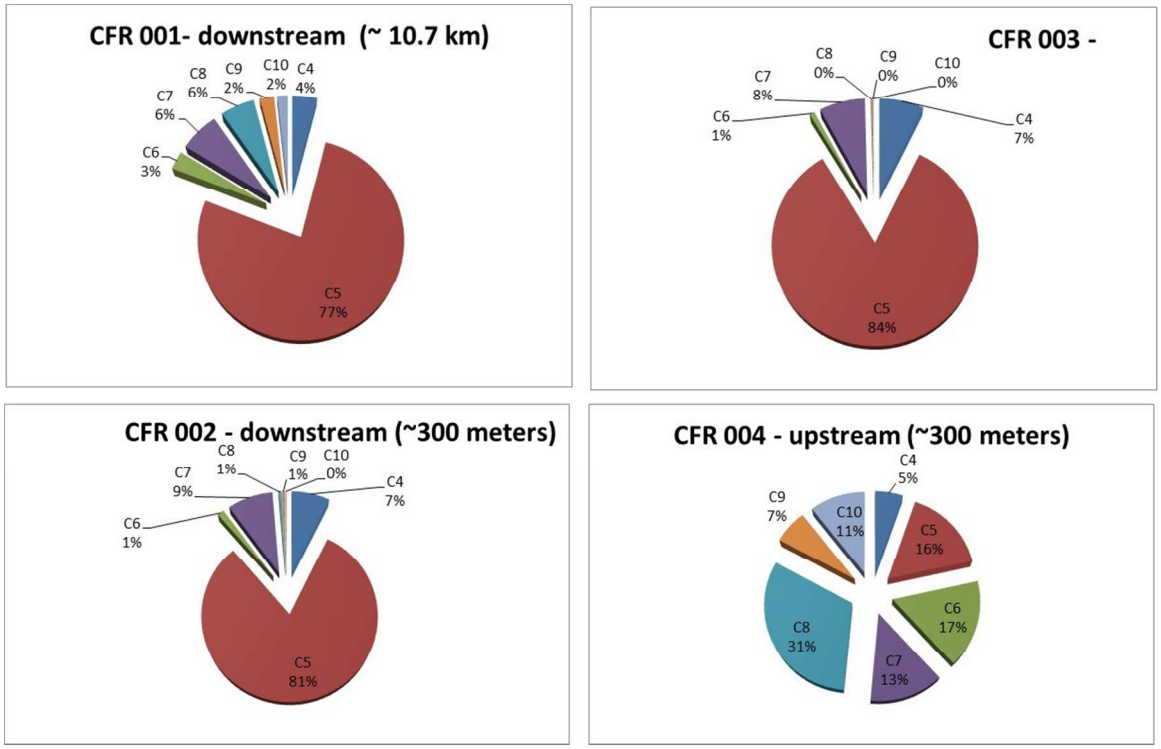


Figure S3. Proportion of PFAAs contribution to the total for select water samples from the Cape Fear River.

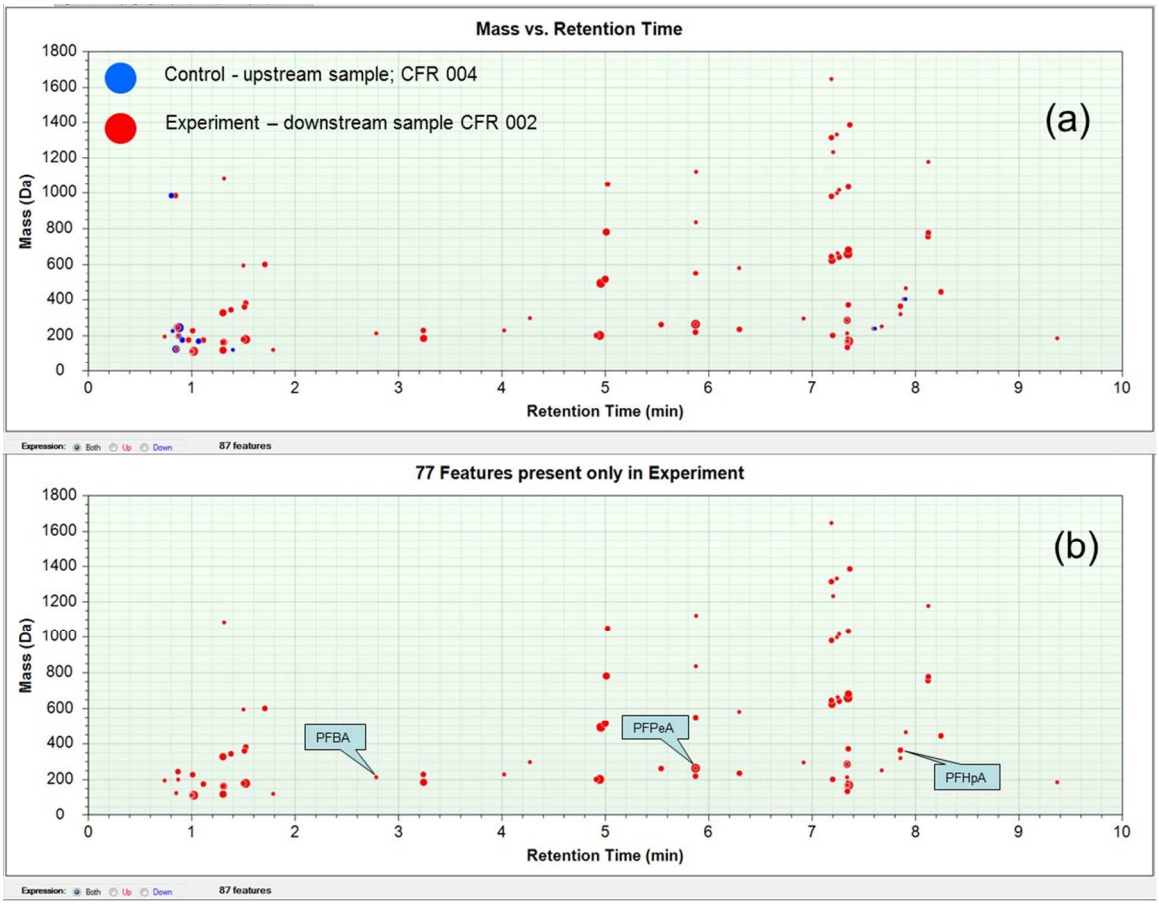


Figure S4. Mass Profiler visualization of molecular features found in (a) control and experimental sample and (b) 77 features unique only to experimental sample, with select peaks previously identified (PFBA, PFPeA and PFHpA). Note: The size of the symbol in this plot is proportional to the area of the peak. Pronounced co-eluting peaks that appear as vertical lines are likely related (i.e. fragments, M-H-, *n-mers*).

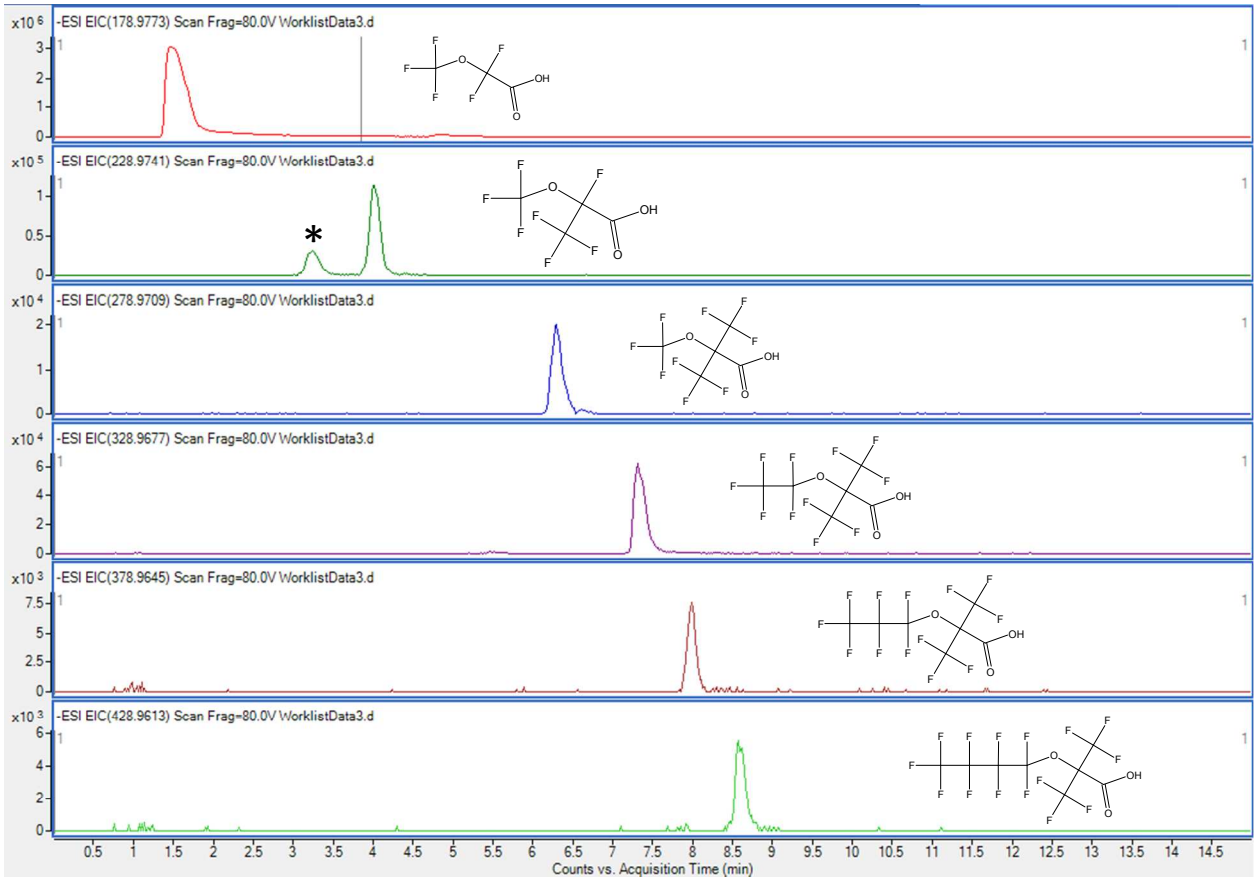


Figure S5. Extracted Ion Chromatogram (EIC) of a suspected homologous series of perfluorinated ether carboxylic acids. Note: The chromatographic peak indicated by an * is the substance associated with this homologous series based on the H^+ and Na^+ dimer co-elution at this retention time. The second later eluting peak in this chromatogram is a similar m/z, possibly an isomer.

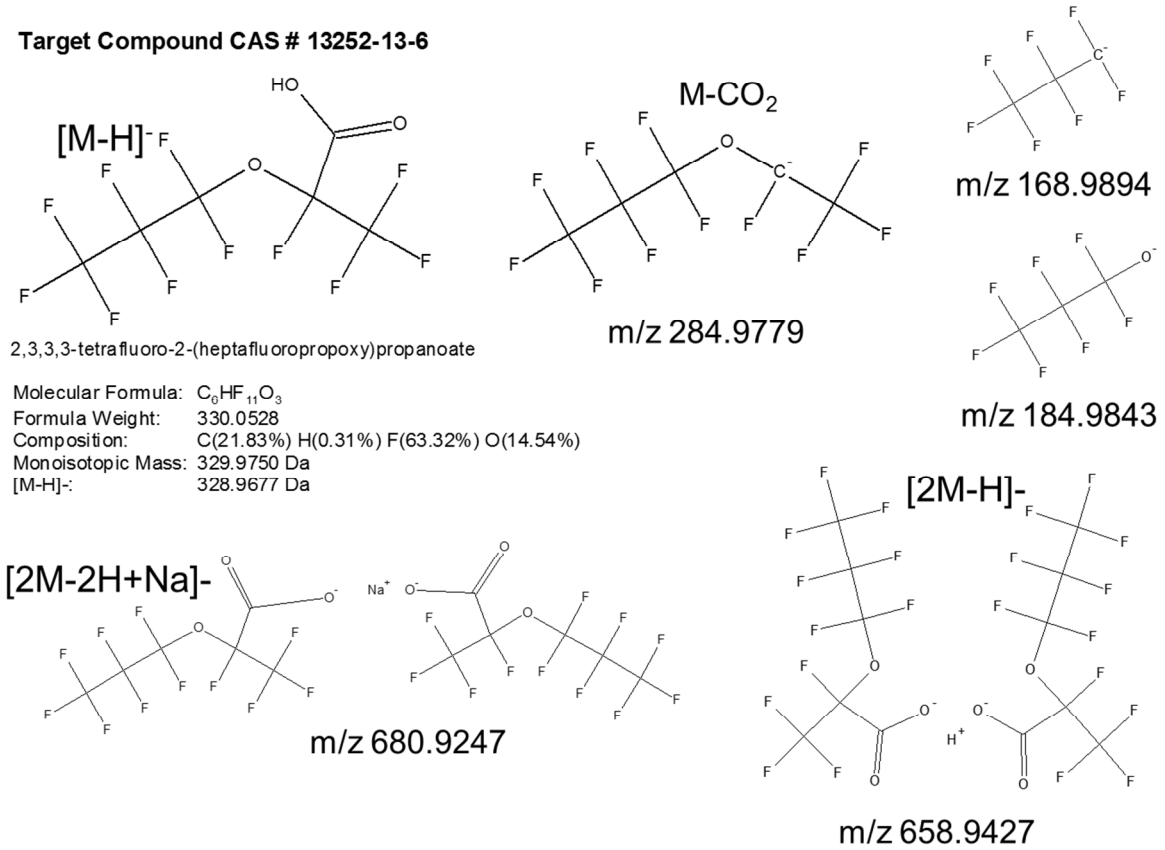
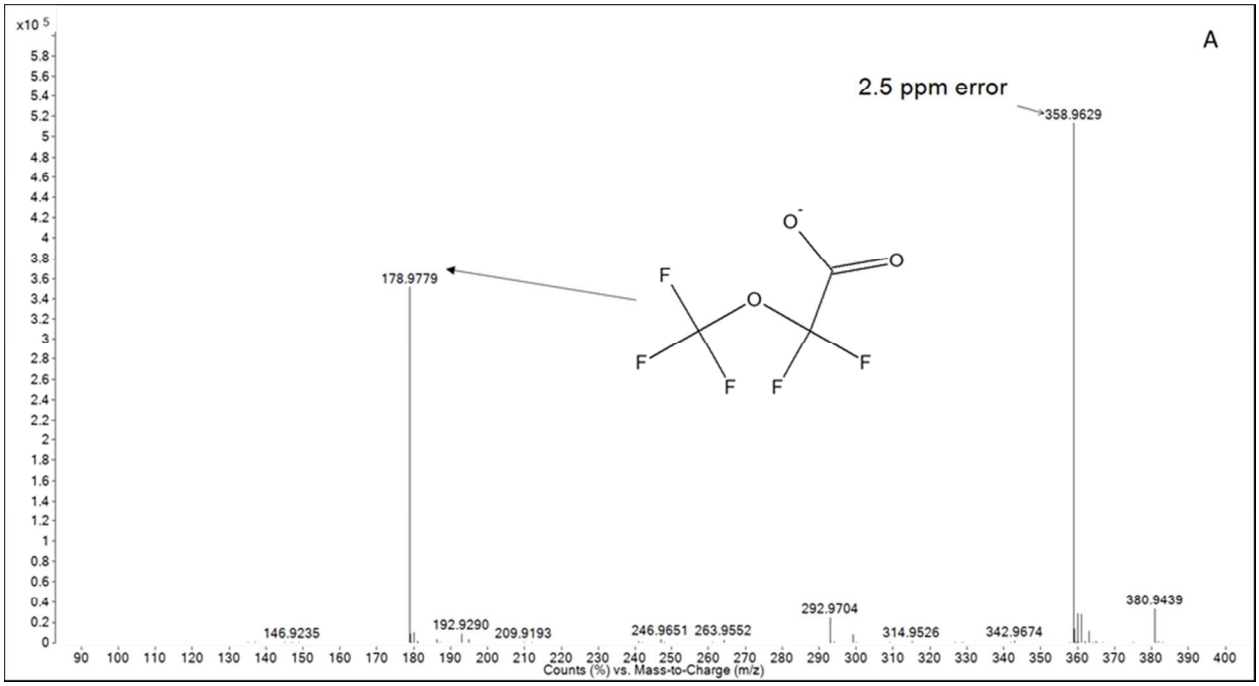
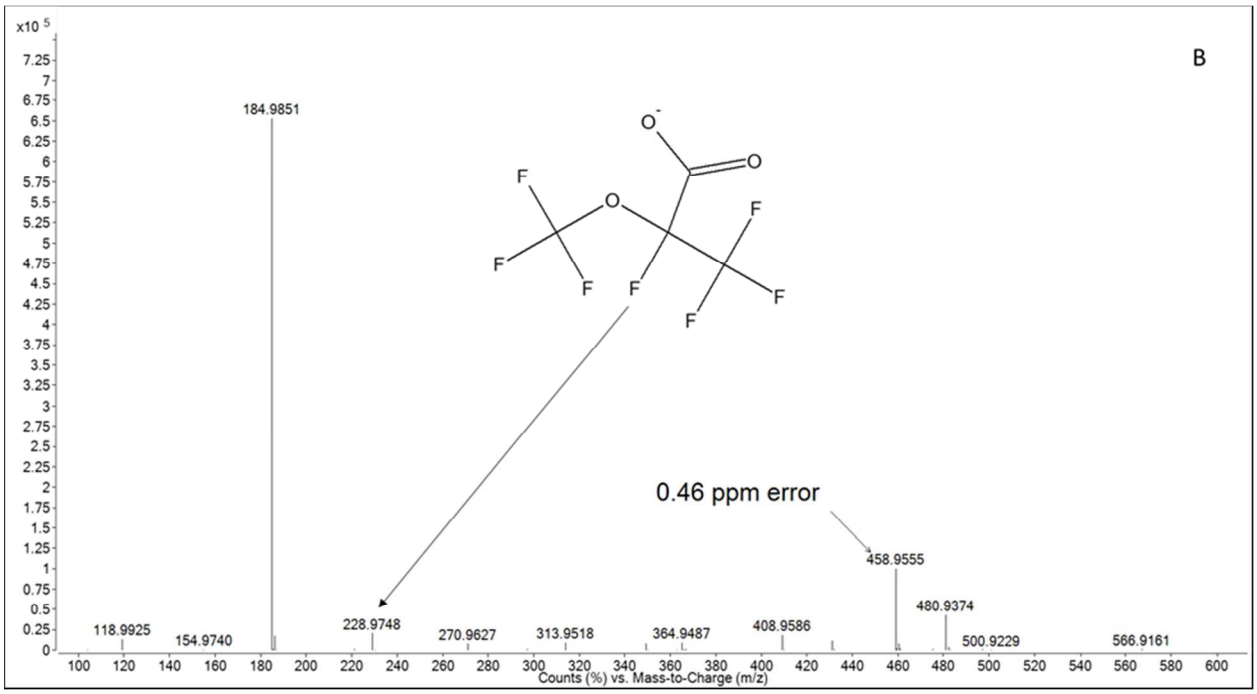


Figure S6. Identified perfluorinated ether carboxylic acid and diagnostic fragment and dimer ions.


A
2.5 ppm error
358.9629
178.9779
146.9235
192.9290
209.9193
246.9651
263.9552
292.9704
314.9526
342.9674
380.9439
Counts (%) vs. Mass-to-Charge (m/z)

92


B
184.9851
0.46 ppm error
458.9555
118.9925
154.9740
228.9748
270.9627
313.9518
364.9487
408.9586
480.9374
500.9229
566.9161
Counts (%) vs. Mass-to-Charge (m/z)

93

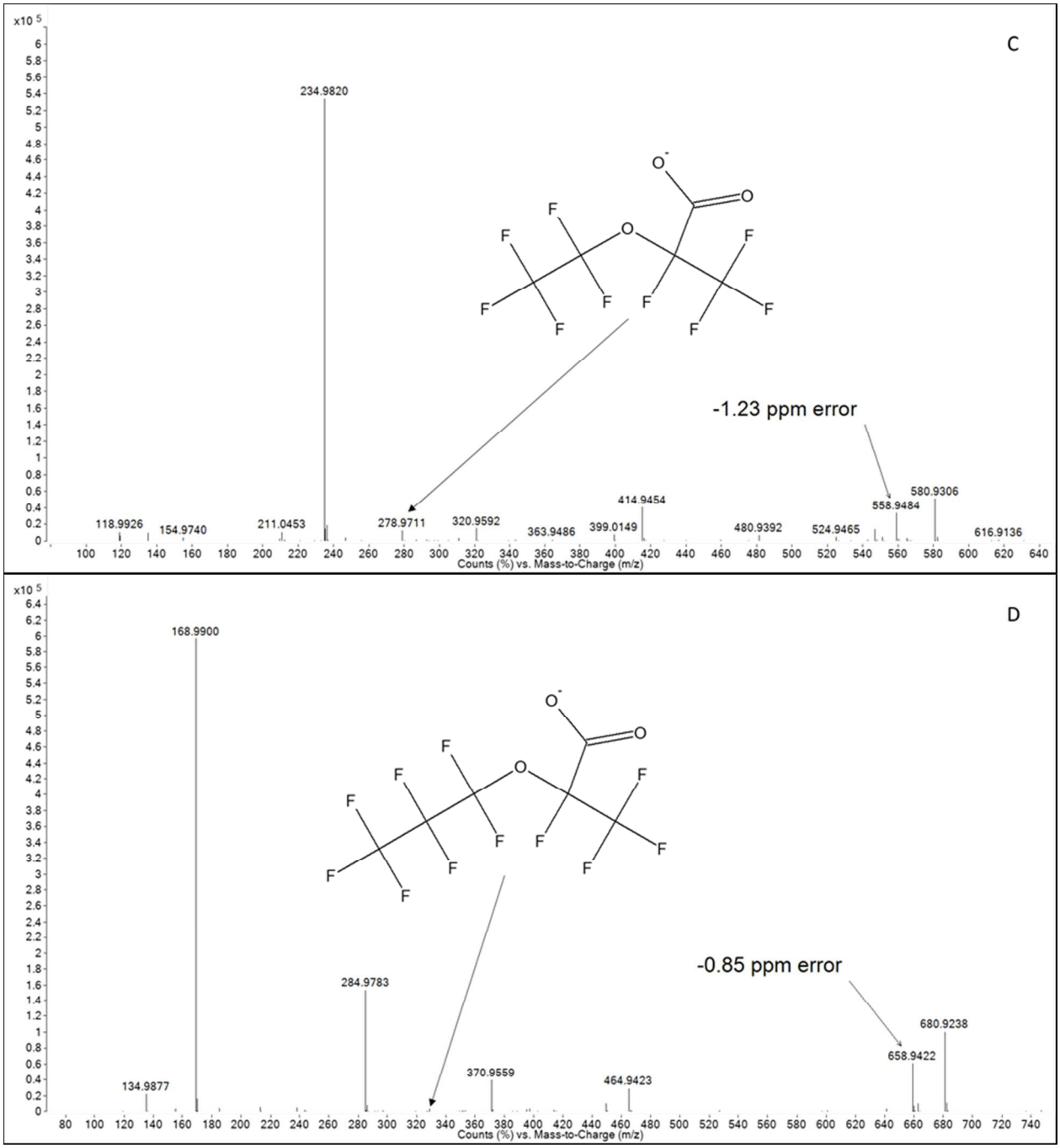


Figure S7 Spectra for Figure S5 chromatographic plot EICs. The spectra shown are for the first four eluting mono ether PFECAs shown in Figure S5. Plot A corresponds to m/z 178.9773; Plot B corresponds to m/z 228.9741; Plot C corresponds to m/z 278.9709; Plot D corresponds to m/z 328.9677. Error values shown are for the corresponding $[2M-H]^-$ (Table 1)

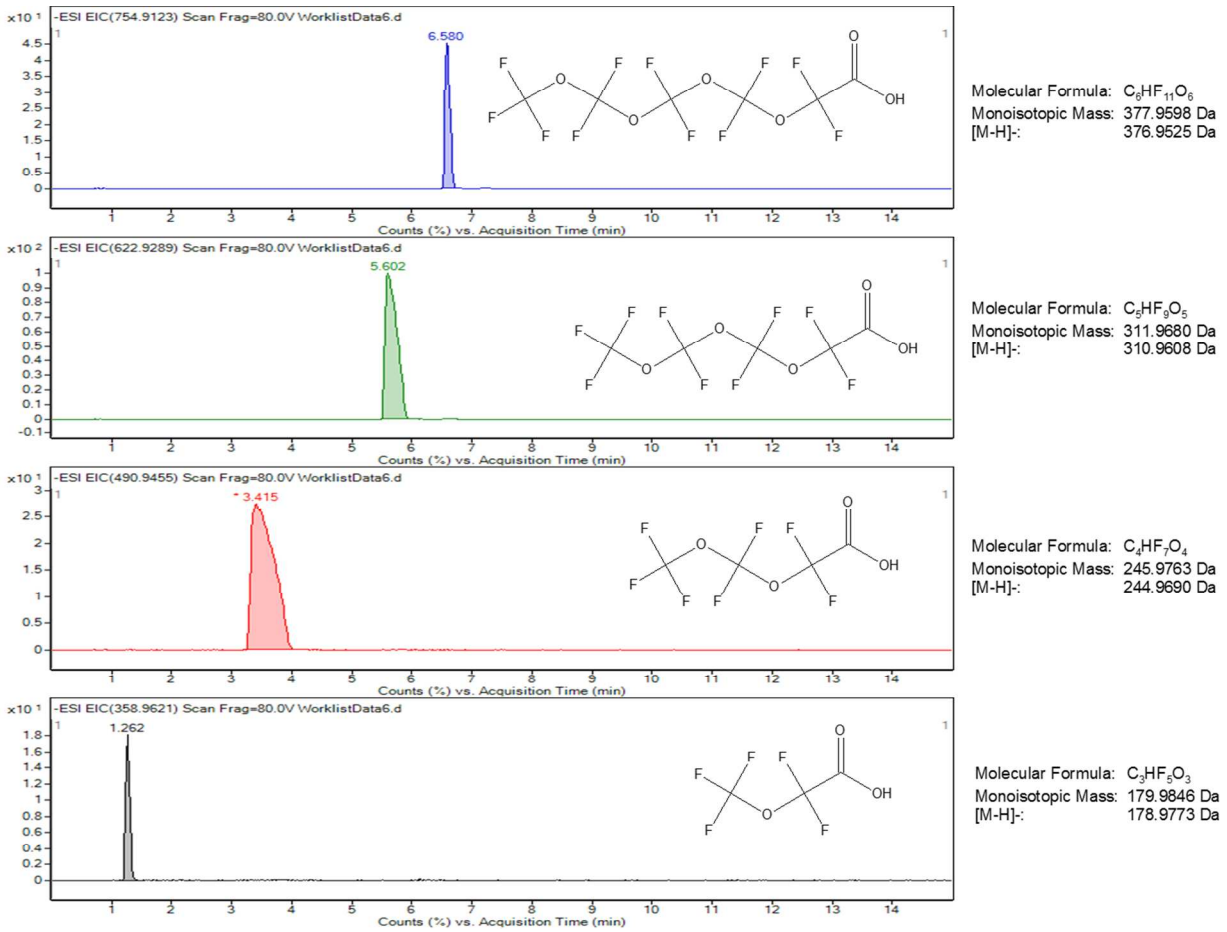


Figure S8. Extracted ion chromatogram of additional perfluorinated ether carboxylic acids homologous series. Proton bound dimer EIC shown for chromatogram. Monomer structure and exact mass shown

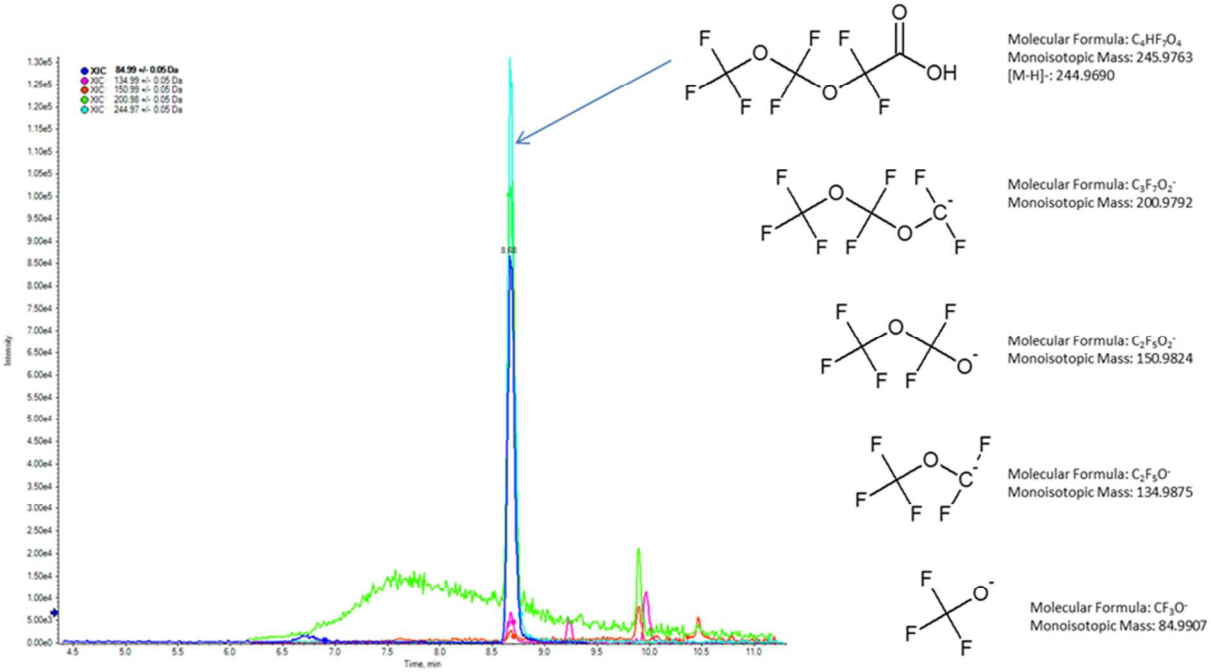
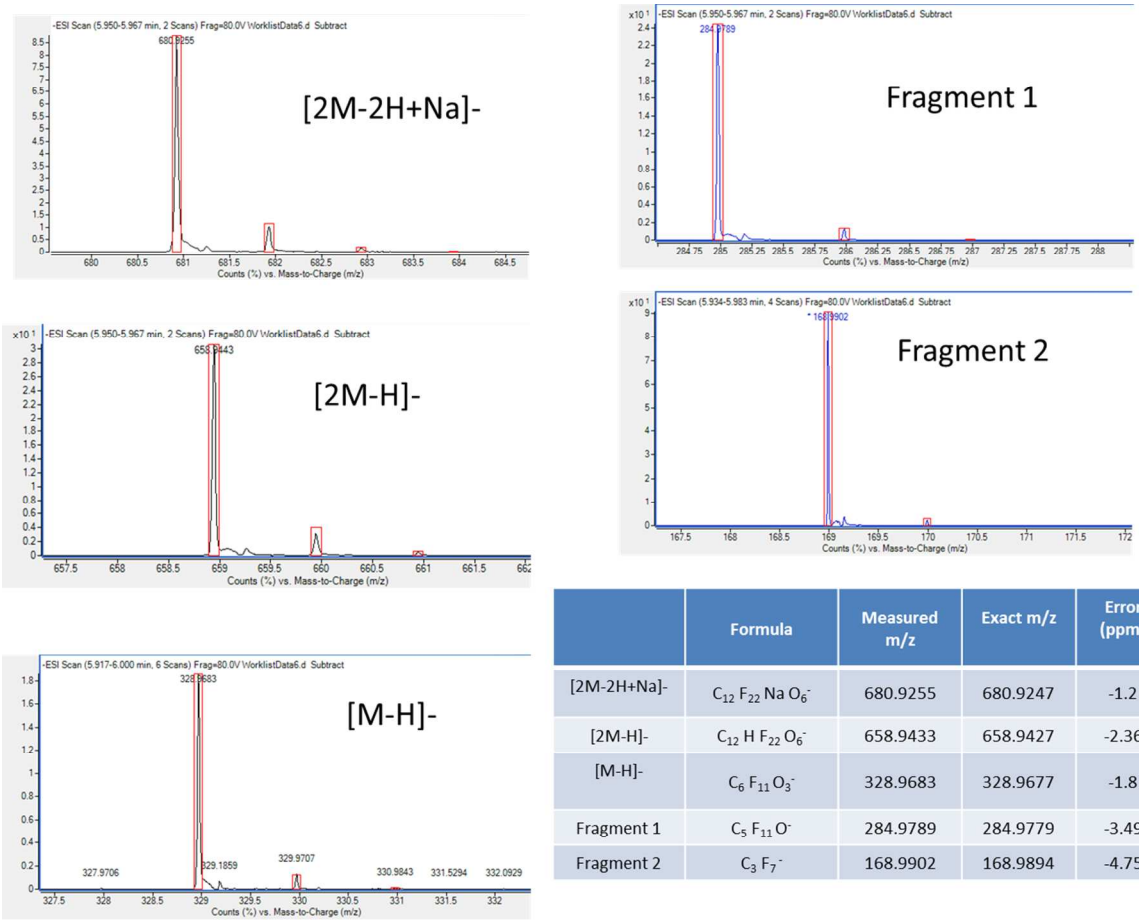
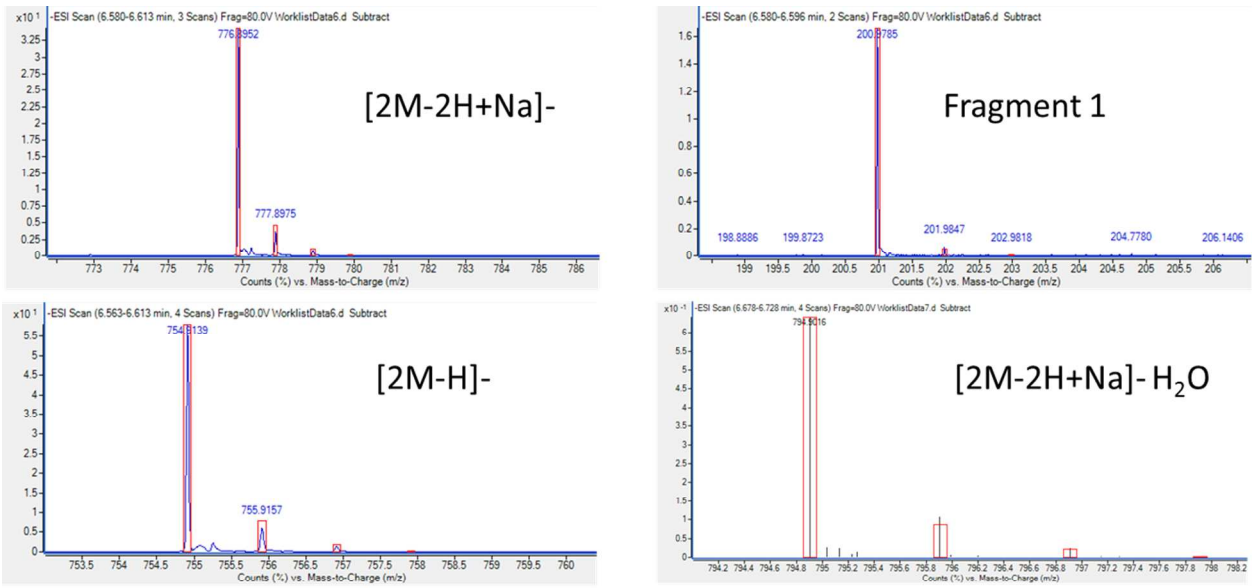


Figure S9. QTOF fragment ions for $C_4HF_7O_4$ (m/z 244.9691) pefluoroether carboxylic acid.



	Formula	Measured m/z	Exact m/z	Error (ppm)	Score
[2M-2H+Na]-	$C_{12}F_{22}NaO_6^-$	680.9255	680.9247	-1.2	98.11
[2M-H]-	$C_{12}HF_{22}O_6^-$	658.9433	658.9427	-2.36	92.96
[M-H]-	$C_6F_{11}O_3^-$	328.9683	328.9677	-1.8	97.85
Fragment 1	$C_5F_{11}O^-$	284.9789	284.9779	-3.49	96.35
Fragment 2	$C_3F_7^-$	168.9902	168.9894	-4.75	84.41

Figure S10. Spectrum, isotope pattern matching and identified adducts and fragment of molecular feature (m/z 328.9683) found in water. The table shows the formula, measured m/z, the exact m/z, the error associated with the measurement and the software scoring of the isotope cluster. The red boxes around each spectrum peak indicate the agreement between the measured and theoretical isotope cluster. The scoring is a bundled measurement of the accurate mass of the monoisotopic peak versus theoretical, the isotope abundance and the isotope spacing.



	Formula	Measured m/z	Exact m/z	Error (ppm)	Score
[2M-2H+Na]-	$C_{12}\,F_{22}\,Na\,O_{12}^{-}$	776.8952	776.8942	-1.31	95.92
[2M-H]-	$C_{12}\,H\,F_{22}\,O_{12}^{-}$	754.9139	754.9122	-2.22	92.66
[M-H]-	$C_{6}\,F_{11}\,O_{6}^{-}$	Not Observed	376.9525	---	---
Fragment 1	$C_{3}\,F_{7}\,O_{2}^{-}$	200.9785	200.9792	3.71	95.18
[2M-2H+Na]- H_2O	$C_{12}\,H_{3}\,F_{22}\,Na\,O_{13}^{-}$	794.9016	794.9047	3.95	84.15

Figure S11. Spectrum, isotope pattern matching and identified adducts and fragment of molecular feature (m/z 376.9525) found in water. The table shows the formula, measured m/z, the exact m/z, the error associated with the measurement and the software scoring of the isotope cluster. The red boxes around each spectrum peak indicate the agreement between the measured and theoretical isotope cluster. The scoring is a bundled measurement of the accurate mass of the monoisotopic peak versus theoretical, the isotope abundance and the isotope spacing.

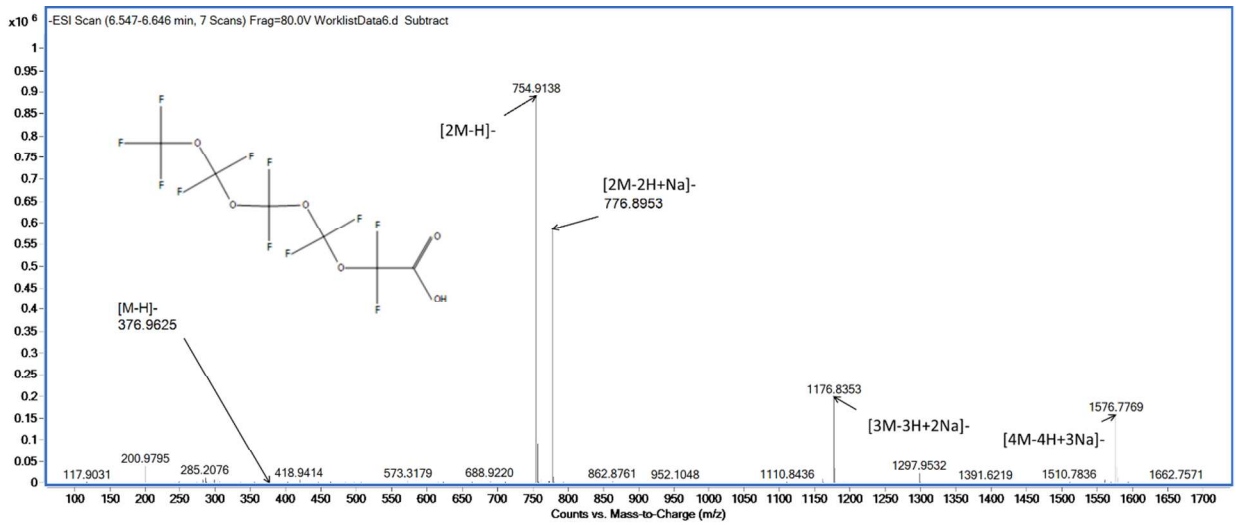


Figure S12. Spectrum of novel perfluorinated ether carboxylic acids showing proton bound and sodium bound *n*-mers found. The structure shown is the parent compound. The various in-source n-mers formed are shown with shorthand nomenclature for dimers, trimers and tetramers.