Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplemental Information for:

Nontarget analysis and fluorine atom balances of transformation products from UV/sulfite degradation of perfluoroalkyl contaminants

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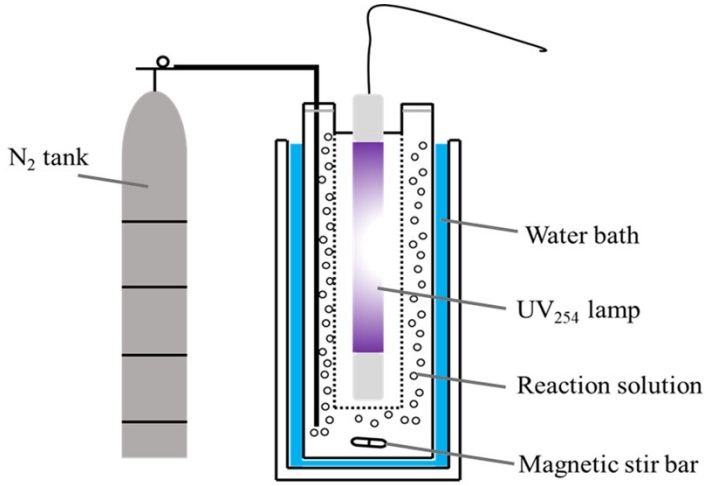


Supplemental Figure 1. Schematic of the custom photoreactor used in this study.

Supplemental Section 1: LC-MS-MS and IC operation parameters

Concentrations of parent PFAS compounds (PFOA, PFOS, PFBS, and GenX) over the course of reaction were measured with an Agilent 6430 liquid chromatography tandem mass spectrometry (LC-MS/MS) system equipped with an C18 column (Agilent Poroshell 120 SB-C18, 3 x 100 mm, 2.7 µm). Injection volume was 5 µL. The mobile phase consisted of HPLC-grade acetonitrile (A) and 20 mM aqueous ammonium acetate (B), with a flow rate of 0.4 mL/min. Gradient elution was used with the following program: 5% B at 2 min, 100% B at 8 min, 5% B at 11 min. Since the samples contained sulfite (a nonvolatile salt), the first 2 minutes of each chromatographic run were diverted to waste instead of to the mass spectrometer. The mass spectrometer operated under negative electrospray ionization with a nitrogen sheath gas pressure of 80 psi, a source temperature of 350 °C, and a spray voltage of 3.2 kV. PFAS were quantified using negative electrospray ionization and multiple reaction monitoring (MRM) using the triple quadrupole mass analyzer. Details of MRM transitions were presented in Table S1.

Fluoride was measured via an ion chromatography system (Thermo Scientific ICS 5000) equipped with an anion column (Dionex IonPac AS11-HC-4 µm, 4 x 250 mm), and a conductivity detector. 30 mM KOH was used as the eluent. The flow rate was 0.9 mL/min. The column temperature was 30 °C.

Table S1. MRM transitions used to quantify PFAS

Compound	MRM transition	Collision energy (eV)
PFOS	499.0 → 80.0	35.0
PFOA	413.0 → 369.0	8.0
GenX	329.0 → 185.0	12.0
PFBS	299.0 → 80.0	35.0

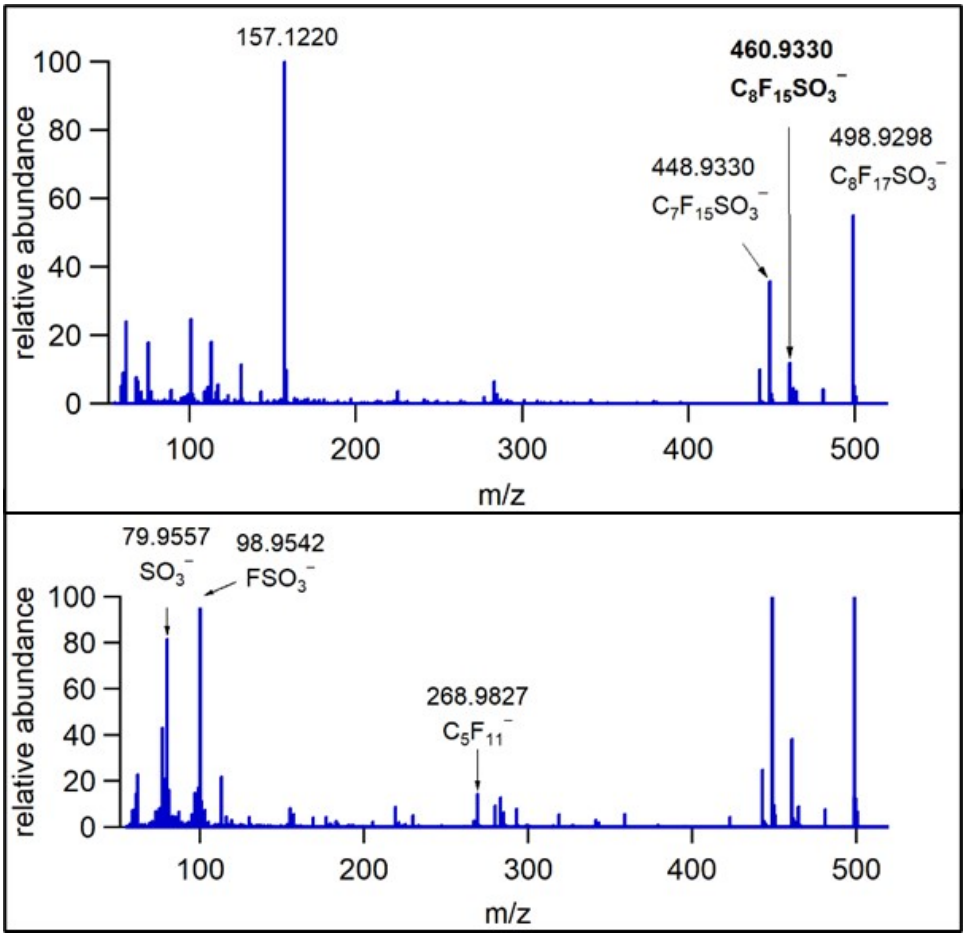
Supplemental Section 2: ESI-HRMS operation parameters

For the high-resolution mass spectrometry analysis using the Orbitrap mass analyzer, electrospray ionization was performed with a spray voltage of 5000 V, capillary temperature of 350 °C, sheath flow pressure of 35 psi, aux flow of 10 a.u. and sweep flow of 1 a.u. The Orbitrap mass analyzer was set to perform both full scan MS and all-ion fragmentation (AIF) from m/z 50–600 in negative ion mode for the entirety of the chromatographic run. AIF was performed with a collision energy of 30.00 eV. Both modes were operated with 70,000 ion resolution.

Supplemental Section 3: mzMine analysis workflow

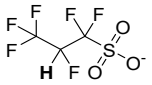
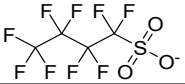
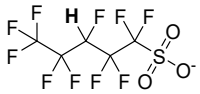
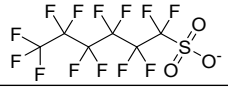
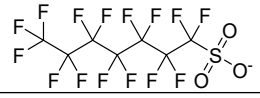
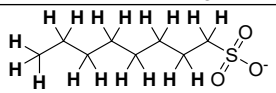
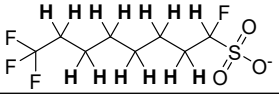
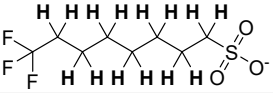
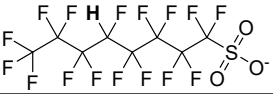
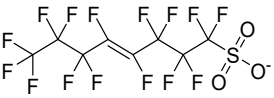
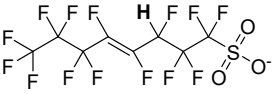
The following workflow was developed within mzMine 2.53 to determine formulae and intensities for peaks present in raw files generated during the high-resolution mass spectrometry analysis using the Orbitrap mass analyzer.

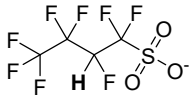
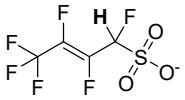
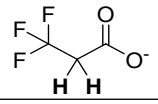
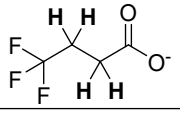
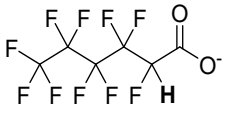
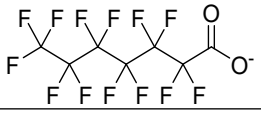
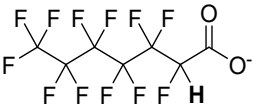
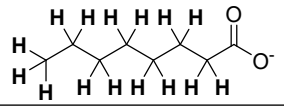
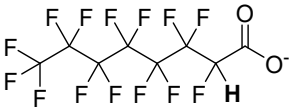
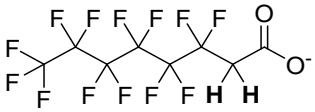
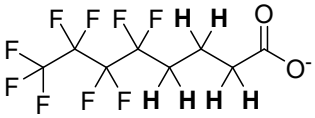
1. All raw data for a single PFAS substrate is imported.
2. Each base peak chromatogram is examined. The baseline level is noted, as well as the height of the smallest peak.
3. Masses from each chromatogram are determined using the exact mass detector with noise cutoffs equal to the baseline level noted in step 2.
4. Chromatograms are built using the ADAP chromatogram builder. The minimum group size was set to 5, group intensity threshold was set to the baseline found in step 2, and the minimum highest intensity is set to the minimum peak height noted in step 2. Mass tolerance was set to 5 ppm.
5. Then, all chromatograms are selected and deconvoluted with the Wavelets (ADAP) algorithm. (Signal to noise of 7 using intensity window estimator, minimum feature height set to the lowest value found for peak height in step 2 among all chromatograms, coefficient to area ratio = 100, peak duration 0 to 3 min, and RT wavelet 0 to 0.2.)
6. Isotopic peak grouping is performed. (m/z tolerance of 5 ppm, retention time tolerance of 5%, maximum charge of 1)
7. Then peak lists of all open files are aligned using the join aligner (m/z tolerance of 5 ppm with a weight of 20, relative retention time tolerance of 5% with a weight of 10).
8. Gap filling is performed using the same m/z and RT range gap filler as the join aligner.
9. Molecular formulas are predicted with constraints based on the parent PFAS compound. For example, for PFOS, the constraints were (C 0-8, H 0-18, O 0-3, S 0-1, and F 0-17). RBDE values were noted but not used as a constraint.

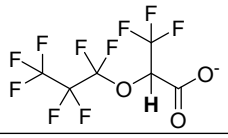
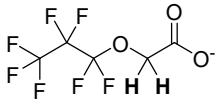
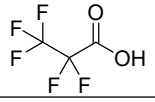
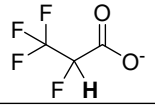


Supplemental Figure 2. HRMS spectra of unsaturated PFOS detected in this study (retention time: 6.57 min). The top spectrum was collected in full-scan mode while the bottom spectrum was collected in all-ion fragmentation (AIF) mode. The RBDE of the calculated formula is 1.5, an increase of 1 over the RBDE of PFOS (0.5). Therefore, the structure must contain one ring or one unit of unsaturation. However, the AIF scan does not show a characteristic peak at [M-80]-, which would indicate a cyclic sulfonate, and does show a peak m/z 79.9557, indicating a linear, unsaturated sulfonate.[1,2] Therefore, we conclude this spectrum represents unsaturated PFOS.

Supplemental Table 1. InChI Keys for transformation products identified in this study.

Transformation products from PFOS			
measured m/z	**formula**	**InChI Key**	**proposed structure**
230.9548	$C_3HF_6O_3S^-$	DMOBTBZPQXBGRE-UHFFFAOYSA-M	 multiple isomers possible
280.9518	$C_4HF_8O_3S^-$	GUDBAXWOSFMPDL-UHFFFAOYSA-M	 multiple isomers possible
298.9428*	$C_4F_9O_3S^-$	JGTNAGYHADQMCM-UHFFFAOYSA-M	
330.9487	$C_5HF_{10}O_3S^-$	GZNYHVDZACVWEW-UHFFFAOYSA-M	 multiple isomers possible
398.9358*	$C_6F_{13}O_3S^-$	QZHDEAJFRJCDMF-UHFFFAOYSA-M	
380.9457	$C_6HF_{12}O_3S^-$	ITTUNFSMLSXTDN-UHFFFAOYSA-M	 multiple isomers possible
448.9332*	$C_7F_{15}O_3S^-$	OYGQVDSRYXATEL-UHFFFAOYSA-M	
193.0894	$C_8H_{17}O_3S^-$	WLGDAKIJYPIYLR-UHFFFAOYSA-M	
265.0525	$C_8H_{13}F_4O_3S^-$	DWKMKCZMBKOFSU-UHFFFAOYSA-M	
247.0614	$C_8H_{14}F_3O_3S^-$	GHMPCZSZHWWMCZ-UHFFFAOYSA-M	
480.9392	$C_8HF_{16}O_3S^-$	VRJQMZSCTPYBEI-UHFFFAOYSA-M	
460.9330	$C_8F_{15}O_3S^-$	KSTCMYVADSAATO-OWOJBTEDSA-M	 multiple isomers possible
442.9420	$C_8HF_{14}O_3S^-$	SQUPGILGWINWLU-OWOJBTEDSA-M	 multiple isomers possible

Transformation products from PFBS			
$C_4HF_8O_3S^-$		NMNMEAKGNXYDIC-UHFFFAOYSA-M	 multiple isomers possible
$C_4HF_6O_3S^-$		FGQWBTWTHOPAFC-OWOJBTEDSA-M	 multiple isomers possible
Transformation products from PFOA			
127.0000*†	$C_3H_2F_3O_2^-$	KSNKQSPJFRQSEI-UHFFFAOYSA-M	
141.0158	$C_4H_4F_3O_2^-$	WTUCTMYLCMVYEX-UHFFFAOYSA-M	
294.9822	$C_6HF_{10}O_2^-$	CYFXTKNPCJAIPM-UHFFFAOYSA-M	 multiple isomers possible
362.9698	$C_7F_{13}O_2^-$	ZWBAMYVPMDSJGQ-UHFFFAOYSA-M	
344.9790	$C_7HF_{12}O_2^-$	HWFPEKMIHWSKHB-UHFFFAOYSA-M	 multiple isomers possible
143.1066	$C_8H_{15}O_2^-$	WWZKQHOCKIZLMA-UHFFFAOYSA-M	
394.9757	$C_8HF_{14}O_2^-$	CLSJUWFCSPJRFC-UHFFFAOYSA-M	 multiple isomers possible
376.9855	$C_8H_2F_{13}O_2^-$	LRWIIEJPCFNNCZ-UHFFFAOYSA-M	 multiple isomers possible
305.0230	$C_8H_6F_9O_2^-$	AQGBOPDJGMNAKJ-UHFFFAOYSA-M	 multiple isomers possible

Transformation products from GenX			
310.9775	$C_6HF_{10}O_3^-$	BLIMGOMLLSPDPB-UHFFFAOYSA-M	
243.0097†	$C_5F_7H_2O_3^-$	PHFJMGZBPBUZQS-UHFFFAOYSA-M	
162.9813	$C_3F_5O_2^-$	LRMSQVBRUNSOJL-UHFFFAOYSA-N	
144.9907	$C_3F_4HO_2^-$	GPKYZQLMEPJAGJ-UHFFFAOYSA-M	

References

(1) De Silva, A. O.; Spencer, C.; Scott, B. F.; Backus, S.; Muir, D. C. G. Detection of a Cyclic Perfluorinated Acid, Perfluoroethylcyclohexane Sulfonate, in the Great Lakes of North America. *Environ. Sci. Technol.* **2011**, *45* (19), 8060–8066. https://doi.org/10.1021/es200135c.

(2) Charbonnet, J. A.; McDonough, C. A.; Xiao, F.; Schwichtenberg, T.; Cao, D.; Kaserzon, S.; Thomas, K. V; Dewapriya, P.; Place, B. J.; Schymanski, E. L.; Field, J. A.; Helbling, D. E.; Higgins, C. P. Communicating Confidence of Per- and Polyfluoroalkyl Substance Identification via High-Resolution Mass Spectrometry. *Environ. Sci. Technol. Lett.* **2022**, *9* (6), 473–481. https://doi.org/10.1021/acs.estlett.2c00206.