Supporting Information

Stability of Per- and Polyfluoroalkyl Substances in Solvents Relevant to Environmental and Toxicological Analysis

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Text S1. Liquid chromatography-mass spectrometry (LC-MS) analysis

LC-MS analysis was performed using an Agilent 1290 Infinity II high-performance liquid chromatograph (HPLC) coupled to an Agilent 6545 quadrupole time-of-flight (QTOF) mass spectrometer. Chromatographic separation was accomplished using a Zorbax Eclipse Plus C18 column (4.6 × 50 mm, 3.5 μm; Agilent). The method conditions were as follows: 0.4 mL/min flow rate; column temperature at 50°C; 100 μL of injection volume; mobile phase A: ammonium acetate buffer (5 mM) in water, and mobile phase B: methanol; gradient: 0-8 min linear from 90:10 A/B to 5:95 A/B, 8-20 min 5:95 A/B; followed by a 5 min post time for equilibration. Compounds were ionized by operating electrospray ionization (ESI) in negative mode. The dual-electrospray source provided purine and hexakis(1H, 1H, 3H-tetrafluoropropoxy)phosphazine as internal reference masses. The instrument was operated in 2GHz extended dynamic range mode with an MS mass range of 70-1200 m/z. Raw data were processed using Agilent MassHunter.

To probe suspect features that may represent reaction products, we looked for integrated peak heights that exhibited a 2-fold or greater change between samples collected at the first time point and the last time point of an experiment. MS spectra collected for each feature of interest were manually checked to identify reaction products, and molecular features identified in the blank were removed from the sample data. Emphasis was placed on chemicals demonstrating a negative mass defect, as described elsewhere.[1] Apart from the dosed PFASs, no additional fluorinated compounds were observed in any of the tested solvents based on the collected LC-QTOF-MS data.

Text S2. PFAS quantitation for LC-MS analysis

Using LC-QTOF-MS data, PFAS quantitation was carried out in a fashion previously described.[2,3] PFAS concentrations were calculated from area ratios (i.e. peak area for the analytical standard divided by the peak area for the isotopically labeled internal standard) and standard curves. Each standard curve included seven calibration points ranging from 10 ng/L to 1,500 ng/L. Calibration standards were analyzed in duplicate, once at the beginning and once at the end of each sample batch. To generate standard curves, area ratios were plotted against known concentrations of the calibration standards. Standard curves were mathematically described by a concentration weighted (1/x), second-order polynomial fit.

The R^2 for perfluoroalkyl acids (PFAAs) was >0.99 and for per- and polyfluoroalkyl ether acids (PFEAs) > 0.98. At the selected ionization conditions, variability in PFEA responses exceeded

those of perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs). Example standard curves are shown in Figure S2. The quantitation limit (QL) was defined as the first point of the standard curve, at which area ratios yielded calculated concentration values within ± 30% error. The QL for LC-QTOF MS was 50 ng/L for PFMOAA and HFPO-TeA, 100 ng/L for PFO2HxA, PFO3OA, PFO5DoA and HFPO-TA, and 10 ng/L for all other PFASs.

Text S3. Quality assurance/quality control (QA/QC) for LC-MS analysis

QC samples included instrument blanks (no isotopically labeled internal standard added), method blanks, initial calibration verification (ICV) samples at 500 ng/L using standards from a second source when possible, and continuing calibration verification (CCV) samples at 500 ng/L. Accuracies of ICVs and CCVs ranged from 82-110% and 72-113%, respectively. Instrument blanks (90:10 water:methanol) were run between samples to verify that the instrument was clean and that there was no carry over after the highest calibration point. The storage time for samples was up to three weeks at room temperature (20.2°C). Approximately 20% of samples were analyzed in duplicate and concentrations of PFASs had relative standard deviations (RSD) of <20% across replicates.

Text S4. Headspace gas chromatography-mass spectrometry (GC-MS) method for Fluoroethers E-1, E-2, and E-3

Concentrations of Fluoroethers E-1, E-2, and E-3 were measured in triplicate by GC-MS using headspace analysis using a method similar to previously developed methods.[4] Triplicate measurements were taken to assess variability in analyte response as mass-labeled standards were not available for Fluoroether E-1, E-2, and E-3. Samples were prepared in 20-mL headspace vials containing 10 mL of ultrapure water and 2.5 g sodium chloride. Ten microliters of either an experimental sample or calibration standard was collected using a gas-tight syringe and injected into the saline water, after which the vial was immediately capped and gently mixed. A headspace autosampler (CTC Analytics CombiPal) was used to first heat the sample to 60°C for 10 minutes with intermittent shaking (5 seconds at 500 rpm then 2 seconds rest). Then a syringe heated to 65°C was used to withdraw 300 µL of headspace from the vial and inject it into the GC-MS (Agilent 7890 GC, Agilent 7010 MS). Using helium (0.7 mL/min) as the carrier gas, analytes were separated on a DB 624 Ultra Inert column (20 m x 0.18 mm x 1.00 µm, J&W). The GC oven

program began at 35°C, held for 0.75 minutes, then ramped to 240°C at 15°C/min. Compounds were ionized with an electron ionization (EI) MS source at 70 eV. Selected-ion monitoring (SIM) was used to quantify Fluoroethers with the most prevalent ion in each spectrum (*m/z* = 101, 169, and 169 for Fluoroethers E-1, E-2, and E-3 respectively). Compound retention time (1.13, 1.61, and 2.61 min for Fluoroether E-1, E-2, and E-3 respectively) and the ratios of major to minor ions were used to verify compound identity. Weighted 4-point calibration curves were developed in duplicate for each compound, and calibration standards were prepared in the solvent considered in each experiment (i.e. ACN, acetone, and DMSO) prior to dilution into saline water as described above.

To verify that volatile losses of Fluoroethers E-1, E-2, and E-3 were negligible from headspace-free containers containing the solvent of interest, 5-day experiments were conducted by adding a mix of Fluoroethers E-1, E-2, and E-3 to solvent (ACN, acetone, or DMSO) in a 25 mL volumetric flask. The volumetric flask was inverted twice to fully mix PFASs, and the first sample set (t_0, n=3, analyzed and quantified on GC-MS) was taken immediately after mixing. A separate set of 5-day samples (n=3) was prepared and transferred to a 20-mL headspace-free amber glass vial and stored for 5 days. The last sample (t=5 days) was taken and analyzed following the headspace GC-MS method. Results indicated no statistically significant difference (t-test, n=3, $p>0.05$) in concentrations between samples collected at t_0 and t=5 days.

To understand mechanisms of HFPO-DA, HFPO-TA, and HFPO-TeA degradation to Fluoroethers E-1, E-2, and E-3, respectively, in polar aprotic solvents (e.g. acetone), we conducted experiments with (1) HFPO-DA, (2) HFPO-TA, (3) HFPO-TeA, and (4) mix of Fluoroethers E-1, E-2, and E-3 (control experiment) in fully deuterated acetone (acetone-D6). The purpose of the control experiment with Fluoroethers E-1, E-2, and E-3 was to verify that the deuterium in acetone-D6 did not exchange with the native hydrogen in Fluoroethers E-1, E-2, and E-3. Briefly, an aliquot of an individual HFPO acid was added to acetone-D6 in a 2-mL glass vial, yielding a starting concentration of ~2 g/L. After ~2 days at room temperature in the dark, ten microliters of sample from the glass vial was transferred to a 20-mL headspace vial. Samples were analyzed in triplicate by GC-MS using headspace analysis as described above, except that no water was included in headspace vials to minimize the potential for deuterium to exchange with native hydrogen from the water. Chemical ionization was used with methane (1 mL/min) as the reagent gas and 125 eV

ionization energy. The source was held at 300°C and the quadrupoles at 150°C. Selected-ion monitoring (SIM) was used to quantify the $[M-F]^+$ for each compound (*m/z* of 267, 433, and 599 for Fluoroethers E-1, E-2, and E-3, respectively) as well as $[M-F+1]^+$ for each compound (*m/z* of 268, 434, and 600 for Fluoroethers E-1, E-2, and E-3, respectively).

Text S5. Gas chromatography-high resolution mass spectrometry (GC-HRMS) analysis for degradation product identification

Samples diluted into 10-mL saline water in 20-mL headspace vials (see Text S4) were further analyzed by GC-HRMS to identify suspected degradation products of PMPA, PEPA, PFO2HxA, PFO3OA, PFO4DA, and PFO5DoA. Standards of Fluoroethers E-1, E-2, and E-3 were run along with the HFPO-DA, HFPO-TA, and HFPO-TeA samples as checks that methods were suitable for these products. Using a Thermo Scientific (Waltham, MA) TriPlus RSH autosampler, the same headspace method from Text S4 was employed; briefly, a 2.5-mL syringe at 65°C sampled 300 µL of headspace after 10-min incubation at 60°C with agitation (5 seconds on, 2 seconds off). The 300 µL were injected into a Thermo Trace 1300 GC coupled to a Q Exactive GC Orbitrap MS. The GC inlet was maintained at 200 °C with a split flow of 5 mL/min and helium carrier gas flow rate of 1.0 mL/min (5:1 split ratio). GC separations were performed using an Agilent DB-624 (30 m × 0.25 mm × 1.40 µm) capillary column. The 14.4-min oven program began at an initial temperature of 35°C held for 0.75 min, then ramped at 15°C/min to 240 °C, with a transfer line temperature of 250°C. Two ionization modes were utilized, electron ionization (EI) and chemical ionization (CI), using an EI/CI combination ion source. Both methods used a source temperature of 270°C and electron energy of 70 eV. The Orbitrap mass analyzer was used for full scan acquisition from 60-650 m/z at 60,000 resolving power. In the CI method only, methane reagent gas (1.5 mL/min) was used to conduct positive CI analyses.

For initial discovery of products, samples were run using EI; its high-signal total ion chromatogram (TIC) facilitated visual recognition of degradation product peaks by comparison of samples to solvent blanks. EI is a hard ionization technique, and the products found provided little molecular information, aside from presence of common perfluoro-terminal fragments (e.g., CF_3^+ [68.9946 m/z]). For more structural information, positive CI was used to target more-intact, higher molecular weight fragments of products that eluted at retention times as determined by EI analyses. The most intact fragments tended to be $[M-F]^+$ for the compounds assessed.

The suspected decarboxylated-PMPA degradation product was later confirmed by retention time and mass spectral matching to a standard of 1,2,2,2-tetrafluoroethyl trifluoromethyl ether (HFE 227), but was not quantified due to the complexity associated with making quantitative measurements using gaseous standards.

Because no degradation products could be determined for the multi-ether PFECAs (PFO2HxA, PFO3OA, PFO4DA, and PFO5DoA), higher concentration (1 μg/mL) samples were prepared in acetone (10 mL in 20-mL headspace vials) from both methanol and water stocks (0.1%, pH>7) and stored at room temperature. EI-GC-Orbitrap analyses were performed periodically over the course of a month, with time points spanning from minutes to weeks after acetone-dilution. Despite the quantified disappearance of the parent ether acids, headspace GC-MS analyses did not reveal any apparent volatile degradation products formed, even in these higher-concentration samples. To assess the potential formation of nonvolatile or thermally labile degradation products for these compounds, a liquid-injection GC-MS method was also used on these same high-concentration samples. In this method, 1 μL of multi-ether PFECA sample in acetone was injected into a programmable temperature vaporizing (PTV) inlet at 60°C, which was then ramped at 14.5°C/s to 150°C for a 1 min transfer step followed by a 2 min cleaning step at 250°C. Still, no byproducts were identified using this method. It is possible that products might elute with the solvent, making them nearly impossible to find, especially when performing unknown analysis. Compared to other PFEAs in this study (e.g., HFPO-DA) that favored one major degradation product, it is also possible that solvent-facilitated degradation of the multi-ether PFECAs resulted in a variety of products, which would have lower abundance in GC-MS analyses, perhaps below limit of detection (LOD).

Text S6. First-order kinetics

The degradation of branched mono-ether PFECAs and multi-ether PFECAs in ACN, acetone, and DMSO can be expressed by first-order kinetics [Equations (1) and (2)], where k is the observed first-order rate constant, t is time, [PFAS] is PFAS concentration, and $[PFAS]_0$ is the initial PFAS concentration.

$$\frac{\mathbf{d[PFAS]}}{\mathbf{dt}} = -\boldsymbol{k}[\mathbf{PFAS}] \quad (1)$$

Integration yields:

$$\ln\left(\frac{[\mathbf{PFAS}]}{[\mathbf{PFAS}]_0}\right) = -\boldsymbol{k}\mathbf{t} \quad (2)$$

The *k* values were obtained from slopes of linear regression lines describing experimental ln (C/C_0) values as a function of time.

Text S7. Arrhenius equation

The temperature-dependence of first-order rate constants describing the degradation of branched mono-ether PFECAs in ACN, acetone, and DMSO was described by the Arrhenius equation:

$$\boldsymbol{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E_a}/\mathbf{RT}} \quad \mathbf{(3)}$$

which was linearized to give:

$$\ln\boldsymbol{k} = \ln\mathbf{A} - \frac{\mathbf{E_a}}{\mathbf{RT}} \quad \mathbf{(4)}$$

where *k* is the temperature-dependent first-order rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and T is absolute temperature in Kelvin.

Text S8. Calculation of molar yield

Molar yield of Fluoroethers E-1, E-2, and E-3 from HFPO-DA, HFPO-TA, and HFPO-TeA, respectively, in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO) after 5 days is shown in Table S12 and calculated from the following equation:

$$[\boldsymbol{Product}]/[\boldsymbol{PFECA}]_0 = \frac{\bar{\boldsymbol{b}}}{\bar{\boldsymbol{a}}} \pm \frac{\bar{\boldsymbol{b}}}{\bar{\boldsymbol{a}}}\sqrt{(\frac{\boldsymbol{S_a}}{\bar{\boldsymbol{a}}})^2 + (\frac{\boldsymbol{S_b}}{\bar{\boldsymbol{b}}})^2}$$

where $\bar{a}$ and $\bar{b}$ are the average concentrations of PFECAs (i.e. HFPO-DA, HFPO-TA, or HFPO-TeA) and Fluoroethers (i.e. E-1, E-2, or E-3) in replicate measurements, respectively; S_a and S_b are standard deviations of concentrations of PFECAs (i.e. HFPO-DA, HFPO-TA, or HFPO-TeA) and Fluoroethers (i.e. E-1, E-2, or E-3) in replicate measurements, respectively.

286 **Table S1. Per- and polyfluoroalkyl substances (PFASs) targeted in this study**

Analyte	Formula	CAS # (hyperlinked to US EPA Chemicals Dashboard)	Source [a]	Mass-Labeled Internal Standard	Solvent
Class 1: Perfluorocarboxylic acids (PFCA)					
Perfluorohexanoic acid (PFHxA)	$C_6HF_{11}O_2$	307-24-4	1	$^{13}C_5$-PFHxA	Methanol
Class 2: Perfluorosulfonic acids (PFSA)					
Perfluorohexane sulfonic acid (PFHxS)	$C_6HF_{13}SO_3$	355-46-4	1	$^{13}C_3$-PFHxS	Methanol
Class 3: Per- and polyfluoroalkyl ether acids (PFEAs)					
Perfluoroalkyl mono-ether carboxylic acids (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)	$C_3HF_5O_3$	674-13-5	2, 3	$^{13}C_4$-PFBA	Basic methanol [b]
Perfluoro-3-methoxypropanoic acid (PFMOPrA) [c]	$C_4HF_7O_3$	377-73-1	4	$^{13}C_4$-PFBA	Methanol
Perfluoro-2-methoxypropanoic acid (PMPA)	$C_4HF_7O_3$	13140-29-9	3	$^{13}C_4$-PFBA	Deionized water
Perfluoro-4-methoxybutanoic acid (PFMOBA) [c]	$C_5HF_9O_3$	863090-89-5	4	$^{13}C_5$-PFHxA	Methanol
Perfluoro-2-ethoxypropanoic acid (PEPA)	$C_5HF_9O_3$	267239-61-2	3	$^{13}C_5$-PFHxA	Deionized water
Hexafluoropropylene oxide-dimer acid (HFPO-DA) = Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	$C_6HF_{11}O_3$	13252-13-6	4, 5	$^{13}C_3$-PFPrOPrA	Methanol
Ammonium salt of hexafluoropropylene oxide-dimer acid = "GenX"	$C_6H_4F_{11}NO_3$	62037-80-3	4	$^{13}C_3$-PFPrOPrA	Methanol
Perfluoroalkyl multi-ether carboxylic acids (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	$C_4HF_7O_4$	39492-88-1	3	$^{13}C_3$-PFPrOPrA	Deionized water
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	$C_5HF_9O_5$	39492-89-2	3	$^{13}C_3$-PFPrOPrA	Deionized water
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	$C_6HF_{11}O_6$	39492-90-5	3	$^{13}C_3$-PFPrOPrA	Deionized water

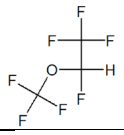
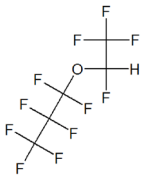
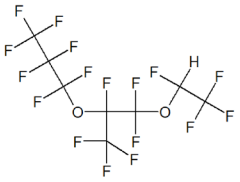
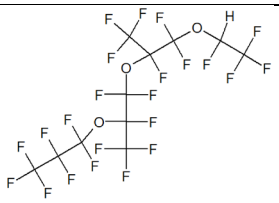
Perfluoro(3,5,7,9,11-pentaoxadodecanoic) acid (PFO5DoA)	$C_7HF_{13}O_7$	39492-91-6	3	$^{13}C_3$-PFPrOPrA	Deionized water
Hexafluoropropylene oxide-trimer acid (HFPO-TA)	$C_9HF_{17}O_4$	13252-14-7	4	$^{13}C_3$-PFPrOPrA	Methanol
Hexafluoropropylene oxide-tetramer acid (HFPO-TeA)	$C_{12}HF_{23}O_5$	65294-16-8	4	$^{13}C_3$-PFPrOPrA	Methanol
Polyfluoroalkyl ether acids					
Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Nafion by-product 2)	$C_7H_2F_{14}SO_5$	749836-20-2	3, 4	$^{13}C_3$-PFHxS	Methanol
1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonate (NVHOS)	$C_4H_2F_8SO_4$	801209-99-4	3	$^{13}C_3$-PFBS	Deionized water
2,2,3,3-tetrafluoro-3-((1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl)oxy)propanoic acid (HydroEVE)	$C_8H_2F_{14}O_4$	773804-62-9	3	$^{13}C_3$-PFPrOPrA	Deionized water
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	$C_7H_2F_{12}O_4$	919005-14-4	1	$^{13}C_4$-PFOA	Methanol
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS, main component of F-53B)	$C_8HF_{16}SO_4Cl$	756426-58-1	1	$^{13}C_4$-PFOS	Methanol
Class 4: Fluorotelomer sulfonate					
6:2 fluorotelomer sulfonate (6:2 FtS)	$C_8H_5F_{13}O_3S$	27619-97-2	1, 4	$^{13}C_2$-6:2 FtS	Methanol

[a] Source: 1 Wellington Laboratories (Guelph, ON, Canada), 2 Fluoryx Labs (Carson City, NV), 3 The Chemours Company (Wilmington, DE), 4 SynQuest Laboratories (Alachua, FL), 5 Cambridge Isotope Laboratories (Tewksbury, MA).

[b] Basic methanol: 95% methanol + 5% deionized water with 2.5 M NaOH

[c] Highlighted chemicals indicate structural isomers. See Figure S1.

Table S2. Structures of 1,2,2,2-Tetrafluoroethyl trifluoromethyl ether and Fluoroethers E-1, E-2, and E-3

Compound	Formula	CAS #	Molecular structure
1,2,2,2-Tetrafluoroethyl trifluoromethyl ether (HFE 227)*	C_3HF_7O	2356-62-9	
Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (Fluoroether E-1)*	$C_5HF_{11}O$	3330-15-2	
2H-Perfluoro-5-methyl-3,6-dioxanonane (Fluoroether E-2)*	$C_8HF_{17}O_2$	3330-14-1	
2H-Perfluoro-5,8-dimethyl-3,6,9-trioxadodecane (Fluoroether E-3)*	$C_{11}HF_{23}O_3$	3330-16-3	

* Source: SynQuest Laboratories (Alachua, FL).

Table S3. Stability of PFASs in deionized water at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (μg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery	Day 30 % RSD
PFHxA	50.6	98.3	1.6	93.0	3.9
PFHxS	49.8	95.3	1.8	90.7	5.4
PFMOAA	57.2	99.3	0.4	94.1	0.7
PFMOPrA	39.3	95.5	1.2	90.4	0.1
PMPA	46.6	94.0	1.5	95.3	7.2
PFMOBA	49.1	97.3	1.1	94.7	8.7
PEPA	46.9	92.3	2.9	96.2	5.6
HFPO-DA (PFPrOPrA)	44.2	94.6	4.0	94.8	11.1
GenX	26.5	95.0	0.2	91.0	10.5
PFO2HxA	43.1	97.4	2.3	97.8	0.2
PFO3OA	42.3	92.6	1.8	92.6	3.9
PFO4DA	41.3	95.8	0.1	89.8	2.0
PFO5DoA	41.0	99.2	4.6	95.0	3.5
HFPO-TA	38.0	99.2	9.9	94.7	1.2
HFPO-TeA	29.3	95.6	1.2	109.7	8.2
Nafion by-product 2	38.6	96.1	0.1	91.7	4.0
NVHOS	56.3	94.9	0.5	96.3	12.6
HydroEVE	34.5	101.1	2.7	102.5	3.7
ADONA	28.4	99.6	2.3	93.5	1.9
F-53B	50.1	102.3	1.9	104.0	14.8
6:2 FtS	40.8	99.5	3.9	102.2	0.8

[a] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

Table S4. Stability of PFASs in methanol at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (µg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery	Day 30 % RSD
PFHxA	50.5	92.1	3.1	97.8	8.0
PFHxS	49.1	97.5	0.5	100.4	1.9
PFMOAA	51.4	104.6	1.5	96.7	1.5
PFMOPrA	43.0	105.4	3.2	97.0	1.4
PMPA	48.0	92.4	3.4	99.5	6.7
PFMOBA	48.0	106.1	5.2	97.0	0.4
PEPA	49.7	92.2	4.1	95.0	2.8
HFPO-DA (PFPrOPrA)	40.9	94.5	5.8	101.5	4.1
GenX	26.8	100.7	4.4	92.3	2.3
PFO2HxA	46.0	95.4	4.8	105.2	7.0
PFO3OA	43.5	93.0	4.9	96.4	2.5
PFO4DA	45.9	92.0	5.8	94.5	4.4
PFO5DoA	46.9	92.9	2.1	98.6	4.9
HFPO-TA	30.7	103.5	1.3	103.2	8.4
HFPO-TeA	34.6	91.8	13.9	93.2	2.9
Nafion by-product 2	44.6	98.9	5.6	101.8	0.9
NVHOS	45.3	96.5	1.6	102.7	2.8
HydroEVE	45.9	93.7	6.1	97.9	5.9
ADONA	28.3	106.5	3.4	103.0	6.7
F-53B	39.0	113.4	7.8	96.1	14.3
6:2 FtS	43.8	101.1	4.8	102.1	5.3

[s] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

Table S5. Stability of PFASs in isopropyl alcohol (IPA) at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (μg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery	Day 30 % RSD
PFHxA	50.0	95.9	13.7	99.4	12.4
PFHxS	57.6	95.2	6.8	98.6	4.2
PFMOAA	47.2	106.9	3.8	101.1	3.7
PFMOPrA	40.6	112.2	8.6	107.0	9.5
PMPA	49.8	89.5	12.5	95.3	1.5
PFMOBA	42.5	110.1	9.6	104.3	12.5
PEPA	50.7	90.9	12.6	94.5	1.2
HFPO-DA (PFPrOPrA)	48.8	91.6	10.0	98.9	4.3
GenX	24.3	111.8	9.8	109.9	15.9
PFO2HxA	47.6	96.0	11.6	98.1	2.8
PFO3OA	43.4	107.3	5.7	110.4	0.8
PFO4DA	44.2	100.1	6.1	104.7	3.5
PFO5DoA	48.3	101.5	2.6	96.0	3.3
HFPO-TA	35.8	107.6	10.5	110.6	9.2
HFPO-TeA	31.5	90.2	5.4	99.4	3.1
Nafion by-product 2	50.1	102.3	6.0	102.7	5.8
NVHOS	45.0	95.1	9.3	101.9	2.7
HydroEVE	48.3	99.6	5.5	103.3	2.9
ADONA	25.0	119.2	14.8	108.1	7.6
F-53B	54.1	120.1	7.5	108.0	3.5
6:2 FtS	42.6	97.1	3.0	105.0	4.5

[a] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

Table S6. Stability of PFASs in acetonitrile (ACN) at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (μg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery [b]	Day 30 % RSD [c]
PFHxA	54.8	95.5	2.1	92.8	10.2
PFHxS	50.0	96.3	2.0	96.4	4.3
PFMOAA	34.7	105.7	2.1	97.6	11.7
PFMOPrA	31.2	107.4	1.2	110.3	7.7
PMPA	52.1	ND [c]	ND	ND	ND
PFMOBA	47.5	104.0	2.0	101.9	2.3
PEPA	54.9	ND	ND	ND	ND
HFPO-DA (PFPrOPrA)	36.6	ND	ND	ND	ND
GenX	48.5	ND	ND	ND	ND
PFO2HxA	50.5	87.5	3.4	66.8	1.7
PFO3OA	34.6	89.3	5.2	65.8	2.5
PFO4DA	57.2	86.5	0.6	59.6	2.0
PFO5DoA	54.0	92.8	10.8	67.5	4.2
HFPO-TA	30.8	ND	ND	ND	ND
HFPO-TeA	20.1	ND	ND	ND	ND
Nafion by-product 2	46.4	101.3	4.1	99.6	6.4
NVHOS	47.6	95.4	2.2	96.2	3.8
HydroEVE	48.4	93.0	3.3	97.8	10.0
ADONA	27.3	104.7	6.7	100.2	5.6
F-53B	43.4	103.2	3.3	106.1	8.2
6:2 FtS	51.0	97.0	0.7	102.0	10.1

[a] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

[c] ND means concentration is below quantitation limit (QL).

Table S7. Stability of PFASs in acetone at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (μg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery	Day 30 % RSD
PFHxA	44.4	95.1	6.4	99.6	10.6
PFHxS	50.4	97.5	2.8	93.1	6.0
PFMOAA	55.4	109.9	0.8	96.8	3.2
PFMOPrA	46.2	103.8	1.1	110.9	8.3
PMPA	49.5	ND [c]	ND	ND	ND
PFMOBA	57.4	109.7	2.2	110.2	17.2
PEPA	51.6	ND	ND	ND	ND
HFPO-DA (PFPrOPrA)	44.7	ND	ND	ND	ND
GenX	50.3	ND	ND	ND	ND
PFO2HxA	38.4	66.4	1.5	18.7	1.1
PFO3OA	42.4	54.0	1.5	10.9	2.1
PFO4DA	48.3	41.3	1.2	ND	ND
PFO5DoA	43.7	60.5	0.4	ND	ND
HFPO-TA	31.0	ND	ND	ND	ND
HFPO-TeA	29.2	ND	ND	ND	ND
Nafion by-product 2	41.3	101.4	3.0	95.3	3.3
NVHOS	41.9	100.9	4.1	95.6	6.5
HydroEVE	41.7	96.6	4.6	100.1	8.9
ADONA	29.4	103.5	0.6	100.5	7.3
F-53B	55.7	97.4	12.6	104.8	14.7
6:2 FtS	44.3	101.8	9.8	109.0	9.5

[a] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

[c] ND means concentration is below quantitation limit (QL).

Table S8. Stability of PFASs in dimethyl sulfoxide (DMSO) at room temperature (20.2°C) for 7 and 30 days

Compound	Initial concentration (μg/L)	Day 7 mean % recovery [a]	Day 7 % RSD [b]	Day 30 mean % recovery	Day 30 % RSD
PFHxA	55.8	97.2	1.6	94.4	10.5
PFHxS	58.6	96.4	3.4	95.3	1.5
PFMOAA	68.8	105.3	2.1	95.1	6.1
PFMOPrA	46.6	109.7	3.0	92.1	4.8
PMPA	41.3	ND [c]	ND	ND	ND
PFMOBA	57.8	100.4	2.4	96.1	3.0
PEPA	40.5	ND	ND	ND	ND
HFPO-DA (PFPrOPrA)	45.7	ND	ND	ND	ND
GenX	57.1	ND	ND	ND	ND
PFO2HxA	42.4	89.3	1.3	58.4	1.3
PFO3OA	43.2	83.2	0.6	51.9	0.4
PFO4DA	43.4	86.3	1.4	60.0	8.9
PFO5DoA	46.6	89.9	4.1	62.8	1.4
HFPO-TA	34.8	ND	ND	ND	ND
HFPO-TeA	25.4	ND	ND	ND	ND
Nafion by-product 2	50.5	90.8	4.7	95.4	3.8
NVHOS	57.8	93.2	4.1	93.3	2.0
HydroEVE	53.3	92.9	7.7	103.4	4.7
ADONA	27.6	109.2	2.6	103.8	1.6
F-53B	48.4	99.9	19.6	100.1	2.0
6:2 FtS	46.2	106.4	6.7	108.0	0.2

[a] For ease of data comparison, all analyte concentrations were normalized to the initial concentration and converted to percent recoveries.

[b] Relative standard deviation (RSD) represents for duplicate measurements.

[c] ND means concentration is below quantitation limit (QL).

Table S9. Summary of the stability of PFASs targeted in this study

Class	Compound	Solvent			
		Acetonitrile (ACN)	Acetone	Dimethyl sulfoxide (DMSO)	Polar protic solvents [a]
PFCA	PFHxA	No deg. [b]	No deg.	No deg.	No deg.
PFSA	PFHxS	No deg.	No deg.	No deg.	No deg.
Mono-ether PFECAs	PFMOAA	No deg.	No deg.	No deg.	No deg.
	PFMOPrA	No deg.	No deg.	No deg.	No deg.
	PMPA	k = 3.03 d^{-1} [c]	k = 19.2 d^{-1}	k = 2.00 d^{-1}	No deg.
	PFMOBA	No deg.	No deg.	No deg.	No deg.
	PEPA	k = 4.75 d^{-1}	k = 27.0 d^{-1}	k = 2.63 d^{-1}	No deg.
	HFPO-DA (PFPrOPrA)	k = 4.96 d^{-1}	k = 45.4 d^{-1}	k = 3.92 d^{-1}	No deg.
	GenX	k = 5.86 d^{-1}	k = 47.9 d^{-1}	k = 4.64 d^{-1}	No deg.
Multi-ether PFECAs	PFO2HxA	k = 0.0136 d^{-1}	k = 0.0578 d^{-1}	k = 0.0168 d^{-1}	No deg.
	PFO3OA	k = 0.0128 d^{-1}	k = 0.0743 d^{-1}	k = 0.0195 d^{-1}	No deg.
	PFO4DA	k = 0.0170 d^{-1}	k = 0.106 d^{-1}	k = 0.0160 d^{-1}	No deg.
	PFO5DoA	k = 0.0129 d^{-1}	k = 0.0732 d^{-1}	k = 0.0139 d^{-1}	No deg.
	HFPO-TA	k = 3.39 d^{-1}	k = 27.8 d^{-1}	k = 3.52 d^{-1}	No deg.
	HFPO-TeA	k = 3.71 d^{-1}	k = 32.1 d^{-1}	k = 3.68 d^{-1}	No deg.
Polyfluoroalkyl ether acids	Nafion by-product 2	No deg.	No deg.	No deg.	No deg.
	NVHOS	No deg.	No deg.	No deg.	No deg.
	HydroEVE	No deg.	No deg.	No deg.	No deg.
	ADONA	No deg.	No deg.	No deg.	No deg.
	F-53B	No deg.	No deg.	No deg.	No deg.
Fluorotelomer sulfonate	6:2FtS	No deg.	No deg.	No deg.	No deg.

[a] All studied PFASs had no measurable degradation in the polar protic solvents water, methanol, and isopropyl alcohol (IPA) in ~30 days.

[b] No deg. means the studied PFAS had no measurable degradation in ~30 days.

[c] Averages of observed first-order rate constants (k) are summarized here. See Table 2 for 95% confidence intervals.

Table S10. First-order rate constants (*k*) of PMPA, PEPA, and HFPO-DA in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO) with different water-to-organic solvent ratios (100% organic solvent, 90:10% (v/v) and 80:20% (v/v) organic solvent:water) at room temperature (20.2°C)

Compound	100% ACN		90% ACN+10% water		80% ACN+20% water	
	k (d^{-1})	R^2	k (d^{-1})	R^2	k (d^{-1})	R^2
PMPA	3.03 [a,b] (2.74, 3.31)	0.906	0.0185 (0.0172, 0.0198)	0.988	No measurable degradation in 30 d	
PEPA	4.75 [b] (4.41, 5.10)	0.945	0.0267 (0.0240, 0.0295)	0.974	No measurable degradation in 30 d	
HFPO-DA (PFPrOPrA)	4.96 [b] (4.39, 5.52)	0.882	0.0380 (0.0342, 0.0417)	0.978	No measurable degradation in 30 d	
Compound	**100% Acetone**		**90% Acetone +10% water**		**80% Acetone +20% water**	
	k (d^{-1})	R^2	k (d^{-1})	R^2	k (d^{-1})	R^2
PMPA	19.2 [b] (17.1, 21.2)	0.909	0.0753 (0.0700, 0.0806)	0.989	0.0151 (0.0136, 0.0166)	0.977
PEPA	27.0 [b] (24.7, 29.3)	0.943	0.128 (0.123, 0.0133)	0.997	0.0260 (0.0242, 0.0278)	0.988
HFPO-DA (PFPrOPrA)	45.4 [b] (43.5, 47.3)	0.988	0.192 (0.155, 0.228)	0.965	0.0329 (0.0296, 0.0362)	0.975
Compound	**100% DMSO**		**90% DMSO +10% water**		**80% DMSO +20% water**	
	k (d^{-1})	R^2	k (d^{-1})	R^2	k (d^{-1})	R^2
PMPA	2.00 [b] (1.73, 2.27)	0.826	0.299 (0.262, 0.335)	0.985	0.0471 (0.0425, 0.0518)	0.976
PEPA	2.63 [b] (2.28, 2.97)	0.838	0.473 (0.412, 0.535)	0.983	0.0587 (0.0562, 0.0611)	0.996
HFPO-DA (PFPrOPrA)	3.92 [b] (3.34, 4.51)	0.819	0.481 (0.313 0.649)	0.987	0.109 (0.101, 0.117)	0.996

[a] Experimental results were analyzed using the regression data analysis tool in Microsoft Excel, and the average rate constant was reported. Values in parentheses represent the lower and upper limit of 95% confidence interval.

[b] Experiments were conducted in replicate starting at different initial concentrations (10, 50 and 100 μg/L).

Table S11. First-order rate constants (*k*) of PMPA, PEPA, and HFPO-DA in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO) at three temperatures [cold (3.4°C), room (20.2°C), and hot (32.4°C)]

Compound	ACN, cold		ACN, room		ACN, hot	
	k **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**
PMPA	0.278 [a] (0.242, 0.313)	0.960	3.03 [b] (2.74, 3.31)	0.906	26.0 (24.3, 27.8)	0.996
PEPA	0.336 (0.309, 0.365)	0.983	4.75 [b] (4.41, 5.10)	0.945	29.8 (27.0, 32.6)	0.991
HFPO-DA (PFPrOPrA)	0.383 (0.365, 0.401)	0.994	4.96 [b] (4.39, 5.52)	0.882	31.8 (27.1, 36.6)	0.978
Compound	**Acetone, cold**		**Acetone, room**		**Acetone, hot**	
	k **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**
PMPA	1.11 (1.00, 1.23)	0.976	19.2 [b] (17.1, 21.2)	0.909	127 (117,138)	0.999
PEPA	1.88 (1.68, 2.07)	0.976	27.0 [b] (24.7, 29.3)	0.943	160 [c] (103, 213)	0.999
HFPO-DA (PFPrOPrA)	1.97 (1.70, 2.23)	0.960	45.4 [b] (43.5, 47.3)	0.988	191 [c] (116, 266)	0.997
Compound	**DMSO, cold [d]**		**DMSO, room**		**DMSO, hot**	
	k **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**	***k*** **(d^{-1})**	**R^2**
PMPA	-	-	2.00 [b] (1.73, 2.27)	0.826	20.0 (17.9, 22.0)	0.992
PEPA	-	-	2.63 [b] (2.28, 2.97)	0.838	24.9 (22.7, 27.0)	0.994
HFPO-DA (PFPrOPrA)	-	-	3.92 [b] (3.34, 4.51)	0.819	43.6 (29.1, 58.1)	0.968

[a] Experimental results were analyzed using the regression data analysis tool in Microsoft Excel, and the average rate constant was reported. Values in parentheses represent the lower and upper limit of 95% confidence interval.

[b] Experiments were conducted in replicate starting at different initial concentrations (10, 50 and 100 μg/L).

[c] The 95% confidence interval was relatively large due to the limited number of sample size (n=3; t=0, 10, and 20 min).

[d] Experiment was not conducted at 3.4°C in DMSO due to the high melting point of DMSO (19°C).

Table S12. Activation energy (E_a) and pre-exponential factor (A) of PMPA, PEPA, and HFPO-DA in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO)

Compound	ACN		Acetone		DMSO [a]	
	E_a (kJ/mol)	lnA (A in d^{-1})	E_a (kJ/mol)	lnA (A in d^{-1})	E_a (kJ/mol)	lnA (A in d^{-1})
PMPA	108.8	46.0	114.7	50.0	140.5	58.3
PEPA	108.5	46.1	107.6	47.4	137.2	57.2
HFPO-DA (PFPrOPrA)	106.7	45.4	112.0	49.5	147.1	61.7

[a] Experiment was not conducted at 3.4°C in DMSO due to the high melting point of DMSO (19°C).

Table S13. Molar yield of Fluoroethers E-1, E-2, and E-3 from the degradation of HFPO-DA, HFPO-TA, and HFPO-TeA, respectively, in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO) at room temperature (20.2°C) in 5 days

PFAS	$[PFAS]_0$	Product	[Product]	$[Product]/[PFAS]_0$ [a]
Solvent: acetonitrile (ACN)				
HFPO-DA	15.6 nmol/L	Fluoroether E-1	20.1 nmol/L	129% ± 14%
HFPO-TA	9.1 nmol/L	Fluoroether E-2	8.2 nmol/L	90% ± 13%
HFPO-TeA	7.1 nmol/L	Fluoroether E-3	6.5 nmol/L	91% ± 10%
Solvent: acetone				
HFPO-DA	15.7 nmol/L	Fluoroether E-1	18.8 nmol/L	120% ± 26%
HFPO-TA	7.6 nmol/L	Fluoroether E-2	8.3 nmol/L	109% ± 16%
HFPO-TeA	7.3 nmol/L	Fluoroether E-3	7.2 nmol/L	98% ± 6%
Solvent: dimethyl sulfoxide (DMSO)				
HFPO-DA	16.4 nmol/L	Fluoroether E-1	15.1 nmol/L	92% ± 3%
HFPO-TA	11.6 nmol/L	Fluoroether E-2	9.8 nmol/L	84% ± 16%
HFPO-TeA	8.9 nmol/L	Fluoroether E-3	7.5 nmol/L	84% ± 18%

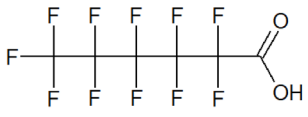
[a] Calculation of molar yield is detailed in Text S8.

Table S14. The percent abundance of $[M-F+1]^+$ ion for Fluoroethers E-1, E-2, and E-3 from the degradation of HFPO-DA, HFPO-TA, and HFPO-TeA, respectively, in fully deuterated acetone

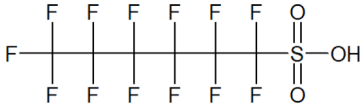
The abundance of $[M-F+1]^+$ ion to the sum abundance of $[M-F]^+$ and $[M-F+1]^+$ ions [a]	
Fluoroether E-1 (C_5HOF_{11}) in deuterated acetone	Degradation product of HFPO-DA in deuterated acetone
4.8 ± 0.02%	70.2 ± 10.6%
Fluoroether E-2 ($C_8HO_2F_{17}$) in deuterated acetone	Degradation product of HFPO-TA in deuterated acetone
7.7 ± 0.02%	76.4 ± 6.3%
Fluoroether E-3 ($C_{11}HO_3F_{23}$) in deuterated acetone	Degradation product of HFPO-TeA in deuterated acetone
10.2 ± 0.03%	79.4 ± 5.1%

[a] *m/z* of $[M-F]^+$ = 267 for HFPO-DA, 433 for HFPO-TA, and 599 for HFPO-TeA.

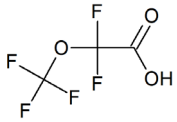
m/z of $[M-F+1]^+$ = 268 for HFPO-DA, 434 for HFPO-TA, and 600 for HFPO-TeA.



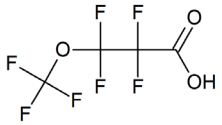
PFHxA



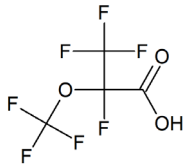
PFHxS



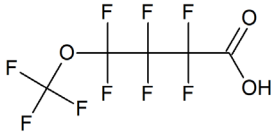
PFMOAA



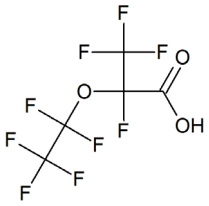
PFMOPrA



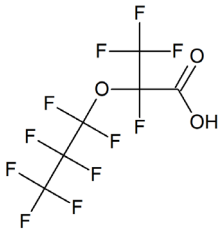
PMPA[a]



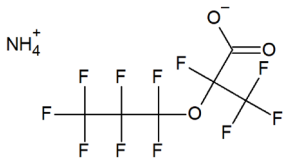
PFMOBA



PEPA[b]

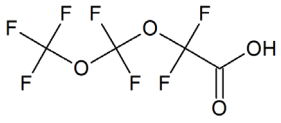


HFPO-DA (PFPrOPrA)

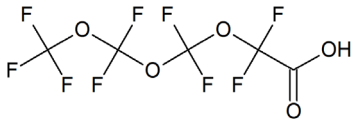


Ammonium salt of HFPO-DA

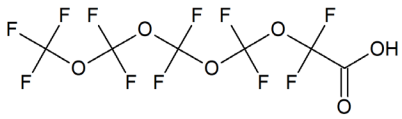
(= "GenX")



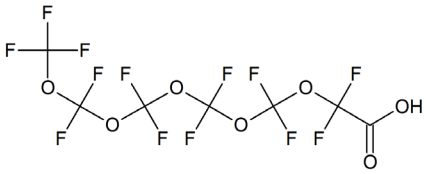
PFO2HxA



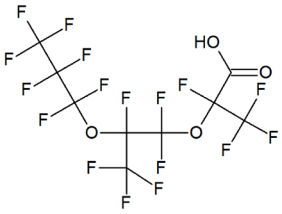
PFO3OA



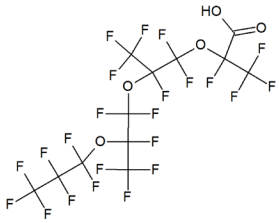
PFO4DA



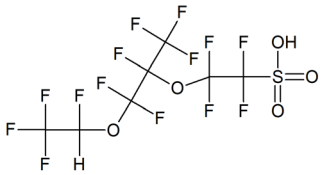
PFO5DoA



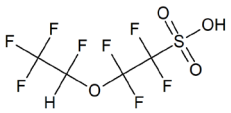
HFPO-TA



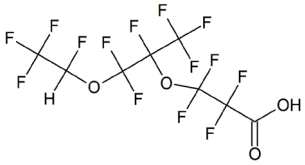
HFPO-TeA



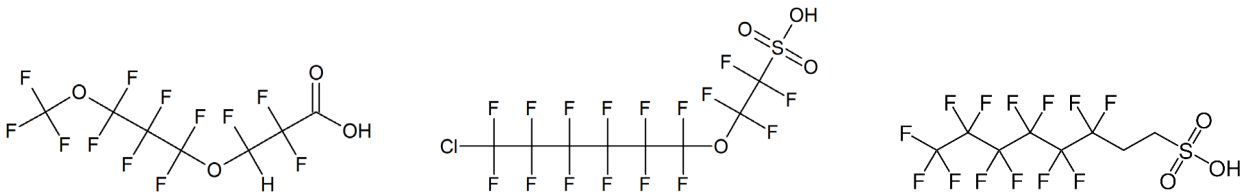
Nafion by-product 2



NVHOS



HydroEVE



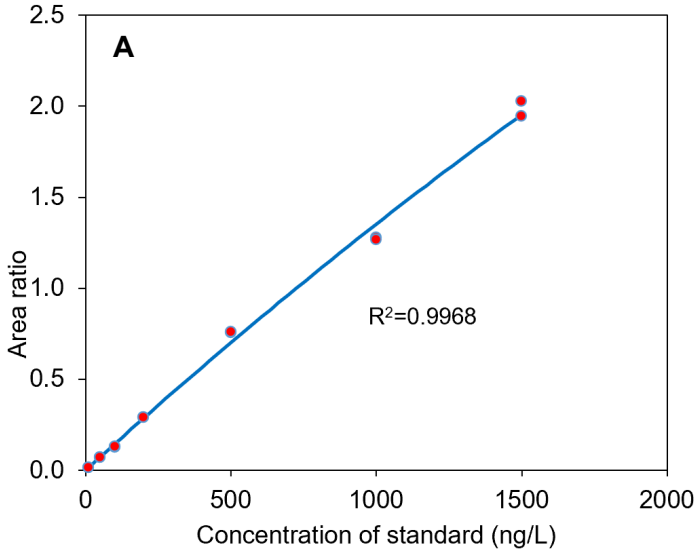
ADONA **9Cl-PF3ONS (main component F-53B)** **6:2 FtS**

Figure S1. Molecular structures of per- and polyfluoroalkyl substances (PFASs) evaluated in this study.

[a] In Sun et al. (2016),[5] this compound was presented as PFMOPrA. However, it is likely that environmental samples contain the branched isomer, PMPA, shown here and in Strynar et al. (2015).[6]

[b] In Sun et al. (2016),[5] this compound was presented as PFMOBA. However, it is likely that environmental samples contain the branched isomer, PEPA, shown here and in Strynar et al. (2015).[6]

403



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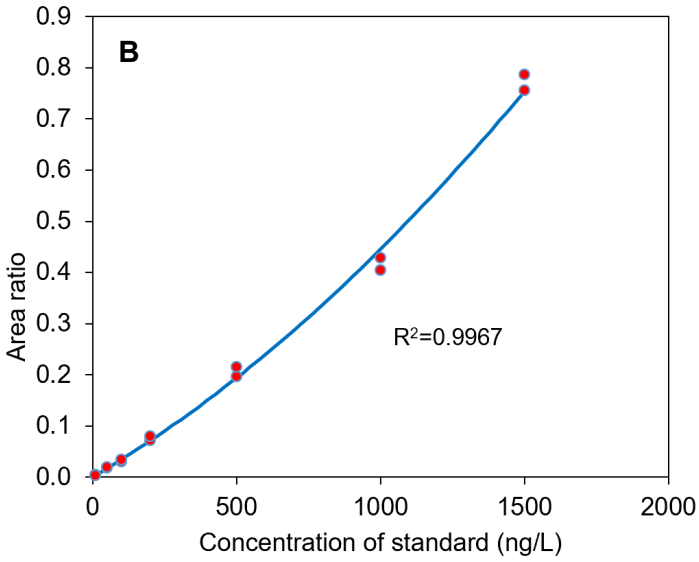


405 **Figure S2. Representative calibration curves for (A) PFHxA and (B) PFO2HxA using LC-**
406 **HRMS.**

407 Red dots represent area ratios (i.e. measured peak area for the native standard divided by measured
408 peak area for the isotopically labeled internal standard), and blue line is the concentration-weighted
409 (1/x) second-order polynomial fit.

410

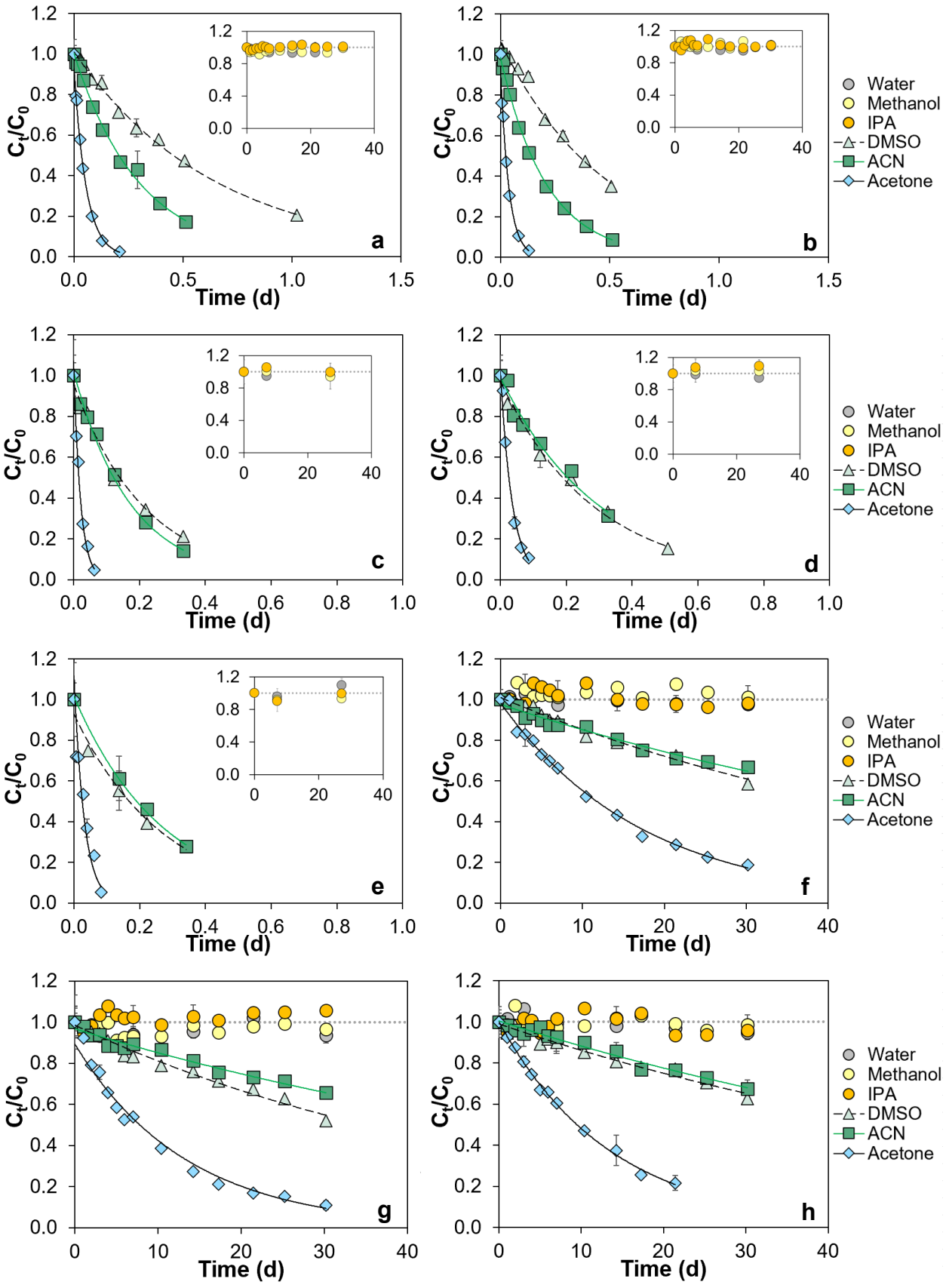

a
b
c
d
e
f
g
h
Water
Methanol
IPA
DMSO
ACN
Acetone
Time (d)
Ct/C0

Figure S3. Stability of (a) PMPA, (b) PEPA, (c) GenX, (d) HFPO-TA, (e) HFPO-TeA, (f) PFO2HxA, (g) PFO3OA, and (h) PFO5DoA in water, methanol, isopropyl alcohol (IPA), dimethyl sulfoxide (DMSO), acetonitrile (ACN), and acetone at room temperature (20.2°C). Curves represent first-order kinetic model results, and the corresponding rate constants are given in Table 2. For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

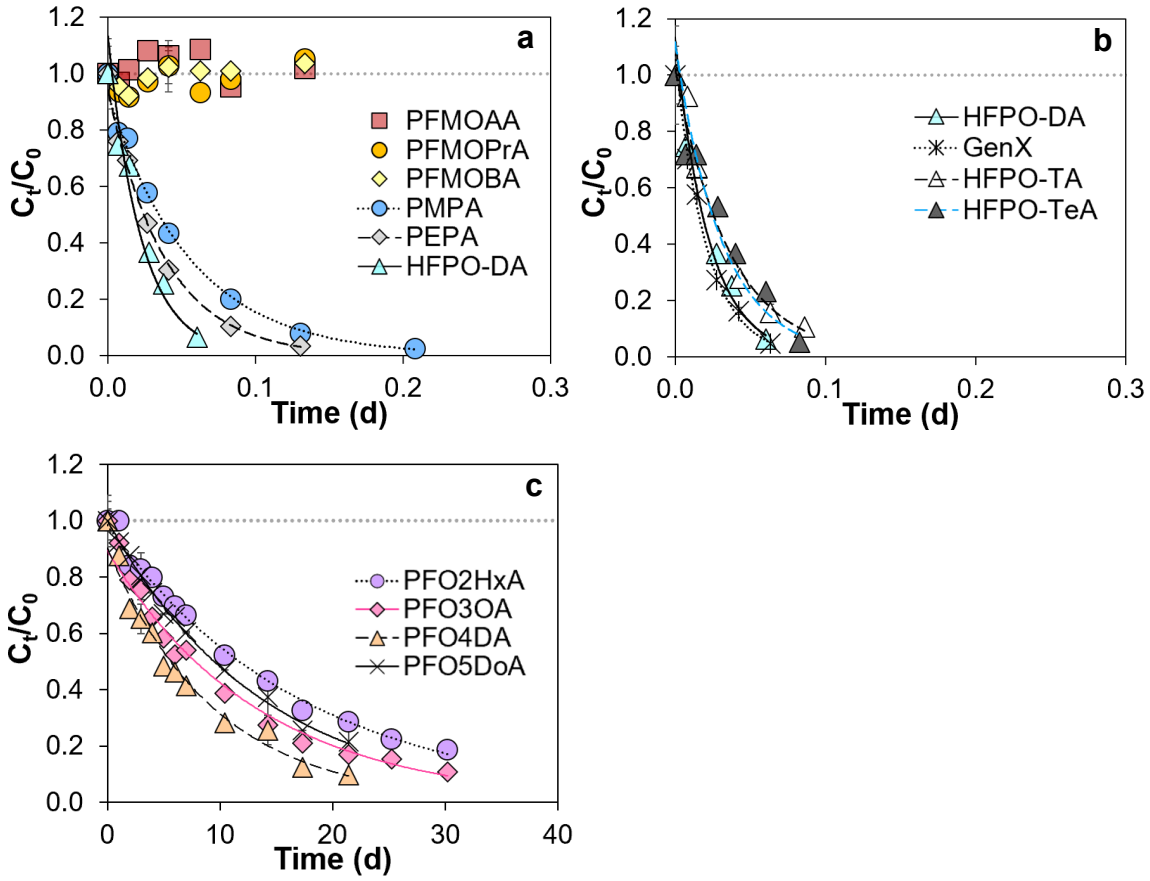


Figure S4. Stability of perfluoroalkyl ether carboxylic acids (PFECAs): (a) mono-ether PFECAs, (b) HFPO homologues, and (c) multi-ether PFECAs in acetone at room temperature (20.2°C).

Curves represent first-order kinetic model results, and the corresponding rate constants are given in Table 2. HFPO-DA is plotted in both panel (a) and (b) for comparison. For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

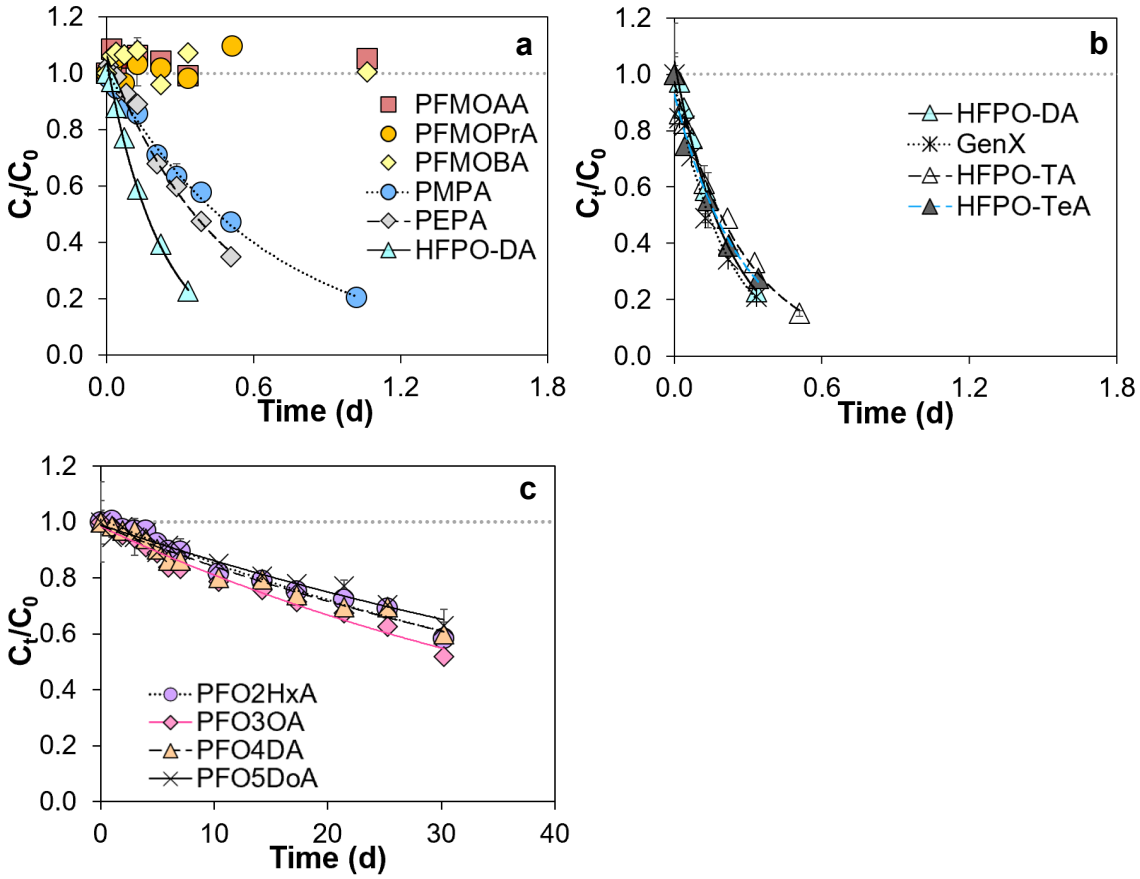
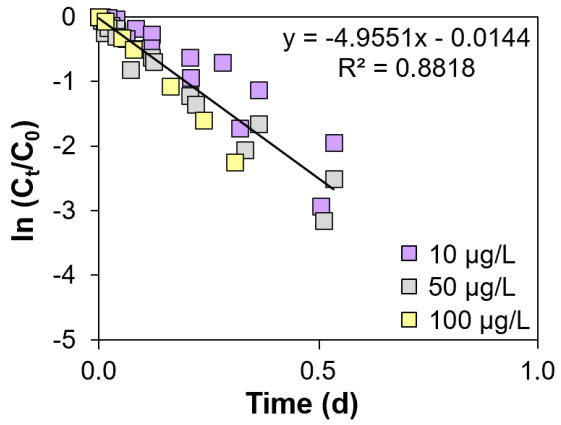
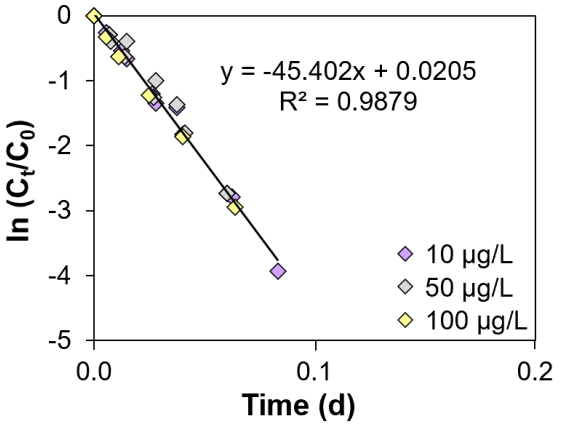


Figure S5. Stability of perfluoroalkyl ether carboxylic acids (PFECAs): (a) mono-ether PFECAs, (b) HFPO homologues, and (c) multi-ether PFECAs in dimethyl sulfoxide (DMSO) at room temperature (20.2°C).

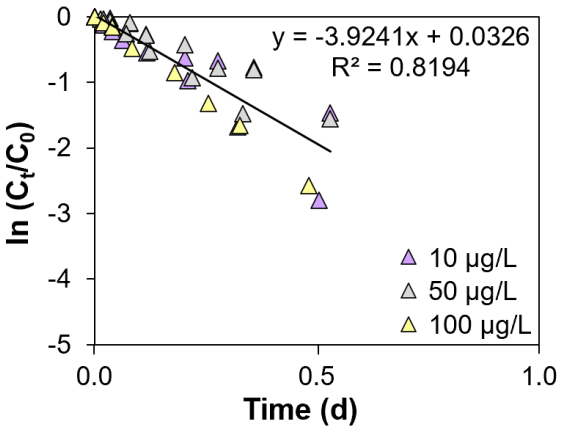
Curves represent first-order kinetic model results, and the corresponding rate constants are given in Table 2. HFPO-DA is plotted in both panel (a) and (b) for comparison. For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.



(a)



(b)



(c)

Figure S6. Stability of HFPO-DA starting at different initial concentrations (10, 50 and 100 µg/L) in (a) acetonitrile (ACN), (b) acetone, and (c) dimethyl sulfoxide (DMSO) at room temperature (20.2°C).

For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

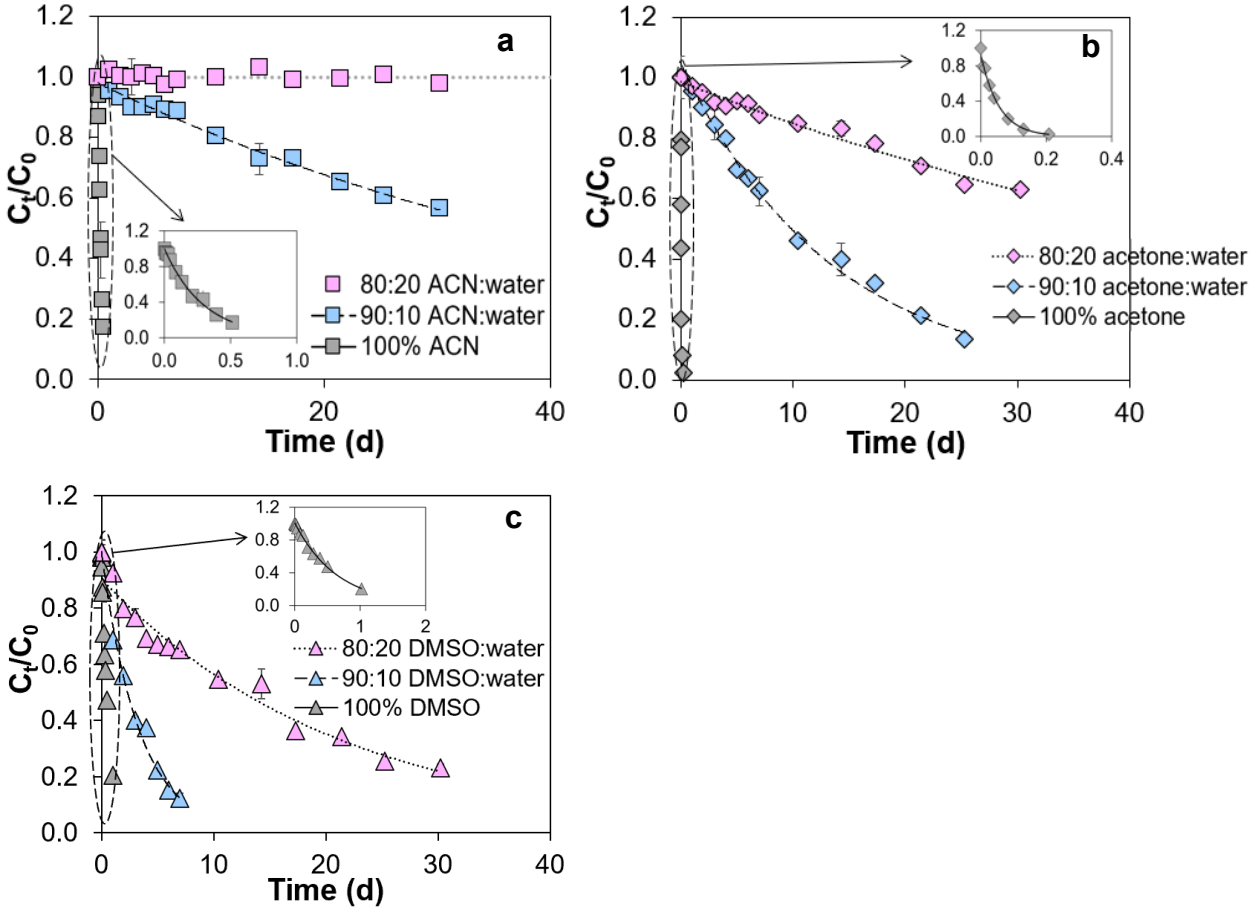


Figure S7. Stability of PMPA in (a) acetonitrile (ACN), (b) acetone, and (c) dimethyl sulfoxide (DMSO) with different water-to-organic solvent ratios at room temperature (20.2°C).

Curves represent first-order kinetic model results, and the corresponding rate constants are given in Tables 2 and S9. The inset in each panel highlights results for PMPA in 100% organic solvent. For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

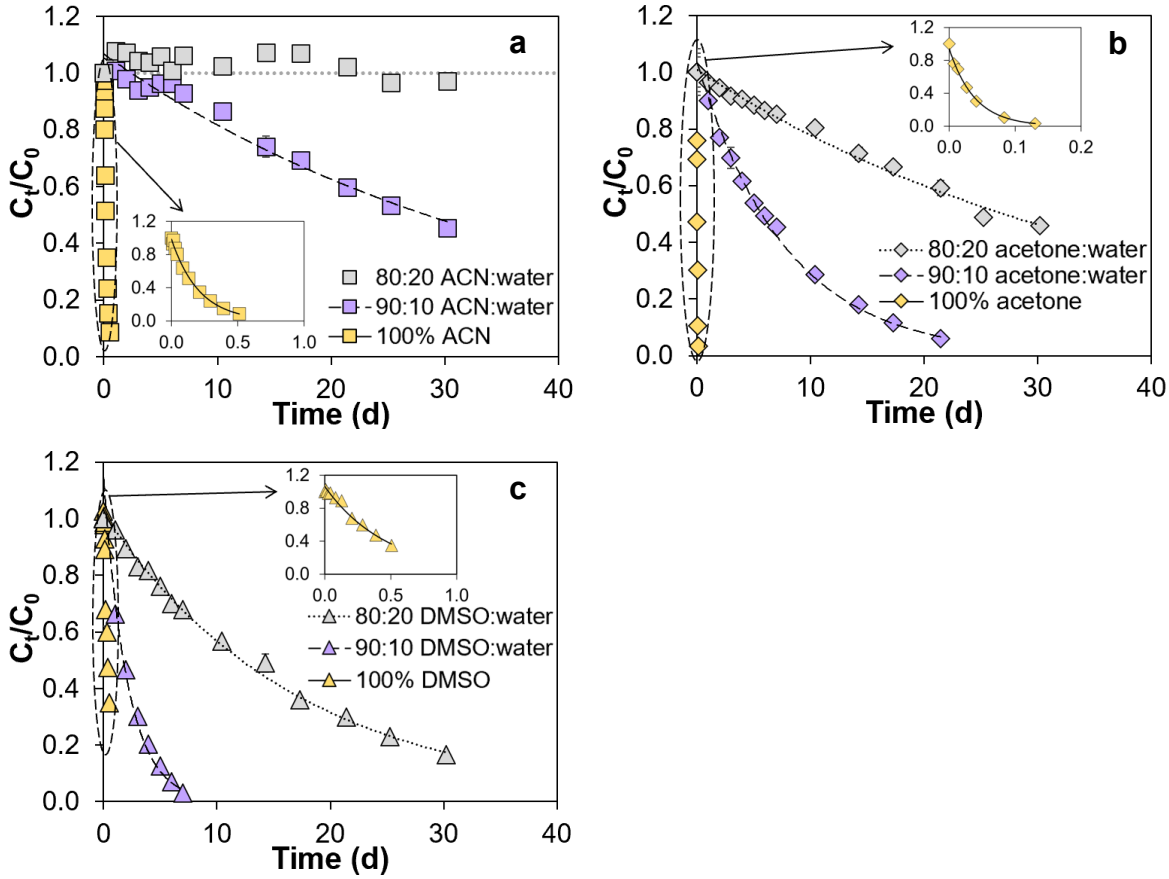


Figure S8. Stability of PEPA in (a) acetonitrile (ACN), (b) acetone, and (c) dimethyl sulfoxide (DMSO) with different water-to-organic solvent ratios at room temperature (20.2°C). Curves represent first-order kinetic model results, and the corresponding rate constants are given in Tables 2 and S9. The inset in each panel highlights results for PEPA in 100% organic solvent. For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

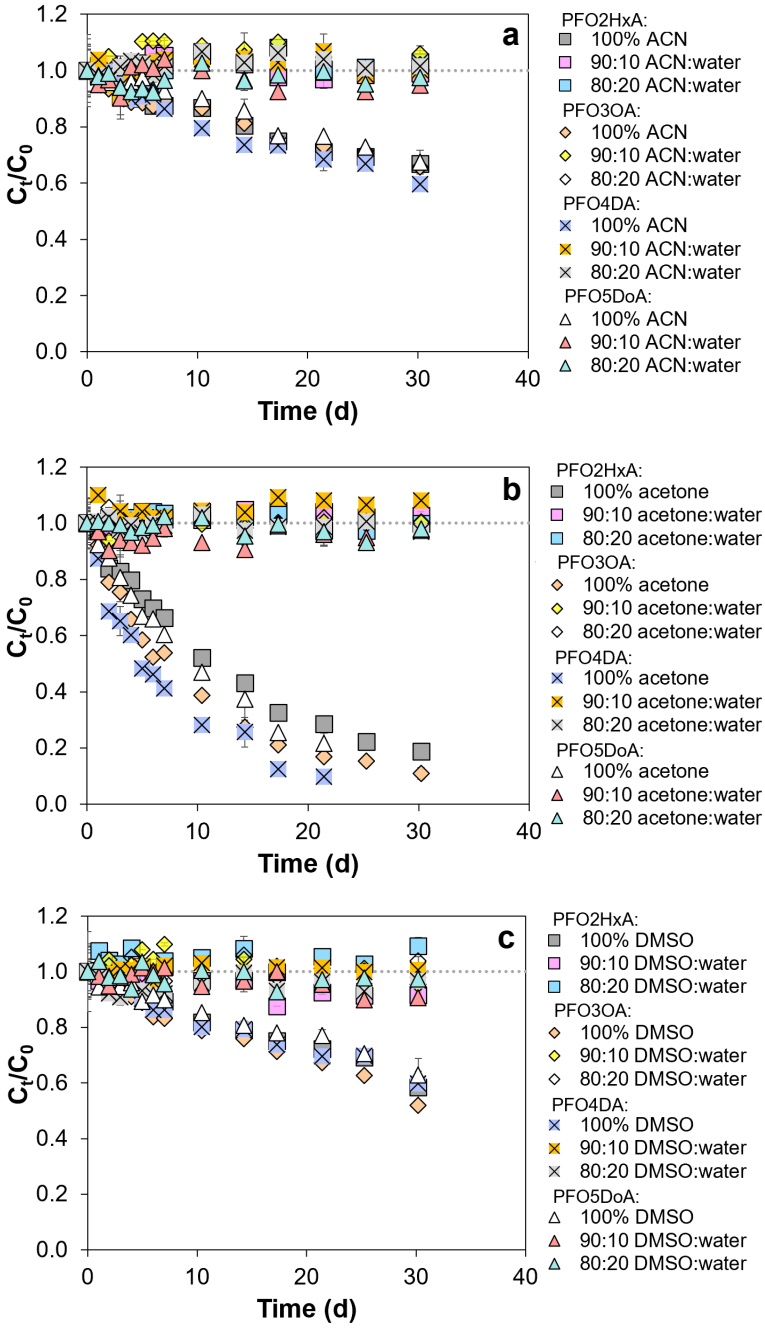


Figure S9. Stability of multi-ether PFECAs in (a) acetonitrile (ACN), (b) acetone, and (c) dimethyl sulfoxide (DMSO) with different water-to-organic solvent ratios at room temperature (20.2°C).

For ease of data comparison, all analyte concentrations were normalized to the initial concentration (C_t/C_0). Error bars represent standard deviations of duplicate measurements. See Figure S1 for compound structures.

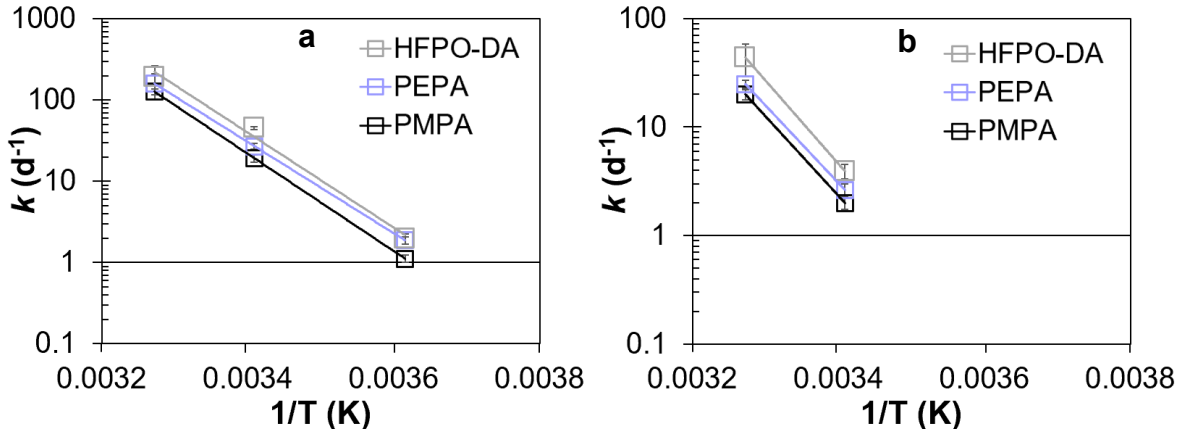


Figure S10. Arrhenius plots describing the temperature-dependence of first-order rate constants of HFPO-DA, PEPA, and PMPA degradation in (a) acetone and (b) dimethyl sulfoxide (DMSO).

The first-order rate constants at different temperatures are given in Table S10. Temperature was recorded at least four times during the test and average temperature was reported. Experiment was not conducted at 3.4°C in DMSO due to the high melting point of DMSO (19°C). See Figure S1 for compound structures.

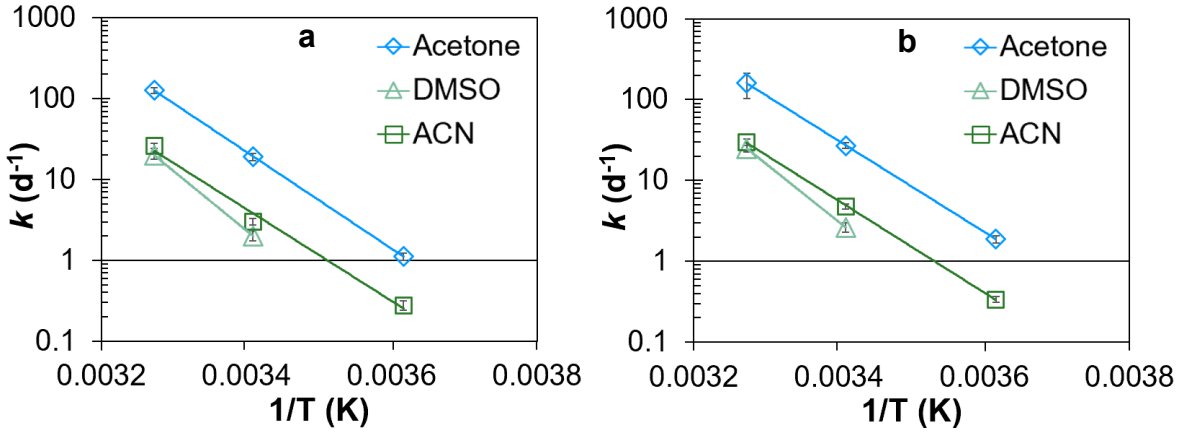
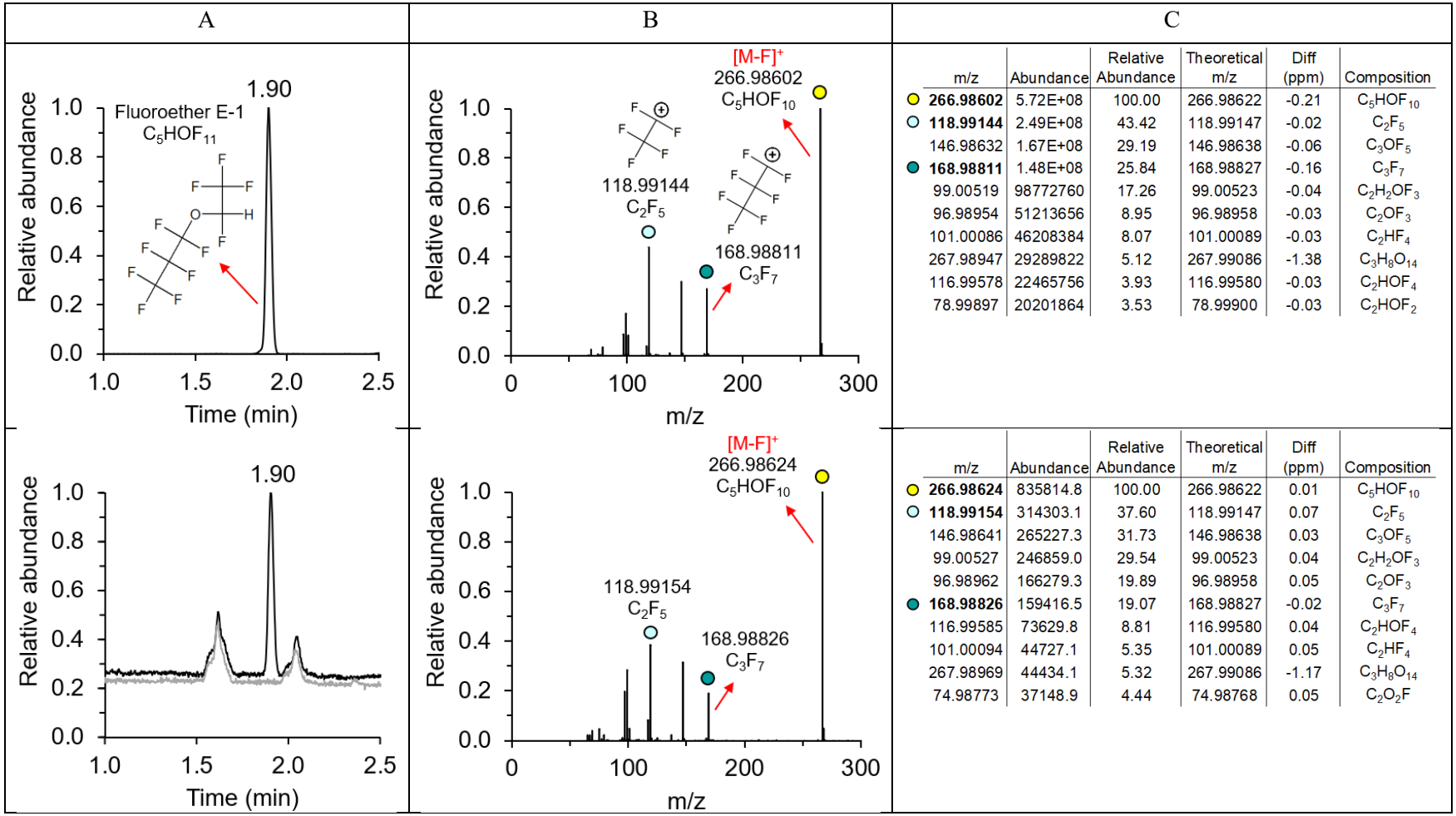


Figure S11. Arrhenius plots describing the temperature-dependence of first-order rate constants of (a) PMPA and (b) PEPA degradation in acetonitrile (ACN), acetone, and dimethyl sulfoxide (DMSO).

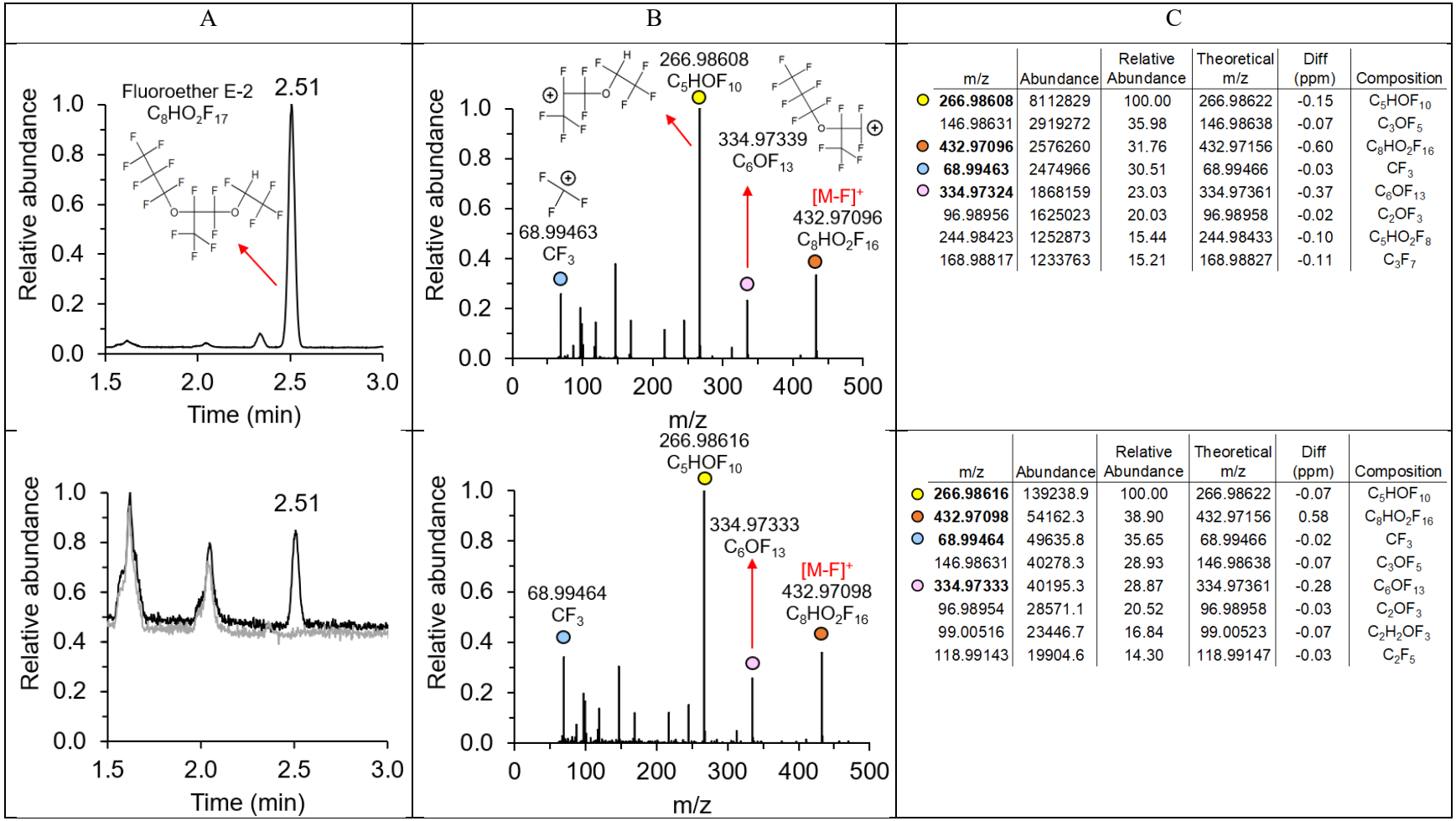
The first-order rate constants at different temperatures are given in Table S10. Temperature was recorded at least four times during the test and average temperature was reported. Experiment was not conducted at 3.4°C in DMSO due to the high melting point of DMSO (19°C). See Figure S1 for compound structures.



m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
266.98602	5.72E+08	100.00	266.98622	-0.21	C_5HOF_{10}
118.99144	2.49E+08	43.42	118.99147	-0.02	C_2F_5
146.98632	1.67E+08	29.19	146.98638	-0.06	C_3OF_5
168.98811	1.48E+08	25.84	168.98827	-0.16	C_3F_7
99.00519	98772760	17.26	99.00523	-0.04	$C_2H_2OF_3$
96.98954	51213656	8.95	96.98958	-0.03	C_2OF_3
101.00086	46208384	8.07	101.00089	-0.03	C_2HF_4
267.98947	29289822	5.12	267.99086	-1.38	$C_3H_8O_{14}$
116.99578	22465756	3.93	116.99580	-0.03	C_2HOF_4
78.99897	20201864	3.53	78.99900	-0.03	C_2HOF_2

m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
266.98624	835814.8	100.00	266.98622	0.01	C_5HOF_{10}
118.99154	314303.1	37.60	118.99147	0.07	C_2F_5
146.98641	265227.3	31.73	146.98638	0.03	C_3OF_5
99.00527	246859.0	29.54	99.00523	0.04	$C_2H_2OF_3$
96.98962	166279.3	19.89	96.98958	0.05	C_2OF_3
168.98826	159416.5	19.07	168.98827	-0.02	C_3F_7
116.99585	73629.8	8.81	116.99580	0.04	C_2HOF_4
101.00094	44727.1	5.35	101.00089	0.05	C_2HF_4
267.98969	44434.1	5.32	267.99086	-1.17	$C_3H_8O_{14}$
74.98773	37148.9	4.44	74.98768	0.05	C_2O_2F

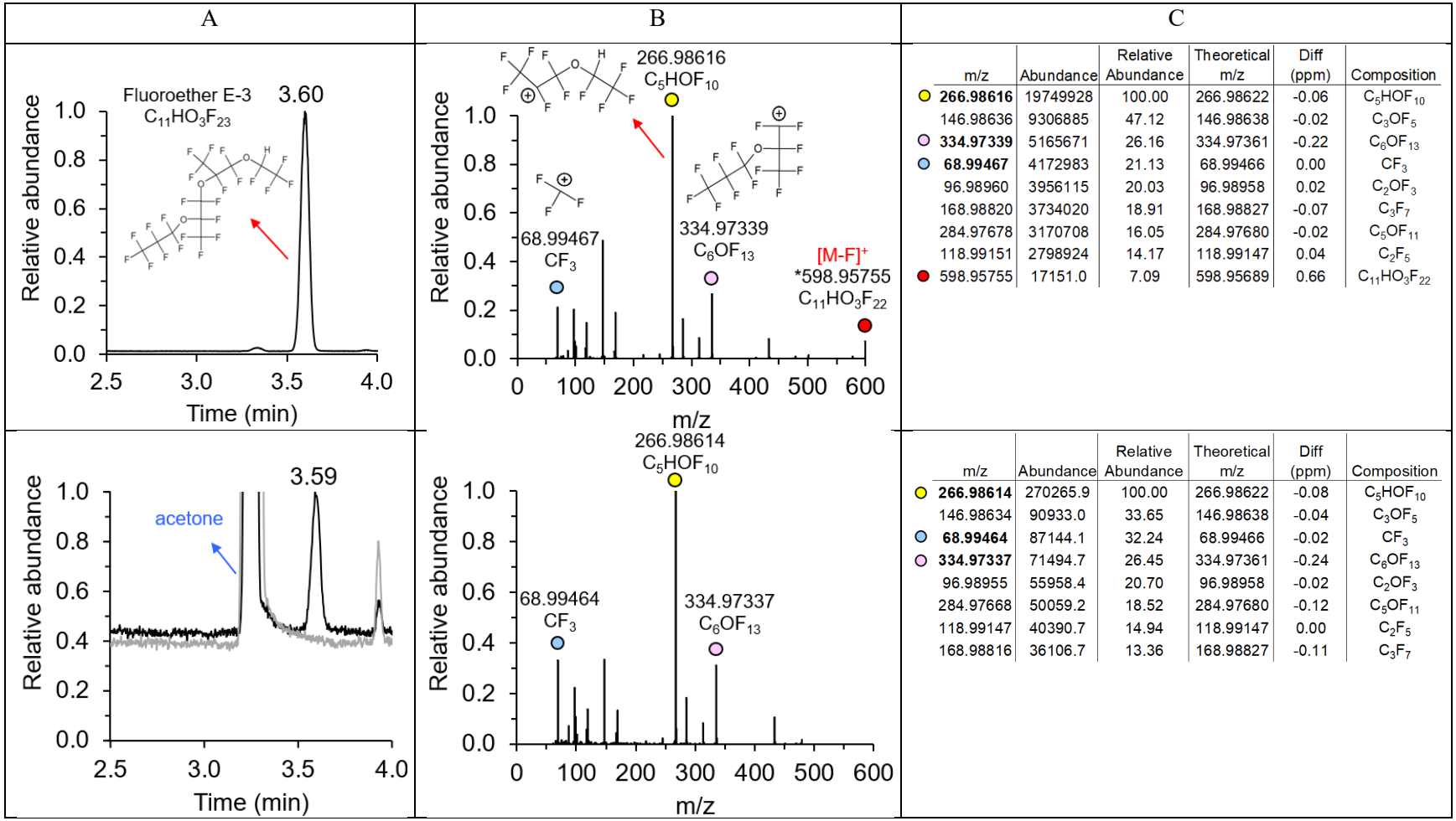
Figure S12. (A) GC−Orbitrap total ion chromatogram (TIC) comparison of Fluoroether E-1 standard (top) and degradation product of HFPO-DA in acetone in 5 days in black color and acetone blank in gray color (bottom); (B) mass spectra of Fluoroether E-1 standard (top) and degradation product of HFPO-DA in acetone in 5 days (bottom); (C) mass spectra list of Fluoroether E-1 standard (top) and degradation product of HFPO-DA in acetone in 5 days (bottom).



m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
266.98608	8112829	100.00	266.98622	-0.15	C_5HOF_{10}
146.98631	2919272	35.98	146.98638	-0.07	C_3OF_5
432.97096	2576260	31.76	432.97156	-0.60	$C_8HO_2F_{16}$
68.99463	2474966	30.51	68.99466	-0.03	CF_3
334.97324	1868159	23.03	334.97361	-0.37	C_6OF_{13}
96.98956	1625023	20.03	96.98958	-0.02	C_2OF_3
244.98423	1252873	15.44	244.98433	-0.10	$C_5HO_2F_8$
168.98817	1233763	15.21	168.98827	-0.11	C_3F_7

m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
266.98616	139238.9	100.00	266.98622	-0.07	C_5HOF_{10}
432.97098	54162.3	38.90	432.97156	0.58	$C_8HO_2F_{16}$
68.99464	49635.8	35.65	68.99466	-0.02	CF_3
146.98631	40278.3	28.93	146.98638	-0.07	C_3OF_5
334.97333	40195.3	28.87	334.97361	-0.28	C_6OF_{13}
96.98954	28571.1	20.52	96.98958	-0.03	C_2OF_3
99.00516	23446.7	16.84	99.00523	-0.07	$C_2H_2OF_3$
118.99143	19904.6	14.30	118.99147	-0.03	C_2F_5

Figure S13. (A) GC−Orbitrap total ion chromatogram (TIC) comparison of Fluoroether E-2 standard (top) and degradation product of HFPO-TA in acetone in 5 days in black color and acetone blank in gray color (bottom); (B) mass spectra of Fluoroether E-2 standard (top) and degradation product of HFPO-TA in acetone in 5 days (bottom); (C) mass spectra list of Fluoroether E-2 standard (top) and degradation product of HFPO-TA in acetone in 5 days (bottom).

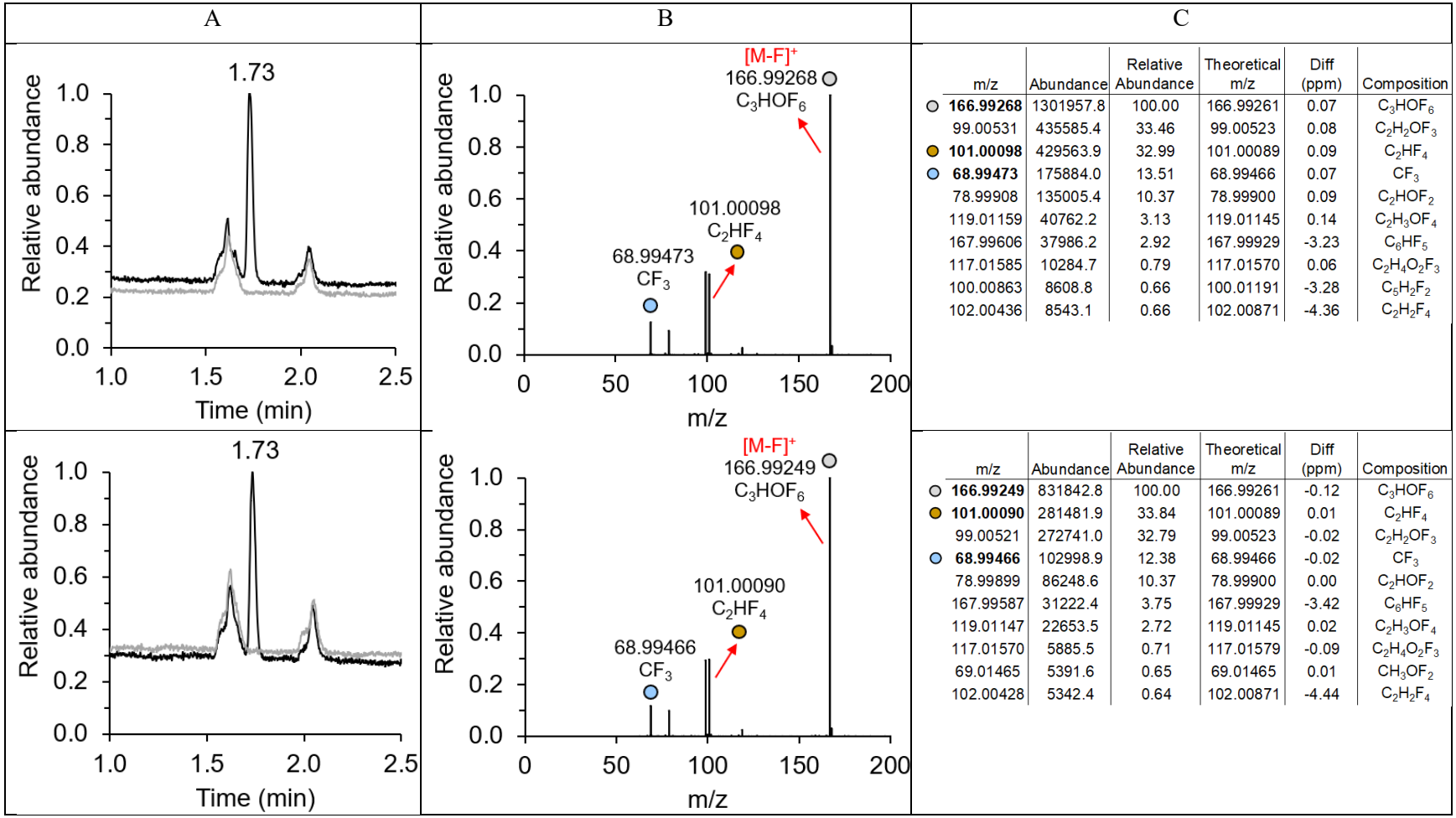


	m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
●	**266.98616**	19749928	100.00	266.98622	-0.06	C_5HOF_{10}
	146.98636	9306885	47.12	146.98638	-0.02	C_3OF_5
●	**334.97339**	5165671	26.16	334.97361	-0.22	C_6OF_{13}
●	**68.99467**	4172983	21.13	68.99466	0.00	CF_3
	96.98960	3956115	20.03	96.98958	0.02	C_2OF_3
	168.98820	3734020	18.91	168.98827	-0.07	C_3F_7
	284.97678	3170708	16.05	284.97680	-0.02	C_5OF_{11}
	118.99151	2798924	14.17	118.99147	0.04	C_2F_5
●	598.95755	17151.0	7.09	598.95689	0.66	$C_{11}HO_3F_{22}$

	m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
●	**266.98614**	270265.9	100.00	266.98622	-0.08	C_5HOF_{10}
	146.98634	90933.0	33.65	146.98638	-0.04	C_3OF_5
●	**68.99464**	87144.1	32.24	68.99466	-0.02	CF_3
●	**334.97337**	71494.7	26.45	334.97361	-0.24	C_6OF_{13}
	96.98955	55958.4	20.70	96.98958	-0.02	C_2OF_3
	284.97668	50059.2	18.52	284.97680	-0.12	C_5OF_{11}
	118.99147	40390.7	14.94	118.99147	0.00	C_2F_5
	168.98816	36106.7	13.36	168.98827	-0.11	C_3F_7

Figure S14. (A) GC−Orbitrap total ion chromatogram (TIC) comparison of Fluoroether E-3 standard (top) and degradation product of HFPO-TeA in acetone in 5 days in black color and acetone blank in gray color (bottom); (B) mass spectra of Fluoroether E-3 standard (top) and degradation product of HFPO-TeA in acetone in 5 days (bottom); (C) mass spectra list of Fluoroether E-3 standard (top) and degradation product of HFPO-TeA in acetone in 5 days (bottom).

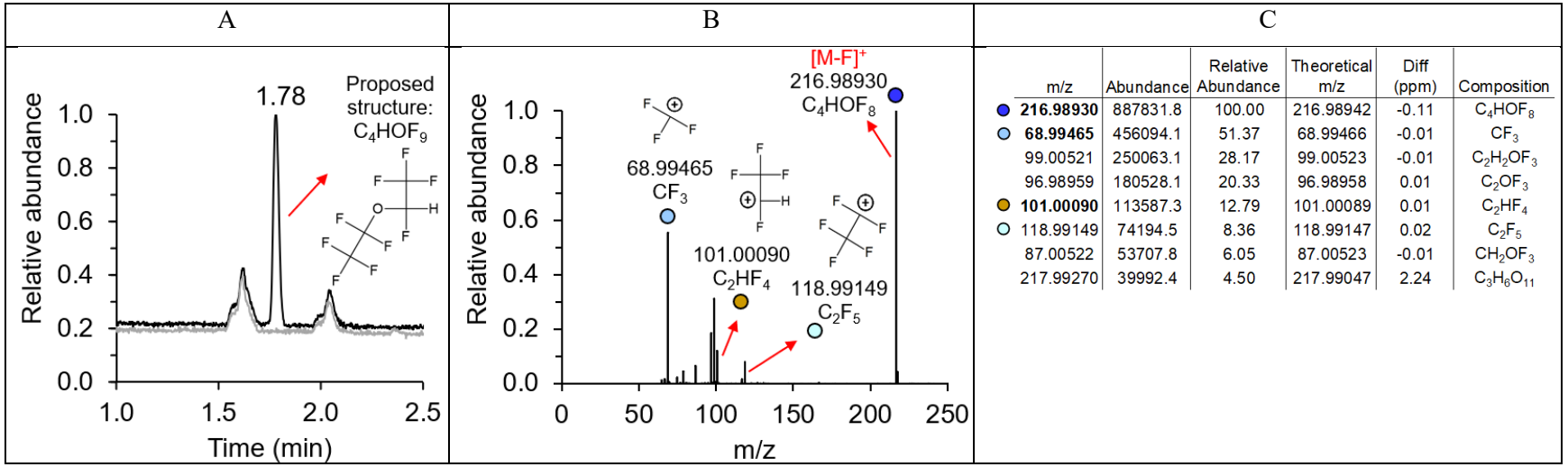
*m/z = 598.95755 was only observed in Fluoroether E-3 standard due to its relatively high abundance.



	m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
○	**166.99268**	1301957.8	100.00	166.99261	0.07	C_3HOF_6
	99.00531	435585.4	33.46	99.00523	0.08	$C_2H_2OF_3$
●	**101.00098**	429563.9	32.99	101.00089	0.09	C_2HF_4
●	**68.99473**	175884.0	13.51	68.99466	0.07	CF_3
	78.99908	135005.4	10.37	78.99900	0.09	C_2HOF_2
	119.01159	40762.2	3.13	119.01145	0.14	$C_2H_3OF_4$
	167.99606	37986.2	2.92	167.99929	-3.23	C_6HF_5
	117.01585	10284.7	0.79	117.01570	0.06	$C_2H_4O_2F_3$
	100.00863	8608.8	0.66	100.01191	-3.28	$C_5H_2F_2$
	102.00436	8543.1	0.66	102.00871	-4.36	$C_2H_2F_4$

	m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
○	**166.99249**	831842.8	100.00	166.99261	-0.12	C_3HOF_6
●	**101.00090**	281481.9	33.84	101.00089	0.01	C_2HF_4
	99.00521	272741.0	32.79	99.00523	-0.02	$C_2H_2OF_3$
●	**68.99466**	102998.9	12.38	68.99466	-0.02	CF_3
	78.99899	86248.6	10.37	78.99900	0.00	C_2HOF_2
	167.99587	31222.4	3.75	167.99929	-3.42	C_6HF_5
	119.01147	22653.5	2.72	119.01145	0.02	$C_2H_3OF_4$
	117.01570	5885.5	0.71	117.01579	-0.09	$C_2H_4O_2F_3$
	69.01465	5391.6	0.65	69.01465	0.01	CH_3OF_2
	102.00428	5342.4	0.64	102.00871	-4.44	$C_2H_2F_4$

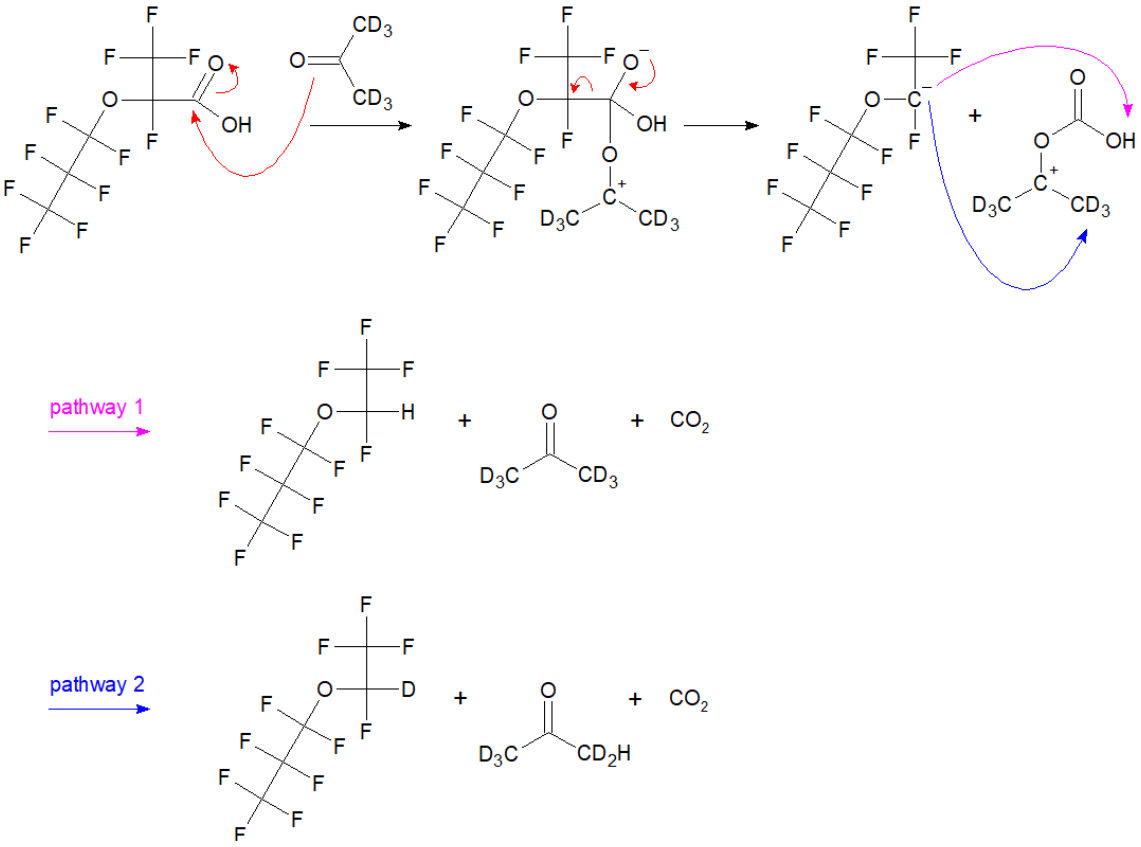
Figure S15. (A) GC−Orbitrap total ion chromatogram (TIC) comparison of degradation product of PMPA in acetonitrile in 5 days (top) and degradation product of PMPA in DMSO in 5 days (bottom); (B) mass spectra of degradation product of PMPA in acetonitrile in 5 days (top) and degradation product of PMPA in DMSO in 5 days (bottom); (C) mass spectra list of degradation product of PMPA in acetonitrile in 5 days (top) and degradation product of PMPA in DMSO in 5 days (bottom). Solvent blanks are depicted in gray color in (A).



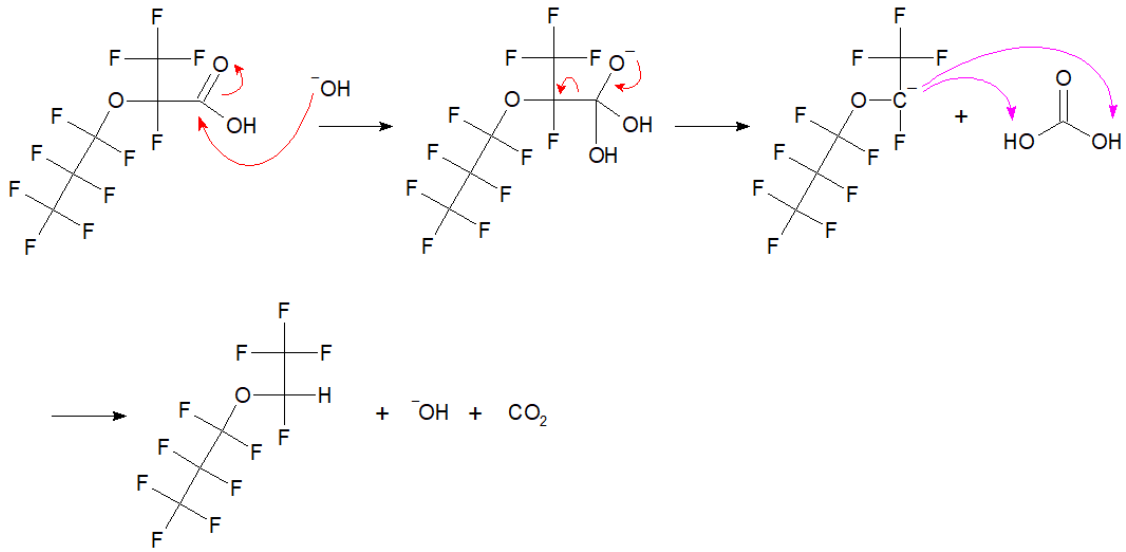
	m/z	Abundance	Relative Abundance	Theoretical m/z	Diff (ppm)	Composition
●	**216.98930**	887831.8	100.00	216.98942	-0.11	C_4HOF_8
●	**68.99465**	456094.1	51.37	68.99466	-0.01	CF_3
	99.00521	250063.1	28.17	99.00523	-0.01	$C_2H_2OF_3$
	96.98959	180528.1	20.33	96.98958	0.01	C_2OF_3
●	**101.00090**	113587.3	12.79	101.00089	0.01	C_2HF_4
●	118.99149	74194.5	8.36	118.99147	0.02	C_2F_5
	87.00522	53707.8	6.05	87.00523	-0.01	CH_2OF_3
	217.99270	39992.4	4.50	217.99047	2.24	$C_3H_6O_{11}$

Figure S16. (A) GC−Orbitrap total ion chromatogram (TIC) of degradation product of PEPA in acetone in 5 days in black color and acetone blank in gray color; (B) mass spectra of degradation product of PEPA in acetone in 5 days; (C) mass spectra list of degradation product of PEPA in acetone in 5 days.

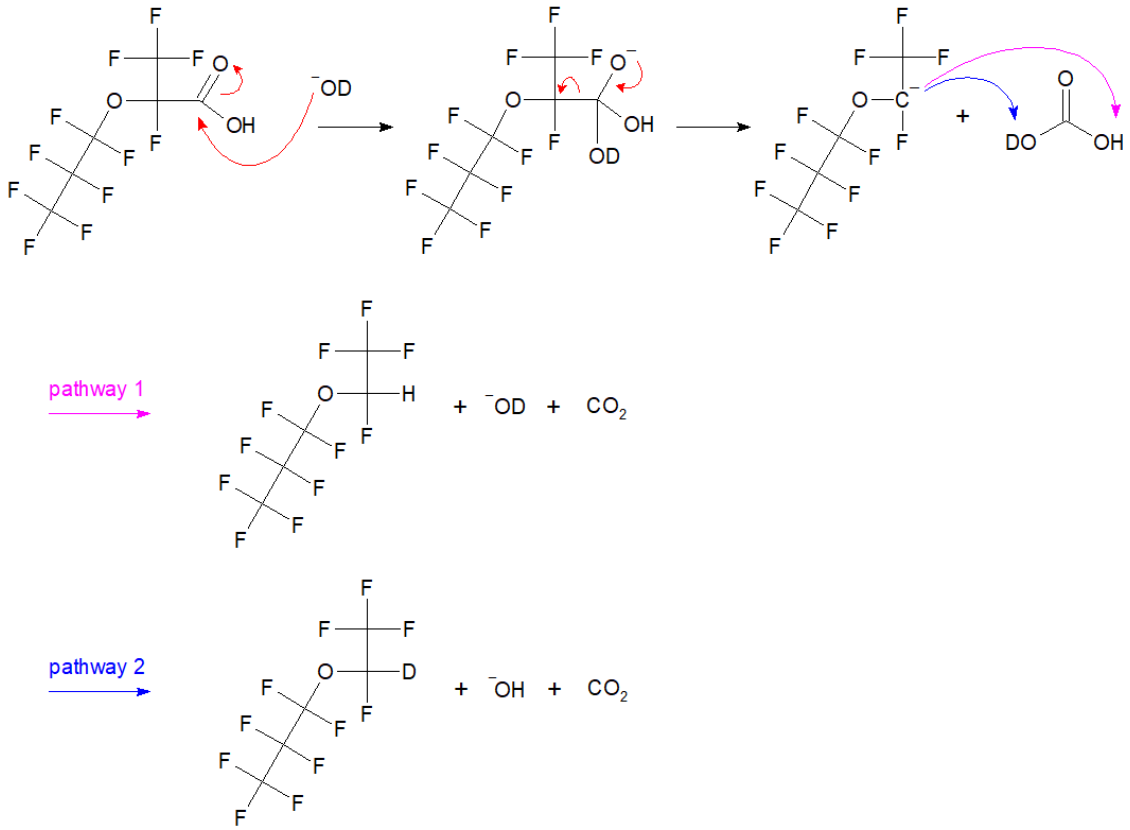
Scheme 1



Scheme 2



531 **Scheme 3**



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Scheme 4 [proposed in Liberatore et al. (2020)[4]]

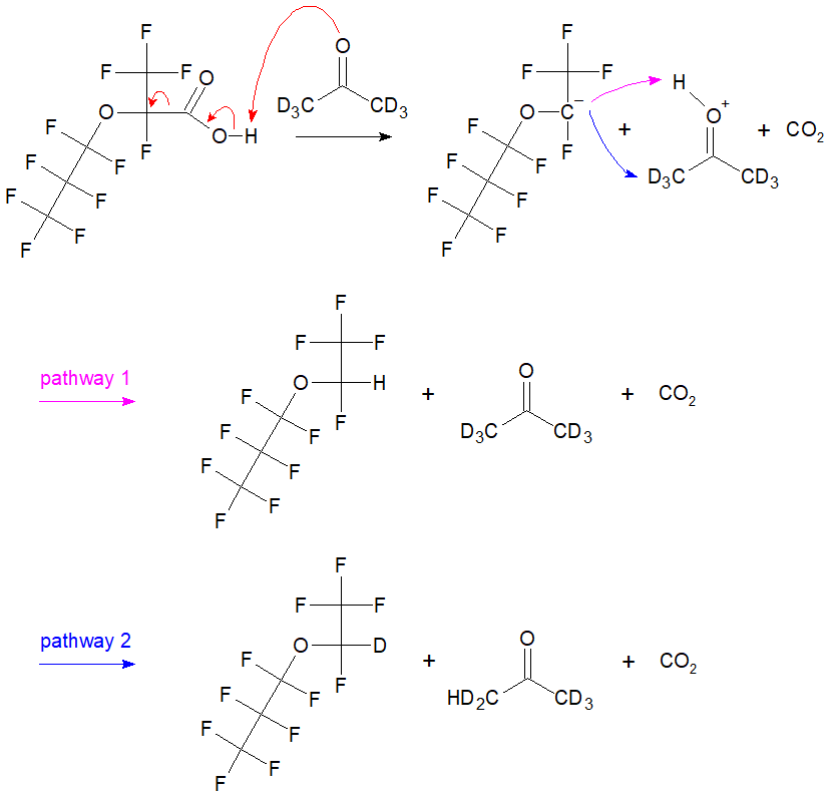

Figure S17. Proposed mechanisms of HFPO-DA degradation of Fluoroether E-1 in deuterated acetone.

Note: arrow shows the direction of electron attack.

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