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Article

Thermal Decomposition of Anionic, Zwitterionic, and Cationic Polyfluoroalkyl Substances in Aqueous Film-Forming Foams

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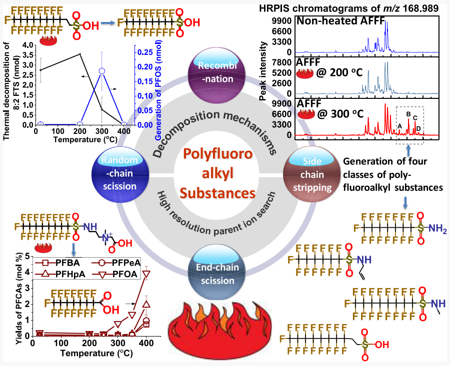

ABSTRACT: In this study, we investigated thermal decomposition mechanisms of cationic, zwitterionic, and anionic polyfluoroalkyl substances, including those present in aqueous film-forming foam (AFFF) samples. We present novel evidence that polyfluoroalkyl substances gave quantitative yields of perfluoroalkyl substances of different chain lengths during thermal treatment. The results support a radical-mediated transformation mechanism involving random-chain scission and end-chain scission, leading to the formation of perfluoroalkyl carboxylic acids such as perfluorooctanoic acid (PFOA) from certain polyfluoroalkyl amides and sulfonamides. Our results also support a direct thermal decomposition mechanism (chain stripping) on the nonfluorinated moiety of polyfluoroalkyl sulfonamides, resulting in the formation of perfluorooctanesulfonic acid (PFOS) and other structurally related polyfluoroalkyl compounds. Thermal decomposition of 8:2 fluorotelomer sulfonate occurred through end-chain scission and recombination reactions, successively yielding PFOS. All of the studied polyfluoroalkyl substances began to degrade at 200−300 °C, exhibiting near-complete decomposition at ≥400 °C. Using a high-resolution parent ion search method, we demonstrated for the first time that low-temperature thermal treatments of AFFF samples led to the generation of anionic fluoroalkyl substances, including perfluoroheptanesulfonamide, 8:2 fluorotelomer sulfonic acid, *N*-methyl perfluorooctane sulfonamide, and a previously unreported compound *N*-2-propenyl-perfluorohexylsulfonamide. This study provides key insights into the fate of polyfluoroalkyl substances in thermal processes.

KEYWORDS: *PFAS, thermal transformation, precursor compounds, thermal generation of PFAS, thermal decomposition of PFAS, decomposition mechanisms, high-resolution PIS*

■ INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic compounds that have been produced for decades and used primarily as surface-active agents in various industrial and commercial products, including nonstick cookware and aqueous film-forming foams (AFFFs) for fire suppression.[1−4] Technical formulations of PFASs have been produced by electrochemical fluorination and telomerization,[5] which form a diverse set of compounds,[1,6−9] including high-volume production chemicals such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), as well as unintentionally produced byproducts. PFASs are recalcitrant to degradation at ambient temperature and are not easily removed in conventional drinking-water and wastewater treatment processes.[10−15] These properties have been responsible for the widespread and lasting environmental contamination problems associated with PFASs. Various advanced technologies, including electrochemical methods,[16−18] photocatalysis,[19,20] biological approaches,[21,22] and plasma-based treatments,[23,24] have been examined to remove or decompose PFAS in contaminated water and soil.

PFASs have been frequently reported to be thermally stable in the literature. Contradictory to this prevailing view, Xiao et al. recently demonstrated that the thermal decomposition of PFOA occurred at low temperatures of 150−200 °C.[25,26] Thermal decomposition of PFOA appears to begin with the hemolytic cleavage of the C−C bond linking the perfluoroalkyl chain and the carboxyl group and proceed through radical-mediated chain propagation reactions.[26,27] Granular activated carbon or other highly porous materials can alter the thermal decomposition pathway of perfluoroalkyl carboxylates (e.g., PFOA) and GenX and substantially accelerate their decomposition at low and moderate temperatures (<400 °C).[26] From a remediation perspective, Crownover et al. examined the decontamination of soil containing perfluoroalkyl substances

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by heating the soil to a specific temperature to vaporize the chemicals (i.e., thermal desorption).[28] A reduction of up to 99.998% of perfluoroalkyl substances in soil was observed after 10−14 days of heating at 200−400 °C under an airflow.[28] Gerhard and co-workers treated soil and granular activated carbon laden with perfluoroalkyl substances by smoldering combustion at much higher temperatures (>900 °C).[29] The authors observed a substantial PFOS removal of up to >99.9995% from the treated media.[29] Strathmann and co-workers recently developed a hydrothermal treatment[30,31] that can effectively decompose a variety of PFASs at near-critical temperature and pressure (350 °C; 16.5 MPa) within 15−30 min.[31]

While these recent studies[25,28−31] have provided significant insight into the fate of PFASs in thermal processes, a fundamental understanding of certain vital aspects is still limited. Previous studies[25,28,29] have focused on perfluoroalkyl substances, whereas a general understanding of the thermal stability and decomposition mechanisms of polyfluoroalkyl substances is lacking. AFFF samples typically contain a significant amount of polyfluoroalkyl substances. The term "polyfluoroalkyl substances" comprises compounds where many, but not all, H atoms attached to C atoms in nonfluorinated analogues have been replaced by F atoms. Polyfluoroalkyl substances (such as polyfluoroalkyl amides and polyfluoroalkyl sulfonamides) are often found to have a perfluoroalkyl chain attached to one or more nonfluorinated moieties.[1] More than 400 sites have been identified in the United States where there are known or suspected releases of PFASs due to the use of AFFFs for fire training.[32] Systematic studies examining the possible decomposition of polyfluoroalkyl substances or AFFFs in thermal processes such as fire training, natural wildfires, and biomass burning for land clearing are scarce and incomplete. The fate of polyfluoroalkyl substances in thermal processes is also an important element of consideration in the selection, modification, and operation of thermal technologies for remediation of AFFF-impacted sites.

This study was carried out to understand the thermal stability and decomposition mechanisms of polyfluoroalkyl substances, which have remained elusive so far. We hypothesized that the thermal treatment of polyfluoroalkyl substances can lead to the formation of other classes of polyfluoroalkyl substances or even perfluoroalkyl substances such as PFOA and PFOS. To test this hypothesis, thermal decomposition of model cationic, zwitterionic, and anionic polyfluoroalkyl substances and four 3M AFFF samples was investigated. Cationic and zwitterionic PFASs account for ∼50% of newly identified PFAS compounds[4] and have been found to compose up to 97% of the total PFAS mass in an AFFF-impact area.[33] Qualitative and quantitative information was obtained using high-resolution mass spectrometry (HRMS) and an innovative high-resolution parent ion search (HRPIS) method developed on a Waters quantitative time-of-flight mass spectrometer (ToF MS).[34] This system allows for the simultaneous acquisition of both MS and MS/MS fragmentation data during a single chromatographic run using alternating low- and high-collision energy scans (MS^E) (Figure 1).[35] The ToF MS^E HRPIS method selectively identifies parent PFAS compounds by employing characteristic fragments as a marker,[34] which has been validated with the certified standards of PFASs and used to identify 90 emerging polyfluoroalkyl substances in commercial surfactant concentrates.[34]

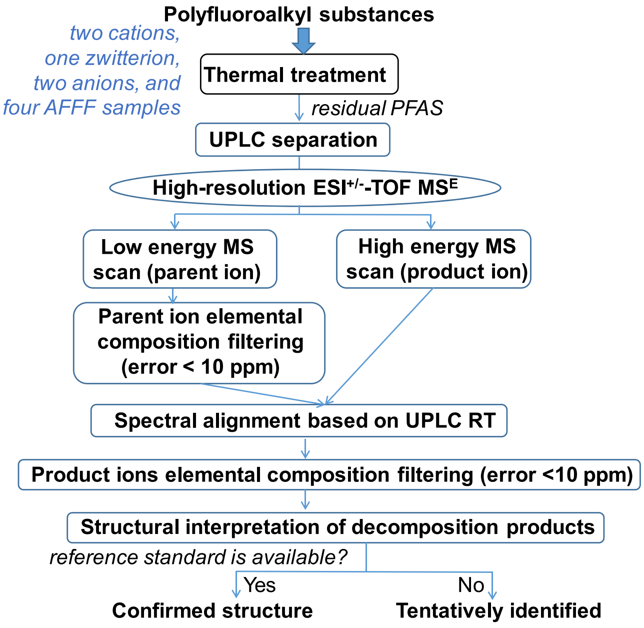


Figure 1. Workflow for identification of thermal decomposition products of polyfluoroalkyl substances using ultra-high-pressure liquid chromatography (UPLC)−ESI-ToF MS^E HRPIS (RT: retention time).

MATERIALS AND METHODS

PFAS Chemicals and AFFF. A few cationic and zwitterionic polyfluoroalkyl substances, such as perfluorooctaneamido ammonium salt (PFOAAmS), perfluorooctanesulfonamido ammonium salt (PFOSAmS), and perfluorooctanesulfonamido betaine (PFOSB) (Table S1), with available genuine standards were included in this study. These substances have been identified in AFFFs and Fluorad brand surfactant samples.[1,34,36] We also included two anionic polyfluoroalkyl substances, 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA) and the sodium salt of 8:2 fluorotelomer sulfonic acid (8:2 FTS) (Table S1), both of which have been frequently found in environmental samples.[37,38] Furthermore, four 3M AFFF samples (Table S2) were included.

To confirm decomposition products of polyfluoroalkyl substances, the reference standards of the following perfluoroalkyl substances (Table S3) were prepared: perfluorobutyric acid (PFBA); perfluoropentanoic acid (PFPeA); perfluoroheptanoic acid (PFHpA); PFOA; and the potassium salts of perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and PFOS.

Thermal Treatment of Model Polyfluoroalkyl Substances. A known quantity of polyfluoroalkyl substance powders was added into a reactor as described previously.[25] The reactor was then capped with a ground-glass stopper and heated within a muffle furnace (Neytech, Vulcan 3-550, USA) from room temperature (22 °C) to a predetermined temperature (100, 200, 300, 400, 500 °C) at a 10 °C/min heating rate.

Thermal Treatment of AFFF. Twenty microliters of an AFFF liquid were dissolved in 50 mL of methanol (Optima; LC/MS grade) and equilibrated for >48 h before use. Then, a 1 mL aliquot of the methanol solution was added to a reactor (without stopper) and dried in a forced-air oven at 25 °C (Cascade Tek, Cornelius, OR). The reactor was subsequently

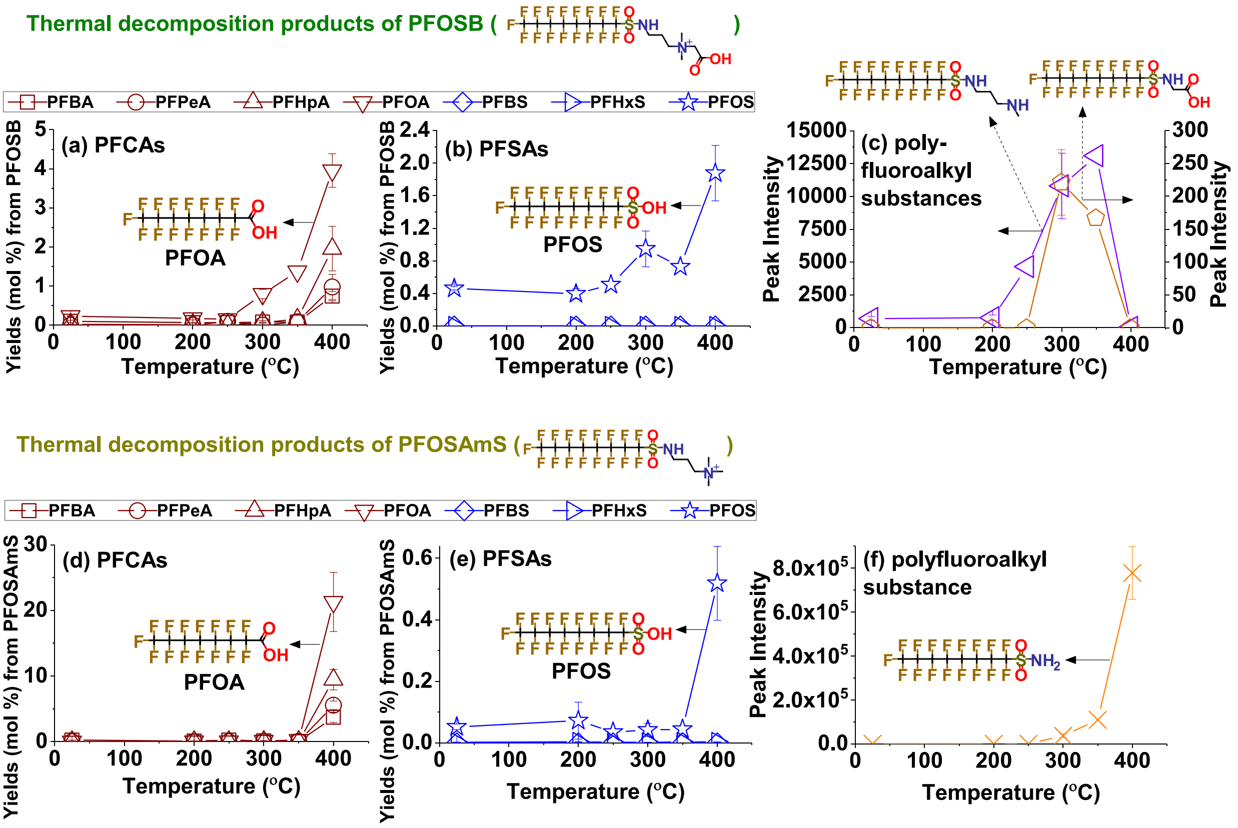


Figure 2. Generation of perfluoroalkyl carbonates, perfluoroalkyl sulfonates, and polyfluoroalkyl substances from zwitterionic (PFOSB) and cationic (PFOSAmS) PFASs during thermal treatments. Detection of these degradants was achieved mainly by HRPIS.

capped with a ground-glass stopper, transferred to the muffle furnace, and heated to a predetermined temperature at a 10 °C/min heating rate.

UPLC and HRMS. Once the temperature reached the target value, the reactor was taken out of the furnace and cooled to ambient temperature. Then, a known volume of methanol and ammonium acetate at 100 mmol/L were added.[25] The residual PFAS and decomposition products in methanol were analyzed using a Waters Acquity ultra-high-pressure liquid chromatography (UPLC) system coupled with a Waters high-resolution quantitative ToF MS (Synapt G2-S, Waters Corporation, Milford, MA) (Figure 1). Chromatography was performed using a Waters Acquity UPLC BEH Shield RP18 column (100 × 2.1 mm^2; 130 Å; 1.7 μm) with a Waters Acquity UPLC BEH Shield RP18 VanGuard precolumn (5 × 2.1 mm^2; 130 Å; 1.7 μm).[39] The mobile phase consisted of eluent A (2 mM ammonium formate in Optima water; LC/MS grade) and eluent B (2 mM ammonium formate in Optima methanol; LC/MS grade).[39] Mass spectrometry analysis was performed using the Synapt G2-S ToF MS with an ESI source either in a negative (ESI$^-$) or positive (ESI$^+$) ion mode. The analyzer was operated with an extended dynamic range at 10 000 resolution (full width at half-maximum (FWHM) at *m*/*z* 554) with an acquisition time of 0.1 s. More details can be found in the Supporting Information.

HRPIS Experiments. The identification of thermal decomposition products of PFASs was conducted in two major steps (Figure 1).[34] In brief, HRPIS was performed after aligning MS and MS/MS extracted ion chromatograms generated from UPLC−ESI-ToF MS^E data using the MassLynx V4.1 software. The parent MS and characteristic MS/MS spectra aligned with characteristic fragment ions were then examined, and the candidate PFAS parent compounds were identified using HRPIS[34] with a mass error tolerance of 10 ppm. The accuracy of HRPIS was evaluated by the difference (error) between the measured mass and the calculated exact mass

$$\text{error (in ppm)} = \frac{[\text{measured mass (Da)} - \text{exact mass (Da)}]}{\text{exact mass (Da)}} \times 10^{-6} \qquad (1)$$

RESULTS AND DISCUSSION

Radical-Mediated Decomposition Pathway. We found that the studied cationic and zwitterionic PFASs gave quantitative yields of PFOA and PFOS during thermolysis (Figure 2). The yield of PFOA from PFOSAmS (cationic), a potential PFOS precursor compound, reached 21.3 mol % at 400 °C (Figure 2). A much more moderate generation of PFOA (<5 mol %) was observed during the thermolysis of PFOSB (zwitterionic; Figure 2) and a cationic polyfluoroalkyl amide (PFOAAmS; Figure S1). The yield of PFOS from both PFOSAmS and PFOSB was minor compared to that of PFOA (Figure 2). These cationic and zwitterionic PFASs also yielded a few polyfluoroalkyl substances (Figure 2).

The results presented in Figure 2 revealed two thermal decomposition mechanisms of polyfluoroalkyl substances: (i) a radical-mediated mechanism leading to the generation of PFOA and homologues and (ii) a chain-stripping mechanism by which the nonfluorinated moiety is eliminated (Figure 3).

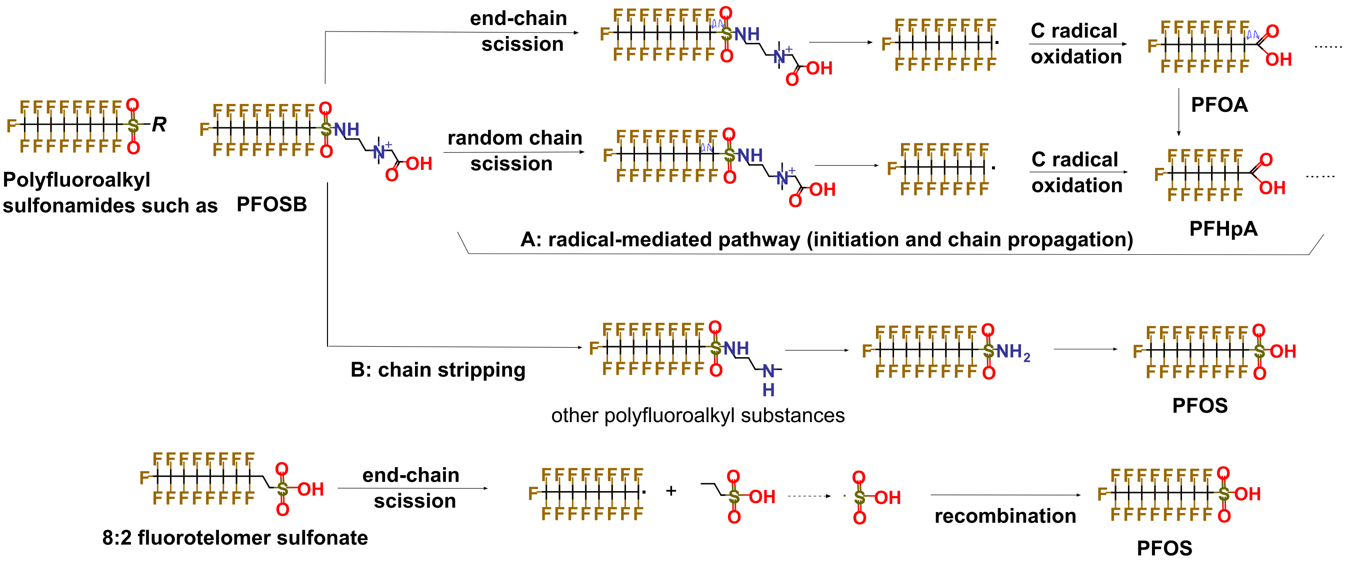
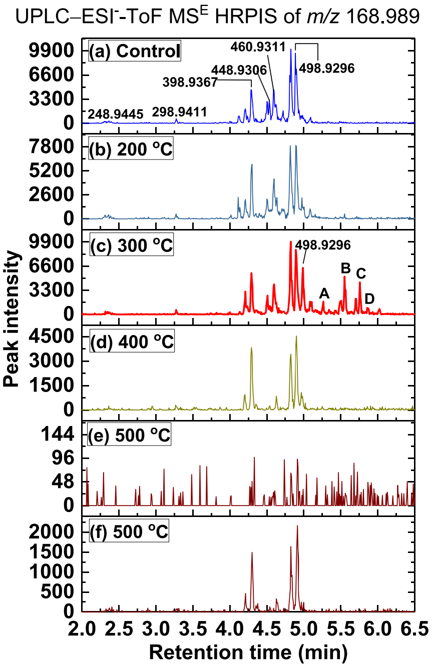
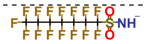
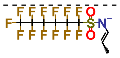
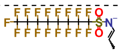


Figure 3. Thermal decomposition pathways of the studied polyfluoroalkyl substances.



	Structure of generated PFAS	Ion formula	m/z^a	m/z^b	Error (ppm)
A		$C_7HF_{15}NO_2S^-$	447.9486	447.9494	-1.8
B		$C_9H_5F_{13}NO_2S^-$	437.9843	437.9839	0.9
C		$C_9H_3F_{17}NO_2S^-$	511.9633	511.9619	2.7
D		$C_{11}H_5F_{17}NO_2S^-$	537.9749	537.9775	-4.8

^{a}: observed m/z; ^{b}: exact m/z.

Figure 4. Thermal decomposition of PFAS in an AFFF sample (#1) at different temperatures (nonheated control to 500 °C) as illustrated by UPLC−ESI$^-$-ToF MS^E HRPIS chromatograms on m/z 168.989 ($C_3F_7^-$).[34] (a−e) Samples were diluted 50 times before UPLC−ESI$^-$-ToF MS^E analysis to achieve satisfactory peak separation in the UPLC system. (f) Undiluted sample. See Figures S4−S6 for UPLC−ESI$^-$-ToF MS^E HRPIS chromatograms on m/z 168.989 of other AFFF samples (#2−#4).

In the first pathway, the thermal decomposition of polyfluoroalkyl substances involves multistep radical chain reactions, including initiation, chain propagation, and termination (Figure 3). Two types of initiation were involved. (1) End-chain scission: PFASs are broken up from the bond between the perfluoroalkyl chain and the nonfluorinated side chain. This creates a perfluoroalkyl radical that further undergoes C radical oxidation yielding PFOA (Figure 3).[39,40] (2) Random-chain scission: the breaking off of a C−C bond at seemingly random locations on the perfluoroalkyl chain. The resultant perfluoroalkyl radicals undergo C radical oxidation, generating perfluoroalkyl carboxylic acids of different chain lengths, including PFHpA (Figures 2 and 3). Thermal decomposition of PFOA also produces PFHpA.[26]

Degradation on Nonfluorinated Side Chains of Polyfluoroalkyl Substances. The second decomposition pathway involves thermal decomposition of the nonfluorinated moiety of cationic/zwitterionic polyfluoroalkyl sulfonamides (e.g., PFOSB), which produced PFOS and other polyfluoroalkyl substances (Figures 2 and 3). A similar phenomenon was observed during the thermal decomposition of anionic polyfluoroalkyl substances, namely, *N*-MeFOSAA and 8:2 FTS (Figures S2 and S3). The generation of PFOS from 8:2 FTS involved recombination reactions in which the perfluoroalkyl

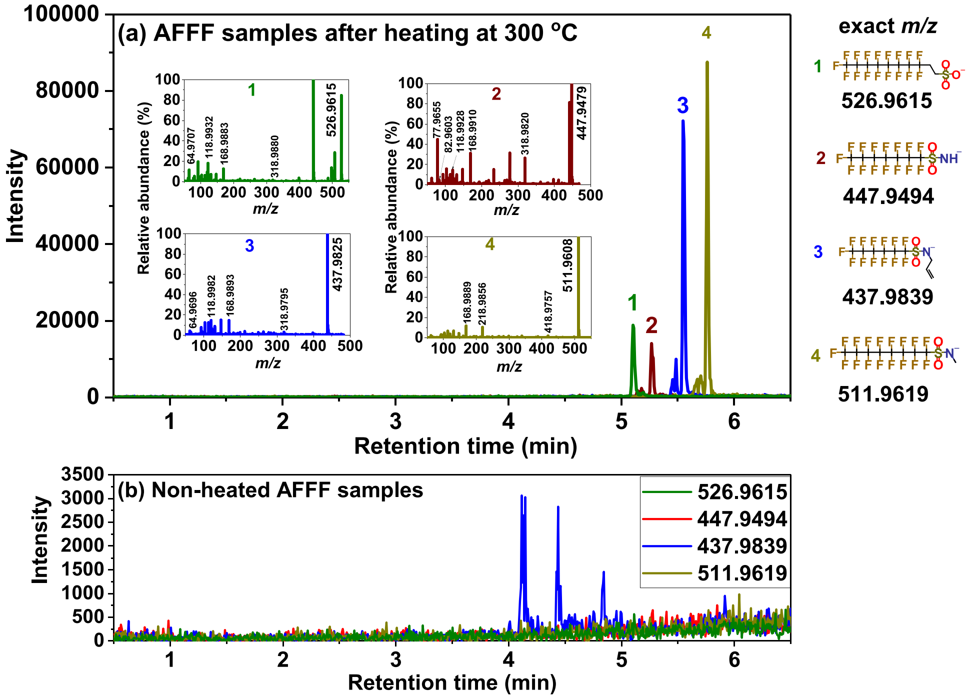


Figure 5. UPLC−ESI⁻-ToF MS^E selected ion current chromatograms. The insets in (a) display the UPLC−ESI⁻-ToF MS^E spectra of four generated polyfluoroalkyl substances. The observed m/z value of compound #1 (8:2 FTS) happened to be the same as its exact mass.

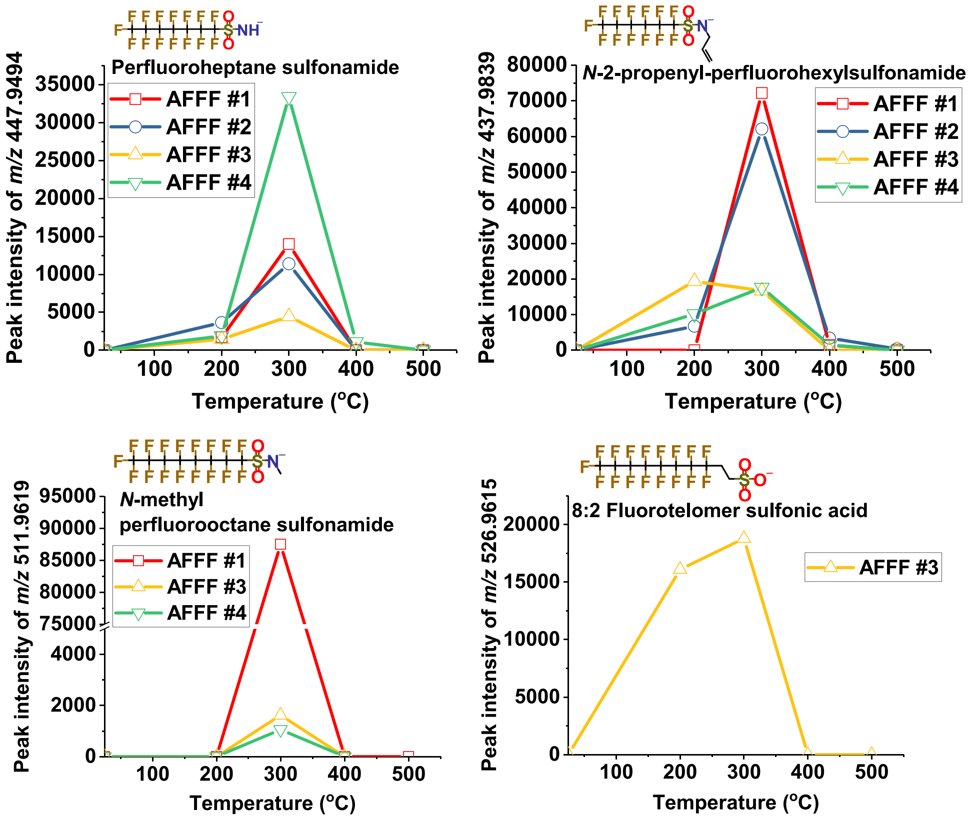


Figure 6. Polyfluoroalkyl substances formed during the thermal treatment of AFFF samples at 200−400 °C as illustrated by UPLC−ESI⁻-ToF MS^E peak intensities of their respective m/z values. All samples were handled in the same manner before the UPLC−ESI⁻-ToF MS^E analysis.

radical recombines with the sulfonate group successively yielding PFOS (Figure 3).

HRPIS Analysis of the Thermal Treatment of AFFF. The HRPIS technique arises from the parent (precursor) ion scan (PIS) carried out on triple quadrupole MS systems for the detection of chlorinated/brominated compounds with the relative abundance ratio of Cl/Br isotopes as a diagnostic tool.[41−45] ^{19}F is the only stable isotope of F. However, we

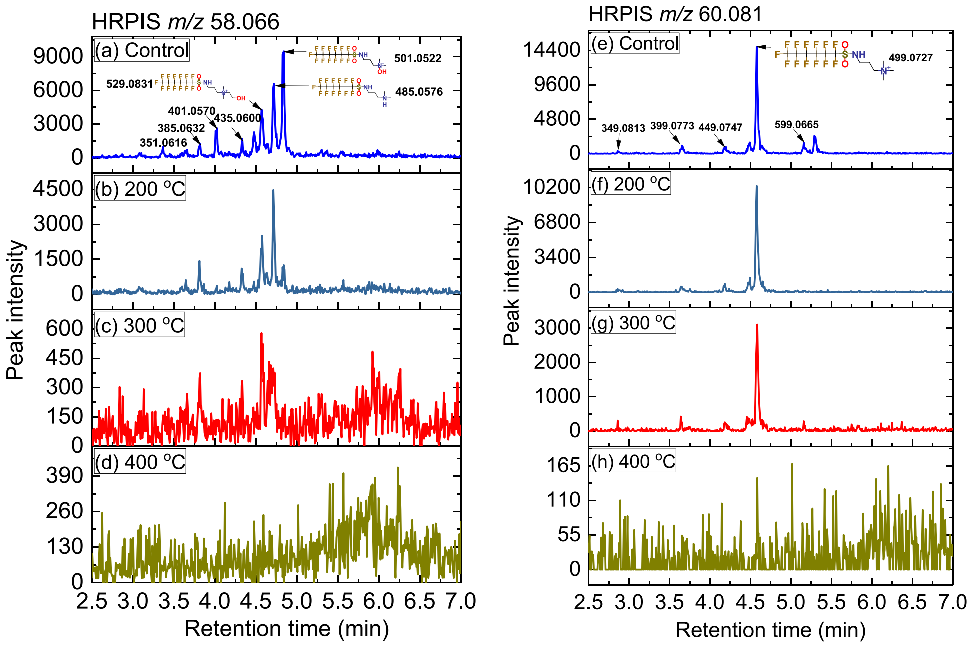


Figure 7. UPLC−ESI$^+$-ToF MS^E HRPIS chromatograms on m/z 58.066 ($-N^{+}$) and m/z 60.081 ($-NH^{+}$) of an AFFF sample (AFFF #2) at different temperatures (nonheated control to 400 °C). UPLC−ESI$^+$-ToF MS^E HRPIS chromatograms of other AFFF samples can be found in Figures S7−S12.

previously demonstrated that anionic PFAS can be selectively detected by performing HRPIS on characteristic fragments (e.g., C_3F_7 (*m/z* of 168.989)) on the UPLC−ESI-ToF MS^E system.[34]

Thermal decomposition of PFASs in AFFFs was illustrated by UPLC−ESI$^-$-ToF MS^E HRPIS chromatograms (Figures 4 and S4−S6). Based on the *m/z* values and the UPLC retention times (RTs), the peaks at RTs of 2.361, 3.274, 4.292, 4.591, and 4.886 min in Figure 4a represent perfluoropropanesulfonate ($C_3F_7SO_3^-$; *m/z* 248.9445), PFBS ($C_4F_9SO_3^-$; *m/z* 298.9411), PFHxS ($C_6F_{13}SO_3^-$; *m/z* 398.9367), perfluoroheptanesulfonate ($C_7F_{15}SO_3^-$; *m/z* 448.9306), and PFOS ($C_8F_{17}SO_3^-$; *m/z* 498.9296), respectively. Interestingly, a few new anionic PFAS compounds were generated as shown in UPLC−ESI$^-$-ToF MS^E HRPIS chromatograms on *m/z* 168.989 (Figure 4c).[34]

The peak at the UPLC RT of 5.265 min corresponds to a PFAS compound with *m/z* 447.9479 (A in Figure 4c). The associated MS^E spectrum illustrates fragments, including SO_2N^- (*m/z* 77.966), FO_2S^- (*m/z* 82.960), and perfluorinated species ($C_2F_5^-$, $C_3F_7^-$, $C_6F_{13}^-$) (Figure 5). After subtracting *m/z* 318.9795 ($C_6F_{13}^-$) and *m/z* 77.9655 (SO_2N^-) from *m/z* 447.9479, the remaining part is $-CF_2H$ (*m/z* 51.005); therefore, we believe this compound to be perfluoroheptanesulfonamide ($C_7HF_{15}NO_2S^-$; 447.9486). A genuine standard for perfluoroheptanesulfonamide is not available. The error between measured and theoretical *m/z* values was −1.8 ppm (Figure 4).

The MS^E spectra at the UPLC RT of 5.108 min indicate another compound with *m/z* 526.9615 and its fragment ions, including HO_2S^- (*m/z* 64.9703), $C_2F_5^-$ (*m/z* 118.9926), $C_3F_7^-$ (*m/z* 168.9894), and $C_6F_{13}^-$ (*m/z* 318.9798) (Figure 5). We tentatively assigned the formula of $C_{10}H_4F_{17}O_3S^-$ to this compound, which was confirmed as 8:2 FTS with the reference standard. Similarly, the compound at the UPLC RT of 5.759 min was confirmed to be *N*-MeFOSA with the corresponding reference standard.

The compound at the UPLC RT of 5.552 min had a previously unreported *m/z* of 437.9825 (Figures 4c and 5), indicating a possible new PFAS. According to its MS^E fragments ($C_2F_5^-$, *m/z* 118.9982; $C_3F_7^-$, *m/z* 168.9893; $C_6F_{13}^-$, *m/z* 318.9795; HO_2S^-, *m/z* 64.9696), we assigned the formula of $C_9H_5F_{13}NO_2S^-$ to the deprotonated form of this compound. This led to four possible structures (Table S4). After considering the other polyfluoroalkyl substances (e.g., *N*-MeFOSA) generated during thermal treatments of AFFF samples, we tentatively assigned it to be *N*-2-propenyl-perfluorohexylsulfonamide (CAS: 67584-48-9) (Figures 4 and 5). The genuine standard of this compound is unavailable.

The occurrence of these anionic polyfluoroalkyl substances indicates that the temperature was sufficient to cause partial decomposition of the nonfluorinated moiety of their parent compounds but was not high enough for the complete stripping of the nonfluorinated group. These four anionic polyfluoroalkyl substances appeared at ∼200 °C and reached maximum abundance at 300 °C (Figure 6). Two compounds, including the newly identified PFASs, were generated in all four AFFF samples. *N*-MeFOSA was generated in three AFFF samples, while 8:2 FTSA was only produced in one AFFF sample after the thermal treatment. All compounds decomposed when the temperature was increased to 400 °C and above.

We also investigated whether cationic/zwitterionic polyfluoroalkyl substances were generated. Xiao et al. previously reported that the UPLC−ESI$^+$-ToF MS^E HRPISs of *m/z* 58.066 ($-N^{+}$) and *m/z* 60.081 ($-NH^{+}$) can be used to identify cationic/zwitterionic polyfluoroalkyl substances in PFAS-based surfactant concentrates.[34] This HRPIS method also appears to function well for AFFF samples. A number of

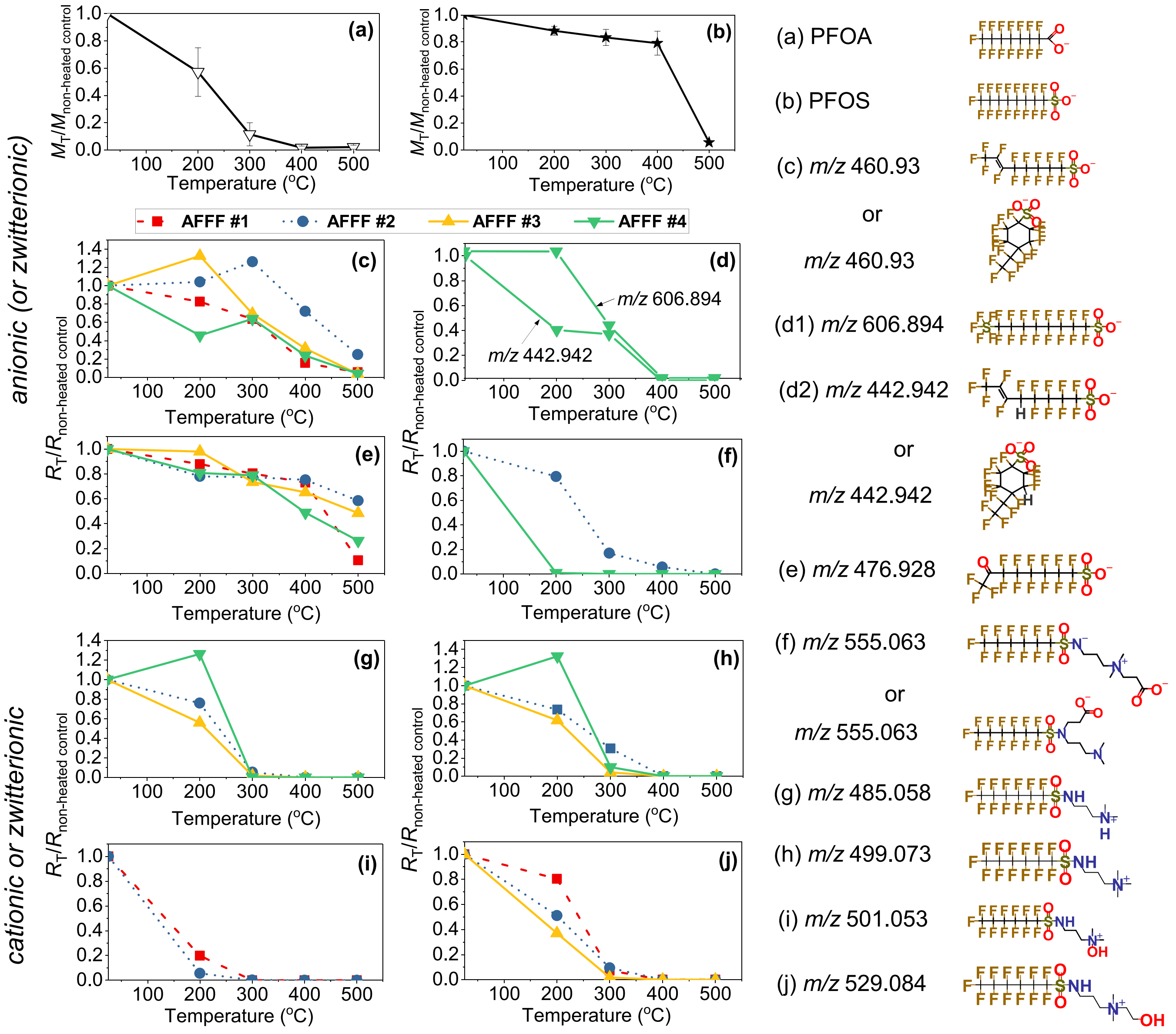


Figure 8. Thermal decomposition of PFASs present in AFFFs at different temperatures. M_T refers to the residual mass of PFOA/PFOS at a given temperature. R refers to the UPLC−ESI-ToF MS peak intensity for polyfluoroalkyl substances in AFFFs that cannot be quantified due to the lack of authentic standards.

cationic or zwitterionic PFAS compounds were identified in raw AFFF, which began to decompose at 200 °C (Figures 7 and S7−S12). The generation of new cationic and zwitterionic polyfluoroalkyl substances was not evident during thermal AFFF treatments (Figures 7 and S7−S12).

Figure 8 illustrates the thermal decomposition of all PFASs in 11 classes identified in AFFFs for this study. Figures S13−S21 display the corresponding UPLC−ESI$^+$-ToF MS and MS^E spectra. These classes were reported by previous researchers in AFFFs and environmental samples.[1,36,46,47] The compound with *m*/*z* 460.93 represents unsaturated perfluorooctane sulfonate or perfluoro-ethyl-cyclohexane sulfonate (class c). Approximately 76−94% reduction of the peak intensity of class c PFAS compounds was observed after the thermal treatment. The PFAS in class d1 is penta-fluoro-perfluoroalkyl sulfonate. The PFAS in class d2 is structurally similar to that in class c, except that one F atom on the perfluorinated chain has been replaced by an H atom. PFASs in both classes d1 and d2 showed complete degradation at 400 °C. The compound with *m*/*z* 476.928 represents a keto-perfluorooctane sulfonate (class e). Compounds in classes f−j are polyfluoroalkyl substances having a relatively long nonfluorinated side chain that is subject to side-chain stripping. As expected, PFASs in these five classes (f−j) were less thermally stable than PFASs in other classes (Figure 8). Substantial thermal decomposition of all polyfluoroalkyl substances in AFFFs was observed at 300 °C (Figure 8), the same temperature at which the generation of the anionic PFAS compounds (e.g., *N*-MeFOSA) was maximized (Figure 6). However, it is practically impossible to pinpoint the precursor compounds of these anionic PFASs (Figures 4−6).

While theoretically all PFAS compounds in a sample can be detected by HRPIS, it is more suitable for the detection of major, high-abundance PFAS species. Certain low-abundance PFAS species may not be detected by HRPIS. Nevertheless, the results of this study clearly indicate that polyfluoroalkyl substances can readily transform into other types of polyfluoroalkyl substances and even perfluoroalkyl substances in thermal processes. Such a transformation may occur in the natural environment at ambient temperature, albeit at a possibly slower rate, which warrants further investigation.

Furthermore, this study contributes to the broader discussion on the relative importance of direct and indirect sources of perfluoroalkyl substances. Our results provide further evidence that perfluoroalkyl substances (e.g., PFOA and PFOS) and certain polyfluoroalkyl substances detected at AFFF-impacted sites (soil/groundwater) may actually be transformation products of polyfluorinated compounds. Transformation of polyfluoroalkyl substances to perfluoroalkyl substances has also been observed in chemical and biological systems.[39,48−51] However, the indirect source of PFOA and PFOS has not received sufficient attention in current regulatory efforts.

Lastly, this study is highly relevant in practice because thermal approaches have been applied for remediation of PFAS-contaminated sites. The findings suggest that moderate thermal treatment (e.g., thermal desorption) of AFFF-contaminated matrices may inadvertently contribute to the generation of certain PFAS compounds. Therefore, it is envisaged that the results of this work will aid in the planning of strategic remediation programs or in improving current thermal remediation practices to limit the unwanted production of PFASs from precursor compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c02125.

> UPLC−chromatography conditions, ToF MS^E, model anionic, cationic, and zwitterionic polyfluoroalkyl compounds (Table S1); AFFF samples (Table S2); PFAS chemicals used to confirm decomposition products of polyfluoroalkyl substances (Table S3); four possible structures for $C_9H_5F_{13}NO_2S$ (Table S4); generation of perfluoroalkyl substances from a cationic polyfluoroalkyl amide during thermal treatment (Figure S1); thermal decomposition of *N*-MeFOSAA and 8:2 FTS and generation of PFOS (Figures S2 and S3, respectively); thermal decomposition of PFAS in AFFF samples as illustrated by UPLC−ESI$^-$-ToF MS^E HRPIS chromatograms on *m/z* 168.989 (Figures S4−S6); thermal decomposition of PFASs in AFFF samples as illustrated by UPLC−ESI$^+$-ToF MS^E HRPIS chromatograms on *m/z* 58.066 and *m/z* 68.081 (Figures S7−S12); and UPLC−ESI$^+$-ToF MS and MS^E spectra of PFASs identified in AFFF samples (Figures S13−S21) (PDF)

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Notes

The authors declare no competing financial interest.

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