

Research Paper

The first quantitative investigation of compounds generated from PFAS, PFAS-containing aqueous film-forming foams and commercial fluorosurfactants in pyrolytic processes



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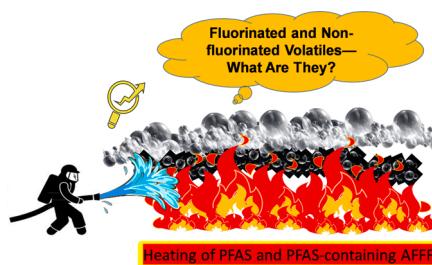
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HIGHLIGHTS

- Compounds emitted from PFAS-relevant commercial products and PFAS upon pyrolysis.
- Approximately 30 non-fluorinated compounds were detected at 200–500 °C.
- 1,4-Dioxane was emitted from multiple heated AFFF and fluorosurfactant samples.
- Perfluoroheptene (C_7F_{14}) thermally decomposed at temperatures as low as 200 °C.
- Most of these compounds were not detected at 890 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Teresa A.P. Rocha-Santos

Keywords:

Thermal transformation
Cationic and zwitterionic PFAS
Perfluoroalkenes
Radical-chain reactions
Aromatics and heteroaromatics

ABSTRACT

Pyrolysis as a thermochemical technology is commonly used in waste management and remediation of organic-contaminated soil. This study, for the first time, investigated fluorinated and non-fluorinated compounds emitted from per- and polyfluoroalkyl substances (PFAS) and relevant products upon pyrolysis (200–890 °C) and their formation mechanisms. Approximately 30 non-fluorinated compounds were detected from PFAS-containing aqueous film-forming foams (AFFFs) and commercial surfactant concentrates (SCs) after heating, including glycols and glycol ethers that were predominant at 200 °C. Oxygen (e.g., 1,4-dioxane) and nitrogen heterocycles and benzene were unexpectedly observed at higher temperatures (300–890 °C), which were likely formed as a consequence of the thermal dehydration, dehydrogenation, and intermolecular cyclization of glycols and glycol ethers. Fluorinated volatiles in six major classes were detected at low and moderate temperatures (200–500 °C), including perfluoroalkenes, perfluoroalkyl aldehydes, fluorotelomer alcohols, and polyfluorinated alkanes/alkenes. Several features of the pyrolyses of PFAS suggest that the underlying decomposition mechanism is radical-mediated. Perfluoroheptene thermally decomposed at 200 °C to shorter-chain homologues following a radical chain-scission mechanism. Most of these volatiles observed at low/moderate temperatures were not detected at 890 °C. Ultra-short-chain fluorinated greenhouse gases (e.g., perfluoromethane) were not found.

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1. Introduction

Thermal treatments such as incineration and pyrolysis are effective methods of destroying hazardous organics and reducing waste volume. However, major environmental concerns are emissions of hazardous substances into the atmosphere with flue gases. Studies in the past have demonstrated the formation of highly toxic *chlorinated* dioxins during the incineration of chlorine-bearing waste materials (Dopico and Gomez, 2015; Dyke et al., 2003; Hutzinger et al., 1985). Incineration of wastes containing *brominated* flame retardants leads to the formation of brominated dioxins and furans (Soderstrom and Marklund, 2002). Performing pyrolysis on solid waste materials in an anaerobic condition may prevent the generation of dioxins and furans while recovering energy and waste materials (Bobek-Nagy et al., 2020; Chen et al., 2022; Liu et al., 2021; Sormo et al., 2020).

Much less attention has been given to compounds generated during thermal treatment of *fluorinated* compounds, particularly per- and polyfluoroalkyl substances (PFAS) that have been mass-produced since the 1960s. Because of the strong carbon–fluorine bond, PFAS are highly resistant to degradation. Compared to hydrocarbon-based surfactants that are only hydrophobic in nature, the perfluorinated chain of PFAS is oleophobic, or oil repelling. These properties have led to their use in surface-active agents or as individual ingredients in various products such as aqueous film-forming foams (AFFFs) (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014), food containers (Glenn et al., 2021; Schaider et al., 2017), baking papers (Kotthoff et al., 2015), clothing (Kotthoff et al., 2015), stain-resistant carpets (Kotthoff et al., 2015), and cosmetics (Whitehead et al., 2021). PFAS-containing AFFFs have been used since the World War II to extinguish hydrocarbon fuel fires at U.S. military sites, municipal airports, refineries, and other industries (Darwin, 2011; Moody and Field, 2000). Data on hazardous compounds emitted from AFFFs upon heating are virtually nonexistent in the literature.

Furthermore, there are currently more than 400 places in the United States where the release of PFAS to soil is known or suspected due to the historical use of AFFFs (DOD, 2017). There is a well-recognized need for remediation of PFAS- or AFFF-contaminated zones (Naidu et al., 2020). Pyrolysis is a commonly used remediation technology to cleanup organic-contaminated soils (Vidonish et al., 2016).

The U.S. EPA has recently identified thermal treatment as one of the three commercially available technological options that can degrade or manage PFAS migration in contaminated materials (USEPA, 2020). Recent laboratory studies have shown that thermal desorption at 200–400 °C and smoldering combustion at > 900 °C were effective in decontamination of soil laden with perfluoroalkyl substances (Crownover et al., 2019; Duchesne et al., 2020). Strathmann and co-workers developed a hydrothermal treatment system (Hao et al., 2021; Wu et al., 2019) that can effectively decompose a variety of PFAS at near-critical temperature and pressure within 15–30 min. Liang et al. showed that the hydrothermal liquefaction at 300 °C can degrade PFAS present in plant biomass (Zhang et al., 2020). Singh et al. systematically investigated PFAS degradation in plasma-based processes in a series of studies (Singh et al., 2019a; Singh et al., 2019b; Singh et al., 2020). Thoma et al. investigated pyrolysis of PFAS-laden biosolids (Thoma et al., 2022).

Our group recently studied thermal air treatment and pyrolysis of PFAS with different chain lengths and functional groups (Alinezhad et al., 2022; Sasi et al., 2021; Xiao et al., 2021a; Xiao et al., 2020, 2021b). We demonstrated that perfluoroalkane carboxylic acids, including perfluoroctanoic acid (PFOA), in spent granular activated carbon (Sasi et al., 2021; Xiao et al., 2020) and soil (Alinezhad et al., 2022) can be degraded at temperatures as low as 150 °C. Thermal decomposition kinetics of PFAS in the spent media (Sasi et al., 2021; Xiao et al., 2020) and soil (Alinezhad et al., 2022) is not affected by the atmosphere, soil texture, and the initial concentration in soil, provided a sufficiently high temperature is applied. The thermal degradation

half-life of perfluoroctanesulfonic acid (PFOS) is only 2.4–3.1 min at 500 °C (Alinezhad et al., 2022). Polyfluoroalkyl substances in AFFFs transform to a few anionic fluoroalkyl substances at low temperatures and exhibit near-complete degradation at ≥ 400 °C (Xiao et al., 2021a).

In spite of the insights offered by these studies, we are far from the goal of arriving a comprehensive understanding of PFAS thermal decomposition. Experimental data on volatiles generated from heated PFAS and relevant materials are sparse, which are urgently needed to develop sustainable thermal-remediation strategies prior to implementing extensive thermal remediation actions on PFAS- or AFFF-impacted sites. Using gas-phase nuclear magnetic resonance (NMR), Krusic and Roe found that the pyrolysis of ammonium perfluoroctanoate generated 1H-perfluoroheptane (C_7HF_{15}) and perfluoro-1-heptene (C_7F_{14}) (Krusic and Roe, 2004). However, because of the generally low sensitivity and selectivity of NMR, it is unclear whether these two species are the only non-polar thermal decomposition products generated from ammonium perfluoroctanoate (Xiao et al., 2021b). Roth et al. tentatively detected C6 non-polar compounds, including perfluorohexane (C_6F_{14}), from an AFFF heated at 300 °C; volatiles from the AFFF at other temperatures were not reported (Roth et al., 2020).

AFFFs also consist of a multitude of non-fluorinated substances such as 2-(2-butoxyethoxy)-ethanol (Bruton and Sedlak, 2017; Harding-Marjanovic et al., 2016). García et al. analyzed non-fluorinated components in a group of AFFFs by using liquid chromatography (LC) and quadrupole time-of-flight mass spectrometry (MS); a number of polar or hydrophobic compounds, including polyethylene glycols, octylphenol polyethoxylates, alcohol ethoxylates, alkyl ether sulfates, alkyl benzene sulfonates, and alkyl sulfates, were found in 3M AFFF samples (Garcia et al., 2019). On the other hand, information on non-polar, non-fluorinated volatiles emitted from AFFFs during heating is not available in the literature. The environmental impact associated with these compounds may be significant.

To address these critical knowledge gaps, we investigate both fluorinated and non-fluorinated volatiles emitted from AFFFs under pyrolysis conditions in the present study. We employed a hybrid analytical technique, thermal desorption–pyrolysis (TD–Pyr) connected to a cryogenic trapping (CT)-gas chromatography (GC)–electron ionization (EI)–MS system to detect (semi-)volatile, mostly non-polar, compounds of AFFFs and PFAS upon heating over a wide range of temperatures (200–890 °C). An EI-MS database was developed in this research and shared publicly, which may benefit peer researchers, policy makers, and the private sector.

In addition to AFFFs, this study also included Fluorad brand fluorosurfactants (FC-100, FC-129, and FC-170C) that have been used in adhesives, cleaners, coatings, emulsions, and leak detector solutions (Table S1 of the Supporting Information, SI). Cationic, zwitterionic, and anionic polyfluoroalkyl substances were detected in FC-100 and FC-129 (Table S2) (Xiao et al., 2017). FC-170C, on the other hand, contains non-ionic PFAS compounds ($(FC_2F_2)_nSO_2-NC_4H_9-(C_2H_4O)_m-OH$) with two different repeating units, n and m ranging from 5 to 8 and 0–14, respectively (Table S2) (Xiao et al., 2017). FC-170C is typically used in electronic etching baths, floor polish emulsions, refractory manufacturing processes, and specialty inks (Table S1). The generation of PFAS-containing solid materials during the manufacturing, distribution, and application of these products is often unavailable. These materials may be disposed of as solid waste and end up in pyrolyzers and incinerators. The environmental impact associated with thermal decomposition products of fluorosurfactants may be significant, which is not well understood.

2. Methods and materials

2.1. PFAS and PFAS-relevant products

Tables S1 and S2a–S2g present the detailed information on PFAS detected in three 3M AFFFs (#1–#3) and three 3M Fluorad brand

surfactant concentrates (SCs) (FC-100, FC-129, and FC-170C). This work also included individual cationic and zwitterionic PFAS—perfluoroocta neamido ammonium salt (PFOAAmS, $C_7F_{15}-C_7H_{16}N_2O_1$), perfluorocta nesulfonamido ammonium salt (PFOSAmS, $C_8F_{17}-C_6H_{16}N_2O_2S_1$), perfluoroctaneamido betaine (PFOAB, $C_7F_{15}-C_8H_{16}N_2O_3$), and perfluoroctanesulfonamido betaine (PFOSB, $C_8F_{17}-C_7H_{16}N_2O_4S$); these PFAS have been detected in AFFFs and Fluorad brand SCs (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014; Xiao et al., 2017), and can decompose to PFOA and/or PFOS in chemical (Xiao et al., 2018), biological (Jin et al., 2020; Mejia-Avendano et al., 2016), and thermal (Xiao et al., 2021a) processes. Perfluorohept-1-ene (C_7F_{14} ; CAS: 355-63-5) was purchased from Santa Cruz Biotechnology (TA, USA).

2.2. Pyrolysis of AFFFs, SCs, and Individual PFAS

Volatile products generated from pyrolyses of AFFFs, SCs, and individual PFAS compounds in an inert atmosphere were detected by TD—Pyr (Frontier 3030D, Frontier Labs Inc., Japan) connected to a CT—GC—EI-MS system (Agilent GC 7890 and 5975C MS; Santa Clara, CA) (see SI). TD—Pyr—GC—EI-MS was previously used to obtain the structural information of biomass or polymers (Asina et al., 2016; Brzono et al., 2017; Kozliak et al., 2016). In this study, TD—Pyr was employed as a furnace with EI-MS as a detector. A multistep heating strategy was applied, including TD at ≤ 300 °C for evolution of low-molecular-weight compounds and Pyr at higher temperatures for thermally stable compounds or thermal degradation products from precursors (see the SI). Following the TD or Pyr step, gaseous products were concentrated in CT, introduced on the GC column, and analyzed by EI-MS. An Ultra Alloy capillary column (30 m; Frontier Labs Inc., Japan) with an inner diameter of 0.25 mm was used. A high-performance, multi-functional pyrolyzer (3030D, Frontier Labs Inc., Japan) is installed on top of the GC (see SI). This system allows for multiple-step heating including TD at ≤ 300 °C for evolution of volatile, low molecular-weight compounds and Pyr typically at temperatures above 350 °C.

Each sample was heated at four temperatures (200, 300, 500, and 890 °C) at a fixed residence time (30 or 120 s) (see SI for more details). Following the different TD-Pyr steps, the gaseous products were concentrated in CT, and introduced on the GC column and analyzed by GC-MS. As samples were analyzed directly and no cleanup was required, the TD—Pyr—CT—GC—EI-MS system could capture products or species that may not be detected by conventional GC—EI-MS approaches. The main disadvantage of TD—Pyr—CT—GC—EI-MS is the high cost of the analytical platform and device maintenance.

2.3. Analyses of Volatile Compounds

Structures of pyrolysis products were deduced primarily from the mass spectra. Data processing included the MS fragmentation pattern evaluation of a potential pyrolyzate based on the highly curated National Institute of Standards and Technology (NIST) 2005 library that contains 190,825 spectra. In contrast to LC—MS systems where no universal library matching is available, the EI-MS mass spectra are rather *uniform and specific* for an organic compound at a typical EI energy of 70 eV (Rivier, 2003). For compounds to be considered correctly identified, the following criteria had to be satisfied:

Criterion 1. Their EI-MS spectra presented a NIST library match quality of $\geq 80\%$ computed by the instrument's built-in software, which compared statistically significant ions using the Agilent's Probability Based Matching Algorithm. Criterion 2. We also manually evaluated the fragmentation pattern match to reference standards available in the public-accessible PubChem GC-MS database.

—2i. We performed cross-platform evaluation by preferably selecting mass spectral data of a reference standard measured by another GCMS system (e.g., Hitachi RMU-6M MS).

2ii. A minimum of three structure-specific or characteristic fragments should be monitored.

2iii. The relative abundances (RAs) of at least three characteristic fragments should not differ by 30% from those of a reference standard.

Criterion 3. Absence of detected compounds in blanks (see SI).

Criterion 4 (optional). We also evaluated the identification results based on whether a compound was detected in multiple AFFF or FC samples. The simultaneous occurrence of a compound in different AFFF or SC samples has a lower probability, which means a higher specificity.

3. Results and discussion

3.1. Non-fluorinated Volatiles of AFFF and SC samples and their formation mechanisms

Figs. 1 and 2 depict the effect of temperature on the formation of non-fluorinated volatiles from AFFF and SC samples. Fig. 3, Figs. S1–S104, and Table S3 present, respectively, EI-MS spectra, raw spectral data, and detection information details for each of the samples. The predominant compounds identified at 200 °C were glycols and glycol ethers, which had a relatively long GC retention time (>4 min) (Figs. 1, 2, and 4). Among them was 2-(2-butoxyethoxy)-ethanol ($C_8H_{18}O_3$; CAS 112-34-5), known by the trade name of Butyl Carbitol, which is a slow evaporating ester solvent found in many AFFFs (>8–20% (w/w) (Bruton and Sedlak, 2017; Harding-Marjanovic et al., 2016) for enhancing film formation and formulation stability. It is on the USEPA list of hazardous air pollutants. All of the detected glycols and glycol ethers belong to the so-called “e-series” glycol ethers made from ethylene oxide.

At a higher temperature (300 °C), several new peaks at a shorter retention time of 2–4 min appeared on TIC chromatograms (Fig. 1). The compound (M) at retention time of 2.8 min was detected in two of 3 M AFFF samples at 300 °C. It generated a few oxygen-containing MS fragments, including CHO^+ (fx1, m/z 29), CH_3O^+ (fx2, m/z 31), C_3H_6O (fx3, m/z 58), and $C_4H_8O_2$ (m/z 88) (Fig. 3). The ions of m/z 31 and m/z 58 represent the successive loss of C_3H_5O (m/z 57) and CH_2O (m/z 30) from M, indicating that it contains multiple oxygen atoms. The oxygen-containing fragmentation ions, such as CH_3O^+ (m/z 31) and C_3H_6O (m/z 58), were also found in glycols and glycol ethers (Fig. 3). However, the much shorter retention time indicates that M is more volatile. We therefore believe it represents an oxygen heterocyclic compound, such as a furan or dioxane. This is substantiated by matching the spectral information of M with that of 1,4-dioxane ($C_4H_8O_2$; CAS: 123-91-1) in both the NIST mass spectral library and the MassBank High Quality Mass Spectral Database analyzed by a Hitachi RMU-6 M MS system (Fig. 3).

The pyrolysis of AFFF samples at moderate temperature (500 °C) yielded a large variety of products, including 1,4-dioxane, amines, long-chain (glycol) ether compounds, and highly volatile aromatics (e.g., benzene) and N-heteroaromatics (pyridine and 3-methyl-pyridine) (Figs. 1–4). Among them were one octylphenol polyethoxylate and one octylphenol that is a known endocrine disruptor (Mayer et al., 2003). Octylphenol polyethoxylates were found in AFFFs and AFFF-contaminated groundwater by García (Garcia et al., 2019). Furthermore, we detected a possible alkene in multiple heated samples (Figs. S5, S19, S25, S38, S43, and S55) with EI-MS fragments typical for alkenes (— CH_2 , m/z 41; — $CH=CH_2$, m/z 55; \times , m/z 70; \times , m/z 83; \times , m/z 97). However, the structure was not resolved. We initially assigned this compound to be 2,4,4-trimethyl-2-pentene. In the following cross-platform evaluation, we found that the RAs of two characteristic fragments (m/z 41 and m/z 97) do not match the reference standard.

At an elevated pyrolysis temperature (890 °C), only aromatics (benzene and 1,4-diphenylerythrene) were detected. Glycols and glycol ethers were not found, suggesting that the pyrolysis of glycols and glycol

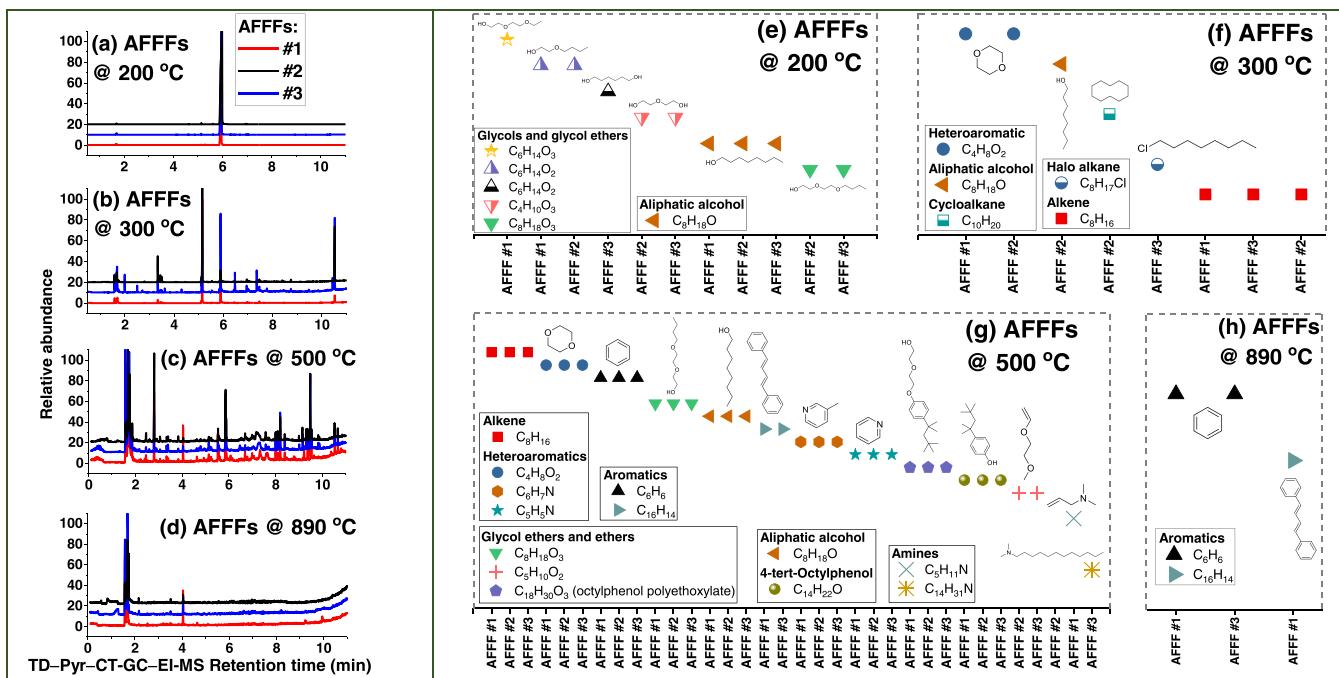


Fig. 1. (a)–(d): TD—Pyr—CT—GC—EI—MS total ion current (TIC) chromatograms of three AFFFs (#1–#3) at 200–890 °C. (e)–(h): Detected non-fluorinated volatiles that meet Criteria 1 and 2 (see Fig. 3).

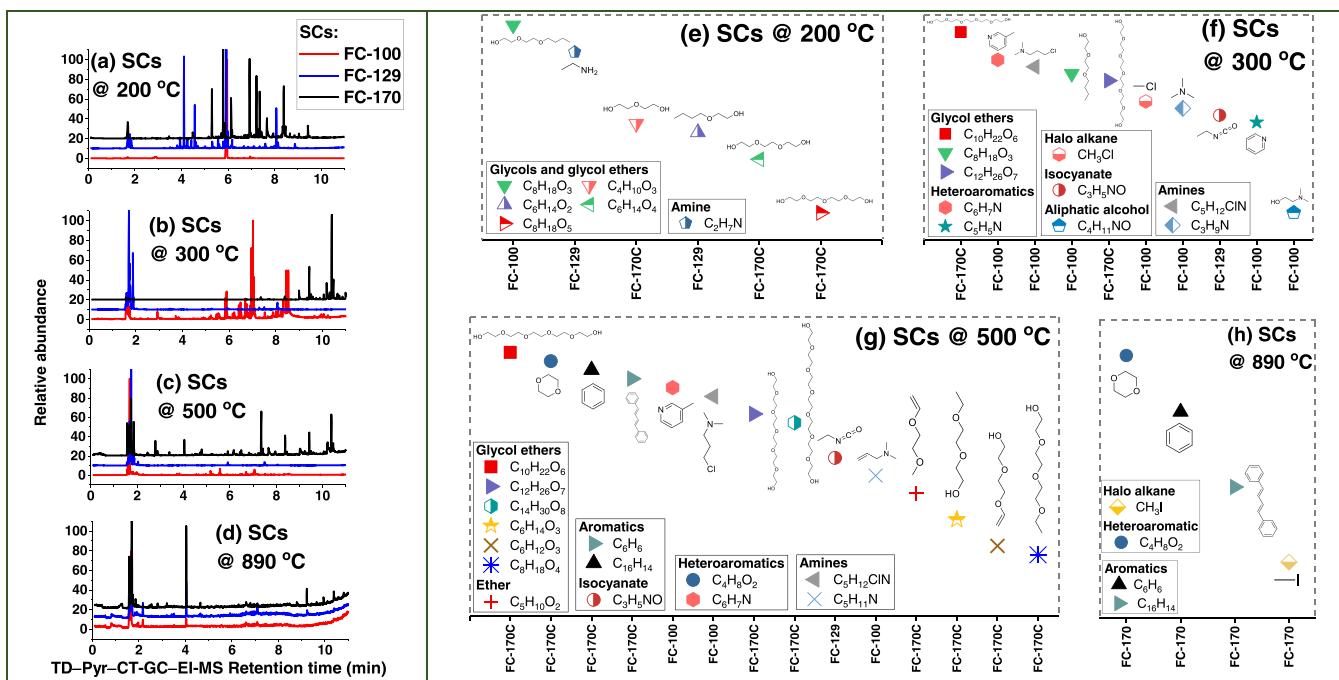


Fig. 2. (a)–(d): TD—Pyr—CT—GC—EI—MS TIC chromatograms of three SCs (i.e., 3M Fluorad brand surfactant concentrates) at 200–890 °C. (e)–(h): Detected non-fluorinated volatiles that meet Criteria 1 and 2 (see Fig. 3).

ethers completed at ~ 890 °C (Figs. 1 and 4).

The pyrolysis of Fluorad brand SCs at 200 °C led to the detection of almost the same group of glycols and glycol ethers found in AFFF samples (Figs. 2 and 3). Therefore, glycols and glycol ethers may be ubiquitously present at sites impacted by 3 M AFFFs and SCs. Octylphenol and octylphenol polyethoxylate were not found in SCs, however. Aromatics (e.g., benzene), heteroaromatics (pyridine and 3-methyl-pyridine), and 1,4-dioxane were detected during SC pyrolyses at 300 and 500 °C. Most of these compounds, other than 1,4-dioxane and aromatics,

were not detected when pyrolysis was conducted at 890 °C.

With a boiling point of 101–102 °C, 1,4-dioxane is used primarily in chlorinated solvents, paint strippers, greases, and waxes (USEPA, 2017). It is flammable and potentially explosive; therefore, it is unlikely that it is added to AFFFs used for firefighting. 1,4-Dioxane is a probable human carcinogen and a common PFAS co-contaminant in the drinking water (Guelfo and Adamson, 2018). It was not identified in AFFFs (Figs. 1e and 2e). We postulate that 1,4-dioxane is formed via the thermal dehydration and intermolecular cyclization of glycols or glycol ethers present in

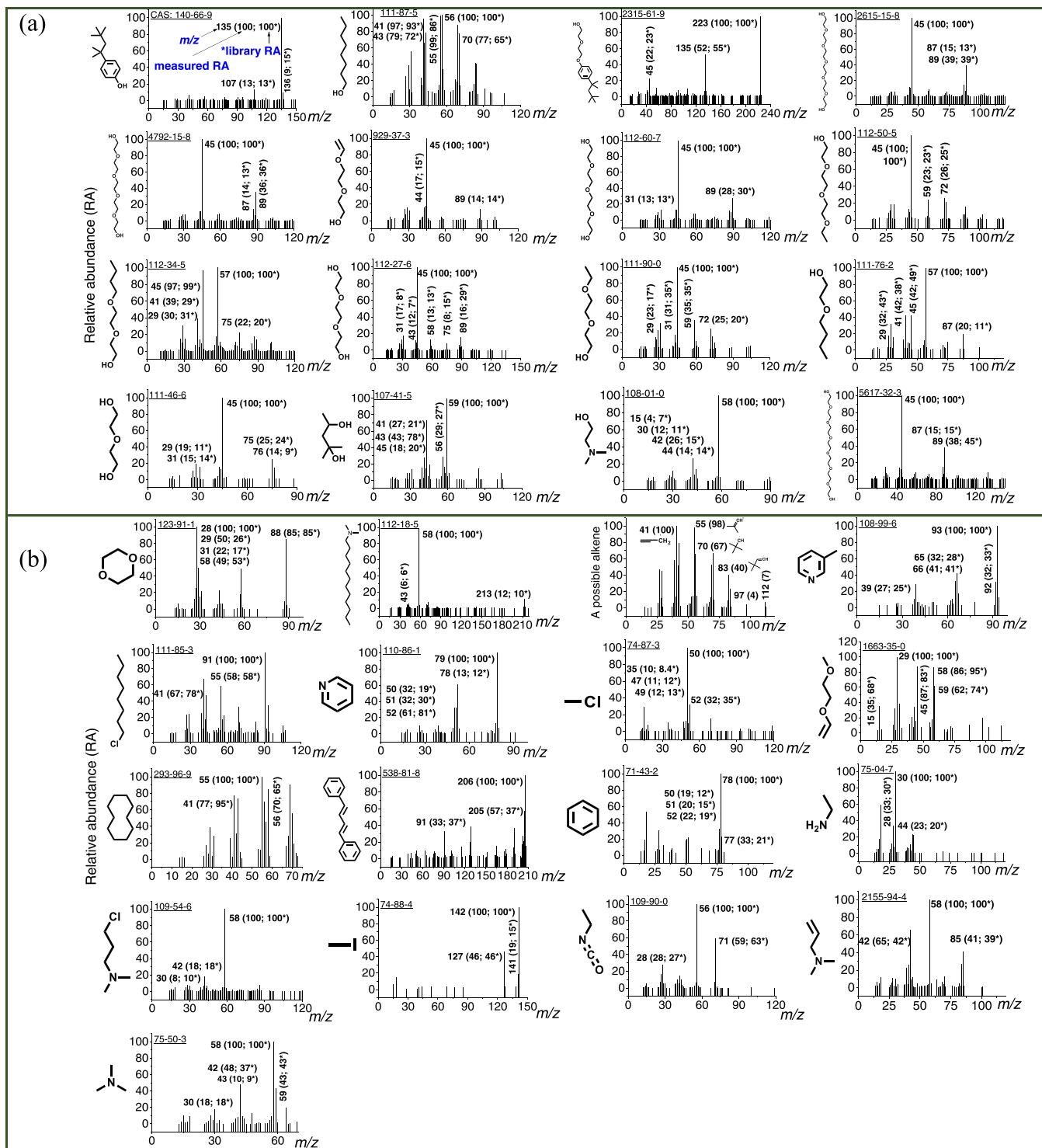


Fig. 3. EI-MS spectra of detected non-fluorinated pyrolyzates of AFFFs and SCs that meet both Criteria 1 and 2: (a) glycols, glycol ethers, alcohols, and phenols; and (b) 1,4-dioxane, aromatics, heteroaromatics, and other species. The numbers in parentheses are RAs of a pyrolyzate's characteristic fragments measured in this study and those of a reference standard obtained from a public-accessible database. See Figs. S1–S103 in the SI for raw mass spectra of these non-fluorinated pyrolyzates.

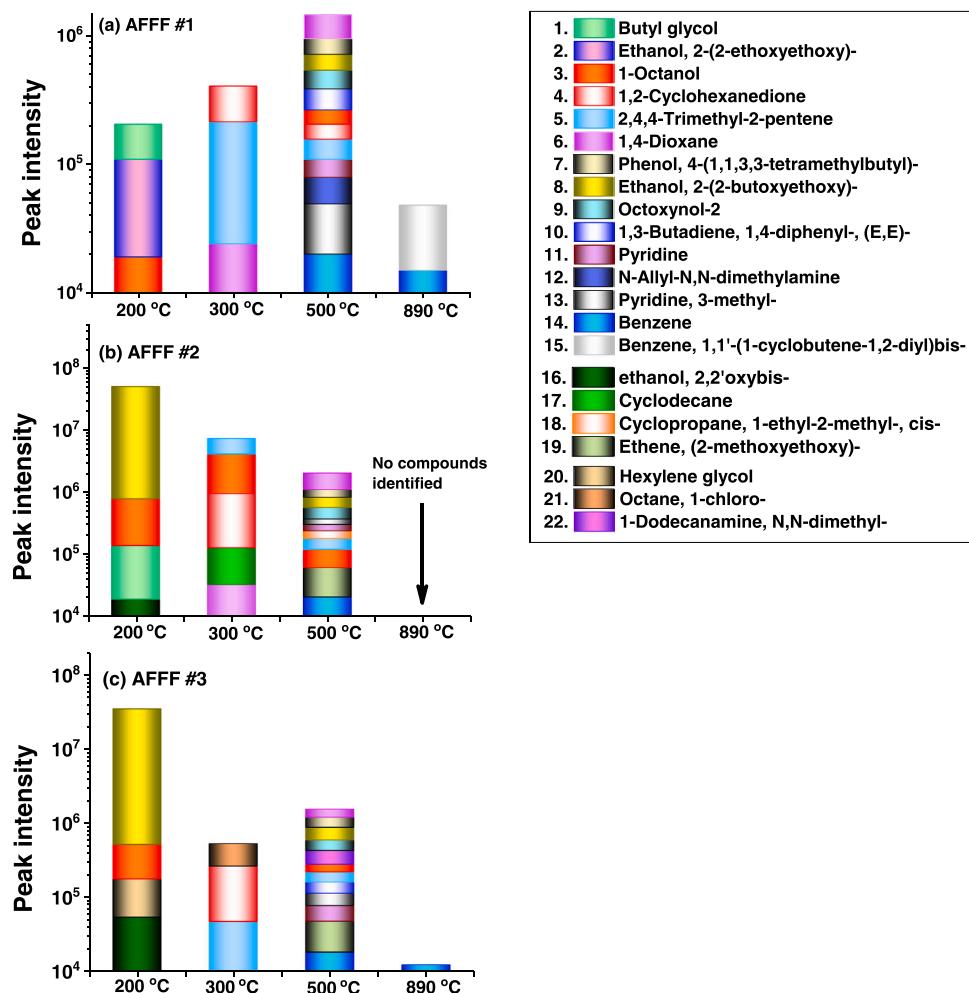


Fig. 4. Relative abundance of non-fluorinated compounds from AFFFs upon pyrolysis at various temperatures as illustrated by TD—Pyr—CT-GC—EI-MS peak intensities. [Fig. S105](#) show the relative abundance of non-fluorinated volatiles identified in SC samples.

AFFFs and SCs, as illustrated in [Fig. 5a](#). In other studies, 1,4-dioxane is formed as a result of ring closing of precursor compounds in the process of synthesis of ethoxylated fatty alcohols ([Bettenhausen, 2020](#)).

The detection of benzene, pyridine, and other (hetero-)aromatics can be attributed to several possibilities: (1) they could be trace components of AFFFs and SCs that do not undergo effective thermal destruction during AFFF and SC pyrolyses; and (2) they could be formed as a consequence of a complex array of pyrolytic processes involving structurally unrelated precursors. The first possibility can be ruled out because these highly volatile compounds such as benzene (boiling point = 80 °C) were not detected in AFFFs ([Figs. 1e, f, 2e, and f](#)). We postulate that benzene is formed from glycols or glycol ethers through thermal dehydration, dehydrogenation, and intermolecular cyclization reactions ([Fig. 5a](#)). Supporting this view, recent findings demonstrate that benzene can be generated as a result of the thermal degradation of propylene glycol ($C_3H_8O_2$) in electronic cigarettes ([Ooi et al., 2019; Pankow et al., 2017](#)). Furthermore, various nitrogen-containing polyfluoroalkyl substances were found in 3M AFFF and SC samples ([Tables S2c, S2d, S2e, and S2](#)). They are structurally similar to PFOS, except that the perfluoroalkyl chain is attached to a nonfluorinated moiety through a sulfonamide group or other polar groups. The thermal degradation of polyfluoroalkyl compounds through a side-chain stripping mechanism ([Xiao et al., 2021a](#)) produces nitrogen-containing species, such as trimethylamine (C_3H_9N ; [Figs. 1, 2, S89, S94, and S100](#)) that can be subsequently involved in the thermal dehydration and intermolecular cyclization of glycols or glycol ethers, leading to the formation of

heteroaromatics (e.g., pyridine) instead of aromatics (e.g., benzene).

3.2. Fluorinated Volatiles of AFFFs, SCs, and Individual PFAS and Their Formation Mechanisms

We found in this study that pyrolyses of AFFFs, SCs, and individual PFAS yielded a number of fluorinated products in six major classes ([Figs. 6 and 7](#)), namely perfluoroalkenes, perfluoroalkyl aldehydes, perfluoroalkanes, fluorotelomer alcohols, and polyfluorinated alkenes and alkanes with a degree of fluorination lower than perfluorinated congeners. Their structures are given in [Tables S4](#). Library match qualities were lower than 80% for most of these fluorinated volatile compounds ([Tables S4](#)). At 300 °C, fluorotelomer alcohols, perfluoroalkyl aldehydes, and per- and polyfluoroalkenes, including perfluoroheptene (C_7F_{14}), were identified from AFFF and SC samples. Pyrolyses of AFFFs, SCs, and individual PFAS at 500 °C yielded perfluoroalkenes, fluorotelomer alcohols, and perfluoroalkyl aldehydes ([Figs. 6 and 7](#)). A majority of these products were also detected at lower temperatures (200 and 300 °C). Polyfluoroalkenes were not observed, however, at 500 °C.

At 890 °C, perfluoroalkenes and perfluoroalkyl aldehydes were the main pyrolyzates; most of the pyrolyzates found at low/moderate temperatures (200–500 °C) were not detected ([Figs. 6 and 7](#)), suggesting the mineralization of PFAS and their volatile pyrolysis products during high-temperature pyrolyses. Our group previously determined the yield of F from PFOA and PFOS at a wide range of temperatures ([Alinezhad et al.,](#)

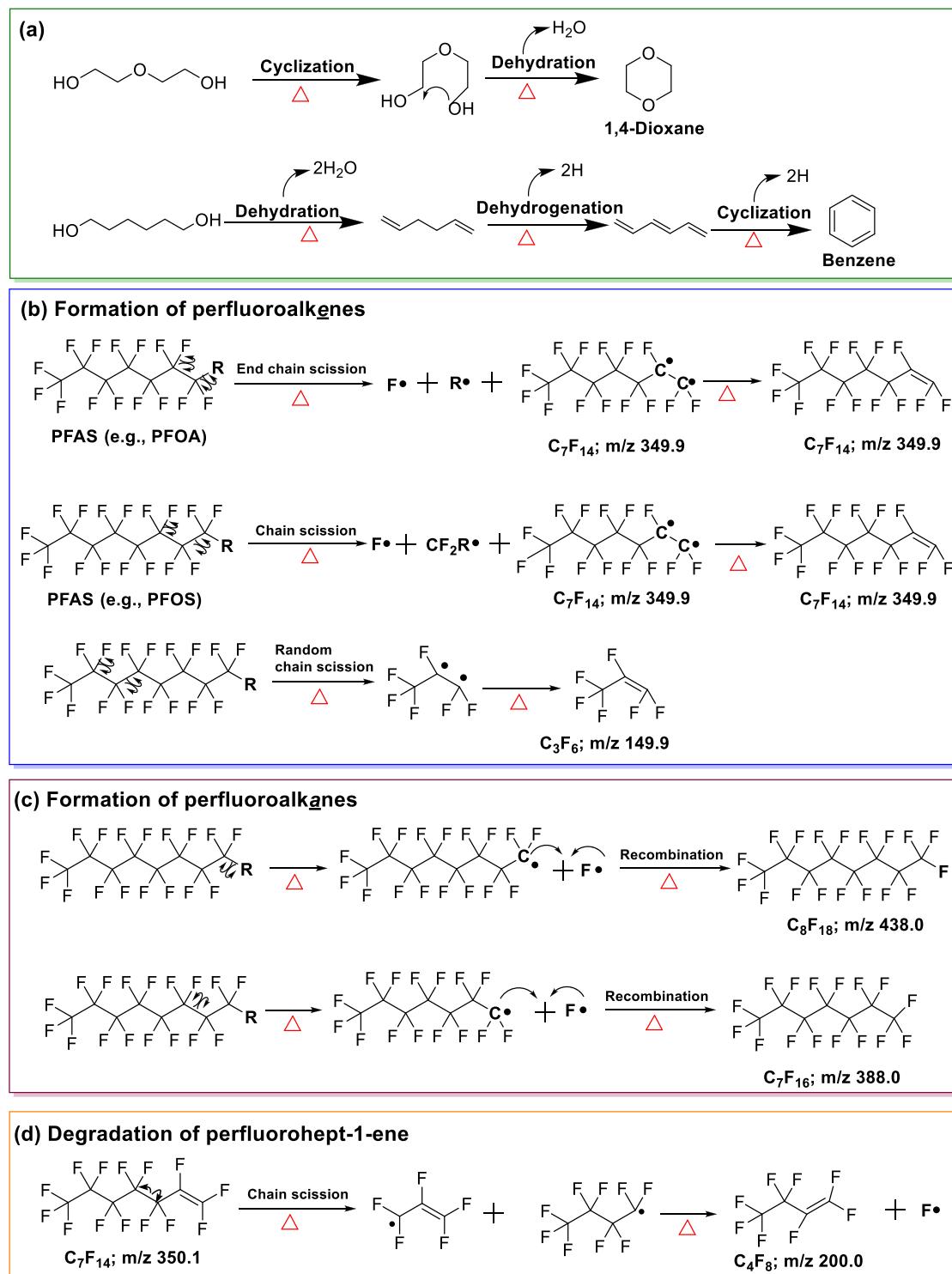


Fig. 5. Possible thermal formation pathways of observed pyrolyzates: (a) 1,4-dioxane and benzene from glycol ether compounds, (b) perfluoroalkenes from PFAS, and (c) perfluoroalkanes from PFAS. (d) A possible degradation mechanism of perfluorohept-1-ene (C_7F_{14}).

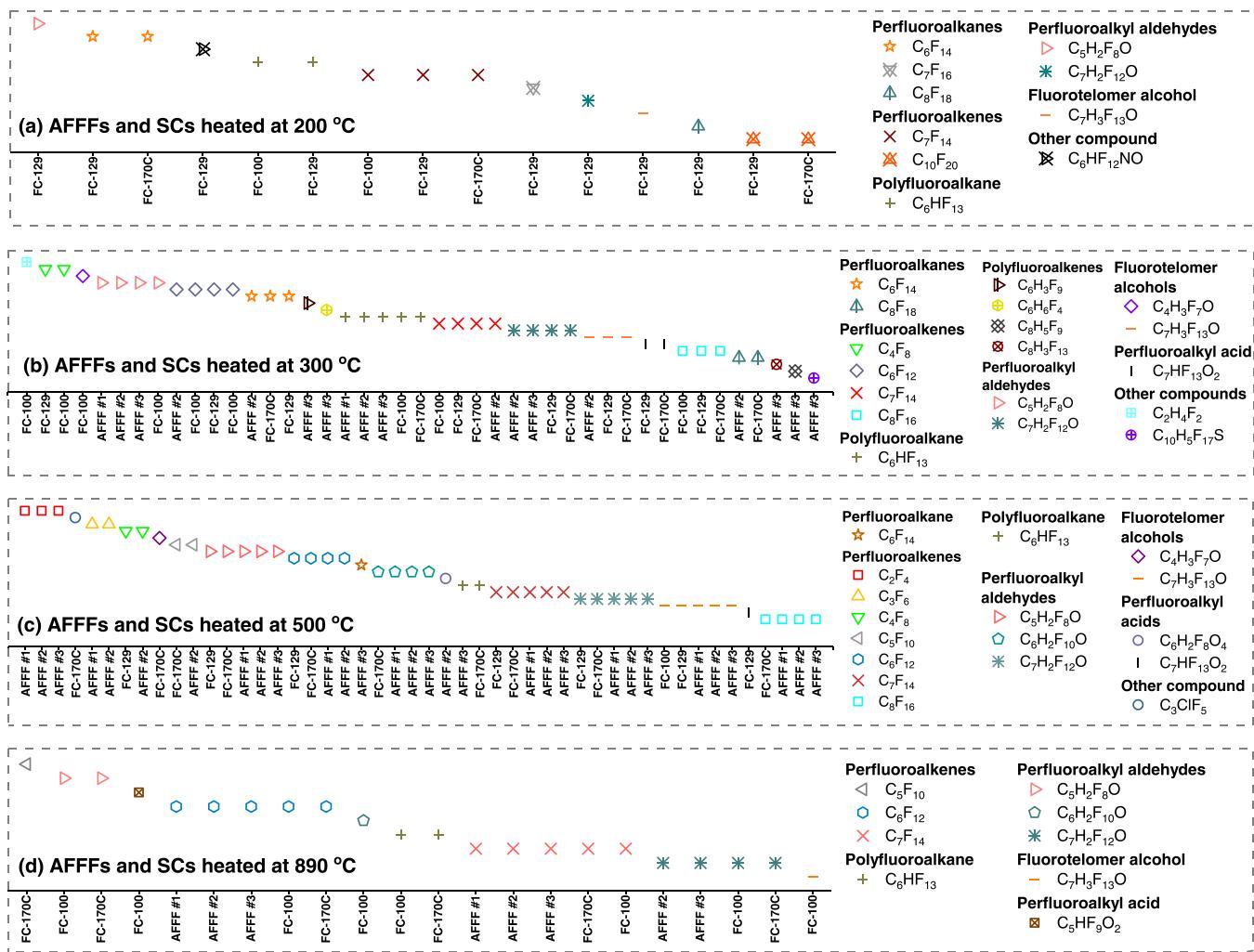


Fig. 6. Possible fluorinated pyrolyzates detected from AFFFs and SCs at different temperatures.

2022; Sasi et al., 2021; Xiao et al., 2020). We found a significant yield of F[−] (up to 92 mol%) from PFOA and PFOS when heated at 700–900 °C (Xiao et al., 2020). Consistent with this finding, Khan et al. calculated the theoretical PFOS thermal decomposition half-life to be only 1 s at 727 °C (Khan et al., 2020).

Interestingly, in spite of the difference in functionalities (Tables S2b–f), PFAS compounds in these AFFF and SC samples (Xiao et al., 2017; Xiao et al., 2021a) yielded a similar profile of fluorinated pyrolyzates (Fig. 6 and Table S4). Likewise, PFOA, PFOS, and their cationic and zwitterionic precursor compounds generated a similar profile of fluorinated pyrolyzates in above-mentioned six classes (Fig. 7 and Table S5). Perfluoroheptene (C₇F₁₄), perfluoroalkyl aldehydes, and polyfluoroalkanes were frequently detected (Figs. 6 and 7). Heating cationic and zwitterionic PFAS compounds also produced a few non-fluorinated species, including trimethylamine (C₃H₉N) (Fig. 7), following a side-chain stripping mechanism (Xiao et al., 2021a).

The detection of fluorinated alkenes and alkanes (Figs. 6 and 7) agrees well with the previously suggested radical chain mechanism (Sasi et al., 2021; Xiao et al., 2021a): the perfluoroalkyl chain of PFAS is broken up from the bond between the perfluoroalkyl chain and the nonfluorinated moiety or at seemingly random locations on the perfluoroalkyl chain. This process forms short-lived perfluoroalkyl biradicals (Sasi et al., 2021; Xiao et al., 2020) that successively relax to yield perfluoroalkenes (Fig. 5b). Chain scission and recombination

reactions may be involved in the thermal formation of perfluoroctane (C₈F₁₈), perfluoroctyl iodide (C₈F₁₇I), and perfluoroheptane (C₇F₁₆) from PFOS precursor compounds such as PFOSAmS (C₈F₁₇–C₆H₁₆N₂O₂SI) (Figs. 5c and 7).

Perfluoroheptene (C₇F₁₄) was the most observed fluorinated pyrolyzate (Figs. 6 and 7 and Tables S4 and S5). Fig. 8 indicates that perfluoro-1-heptene (CAS: 355–63–5; boiling point: 81 °C) was partially degraded at 200 °C, generating perfluorobutene (C₄F₈) and a few other products following a radical cleavage mechanism (Fig. 5d). For example, there is equivocal information regarding whether short-chain perfluorocarbons, including perfluoromethane (CF₄, *m/z* 88.0) and perfluoroethane (C₂F₆, *m/z* 138.0), are generated from heated PFAS. Previous researchers postulated that heating of PFOS generates perfluoromethane (CF₄, *m/z* 88.0) and perfluoroethane (C₂F₆, *m/z* 138.0) (Winchell et al., 2021); however, no mass spectral evidence and literature data are available to support their hypothesis. In the current study, perfluoromethane and perfluoroethane were not detected during pyrolyses of AFFFs, SCs, PFOA, PFOS, cationic/zwitterionic PFAS, and perfluoroheptene, but this does not preclude their formation in small quantities. Short-chain polyfluoroalkanes (or hydrofluorocarbons) on the IPCC (Intergovernmental Panel on Climate Change) list of greenhouse gases were also not observed in this study.

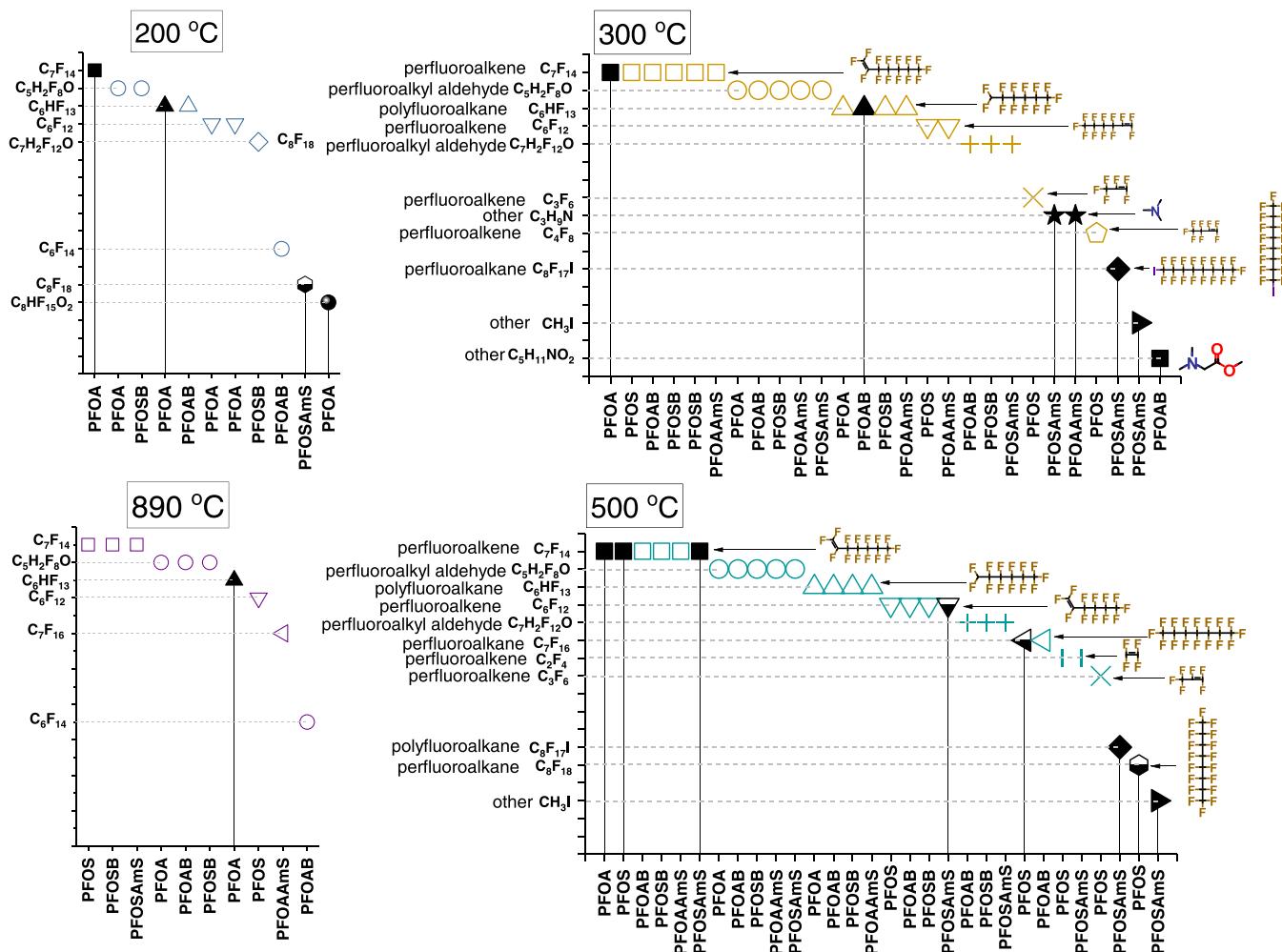


Fig. 7. Pyrolysis products of individual PFAS compounds (PFOA and PFOS in a previous study (Alinezhad et al., 2022) and four cationic and zwitterionic precursor compounds measured in this study). Solid symbols: library match quality of $\geq 80\%$; half-filled symbols: library match quality of 70–80%; open symbols: library match quality of $\leq 70\%$.

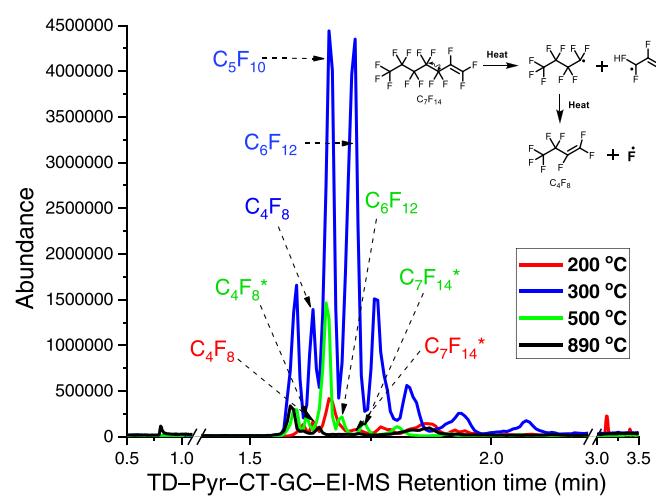


Fig. 8. TD-Pyr-CT-GC-EI-MS chromatograms of perfluorohept-1-ene (C_7F_{14}) heated at different temperatures and a possible degradation pathway. The substances with an asterisk (*) had a NIST library similarity of $\geq 80\%$.

4. Conclusions

The present study contributes to the relevant literature in multiple dimensions. There are many aspects of PFAS thermal stability and transformation where our understanding is incomplete. Our team recently analyzed polar, non-volatile thermal decomposition compounds of PFAS and AFFFs (Sasi et al., 2021; Xiao et al., 2021a). Prior to this study, information on volatile products emitted from PFAS, AFFFs, and SCs during heating was very limited. This work contributes to the existing literature on thermal degradation mechanisms and pathways of PFAS at low, moderate, and elevated temperatures. Evaporation and degradation of PFAS can occur at temperatures as low as 200 °C (Figs. 6 and 7); therefore, the public should be mindful of possible exposure to PFAS and their degradation products during baking and other relevant thermal processes involving PFAS. Our results further imply that fire-fighting applications using AFFFs at military sites, municipal airports, refineries, and other industries may be associated with *occupational* health risks due to the exposure to toxic volatile compounds formed from AFFFs under heating conditions. The uncontrolled heating of AFFFs or materials containing SCs is a hazardous threat to the environment and human health and should therefore be avoided. This study is also highly relevant in practice, because thermal approaches have

been applied for remediation of AFFF-contaminated sites and PFAS-containing materials (USEPA, 2020). Our results indicate that moderate thermal treatments of AFFFs and SCs may inadvertently contribute to the generation of aromatics and heteroaromatics (Figs. 1–4), and that post-treatments should be available to minimize volatile emissions. It is envisaged that this research will aid in the planning of strategic remediation programs or in improving current thermal remediation practices to limit the unwanted production of volatiles from AFFFs. Lastly, it has been known that 1,4-dioxane coexists with PFAS in (AFFF-contaminated) drinking water and groundwater (Guelfo and Adamson, 2018; MPCA, 2021). 1,4-Dioxane is a major co-contaminant of PFAS at U.S. Department of Defense sites (NAVFAC, 2021; SERDP, 2015). The mechanisms, however, are not clear for the co-occurrence of these structurally different compounds used in different applications. This study shows that one possible mechanism is the *de novo* formation of 1,4-dioxane during heating of AFFFs.

Environmental Implication

Per- and polyfluoroalkyl substances (PFAS) are hazardous to human health and the environment. Recent studies have shown that thermal treatments are effective in degrading PFAS. This present study reports non-fluorinated and fluorinated compounds emitted from PFAS and PFAS-relevant products and explore their formation pathways. This information is urgently needed to understand PFAS thermal degradation mechanisms and develop sustainable thermal-remediation strategies prior to implementing extensive thermal remediation actions on PFAS-impacted sites. Our results indicate that the uncontrolled heating of AFFFs or materials containing SCs is a hazardous threat to the environment and human health and should therefore be avoided.

Authors Credit Statement

The authors contributed to the manuscript and Supplementary document preparation and the overall conception and design of the study, experimental design, data analysis and plotting, and thermal degradation pathways.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

This work was mainly supported by the U.S. National Science Foundation CAREER Program (2047062; F.X.). B.S. was supported by the University of North Dakota Pilot Postdoctoral Program from the Office of Vice President for Research & Economic Development. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF.

Appendix A. Supporting information

TD—Pyr—CT-GC—EI-MS method, applications of typical 3M Fluorad brand fluorosurfactants (Table S1), AFFF and SC samples and cationic and zwitterionic PFAS used in this study (Table S2), non-fluorinated volatiles from AFFFs and SCs heated at different temperatures (Table S3), fluorinated volatiles from AFFFs and SCs heated at different temperatures (Table S4), pyrolysis products of individual PFAS

chemicals (PFOA, PFOS, PFOAB, PFOSB, PFOAAmS, PFOSAmS) (Table S5), raw TD—Pyr—CT-GC—EI-MS spectra of volatiles detected from AFFFs and SCs at different temperatures (Figs. S1–S93), raw TD—Pyr—CT-GC—EI-MS spectra of pyrolyzates of individual PFAS chemicals (Figs. S94–S104), relative peak abundance of non-fluorinated compounds from SCs upon pyrolysis (Fig. S105), and raw TD—Pyr—CT-GC—EI-MS spectra of a blank sample (Fig. S106).

Appendix B. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129313.

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