# AFFF: PFAS Composition, Precursors and Biodegradation

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## Abbreviations:

AmPr-FASA = Aminopropyl perfluoroalkyl sulfonamide; AmPr-FAAd = Aminopropyl perfluoroalkyl amido acid; AmPr-FASAPrS = N-dimethyl ammoniopropyl perfluoroalkane sulfonamido propyl sulfonate; BiFOSA = Bis(perfluoro-octylsulfonyl) amine; DPOSA = 6:2 FTNO or Capstone A (see FTNO); EOF = Extractable Organic Fluorine; EtOH-AmPr-FHxSA = N-hydroxyethyldimethylammoniopropyl perfluorohexane sulfonamide (also N-HOEAmP-FASA); EtOH-AmPr-FHxSA-EtOH = N-hydroxyethyldimethylammoniopropyl perfluorohexane sulfonamido ethanol (also N-HOEAmP-FASE); EtOH-AmPr-PFHxSAPrS = Ethanol-aminopropyl-perfluorohexane sulfonamide propyl sulfonate (may refer to FTSAPr-AmHOPrS); FASA = Perfluoroalkyl sulfonamide; FOSAC = Perfluorooctane sulfonamido carboxylate; FTAA = Fluorotelomer sulfonamide alkyl amine; FTAB = Fluorotelomer sulfonamido betaine or FTSA-PrB (6:2 FTAB = Capstone B); FTB = Fluorotelomer betaine; FTCA = Fluorotelomer carboxylic acid; FTNO = Fluorotelomer sulfonamide amine oxide; FTS or FTSA, fluorotelomer sulfonic acid; FTSAm = Fluorotelomer sulfonamide; FTSaAm = Fluorotelomer sulfonamido N,N-dimethyl amine (= FTAA or FTSAPr-DiMeAn); FTSAPr-AmHOPrS = Fluorotelomer sulfonamide propyl amine hydroxypropyl sulfonate; FTSAS = Fluorotelomer thioether amido sulfonate (also FTAoS); FTSHA = Fluorotelomer thiohydroxyl ammonium; FTTh-PrAd-DiMeEtS = Fluorotelomer thioether propyl amide dimethyl ethyl sulfonate (also FTSAS); FTTh-OHPrTAm = Fluorotelomer thioether hydroxypropyl tertiary amine (also FTSHA); FTTh-PrAm = Fluorotelomer thioether propyl amine; FTUCA = Fluorotelomer unsaturated carboxylic acid; HRMS = High resolution mass spectrometry; LC-IMS-MS = Liquid Chromatography-Ion Mobility Spectrometry-Mass Spectrometry; N-AmCP-FHxSA = N-Ammoniocarboxypropyl- perfluoroalkane sulfonamide; N-AP-FASA = N-(3-(dimethylamino)propyl) perfluoroalkane sulphonamide; N-CMAmP-FASA = N-Carboxy methyldimethyl ammoniopropyl perfluoroalkane sulfonamide; N-TAmPFASA = N-Trimethylammoniopropyl-perfluoroalkane sulfonamide; NTA = Non-target analysis; OBS = Sodium p-perfluorous nonenoxybenzene sulfonate; PFAA = Perfluoroalkyl acid; PFAS = Per- and polyfluoroalkyl substances; PFASAC = Perfluoroalkyl sulfonamide amino carboxylate (or PFSaAmA) ; PFASAm = Perfluoroalkyl sulfonamido amine; PFASB = Perfluoroalkyl sulfonamido betaine; PFASNO = Perfluoroalkyl sulfonamidoamine oxide; PFBA = Perfluorobutanoic acid; PFCA = Perfluoroalkyl carboxylic acid; PFHxA = Perfluorohexanoic acid; PFHxS = Perfluorohexane sulfonate; PFHxSAm = Perfluorohexane sulfonamido amine; PFHxSAmA = Perfluorohexane sulfonamido amino acid; PFOS = Perfluorooctane sulfonic acid; PFOSA = Perfluorooctane sulfonamide; PFOSAm = Perfluorooctane sulfonamido amine; PFOSB = Perfluorooctane sulfonamido betaine; PFPeA = Perfluoropentanoic acid; PFOA = Perfluorooctanoic acid; PFOAAm = Perfluorooctane amido amine; PFOAAmS = Perfluorooctane amido sulfonate; PFOAB = Perfluorooctane amido betaine; PFSA = Perfluoroalkyl sulfonate; QTOF = Quadropole time of flight; SO- and $SO_2$ -FTSAS = Sulfoxide derivatives of FTSAS; SSA = Suspect screening analysis; TAmPr-FASA = N-Trimethyl ammonio propyl perfluoroalkane sulfonamide; TOP = Total Oxidizable Precursor; TOF = Total Organic Fluorine; U-PFBOH = Unsaturated perfluorobutanoic alcohol; U-PFHxOH = Unsaturated perfluorohexanoic alcohol; U-PFPeOH = Unsaturated perfluoropentanoic alcohol; U-PFOSNO = Unsaturated perfluorooctane sulfonamido amine oxide; UPLC = Ultra Performance Liquid Chromatography

## *Abstract*

Aqueous film-forming foams (AFFFs) are widely used for fire suppression but are a major source of environmental contamination due to their content of per- and polyfluoroalkyl substances (PFAS). AFFFs are primarily based on two chemistries: electrochemical fluorination (ECF) and fluorotelomerization (FT), each with distinct PFAS profiles and environmental behaviors. Analytical investigations have revealed a complex mixture of known and novel PFAS in both ECF and FT-based foams. A major part of these PFAS compounds may over time degrade into perfluorinated end products. FT-based AFFFs predominantly contain 6:2 fluorotelomer structures such as FTSAS, FTAB, and DPOSA, but other homologues such as 8:2 can be found as well. ECF-based foams are typically dominated by PFOS, but sulfonamide precursors can be equally important. In addition to an increased range of direct AFFF component analysis, the Total Oxidizable Precursor (TOP) assay has proven effective in identifying hidden PFAS precursors. Biodegradation studies show that FT-based PFAS degrade under aerobic conditions, but with a terminal product yield often below 10% over the time studied. FT betaine structures have been found to be particularly persistent. ECF-based PFAS exhibit a wide range of degradation behaviors, with quaternary ammonium and betaine structures showing the highest persistence. Structural features such as nitrogen head groups and perfluoroalkyl chain length significantly influence degradation rates and product yields. Despite some precursor degradation, many PFAS remain in the environment for a very long time, highlighting the need to use extended analytical methods and mass balance approaches. These findings underscore the

importance of comprehensive PFAS characterization in AFFFs to inform environmental risk assessments and guide remediation strategies.

## *Introduction*

Aqueous film-forming foams (AFFFs) are widely used chemical formulations designed to suppress hydrocarbon-based fires by forming a film that cuts off oxygen and prevents reignition (Harding-Marjanovic et al., 2015; Place and Field, 2012). These foams may contain per- and polyfluoroalkyl substances (PFAS), which are persistent, bioaccumulative, and potentially toxic (Place and Field, 2012; Luo et al., 2020). AFFFs have been extensively deployed at military, industrial, and municipal sites, leading to widespread contamination of soil, groundwater, and surface water (e.g. Backe et al., 2013; D'Agostino and Mabury, 2017).

Two major types of AFFF formulations exist based on their fluorochemical production method: electrochemical fluorination (ECF) and fluorotelomerization (ITRC, 2023). ECF-based AFFFs, historically produced by 3M, contain fully fluorinated perfluoroalkyl acids such as PFOS and PFHxS and started to be phased out around 2002 due to environmental and health concerns (Place and Field, 2012; ITRC, 2023). In contrast, fluorotelomer-based AFFFs, which became predominant after 2001, contain polyfluorinated precursors that can degrade into perfluoroalkyl carboxylates (ITRC, 2023). Despite reformulation efforts, fluorotelomer AFFFs for a long time contained significant levels of long-chain PFAS (incl 8:2 FT structures) or their degradation products (ITRC, 2023).

The complex and variable composition of AFFF formulations, including both known and unidentified PFAS, complicates environmental assessments (Luo et al., 2020; ITRC, 2023). Targeted PFAS analyses often account for only a small fraction of total organofluorine content in AFFF-impacted environments (Luo et al., 2020). As a result, comprehensive characterization of AFFF formulations is essential to understand their environmental fate and transport (Barzen-Hanson et al., 2017; ITRC, 2023). This is particularly important for assessing contamination in soil and groundwater, where legacy and modern AFFF use has left a persistent PFAS footprint. Investigation into the composition and degradation of AFFF-derived PFAS is thus critical for effective environmental management and remediation strategies.

## *Analytical investigations of AFFF*

Comprehensive analysis of AFFF typically make use of a suite of techniques to allow for an, as complete as possible, characterization. Given the complexity and number of unknown PFAS compounds in both ECF and FT produced foams high-resolution mass spectrometry (HRMS) is employed as detectors with QTOF (Quadrupole Time-of-Flight) and Orbitrap being the most common examples. The chromatographic part of the system is most frequently a UPLC (ultra performance liquid chromatography) instrument, though GC (gas chromatography) has also been utilized. Regarding HRMS applications there are, simplified, two variants, non-target analysis (NTA) based on investigation of elemental compositions derived from absolute masses obtained without any prior knowledge of possible compounds and an NTA sub-category, suspect screening analysis (SSA) where a list of absolute masses is matched with known substances, denoted "suspects" (see e.g. Manz et al, 2023). A drawback is that full quantification cannot be achieved, frequently semi-quantifcation versus a known PFAS is performed instead.

HRMS characterization is almost always accompanied by a regular "target" PFAS analysis. This analysis covers legacy, often regulated, PFAS such as PFOS, PFOA and PFHxS. Targeted determination is dependent upon the availability of analytical standards limiting the number of analytes to approx 100-150. Target PFAS, with the exception of some ECF AFFF, do normally correspond to a very limited share of the total organo-fluorine content. Discovery of prevalent AFFF components can trigger manufacturing of new standards which has happened with e.g. 6:2 FTAB, DPOSA and 6:2 FTSAS.

Other complimentary methods are TOP (total oxidizable precursors), EOF (extractable organic fluorine) and TOF (total organic fluorine). These can provide further information, not at least for construction of mass balances but also, as for TOP, further structural confirmations. Concerning AFFF composition, concentrates typically contain <2% fluorosurfactants (PFAS) and 15-18% "ordinary" surfactants (ITRC, 2023), although higher PFAS levels have occasionally been found.

### *Characterization of Fluorotelomer (FT) Based AFFF*

During the first half of the 2010's a number of fundamental papers characterizing the content of FT AFFF products were published, laying the foundation for our current understanding. Place and Field (2012) investigated AFFF products from US manufacturers such as National Foam, Ansul, Chemguard, Angus, Buckeye, and Fire Service Plus. National Foam AFFF featured 4:2 to 10:2 fluorotelomer sulfonamide betaines (FTAB), while Ansul and Chemguard products were dominated by 6:2 and 8:2 fluorotelomer thioether amido sulfonates (FTSAS/FtTAoS). Angus AFFF included both FTSAS and hydroxylated quaternary amine derivatives. Buckeye AFFF contained unique x:y:z fluorotelomer betaines (FTB), and Fire Service Plus AFFF shared a similar structure. Six telomer-based AFFF formulations were examined by Backe et al (2013), revealing a diverse suite of fluorotelomer surfactants. FTSASs, particularly the 6:2 homologue, was the dominant PFAS found in Ansul, Chemguard, and Angus products. Other telomer PFAS classes such as fluorotelomer sulfonamido betaines, sulfonamido amines, and betaines were present in National Foam and Fire Service Plus formulations. Fluorotelomer sulfonates (FTS) were detected only in formulations containing sulfonamido betaines, suggesting they may be degradation products of FTSASs.

In the study by D'Agostino and Mabury (2014) FT-based PFASs were dominant in post-2002 AFFF formulations. FTSASs with chain lengths from C4 to C14, along with their sulfoxide derivatives and hydrolysis products were frequently seen. Fluorotelomer sulfonamide alkylbetaines (FTABs) and their amine intermediates were found in a number of foams, with C4 to C12 congeners detected. Fluorotelomer betaines (FTBs) and fluorotelomerthiohydroxyl ammonium compounds (FTSHAs), including sulfoxides, were also present, particularly in one formulation. Similarly, Weiner et al. (2013) identified 6:2 FTSAS as a major component in many AFFFs. It was detected in 71% of the foams, with concentrations ranging from 1 to 7,000 mg/L. Five foams contained over 1,000 mg/L of 6:2 FTSAS, and these also showed high levels of its sulfoxide derivative, indicating oxidative sensitivity. 6:2 FTS was present at 1-49% of the FTSAS concentration. Minor amounts of 4:2 and 8:2 FTSAS were also detected. The presence of 6:2 FTS in the same samples supports the hypothesis that it is a breakdown product of 6:2 FTSAS.

Subsequent studies have contributed to further elucidation and detection of additional AFFF classes as well as possible degradation and by-products. Dauchy et al. (2017) analyzed nine concentrates. Only three of the targeted PFAS— 6:2 FTSA, 6:2 FTAB, and 6:2 FTAA (FtSaAM) —were quantified, with concentrations ranging from <5 to 3,200 mg/L. These compounds were found in various combinations across the samples. Additionally, thirteen other PFASs were identified including 6:2 FTSAS and 6:2 FtTHN, which were present in several concentrates with high relative intensity ratios (i.e. concentration). PFOSAm, a PFOS precursor, was detected in one concentrate, possibly due to tank reuse. C4 to C8. Liu et al (2022) detected a similar range: 6:2 FTS, 6:2 FTAB, 6:2 FTAA, and 6:2 FTSAm. DPOSA dominated in one foam. The product VF-9129 uniquely contained EtOH-AmPr-PFHxSAPrS (or

6:2 FTSAPr-AmHOPrS; Shojaei et al., 2022a), a complex telomer-based PFAS. Another sample featured OBS (sodium p-perfluorous nonenoxybenzene sulfonate), a novel PFAS recently linked to environmental contamination in China. The study also indicated the existence of polymer-based products at least on the Chinese market. Concentrations of neutral PFAS like 6:2 FTOH could reach up to 4.1 g/L in these.

Dubocq et al. (2020) investigated 24 AFFF. DPOSA (6:2 FTNO), another FT surfactant, was semi-quantified at 4.7-6.0 mg/L in two samples and 6:2 FTAB was detected at 36-120 mg/L in two as well. 6:2 FTSAS reached 2800 mg/L in one sample while lower levels were observed in some other formulations. Among “regular” PFAS, 6:2 FTS was the most prominent, found at concentrations up to 39 mg/L. The combined fluorine from these compounds explained only up to 32% of the total organofluorine in the best case, a figure that is in contrast to some other reports. The study by Barzen-Hanson et al. (2017) confirmed previously reported fluorotelomer PFASs such as 6:2 and 8:2 FTSAS and FTAB in National Foam and Ansul AFFF products. Overall, there was a limited diversity of telomer-based PFASs suggesting fewer unintended byproducts compared to ECF-based formulations. Ten AFFF formulations were screened using liquid chromatography - ion mobility spectrometry - mass spectrometry (LC-IMS-MS; Luo et al., 2020). In total 124 substances were detected. Major components included 6:2 FTAB, 6:2 FTSAS, and 6:2 FTAA. The study also pointed to the possibility that many analytes were degradation products or manufacturing byproducts, such as 6:2 FTS and 6:2 FTSH.

In the work by Liu et al. (2023) an Ansulite AFFF formulation was investigated with fluorotelomer betaines (FTBs) being the dominant constituents. The most abundant compounds were 5:1:2 FTB (3500 mg/L), 7:1:2 FTB (3300 mg/L), and 9:1:2 FTB (840 mg/L), followed by 5:3 FTB (820 mg/L) and 7:3 FTB (740 mg/L). Together, these accounted for over 93% of the total PFAS concentration, which summed to approximately 10,300 mg/L. In a paper by the same authors (Liu et al., 2024) 14 FT-based AFFFs were characterized and found to be dominated by zwitterionic and cationic FT precursors, particularly n:2 FTAB (6,100-37,000 mg/L) and n:1:2 FTB (up to 12,000 mg/L). An Ansulite product was notable for its high level of 6:2 FTSAS (3,900 mg/L), and 6:2 FTSHA (FTTh-OHPrTAm; 1,600 mg/L), together accounting for over 90% of total PFAS. As in the study mentioned above FT AFFFs showed lower PFAS diversity (10-50 individual PFAS per foam) and total concentrations (6,100-48,000 mg/L) compared to ECF AFFFs. Seven novel FT-derived PFAS classes were identified, though they contributed less than 1% of total PFAS, with some still reaching hundreds of mg/L.

Li et al. (2024) found that FT-based PFAS dominated nine of the 13 foam samples, contributing 44-100% (average 85%) of total target PFAS. Major substances comprised 6:2 FTAB, 6:2 FTSA, 6:2 FTSAS, 6:2 FTAA (FTSaAm) and 6:2 FTSA-HOPrS, with 6:2 FTAB found in all tested foams. A comprehensive analysis of PFAS in the Buckeye Platinum Plus C6 AFFF formulation was performed by Shojaei et al. (2022a). The dominant compound was 6:2 FTSAPr-AmHOPrS, with a concentration exceeding 13,000 mg/L, representing ~90% of the total PFAS load. Shojaei et al. (2022b) analyzed two fluorotelomer-based aqueous film-forming foams (FT-AFFFs) using a combination of suspect screening and semiquantitative (SQ) analysis to determine PFAS composition, alongside the TOP assay (see below). In both formulations, 6:2 fluorotelomer sulfonate (6:2 FTS) was the most abundant target PFAS, present at approximately 10 mg/L. In the first AFFF, 6:2 FTSAPr-AmHOPrS was the predominant PFAS constituent, detected at a concentration of 12,000 mg/L, with minor contributions (up to ~10%) from structurally similar 6:2-based compounds. The second foam formulation contained 6:2 FTS (170 mg/L) and 8:2 FTSAS (530 mg/L), along with their oxidized derivatives, 6:2 SO-FTSAS and 8:2 SO-FTSAS, at concentrations of 32 mg/L and 130 mg/L, respectively. Several minor substances were also identified, including 6:2 FTAB (6.8 mg/L).

Screening identified 14 major PFAS compounds in nine contemporary FT AFFF products (Ruyle et al., 2021). All 14 were 6:2 FT-based compounds, which together accounted for 96 ± 1% of PFAS peak area in negative ion mode and 92 ± 6% in positive ion mode. Nine of the most abundant compounds comprised 6:2 FTAB, 6:2 FTSAS, SO-6:2 FTSAS, 6:2 FTSHA, 6:2 FTTh-PrAm, 6:2 FTS, DPOSA (6:2 FTNO), EtOH-AmPr-PFHxSAPrS (or more likely 6:2 FTSAPr-AmHOPrS; Shojaei et al., 2022a) and 6:2 FTSO-OHPrTAm, while five structures remained unidentified. Most of the compounds listed confirm other studies, and also the predominance of 6:2 FT structures in current foams. Total extractable organofluorine (EOF) in the AFFF samples ranged from 4,200 to 16,000 mg/L F, while targeted PFAS explained ≤1%. Also in the work published by the Swedish Chemical Agency (KEMI, 2015), covering six modern foams from 2014, 6:2 FT structures were the main PFAS constituents in all. 6:2 FTAB, 6:2 FTSAS or mixes were frequent while one sample contained DPOSA and 6:2 FTAA.

### *Characterization of ECF Based AFFF*

Composition of electrochemical fluorination (ECF) AFFF, mainly 3M formulations, has also been subject for intense research. Regarding the content of many legacy ECF foams, especially 3M manufactured, the major PFAS constituent is PFOS with concentrations ranging from 5,000-40,000 mg/L, most products having <10,000 (Houtz et al, 2013; Liu et al, 2024). In turn PFOS made up 25-55% of the total PFAS content. These formulations also typically contain significant amounts of other PFSA, in particular PFHxS, as well as PFCA e.g. PFOA. A feature of ECF produced PFAS is that both linear and branched isomers of the perfluorinated moiety are formed, for PFOS around 30% branched. The presence of branched PFAS can assist evaluation not at least regarding the origin of end products and during TOP (van Hees, 2018).

Besides PFSAs and PFCAs ECF foams also contain precursors such as C4-C8 sulphonamides. Place and Field (2012) identified several ECF substances in 3M AFFF formulations used by the U.S. military. As expected, major components were consistently C6-C8 PFSA, including PFOS. Additionally, zwitterionic C4-C6 perfluoroalkyl sulfonamides with carboxylic acid and tertiary amine functionalities were detected in products manufactured after 1992. Similar observations were made by Backe et al. (2013) who analyzed five 3M AFFF formulations. These contained high concentrations of PFOS, 8-12 times higher than PFHxS. Lower levels of PFCA were also found. In addition, cationic perfluoroalkyl sulfonamidoamines (C4-C8 PFSaAm) and zwitterionic perfluoroalkyl sulfonamide amino carboxylates (C4-C8 PFSaAmA or PFASAC) were detected, with C6 being the most prevalent homologue. In line with Place and Field (2012) these novel PFAS were more abundant in formulations manufactured after 1993, indicating a shift in composition over time.

D'Agostino and Mabury (2014) discovered several ECF-based PFASs in AFFF formulations including one from Angus Fire. These included PFSaAmAs, their amine intermediates, and dicarboxylate side products, with chain lengths ranging from C4 to C8. Additionally, perfluoroalkyl sulfonamidoamine oxides (PFASNOs) were found in two foams, with C6-C9 congeners confirmed. These ECF-derived surfactants are potential precursors to perfluoroalkyl sulfonates (PFSAs), such as PFOS, due to known biotransformation pathways. Thirty-four novel classes of ECF compounds were discovered by Barzen-Hanson et al. (2017). Many shared a common sulfonamide-based structure and varied by 50 Da, indicative of $CF_2$-based homologues. The classes included anionic, zwitterionic, and cationic species. Notable examples were perfluoroalkyl sulfonamides, sulfonamido betaines, and trimethylammonium derivatives (chain lengths C3 to C8). A higher chemical complexity and diversity of the formulations was found for products manufactured before 1993.

Seven ECF AFFFs were analyzed in the paper by Liu et al. (2024). As anticipated, these were rich in PFSAs, especially PFOS, followed by PFHxS. The foams also contained a wide variety of zwitterionic and cationic ECF precursors, including sulfonamides and amides with ethanol, propane sulfonate, and quaternary ammonium headgroups. Notably, 14 novel ECF-derived PFAS classes were detected, including AmPr-FASAPrS and TAm-OHPr-EtFASA, with some classes exceeding 2000 mg/L. Total PFAS concentrations in ECF AFFFs ranged from 11,000 to 120,000 mg/L, with 102-224 individual PFAS detected per sample. Dong et al. (2024) identified nine major PFAS classes as components of a ca 1999 3M AFFF. Among these, ECF precursors comprised TAmPr-FASA (C4-C6), AmPr-FASA (C4-C8), and AmPr-FAAd (C6-C7).

Shojaei et al. (2022b) investigated an ECF-based AFFF using a combination of suspect screening, semiquantitative (SQ) analysis to assess the total PFAS composition in combination with the TOP assay (see below). The dominant conventional target PFAS identified in the formulation was PFOS, present at 6,500 mg/L, followed by perfluorohexane sulfonate (PFHxS) at 430 mg/L. Suspect screening revealed the presence of 189 PFAS in the product. The major constituents were primarily C6 sulfonamide derivatives, including EtOH-AmPr-FHxSA (930 mg/L), EtOH-AmPr-FHxSA-EtOH (1,400 mg/L), EtOH-AmPr-PFHxSAPrS (1,900 mg/L), and AmPr-FHxSA (290 mg/L). Lower concentrations of analogous C4–C5 and C7–C8 sulfonamide derivatives were also detected.

In an investigation of current Chinese AFFF formulations several ECF-based PFAS in were identified while PFOS was still the dominant compound.  (Liu et al., 2022). Zwitterionic PFAS such as PFASNO (C6 and C8), sulfonamido amines (PFASaAm), and sulfonamides (PFASA) were also present. These compounds are known to transform into perfluoroalkyl acids (PFAAs) under environmental conditions. Li et al. (2024) also studied contemporary Chinese firefighting foams and detected 14 PFAS classes of sulfonamides. These included novel compounds such as bis(perfluoro-octylsulfonyl) amine (BiFOSA) and unsaturated perfluorooctane sulfonamido amine oxide (U-PFOSNO). Some AFFF were characterized by high levels of C8 homologues like PFOSNO and FOSAC, consistent with other reports. In four foam samples, sulfonamides and PFSAs contributed 61-68% of total PFAS.

### *TOP Assay - Chemical Oxidation of Precursors*

As the investigations summarized above show thousands of PFAS compounds may exist in AFFFs and it is not analytically possible to determine all, at least not fully quantitatively. In addition to detection of these individual substances, there is a potential need to assess the pool of PFAS that with time may decompose to perfluorinated compounds.

It is known that precursors can be chemically oxidized to corresponding perfluorinated substances. Houtz and Sedlak (2012) developed a laboratory method, which was named TOP (Total Oxidizable Precursors) assay, based on oxidation using hot persulphate in an alkaline solution. Under these conditions hydroxyl radicals are formed reacting with both telomers and ECF (mainly sulfonamide) precursors. The parameters were selected in a way, so PFCA and PFSA initially present were not affected.

In comparison to naturally occurring biodegradation in the TOP assay sulfonamide containing precursors form a corresponding Cn PFCA e.g. in the case of PreFOS, PFOA is the resulting product. As in the environment FT (n:2) oxidation is more complex and a series of PFCAs are produced, which includes the Cn+1, Cn, Cn-1 etc down to the C4 acid. For the telomers investigated the greatest yield was seen for the Cn-1 PFCA followed by the Cn and then Cn-2 compounds (Houtz and Sedlak, 2012). The TOP assay has been used for a number of environmental matrices such as effluent waste water, run-off, river and ground waters as well as soil and products like AFFF.

### *TOP Assay of AFFF - Fluorotelomer and ECF Products*

Houtz et al (2013) investigated foams from manufacturers such as Ansul, Chemguard, National Foam, and Buckeye containing sulfonamido betaines (FTAB), sulfonamido amines (FTAA), and thioamido sulfonates (FTSAS; see above). Upon oxidative conversion using the TOP assay, these precursors yielded substantial amounts of PFCA, primarily PFHxA and PFPeA, with recovery rates ranging from 61% to 200%. Buckeye AFFF, high in fluorotelomer betaines (e.g. 7:1:2 FTB), produced a broader PFCA profile including PFHpA and PFOA. These results demonstrated the high precursor content and transformation potential of FT AFFFs. In the same article 3M AFFF formulations (1988-2001), containing sulfonamide-based precursors such as PFHxSAm and PFHxSAmA, were oxidized. These precursors were efficiently oxidized to PFHxA with recovery rates 73% to 150%.

TOP conversion was applied to selected AFFF to assess the presence of unidentified precursors (Dauchy et al., 2017). In two samples where no dominant PFASs were initially identified, the TOP assay revealed substantial levels of oxidizable precursors, generating total PFCA concentrations around 20,000 mg/L. The oxidation products included long-chain PFCAs such as PFDA to PFTeDA. These findings underscore the applicability of the TOP assay in revealing hidden PFAS content in modern AFFF products.

Nearly all oxidizable PFAS precursors in the foams studied were transformed into PFCAs at TOP, confirming its high efficiency (Li et al., 2024). However, NTA after TOP assay uncovered 1-56% more PFAS and 8-56% more fluorine equivalents than target analysis alone. Six additional PFAS were identified post-TOP, including three novel double-bond perfluorinated alcohols (U-PFHxOH, U-PFPeOH, U-PFBOH). These findings suggest that conventional TOP assays may underestimate PFAS precursor levels. Liu et al. (2024) showed that TOP assay produced high levels of PFCA from both FT and ECF AFFFs with ECF foams forming mainly PFHxA (54-76%) and FT foams PFPeA (34-43%) and PFBA (19-22%). In FT AFFFs, known precursors explained nearly all TOP-derived PFCAs, while in most ECF AFFFs, 19-53 mol% of precursors remained unidentified. The sum of TOP-derived precursors and targeted PFAAs correlated well with TOF in ECF AFFFs (87 ± 12% recovery), but less so in FT AFFFs (51 ± 8%), likely due to fluorine loss during oxidation. These results highlight the utility and limitations of TOP and EOF/TOF in assessing PFAS mass balance.

In addition to suspect screening and semiquantitative (SQ) analysis, Shojaei et al. (2022b; see above) also performed the TOP assay on the three AFFF formulations investigated. Results from the TOP assay were compared with SQ data obtained from the screenings. On a molar basis, comparable PFAS levels (14–40 mmol/L) were observed for both the ECF-based AFFF and the FT formulation containing 6:2 FTSAPr-AmHOPrS. In contrast, for the second FT foam—characterized by the presence of 6:2 and 8:2 FTSAS/SO-FTSAS—the semiquantitative analysis accounted for only ~10% of the PFAS molar concentration indicated by the TOP assay. The underlying reasons for this discrepancy remain unclear. Suspect screening was also conducted post-TOP assay. Three PFAS classes—hydrogen-substituted perfluoroalkyl carboxylic acids (H-PFCAs), unsaturated perfluoroalkyl ether carboxylic acids (UPFECAs), and perfluoroalkyl cyclopentane carboxylic acids (PFCPeCAs)—showed significant concentration increases, suggesting they may represent novel TOP end products. Conversely, five other PFAS classes, including chlorinated perfluoroalkyl sulfonic acids (Cl-PFSAs) and ketone-substituted perfluoroalkyl sulfonic acids (K-PFSAs), were resistant to oxidation. The authors concluded that these recalcitrant compounds should be quantified prior to TOP assay to avoid underestimation of total PFAS content.

TOP assay, combined with Bayesian inference, was used to quantify precursor concentrations and chain lengths in AFFF samples (Ruyle et al., 2021). The analysis showed that targeted PFAS and oxidizable precursors together accounted for 104 ± 19% of extractable organofluorine (EOF), confirming a near-complete fluorine mass balance. Changes in C4-C8 PFCAs were used to infer precursor levels. Notably, 6:2 FT precursors made up 90 ± 1% of the total oxidizable PFAS in contemporary AFFF, with 6:2 FTSA—one of the few targeted analytes—representing less than 3% of this group.

### *TOP Assay and Suspect Screening of Highly Contaminated Soils*

Characterization of source zone soils polluted by AFFF can be important for a more comprehensive environmental assessment, not at least to gain qualitative and quantitative information on precursors that may degrade over time and e.g. cause groundwater contamination. TOP assay is one of the analytical tools that can be used for this purpose and can also reflect the type(s), “backbone structures”, of AFFF that caused the pollution. Suspect screening combined with semi-quantification is also becoming an important method for a more direct assessment.

In AFFF-impacted soils and aquifer solids, the TOP assay revealed extensive precursor presence and transformation (Houtz et al, 2013). In a surficial soil oxidation yielded up to 20,000 µg/kg PFHxA and 13,000 µg/kg PFPeA. Lower contents were found in an aquifer solid with TOP producing 1,000 µg/kg PFHxA and 870 µg/kg PFBA. Across all samples, PFHxA was the dominant oxidation product, often exceeding predicted levels, indicating the presence of unidentified C6 precursors. Unidentified precursors accounted for 13-20% of total PFAS. In the work by Casson and Chiang (2018) the source area soils, where 3M AFFF had been mainly used, contained high concentrations of PFASs, particularly PFOS and the precursor PFOSA. TOPA results revealed substantial increases in PFCA concentrations post-oxidation, for example, in one soil PFCAs rose from 140 to 15,000 µg/kg with PFHxA as major conversion product.

Wang et al (2025a) applied the TOP assay to ten AFFF-impacted soil samples in Sweden, revealing significant increases in PFCAs post-oxidation, rising from 0.7 to 12,400 µg/kg DW. The C4-C6 PFCA (70-86%) formed indicated mainly short-chain precursors with C5 (PFPeA) as major PFCA, followed by C6 (PFHxA) and C4 (PFBA), likely reflecting initial FT 6:2 and ECF C6-sulphonamide precursors. One site, however, showed a distinct profile, possibly suggesting the presence of ECF C8-sulphonamides. Despite combining TOP and target analysis, 20-94% of extractable organofluorine remained unexplained, likely due to non-oxidizable PFAS, incomplete precursor conversion, and undetected ultra-short-chain PFAS.

In a parallel paper to the one mentioned above Wang et al. (2025b) investigated five of the ten soils subjected to TOP conversion and confirmed 4:2 to 14:2 FTABs, with 6:2 and 8:2 being the most abundant, comprising on average 57% and 21% of the FTAB class, respectively. In two soils N-TAmP-FASA was found including both C6 and C8. Other PFAS identified included 6:2 FTSHA-sulfoxide and additional C6- and C8-sulphonamides. In additional work, van Hees and Karlsson (2024) conducted suspect screening—based on the findings of Wang et al. (2025b)—in combination with full (target) and semiquantitative (SQ) analysis of two contrasting soils from the dataset: one predominantly impacted by FT-based AFFF, and the other by ECF-based AFFF contamination, primarily PFOS. In the FT-impacted soil, FTABs were the major AFFF-related compounds, with approximately equal concentrations of the 6:2 and 8:2 homologues (~8,000 µg/kg dry matter), and notable contributions from the 10:2 and 12:2 variants. In the ECF-impacted soil, PFOS was the dominant PFAS, detected at 21,000 µg/kg dry matter, followed by PFHxS at 1,700 µg/kg. A total of six C6-, two C8-, and one C5-sulfonamide precursors were identified, ranging from 5 to 210 µg/kg dry matter. Examples include N-TamP-FHxSA/FOSA, N-AP-FHxSA, EtOH-AmPr-FHxSA-EtOH (N-HOEAmP-FHxSE), N-CMAmP-FHxSA/FOSA, and N-AmCP-FHxSA.

Shojaei et al. (2022b) also applied semiquantitative (SQ) suspect screening and the Total Oxidizable Precursor (TOP) assay to AFFF-impacted soils to evaluate total PFAS concentrations and transformation behavior. PFOS was the most abundant PFAS in soil A, reaching 510 µg/kg, with PFHxS, PFNS, and PFDS also present at significant concentrations (20–150 µg/kg). In soil B, PFOA was dominant at 240 µg/kg, while soil C exhibited a high PFOS concentration of 1,250 µg/kg. Fluorotelomer sulfonates (4:2, 6:2, and 8:2 FTS) were detected across all three soils, ranging from 0.1 to 30 µg/kg. SQ analysis identified a wide range of PFAS classes, with total concentrations spanning from 1.3 to 13.5 µmol/kg (approximately 650 to 6,500 µg/kg). The TOP assay revealed a 30% and 50% increase in oxidizable precursors in soils A and C, respectively, while soil B showed minimal change. Several PFAS classes, including hydrogen-substituted perfluoroalkyl carboxylic acids (H-PFCAs) and unsaturated perfluoroalkyl ether carboxylic acids (UPFECAs), increased following TOP treatment, indicating their role as novel oxidation end products. On a molar basis, good agreement was observed between the sum of SQ and TOP results for soils A and B. In contrast, for soil C, the semiquantified PFAS concentrations were approximately 25–30% higher than those estimated by TOP. Suspect screening identified numerous individual compounds, revealing substantial variability in PFAS composition. Among the major ECF precursors, EtOH-AmPr-FHxSA, AmPr-N-MeFHxSA, EtOH-AmPr-FHxSA-EtOH, and TAmPr-FOSA (~50–1,000 µg/kg) were prominent, with the highest concentrations found in soil C. Fewer FT precursors were detected; however, 6:2 FTAA was present at significant levels (~25–850 µg/kg), along with minor contributions from its 8:2 homologue and 6:2 FTSA-PrAn. Again, soil C exhibited the highest level of contamination. The study also evaluated basic and basic + acid extractions for all three soils, along with two extract dilutions. In one soil, TOP yield increased by 35%, corresponding to approximately 10% of the total target + TOP-derived PFAS, while no effect was observed in the other two soils. The authors concluded that combining TOP and SQ methodologies provides a more representative estimate of total PFAS concentrations in soil matrices.

Capitain et al. (2025) developed a matrix-matched semi-quantification method for NTA in an AFFF-contaminated soil profile, enabling estimation of 96 tentatively identified compounds alongside 28 fully quantified PFAS. The approach utilized ionization class-specific average calibration curves (ACCs) for a number of PFAS classes. In the topsoil layer the total PFAS concentration reached 15,000 µg/kg, with cationic PFAS dominating (74%), including major compounds such as 6:2 FTSHA-sulfoxide (2,300 µg/kg) and 6:2 FTSHA-sulfdioxide (1,900 µg/kg). Quantified PFAS included PFOS (1,700 µg/kg), 6:2 FTAB (3,200 µg/kg), and 5:1:2 FTB (1,100 µg/kg). The fluorine mass balance was closed, with F from PFAS matching the measured EOF. PFAS concentrations decreased with depth, with transformation products such as PFHxA and PFHxS peaking in the saturated zone. The study demonstrated the critical role of semi-quantification in comprehensive PFAS site characterization.

### *Biodegradation of AFFF Precursors*

As the articles cited above demonstrate AFFFs contain complex mixtures PFAS, both ECF-derived and FT-based compounds. Upon environmental release, precursors can undergo microbial biotransformation, ultimately yielding highly stable perfluoroalkyl (typically PFSA and PFCA) end-products. The transformation processes primarily affect the non-fluorinated head groups. FT-based compounds may also undergo degradation of the hydrocarbon spacer adjacent to the fluorinated tail as well as partial unzipping of the tail itself.

Aerobic conditions favour transformations, while anaerobic pathways are less understood. The transformations often involve semi-stable intermediates like fluorotelomer sulfonates (FTS) and fluorinated sulfonamides (FASA). Some compounds, such as CMeAmPr-FASAA, are detected in the environment but not in AFFF, suggesting in situ formation. Understanding these pathways is essential for environmental monitoring, risk assessment and source attribution. However, predictive models for

PFAS biotransformation remain limited due to the unique chemical properties of these substances (Choi et al, 2022).

*Biodegradation of Fluorotelomer (FT) Based AFFF*

Microbial biotransformation of fluorotelomer precursors, particularly n:2 fluorotelomer surfactants, has been extensively studied. These include compounds like 6:2 FTAB, 6:2 FTAA, and 6:2 FTSAS, which share common transformation pathways leading to intermediates such as FTSs and FTOHs. The degradation primarily occurs at the head group via N-dealkylation and sulfur oxidation. The topic was reviewed by Choi et al (2022). Among the studies listed, not discussed below, for example, 6:2 FTAB showed a 70% reduction in 7 days under aerobic conditions in a pure bacterial culture with a 71-99% mass balance, and 6:2 FTAA had 53 ± 6% remaining after 109 days with over 12-16% recovered as products (>50% 6:2 FTS). Under anaerobic (sulphur-reducing) conditions, 6:2 FTSAS showed ~75% reduction over 282 days. These transformations can yield PFCAs through intermediates like FTOH and FTCA. However, field detection of intermediates is limited with the exception of e.g. FTS substances, suggesting low environmental stability. The authors concluded that FT degradation is influenced by environmental conditions and the structure of the head group.

Commonly biodegradation experiments have been carried out in inoculated microcosms. Weiner et al. (2013), tested 6:2 FTSAS (trade name Lodyne) using activated sludge from a wastewater treatment plant (WWTP) under aerobic conditions. The compound degraded rapidly, with only 0.05% remaining after 51 hours and falling below the limit of quantification (LOQ) at the end of the experiment (42 d). Detected degradation products included 6:2 FTOH (final yield: 6.2%), 5:3 FTCA (17%), 6:2 FTUCA (3.4%), PFPeA (3.2%), and smaller amounts of PFHxA and PFHpA. Harding-Marjanovic et al. (2015) also investigated the aerobic biotransformation of FTSAS in soil microcosms amended with Ansul AFFF, focusing on 6:2, but also 4:2 and 8:2 homologues. Complete biotransformation of all three FTSASs occurred within 45 days in live microcosms, resulting in transformation products such as FTS, FTCA, FTUCA and PFCA (PFHxA, PFPeA, and PFBA). Two novel intermediates, 6:2 SO-FTSAS and 6:2 $SO_2$-FTSAS, were identified suggesting sequential oxygenation of the thioether moiety. Quantified transformation products accounted for ~10% (mol/mol) of the FTSAS added. A TOP assay recovered 75-100% of the FTSAS as PFCAs and the distribution of PFCA (C4:C5:C6) formed indicated oxidation of 6:2 FT precursors i.e. 6:2 FTSAS and related 6:2 transformation substances. The studies confirm that FTSAS is a precursor to persistent PFCAs in the environment with potentially slow transformation rates of intermediates potentially leading to long-term release.

Aerobic biodegradation of 6:2 FTAA and 6:2 FTAB was also performed in WWTP sludge over 109 days by D'Agostino and Mabury (2017). The most abundant degradation product was 6:2 fluorotelomer sulfonamide (FTSAm), accounting for nearly 7% of FTAA and 1% of FTAB in the active experiments. Both compounds also degraded into 6:2 FTOH, 6:2 FTCA, 6:2 FTUCA, 5:3 FTCA, and PFCAs (PFPeA, PFHxA - and for FTAA - PFBA). FTAA underwent more extensive transformation, with only 1-9% of the unaccounted FTAA remaining in the aqueous phase or solids, compared to 33-74% for FTAB. Total quantifiable degradation products accounted for 12-16% of FTAA loss and 3-6% for FTAB. Concentrations of FTCA and FTUCA peaked around day 45, indicating their role as intermediates. Final PFCA yields were 2.1% (6:2 FTAA) and 0.6% (6:2 FTAB). The slow degradation—especially for FTAB—suggests persistence in aerobic environments.

6:2 FTAB was also investigated by Fang et al. (2024a) alongside 6:2 FTS and DPOSA (6:2 FTNO)—in aerobic sludge over 100 days. Their degradation (disappearance) followed first-order kinetics with half-lives of 29 days for 6:2 FTSA, 1.2 days for 6:2 FTNO, and >100 days for 6:2 FTAB. DPOSA rapidly transformed into 6:2 FTAA ($t_{1/2}$ ≈ 11.5 days), which further degraded to 6:2 FTSAm, but not to PFCA. In contrast, 6:2 FTS yielded several PFCAs, including PFHpA (7%), PFHxA (5%), and 5:3 FTCA (7%) by day 100. Novel transformation products such as 6:2 FTUSA and Ketone-6:2 FTSA were detected. 6:2 FTAB showed minimal transformation, with no major products seen, likely due to strong sorption and lack of specific microbial enzymes. In another report by Fang et al. (2024b) 6:2 FTS, 6:2 FTAB, 5:3 FTB and 5:1:2 FTB were investigated as well, but in aerobic wetland soil over 100 days with two different carbon sources. 6:2 FTS showed the highest degradation, with only 1-12% remaining ($t_{1/2}$ = 17-26 days). 6:2 FTAB was more persistent, with 20% degraded, primarily via sulfonamide hydrolysis. The final PFCA yields from 6:2 FTS reached 13% (mainly PFHxA and PFHpA). In contrast, 6:2 FTAB yielded 0.8% PFHxA and 0.7% PFHpA at most. Both 5:3 FTB and 5:1:2 FTB showed extreme persistence, with no significant degradation or product formation. Liu et al. (2023) came to the same conclusion that both 5:3 and 5:1:2 FTBs are highly persistent in aerobic soils, displaying negligible degradation over 120 days in four different soils. The studies highlight that terminal nitrogen-containing groups significantly influence PFAS stability and transformation, especially the betaine moiety.

For comparison, Yan et al. (2024) investigated the biotransformation of 6:2 FTS in flow-through columns packed with AFFF-impacted soil under environmentally relevant conditions (305 days) instead of using microcosms. Reducing the pore-water velocity from 3.7 to 2.4 cm/day led to a decrease in 6:2 FTS effluent concentrations, from 71% to 55%, while increasing late-stage PFCA yields from 0.3 mol% to 1.0-1.4 mol%. Flow interruptions of 2 and 7 days further enhanced degradation, with product yields temporarily doubling. Most degradation occurred in the first quarter of the column. Compared to microcosms, column systems showed lower rates (~0.04 vs. 0.137 cm/g/d) but achieved similar or greater transformation yields more efficiently.

*Biodegradation of ECF Based AFFF*

Biotransformation of ECF-derived PFAS has gained attention more recently, focusing on classes such as quaternary ammonium surfactants, amine oxides, and betaines. These compounds share structural pattern that undergo similar degradation pathways, primarily involving N-dealkylation, hydrolysis, and oxidation. Some examples from the review of Choi et al (2022) include PFOAAmS which had a $DT_{50}$ (time for 50% disappearance) of 127 days and yielded 30% PFOA in aerobic soil, while PFOANO had a $DT_{50}$ of 3-7 days with 15-21 mol% PFOA yield. Sulfonamide-containing compounds like PFOSNO had $DT_{50}$ of 15 days. These transformations often bypass intermediate stages like FOSA, directly forming terminal PFCA and PFSA. Notably, tertiary sulfonamides, abundant in 3M products, are less studied but appear to be persistent in soils.

Liu et al. (2021) investigated the aerobic soil biodegradation (90-150 d; OECD 304 mod) of four ECF-based PFAS: perfluorooctane amido betaine (PFOAB), perfluorooctane sulfonamido betaine (PFOSB), perfluorooctane amido amine (PFOAAm), and perfluorooctane sulfonamido amine (PFOSAm). PFOAB degraded with $DT_{50}$ values of 266-630 days and yielded PFOA at 6-33 mol%, while its intermediate PFOAAm had a much shorter $DT_{50}$ of 14 days. PFOSAm showed moderate degradation ($DT_{50}$ = 48 days in one soil) and produced PFOS at 2.7 mol% yield. PFOSB was highly persistent ($DT_{50}$ = 675 days), with a PFOS yield of only 1.5 mol%, while its coexisting PFOSAm impurity contributed less to PFOS formation. The environmental stability of the compounds followed the order: quaternary ammonium ≈ betaine ≫ tertiary amine > amine oxide. These results demonstrate that the nitrogen-containing head group, rather than molecular weight, is the key determinant of degradation potential and product yield for ECF-derived PFAS in aerobic soils.

Biotransformations of several 3M AFFF components were observed in aerobic soil microcosms over 308 days, with AmPr-FASA (C4-C8) decreasing by 47-94% and TAmPr-FASA (C4-C6) by up to >99% in live treatments. Major transformation products included FASA (C3-C6, C8) and PFCA/PFSA (e.g., PFHxS, PFBA), which also increased under biotic conditions. M-AmPr-FASA and OAmPr-FASA were detected as intermediates. Structural features strongly influenced stability. In line with other reports compounds with quaternary ammonium groups (e.g. TAmPr-FASA) were more stable than those with tertiary or secondary amines, and carboxamide-based PFAS (e.g., AmPr-FAAd) were less stable than sulfonamide analogues. Additionally, the presence of carboxyalkyl groups on one or both nitrogen atoms enhanced resistance to transformation. Moreover, a longer perfluoroalkyl chain length reduced the biodegradation which was shown for a number of compound classes. It was speculated that higher adsorption to the soil in the microcosms was the main reason for the observation (Dong et al., 2024).

### *Discussion - Composition of AFFF*

FT-based AFFFs have likely existed since the 1970’s but have become predominant after 2002. They contain a diverse array of polyfluorinated precursors that degrade into PFCA, commonly with FTS substances as intermediates. Key PFAS classes include fluorotelomer thioether amido sulfonates (FTSAS), fluorotelomer sulfonamido betaines (FTAB), and DPOSA (6:2 FTNO). While 6:2 homologues are most common, 8:2 compounds like 8:2 FTSAS and 8:2 FTAB are also frequently detected, especially in older formulations. However, 8:2 FT structures have been reduced over time, for example through US-EPA:s voluntary PFOA Stewardship Program and foams should from 2015 be more or less be entirely 6:2 FT based (ITRC, 2023). In some cases, as for FTSAS, sulfoxide derivatives can also be of importance. Other notable constituents in foams include complex structures such as 6:2 FTSAPr-AmHOPrS, 6:2 FTSHA and 6:2 FTTh-PrAm. Potential by- or decomposition products such as 6:2 FTSA, 6:2 FTAA and 6:2 FTSAm are common as well, sometimes even to be labelled as major constituents. TOP assay results confirm that FT AFFFs yield a broad PFCA profile, reflecting the transformation of mainly 6:2 but also 8:2 precursors. Concentrations of PFAS in FT AFFF vary widely from <1,000 to 48,000 mg/L.

ECF-based AFFFs, primarily produced by 3M, are dominated by fully fluorinated PFSAs, especially PFOS with concentrations ranging from 5,000 to 40,000 mg/L making up 25-55% of the PFAS content. These formulations also contain PFCA like PFOA and a wide variety of sulfonamide-based precursors, including C4-C8 sulfonamido amines and sulfonamido amino carboxylates. Taken as a whole, C6 seems to be the most abundant sulfonamide homologue at least in products from the 1990’s, a finding that is also supported by the predominant formation of PFHxA at TOP oxidation of these foams. A characteristic of ECF chemistry is the presence of both linear and branched isomers, which can aid in source attribution. The chemical complexity of ECF AFFFs is higher than FT-based ones, with up to 200+ individual PFAS detected per sample.

These findings emphasize the need to identify major AFFF compounds for accurate environmental risk assessment and remediation planning. An increased number of semi-quantifications in combination NTA/SSA as well as more standards becoming available for regular targeted analysis are responses to this demand and assist a more detailed understanding. It is not only a matter of obtaining a better estimate of the total PFAS load but also to better comprehend potential, mobile, degradation products that may pose a risk, besides soils, to surface and groundwaters.

### *Discussion - Biodegradation of AFFF*

Biodegradation of FT-based AFFF compounds has been widely studied in aerobic soil and sludge microcosms. The degradation pathways typically involve initial oxidation or hydrolysis of the head group, forming intermediates like FTSs, FTOHs and FTUCAs, which can further degrade into PFCAs.

However, the recorded overall transformation efficiency is often moderate. Studies in soils and WWTP sludges confirm that even under favorable conditions, only a fraction of the original compound is converted to terminal products like PFHxA or PFPeA, often <10% over a 100 days experiment. However, this formation will long term be of key importance in risk assessment. The degradation (or disappearance) order in the studies cited above generally followed: FTSAS > FTSA > FTAA > FTAB with $DT_{50}$ from a few up to >100 days. Betaine structures were the most persistent, for example FTBs showed negligible or no transformation. These findings underscore the importance of head group chemistry and molecular structure in determining environmental persistence. There is also a need to better understand and quantify rate-determining intermediates that potentially could reach appreciable levels in especially soils.

ECF-based AFFF compounds, particularly those containing sulfonamide and amine functionalities, also show a wide range of biodegradation behaviors. While some precursors like PFOSAm and PFOAAm degrade moderately under aerobic conditions, others such as PFOSB and quaternary ammonium derivatives are highly persistent. The transformation pathways may bypass intermediate stages and lead directly to stable end-products like PFOS or PFOA. Though yields are generally low for sulfonamides, frequently 1-3% over the test duration for PFOS while PFOA figures can be higher 30% for that type of ECF precursor. Half-lives ($DT_{50}$) ranged between 3-675 days. Also, for ECF molecules structural features such as the type of nitrogen group and the presence of carboxyalkyl substituents significantly influence degradation rates with the order of persistence quaternary ammonium ≈ betaine ≫ tertiary amine > amine oxide quoted. Longer perfluoroalkyl chains, possibly due to higher sorption to soil further reduce bioavailability and transformation. Despite some degradation occurring over extended periods, results suggest many ECF-derived PFAS remain in the environment for decades. It can be noted that seven of the nine AFFF sulphonamides identified in soil in the work by van Hees and Karlsson (2024) had a quaternary substitution of the terminal nitrogen atom. As for FT formulations these results underscore the importance of identifying persistent structures in ECF AFFFs to better predict long-term contamination and inform remediation strategies.

## *Disclaimer*

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