Novel per- and polyfluoroalkyl substances in an active-use C6-based aqueous film forming foam

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ABSTRACT

Studies have identified hundreds of per- and polyfluoroalkyl substances (PFAS) in aqueous film forming foam (AFFF) using high resolution mass spectrometry (HRMS), and there is increasing reliance on HRMS with suspect screening in areas such as PFAS fate and transport. Characterization of active-use AFFF formulations is crucial for maintaining representative lists of PFAS for such efforts. Herein, targeted analysis, total oxidizable precursor assay (TOP), suspect screening, and non-targeted analysis were used to characterize PFAS in an AFFF currently certified for use by the U.S. military. The sum of PFAS identified during targeted analysis and suspect screening was compared to TOP, demonstrating that > 90% (20.2 mM) of the estimated total PFAS concentration (22.4 mM) was comprised of "unknown" PFAS. Tandem and multi-stage tandem mass spectra were used to annotate 10 PFAS within 9 classes, 8 of which have never been reported. A subset are fluorotelomer-based isomers of legacy, electrochemically synthesized PFAS. Thus, suspect screening efforts that rely solely on accurate mass matching may mis-annotate PFAS presented here as isomers that will have key differences in properties such as biotransformation pathways. The total estimated concentration of the 10 PFAS was ~20 mM, which agrees with the "unknown" fraction (20.2 mM) identified by TOP.

1. Introduction

Per and polyfluoroalkyl substances (PFAS) have been used in aqueous film-forming foam (AFFF) since the 1960s when the U.S. Navy Research Laboratory initiated development of foams that combined various 3M surfactant mixtures and other components for use as firefighting agents (Tuve et al., 1964). Military specification MIL-F-24385 was developed in 1969 (U.S. Navy, 1969) establishing criteria that AFFF formulations must meet to be listed on the Qualified Products List (QPL) for use at military facilities. 3M, Ansul, National Foam, Angus, Chemguard, Buckeye, and Fire Service Plus manufactured AFFF listed on the QPL from 1972 to 2014 (Place and Field, 2012; U.S. Navy, 2021a, 2021b). Currently the QPL has six 6% and ten 3% AFFF formulations, made by Tyco Fire Products (Ansul Brands), Perimeter Solutions (Solberg), Buckeye Fire Products, National Foam, Dafo FomTec AB, and Viking Corporation (Department of Defense, 2021). Since 1972, over 60 AFFF certifications are documented on the QPL. Each AFFF on the QPL may contain dozens to more than 100 PFAS, (Place and Field, 2012; Barzen-Hanson et al., 2017a) and may have been used broadly in the U. S. and internationally in training and emergency response.

Although the evolutionary history of AFFF composition is not fully understood, significant progress has been made in understanding PFAS in formulations from 1984 to 2017 (Place and Field, 2012; Backe et al., 2013; Barzen-Hanson et al., 2017b; Ruyle et al., 2021; D'Agostino and Mabury, 2014). Over 35 classes of anionic, cationic, and zwitterionic PFAS have been identified in AFFF formulations from this time period (Place and Field, 2012; Backe et al., 2013; Barzen-Hanson et al., 2017b; Ruyle et al., 2021; D'Agostino and Mabury, 2014). Additionally, studies have found that AFFFs containing PFAS generated by electrochemical fluorination (ECF) had a market share of greater than 50% through 2000 (Prevedouros et al., 2006). At this time, 3M began phase-out of perfluorooctane sulfonate (PFOS) and PFOS precursors, and there was a corresponding increase in use of fluorotelomer (FT)-based PFAS in AFFF, as evidenced by characterization of AFFF formulations from pre- and post- 2000 (Place and Field, 2012; Barzen-Hanson et al., 2017a; Ruyle et al., 2021).

PFAS composition has been characterized in 2 of 16 AFFFs currently on the QPL (Ruyle et al., 2021; Han et al., 2021). A recent study

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characterized Chemguard C306-MS 3 % and C606-MS 6 % and 7 FT-based AFFFs that are not currently on the QPL (Department of Defense, 2021; Ruyle et al., 2021). This study identified 14 PFAS that purportedly make up the majority of FT-based PFAS in contemporary AFFF (Ruyle et al., 2021). The applicability of these PFAS to the composition of active-use DOD AFFFs is unknown. Structures for 12 of 14 primary PFAS were proposed without structural confirmation via library spectral matching, and the spectra were not published as part of the study (Ruyle et al., 2021). In addition to confirming structural annotations, publication of spectra allows for their inclusion in libraries such as MassBank (HighChem, 2021) and the NORMAN network (Norman Association, 2021) that will support more confident identification of these compounds in future studies.

Several studies have characterized Buckeye BFC 3MS Premium 3 % (i.e., Premium 3MS) that was active on the QPL beginning in 2004 (Place and Field, 2012; Barzen-Hanson et al., 2017a; Han et al., 2021). Premium 3MS is no longer on the QPL and was eventually replaced by Buckeye Platinum Plus C6 3% MS-AFFF (i.e., Platinum Plus C6), which has been listed on the QPL since 2020. Additionally, Platinum Plus C6 is being used in a suite of studies as a benchmark formulation for comparison of the ecotoxicity of PFAS-based AFFF vs. recently-developed, fluorine-free AFFF formulations (SERDP, 2021). The PFAS composition of Platinum Plus C6 3% has never been characterized.

The objective of this study was to apply a combination of HRMS approaches to identify the total PFAS concentration and composition of Platinum Plus C6. Specifically, it was characterized using targeted analysis, including the total oxidizable precursor (TOP) assay (Houtz and Sedlak, 2012). Samples were also analyzed by high performance liquid chromatography quadrupole-time of flight mass spectrometry (HPLC-QToF-MS) coupled with suspect screening. TOP assay results were compared to concentrations of PFAS identified during suspect screening and estimated using semiquantitative (SQ) approaches to determine the fraction of oxidizable precursors attributable to PFAS present on existing suspect lists. Nontargeted data processing methods were used to structurally annotate additional PFAS in HPLC-QToF-MS data comprising the remaining fraction of unknown PFAS, and structure annotation was validated by HPLC coupled to high-field orbital trapping mass spectrometry (HPLC-Orbitrap-MS).

2. Materials and methods

2.1. Materials and AFFF sample preparation

Native and mass labeled internal standards (IS), other materials, preparation of AFFF samples by serial dilution, and application of the TOP assay (Houtz and Sedlak, 2012; Houtz et al., 2013) are described in Section S1, Table S1 and Section S2.

2.2. Data acquisition and processing

Analyses were performed using two instrument platforms: HPLC-QTOF-MS (Sciex X500R) and HPLC-Orbitrap (ThermoFisher Orbitrap Fusion Lumos). Select targeted concentrations were confirmed using a triple-quadrupole HPLC-MS/MS system (ThermoFisher TSQ Altis).

During HPLC-QTOF-MS analysis, each sample was analyzed in triplicate in both electrospray ionization negative (ESI-) and ESI positive (ESI+) modes and data were acquired in multiple reaction monitoring high resolution (MRMHR) mode (targeted analysis) and a data independent, SWATH® acquisition method (suspect screening). Similar to previous work, suspect PFAS concentrations were estimated using structurally similar standards and, when available (ESI- only), IS (Nickerson et al., 2021). Additional information regarding chromatographic conditions, mass spectrometer parameters, quantification of targeted analytes and identification and semiquantitative (SQ) estimates of suspect PFAS and their concentrations is available in the SI (Section S3, Table S2).

Nontargeted analysis (NTA) was used to screen for additional, unknown PFAS by reprocessing HPLC-QToF-MS SWATH data after removing (i.e., filtering) features already identified during suspect screening (Section S3, Fig. S1). Remaining peaks with an area > 100,000 and a Kendrick Mass Defect (KMD, Eq S2-S4) characteristic of PFAS (>0.85 or < 0.15) were selected for further analysis. Data were also screened for homologous series of unknown PFAS (Section S3) (Loos and Singer, 2017). Peaks with a KMD in the target range were screened for fragments characteristic of PFAS, (Barzen-Hanson et al., 2017a; Backe et al., 2013) which were used to assign tentative structures to newly identified PFAS. All spectra of PFAS identified during NTA of SWATH data were confirmed by analyzing samples in a data-dependent acquisition mode (i.e., Independent Data Acquisition [IDA] mode). *In silico* fragments were generated for putatively annotated PFAS using the Analytics module of Sciex OS (1.5) and compared to IDA MS/MS spectra.

Additional evidence for structure annotations of novel PFAS in Platinum Plus C6 was obtained by multi-stage tandem mass spectrometry using HPLC-Orbitrap-MS. PFAS with tentative annotations from HPLC-QToF-MS analysis were analyzed by HRMS (240,000 FWHM at m/z 200), MS/MS, and MS^3 using a data-dependent-analysis approach (stepped collision energies) with targeted inclusion lists corresponding to novel PFAS of interest in ESI+ and ESI- modes. Internal mass calibration was used to achieve mass accuracy < 1 ppm, facilitating molecular formula assignment for precursor and fragment ions in spectra.

Fragmentation trees (MS, MS/MS, and MS^3 spectra for a single compound) were assembled and analyzed by MassFrontier 8.0 (ThermoFisher), which is a rules-based spectral interpretation program that performs *in silico* fragmentation of proposed structures using a library of curated fragmentation mechanisms. Generated fragments are matched against experimental spectra, and the provenance of MS/MS or MS^3 fragment ions is assessed and tracked. Spectra are thus rationalized against proposed structures, and the relative match provides confirmation for fragment ion structure assignments and a method to quantitatively distinguish among isobaric or isomeric candidate structures. After structure annotation, concentrations of new PFAS were estimated using the SQ approach followed for suspect PFAS, (Nickerson et al., 2021, 2020) and names were assigned following the same approach used in recent studies (Section S3) (Nickerson et al., 2021).

2.3. Quality control

For targeted analysis, details regarding the type, frequency, and acceptance criteria for quality control samples are in the Supporting Information along with information regarding IS recoveries, and quality control criteria for the TOP assay (Section S3).

Quality control measures for initial peak selection and subsequent identification using suspect screening analysis, and determination of confidence levels followed methods similar to previous studies (Section S4) (Nickerson et al., 2020; Xiao et al., 2017; Schymanski et al., 2014). Concentrations of PFAS identified during suspect screening and NTA were estimated using response factors for structurally similar calibrant-IS pairs or, when no IS was available (i.e., ESI+ PFAS), based only on calibrant response (Nickerson et al., 2020). Calibrant-IS pairs or calibrants were selected by comparing response factors of available standards to those of PFAS in multiple dilutions of AFFF (Section S4, Figs. S2-S3, Table S3).

3. Results and discussion

In this section, PFAS acronyms are defined in the Supporting Information in Table S1 (targeted analysis), Table S3 (suspect screening), and Table S6 (newly identified PFAS).

3.1. Targeted analytical results

Eleven PFAS were detected during HPLC-QTOF-MS analysis of

Platinum Plus C6 ranging from 8.04 (PFPeS) to 9130 ug/L (6:2 FTS, Table S4). C6 PFAS (6:2 FTS, PFHxA, and PFHxS) comprised 78% of the total molar concentration of targeted PFAS detected (39.3 μmol/L). A prior study that characterized Premium 3MS found ~5254 μmol/L of 6:2 FTSA-PrB (i.e., 6:2 FTAB in prior work) and 222 μmol/L 6:2 FTS (Han et al., 2021). In the Platinum Plus C6, 1.63 μmol/L and 20.3 μmol/L of 6:2 FTSA-PrB and 6:2 FTS were detected, respectively, suggesting significant changes in the PFAS composition of new Buckeye AFFF.

Following application of the TOP assay, the total PFAS concentration increased from 39.3 μmol/L (i.e., total target PFAS) to ~22,400 μmol/L, indicating that 99.98% of PFAS in Platinum Plus C6 was not identified during targeted analysis (Table S4, Fig. S4, Fig. S5, Fig. 1). The largest increases were PFPeA ($\Delta = 12,550 \mu mol$), PFBA ($\Delta = 6,700 \mu mol$), and PFHxA ($\Delta = 2,660 \mu mol$). The formation of C4-C6 PFCAs is consistent with prior studies investigating the fate of 6:2 FT-based PFAS during TOP (Houtz and Sedlak, 2012). Previous characterization of Premium 3MS measured ~19,000 $\mu mol/L$ total PFAS after TOP, (Han et al., 2021) which compares well to the newer Platinum Plus C6. However, in prior work the increase in PFOA (~1450 $\mu mol/L$) was similar in magnitude to that of PFHxA and PFHpA (~1900 and ~1900 $\mu mol/L$, respectively), (Han et al., 2021) suggesting a higher concentration of PFAS with > 6 fluoroalkyl carbons. This again highlights differences in the older Premium 3MS vs. the new Platinum Plus C6. Further discussion of TOP results is presented in the Supporting Information (Section S5, Fig. S4). We note here as in Section S5 that multiple lines of evidence (e.g., multiple AFFF dilutions and combinations of persulfate and sodium hydroxide) were used to ensure complete oxidation during the TOP assay.

3.2. Suspect screening analysis

Suspect screening identified 7 suspect PFAS in 6 classes (Table S3). The total estimated concentration of suspect PFAS was 1970 $\mu mol/L$, and > 99% was comprised of C6 FT-based precursors, consistent with expectations for Platinum Plus C6. The most prevalent class was n:2 FTSAPr-DiMeAn (Table S3), which is a zwitterionic class of PFAS previously detected in FT-based AFFF (Place and Field, 2012;
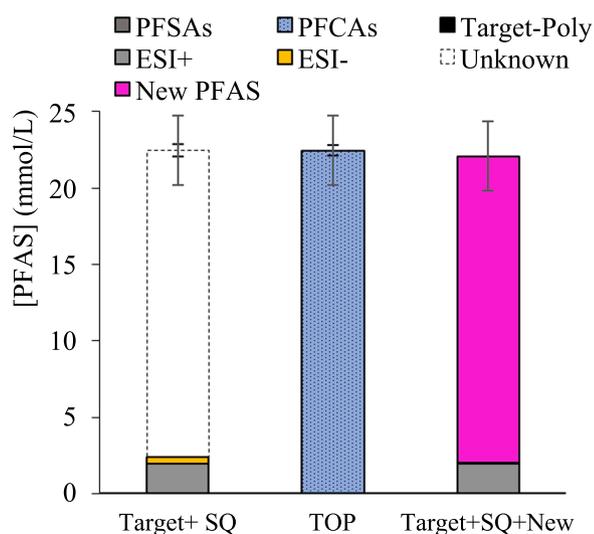
Fig. 1. Targeted concentrations of PFCAs, PFSAs, and precursors with semi-quantitative (SQ) estimates of ESI- and ESI+ suspect PFAS (Targeted + SQ) compared to the total PFAS concentration estimated by TOP (sum of PFCAs and PFSAs after oxidation; TOP), and the sum of Target+SQ and semiquantitative estimates of newly identified PFAS (TOP+SQ+New). ESI- PFAS and PFCAs were present, but at minor concentrations not visible on the scale shown. The difference between TOP and Target+SQ is an estimate of the concentration of PFAS not identified through targeted or suspect screening analysis ("Unknown" in legend).

Barzen-Hanson et al., 2017a; D'Agostino and Mabury, 2014; Moe et al., 2012). Previous work suggests this class of PFAS may be a byproduct of fluorotelomer betaine synthesis (Place and Field, 2012; Norman, 1989). When compared to TOP, suspect PFAS comprised only a small fraction of the total PFAS concentration of ~22,400 μmol, and 91% (~20,400 μmol) of the PFAS concentration was not identified (e.g., "Unknown" in Figure 1). The suspect list used herein was primarily PFAS identified in AFFF or AFFF-impacted media, so results suggested that Platinum Plus C6 was comprised largely of as-yet unidentified PFAS.

Multiple ECF-based precursors were originally matched to observed HPLC-QToF-MS peaks during processing of suspect screening data, some with confidence level 2a (e.g., library compounds, Table S5, Fig. S6). These matches were unexpected because Platinum Plus C6 is known to be a FT-based product. We found that while these analytical features did show some MS/MS fragments that matched ECF-based PFAS resulting in a high library fit (> 70), additional, FT fragment ions were also present. The ultimate annotated structures of these features and their estimated concentrations are presented in Section 3.3, but their original misidentification is notable as these features comprise a significant fraction of the overall PFAS composition of Platinum Plus C6 and were fully isomeric with previously reported AFFF-derived PFAS of a different manufacturing provenance.

3.3. Nontargeted analysis

NTA approaches were used to structurally annotate additional PFAS in the "unknown" fraction evident in TOP data. No homologous series were identified, suggesting that PFAS composition was dominated by a single, C6 chain length. Filtering of features for KMDs characteristic of PFAS and peak intensity greater than 10^5 in a 1000x dilution of Platinum Plus C6, resulted in 155 observed features. Of these, 24 had MS/MS spectra characteristic of PFAS based on fragments identified in prior studies (Barzen-Hanson et al., 2017b; D'Agostino and Mabury, 2014). Structural elucidation was possible for 10 PFAS from 9 classes of n:2 fluorotelomer sulfonamides (Tables S6, Figs. S7-S19). To our knowledge, none have annotated spectra published in prior studies, none are present on curated lists of PFAS, Classes 2–9 are novel, and one (Class 1) has an assigned CASRN and was reported in a single study (Ruyle et al., 2021). Structures were discovered in SWATH ESI- and ESI+ data followed by validation of MS/MS spectra through IDA data acquisition, confirmation via *in silico* fragmentation (Figs. S7-S19), and structural confirmation using HPLC-Orbitrap MS/MS and MS^3 spectra (e.g., Fig. 2, Fig. S20).

3.3.1. Class 1

The primary class of PFAS in Platinum Plus C6 was n:2 FTSAPr-AmHOPrS, which was detected in both ESI+ (Fig. 2, Fig. S7) and ESI- (Fig. S8) and is the only class for which more than one homologue (n = 4,6) was detected. Class 1 is documented in multiple patents, (Getty et al., 2014.; Bertocchio et al., 1980) and the C6 homologue has an assigned CASRN (76201–56–4). The n = 6 homologue (ESI+ m/z 651.0861) of Class 1 was the most abundant compound in Platinum Plus C6 and exceeded the concentration of the n = 4 homologue (ESI+ m/z 551) by ~3 orders of magnitude. As described above, 6:2 FTSAPr-AmHOPrS was originally annotated as EtOH-AmPr-FHxSAPrS, an ECF-based perfluoroalkyl sulfonamide (Table S5).

Ruyle et al. (2021) also recently proposed the Class 1 structure for 6:2 FTSAPr-AmHOPrS (Fig. 2) for Formula 9 of their study ($C_{16}H_{23}F_{13}N_2O_6S_2$). Although depicted as an FT-based structure, the previous study assigned Formula 9 the name of the ECF isomer (i.e., EtOH-AmPr-FHxSAPrS) (Ruyle et al., 2021). The structure of Formula 9 was not supported by MS/MS spectra for confirmation of the FT-based structure vs. the ECF-based name presented. Formula 9 was assigned a confidence level of 2b (i.e., no library MS/MS spectra) (Ruyle et al., 2021; Schymanski et al., 2014). Thus, it appears that the structure was assigned to Formula 9 based on knowledge of the FT-based origin of the
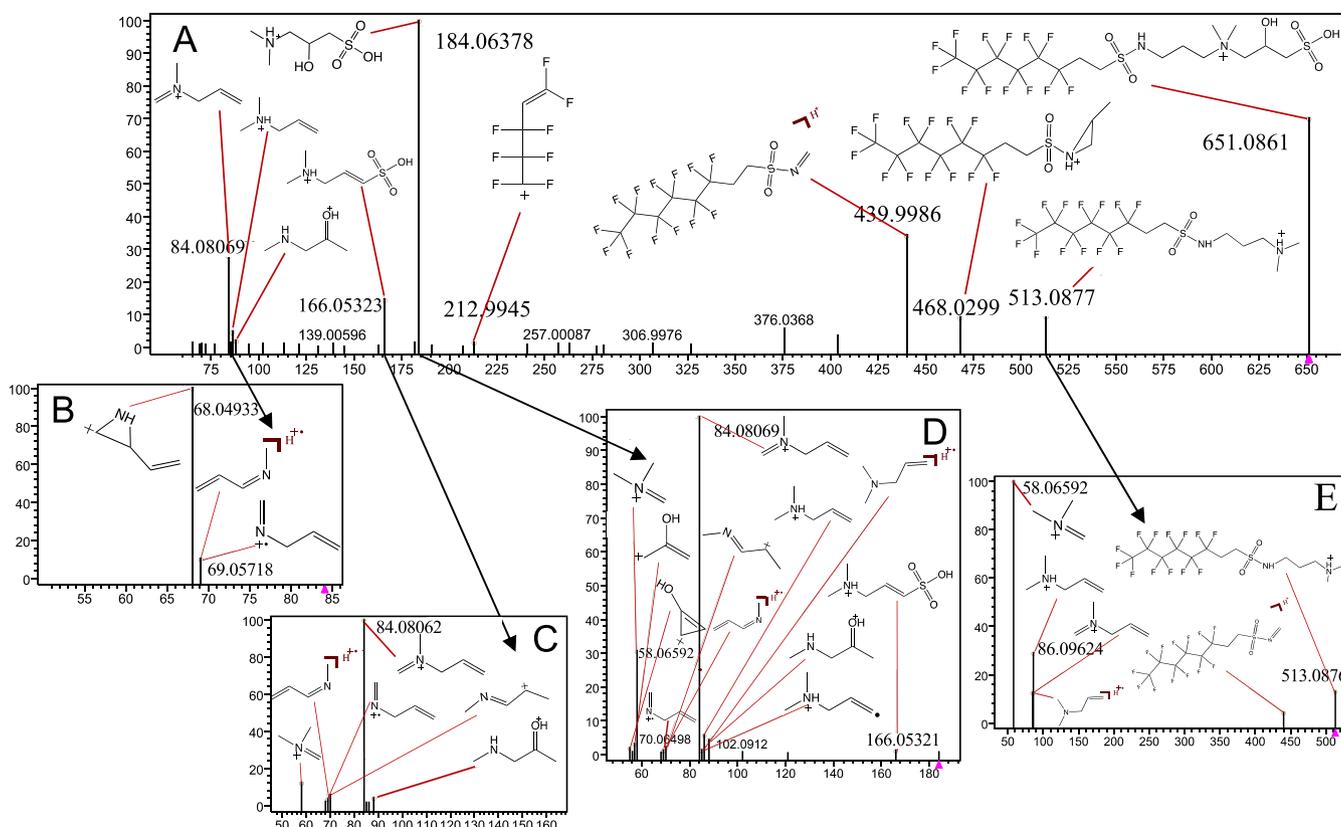
Fig. 2. Orbitrap ESI+ HCD MS/MS spectrum (A) for precursor *m/z* 651.0861, showing structure annotation consistent with compound 6:2 FTSAPr-AmHOPrS. Also shown are structure-annotated MS3 spectra for MS/MS fragment ions 84.0807 (B), 166.0532 (C), 184.0638 (D), and 513.0877 (E). All fragment ion peaks were annotated using MassFrontier 8.0 software using both library and curated fragmentation mechanisms. Theoretical and observed fragment *m/z*, associated mass errors, and relevant fragmentation mechanisms for (A) are shown in Fig. S7.

AFFFs analyzed. Reference spectra and are also not available in NIST, mzCloud, MONA, the NORMAN suspect list, or in the peer reviewed literature. If the Formula 9 structure in Ruyle et al. is correct, then 6:2 FTSAPr-AmHOPrS was detected at levels greater than the solvent blank (based on relative peak areas) of 2 FT-based AFFFs: Angus Fire Tridol® M[C6] 3% and 6%. Neither AFFF is currently listed on the QPL (Department of Defense, 2021). This is the first study to confirm occurrence of Class 1 in a Buckeye AFFF or in an AFFF still certified for use, and it confirms product formulation changes suggested by the results of targeted analysis and TOP. Another key outcome is the generation of annotated MS/MS spectra (Fig. 2a) that can be used in future studies to differentiate this class from ECF-based isomers. Additional description of Class 1 is in the Supporting Information (Section S6).

Further evidence for annotation of Class 1 as n:2 FTSAPr-AmHOPrS was provided by HPLC-orbitrap MS[3] spectra of MS/MS fragments, which were consistent with fragmentation of predicted secondary product ions through known collision induced dissociation (CID) mechanisms from this precursor structure (Fig. 2b-e). Attempts to annotate the observed MS/MS and MS[3] spectra for the ESI+ precursor (*m/z* 651.0861) with fragments derived from the structure of the ECF-derived EtOH-AMPr-FHxSAPrS yielded no plausible mechanisms explaining primary fragment ions (e.g., *m/z* 513.0877, 468.0299, 184.0638, or 166.0532) from that precursor structure (Fig. S19). Finally, multiple matching approaches yielded a very poor match between the observed MS/MS spectrum for ESI+ *m/z* 651.0861 and the library-curated reference MS/MS spectrum of EtOH-AmPr-FHxSA-PrS (e.g., dot-product match score = 2.4, NIST library match score = 0.18).

3.3.2. Classes 2–9

Newly identified Classes 2–9 (Figs. S9-S18, Section S6) are estimated

to be present at concentrations approximately 0.06–7.3% of the concentration of Class 1, so as discussed below, they represented minor components of Platinum Plus C6 and may be unintended impurities. However, such impurities may be useful for forensic applications in future studies. The structures of Classes 2–6 represent variations of Class 1 (Section S6). Classes 7–9 (Section S6) were essentially "dimeric" compounds, containing two 6:2 FT alkyl chains on central functional groups or hydrocarbon structures. For example, Class 7 (*m/z* 836, ESI-only, Fig. S16) is comprised of two 6:2 sulfonamides that share the same terminal nitrogen. Additional description of Classes 2–9 is provided in Section S6 of the Supporting Information.

3.4. Total PFAS in platinum plus C6

SQ estimates of all newly identified PFAS were summed yielding a concentration of ~20,000 *μM*). When total PFAS is estimated as the sum of detected targeted analytes (40.92 *μM*), suspect PFAS (2000 *μM*), and newly identified PFAS, this yields a value of ~22,000 *μM* (Fig. 1). This compares well to 22,400 *μM*, the total PFAS concentration from the sum of targeted analytes and TOP. Studies have shown that 6:2 FTS forms ~80 % C4-C7 PFCAs during TOP application (Houtz and Sedlak, 2012). If also true of the 6:2 FT-based PFAS identified herein, then 100% recovery of all PFAS in Platinum Plus C6 would exceed the TOP-based total PFAS concentrations by ~20%. In addition to analytical variability, which is expected to be within ±30 %, SQ estimates of PFAS identified during suspect screening and nontarget analysis are subject to uncertainty due to a lack of authentic analytical standards. These factors may prevent observation of 20% differences in mass balance between TOP- and SQ-based estimates of total PFAS. Additionally it is possible that TOP concentrations reflect oxidation of multiple, minor PFAS

components of the AFFF that were not captured during NTA as a result of low abundance in the AFFF dilutions analyzed.

4. Conclusions

In this study, 9 classes of PFAS comprised of 10 individual compounds were identified that comprised ~90% of the total molar PFAS concentration measured in Platinum Plus C6. To our knowledge, none are included in current curated lists of PFAS, and only 1 (6:2 FTSAPr-AmHOPrS) can be located by CASRN search. None have published MS/MS spectra. Platinum Plus C6 is currently approved for use on the DoD QPL confirming potential for ongoing release of these PFAS during emergency response or training activities. Analytical standards for these PFAS are not available, but mass balance results highlight that the molar mass of these compounds can be evaluated using the TOP assay followed by targeted analysis of TOP endpoints (i.e., PFCAs).

Incorrect annotation in a prior study of the dominant PFAS in Platinum Plus C6 at *m/z* 651.0861 (ESI+) as the ECF-based EtOH-AmPr-FHxSAPrS should serve as a cautionary note against using suspect lists of known compounds for screening LC-HRMS data to arrive at tentative compound identifications using accurate-mass matches alone. Risks include erroneous attribution of significant fractions of PFAS mass to the wrong PFAS, class, and manufacturing origin. Additionally, PFSAs are the terminal degradation products of ECF-based PFAS whereas FT-based precursors degrade to terminal PFCAs, (Harding-Marjanovic et al., 2015; Liu and Mejia Avendaño, 2013) so, mis-annotation could have important implications for source attribution, fate and transport, and management of PFAS-impacted sites.

Without additional information from MS/MS (and in this case MS³) spectra, spurious and incorrect annotations of isomeric compounds are inevitable, as demonstrated by use of ECF-based nomenclature in prior studies to describe the FT-based structure presented here as Class 1 (i.e., 6:2 FTSAPr-AmHOPrS). Advanced NTA methods (e.g., empirical and *in silico* MS/MS library spectra and rule-based fragment elucidation (Getzinger et al., 2021)) should be rigorously applied to data before structure annotations are made. Formulas, *m/z*, names, SMILES codes, InChi Keys, spectra and other information regarding PFAS Classes 1–9 can be added to publicly available spectral databases and PFAS lists (e.g., Organisation for Economic Cooperation and Development, National Institute of Technology and Standards, and EPA Comptox Dashboard) (OECD, 2022; NIST, 2021; USEPA, 2020). This will facilitate more confident annotation of these PFAS in future studies, reduce knowledge gaps caused by protection of product formulations as confidential business information, and contribute to an overall understanding of PFAS releases when products such as AFFF are used.

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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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2022.100061.

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