Identification of Poly- and Perfluoroalkyl Substances Transformation Products in Aqueous Film-Forming Foam Impacted Wastewater

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Introduction

The current and historic usage of aqueous film-forming foam (AFFF) at military and civilian sites have drawn much attention in recent years due to possible linkage to poly- and perfluoroalkyl substances (PFASs) contamination in water systems [1, 2]. Recently, PFASs were measured at relatively high levels in effluent in some San Francisco Bay Area wastewater treatment plants that were impacted by AFFF usage [3]. However, PFASs identified using targeted analysis methods are only a small portion of the PFAS known to be present in AFFF formulations. As a follow-up study, high resolution mass spectrometry (HRMS) was commissioned to investigate the PFASs at an airport wastewater treatment plant during an AFFF introduction event [4]. AFFF-derived PFASs and their transformation products were identified using high resolution quadrupole time of flight mass spectrometry (QTOF/MS). Using a combination of targeted and non-targeted approaches, molecular features that were extracted from the raw total scan chromatography were tentatively identified with compounds from an in-house PFAS database. For compounds without a database match, chemical formulas were generated based on exact mass, isotope distribution and isotope spacing. We preliminarily identified the presence of various PFASs known to be present in fluorotelomer-based AFFF formulations, including 6:2 fluorotelomermercaptoalkylamido sulfonate (FTSAS), 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB), their homologues from 4:2 to 12:2, as well as various transformation products, primarily derived from the biological oxidation of 6:2 FTSAS within the treatment plant. We identified novel PFASs and proposed their structures. The integrity of the analysis was validated by standardized sample analysis procedures using Agilent MassHunter Qual and Mass Profiler Professional (MPP) software for multivariate analysis, and high match scores/fragments patterns for the assignments. Available isotope labeled and natural PFAS standards were used as positive controls. The unknown screening approach combined with the profile comparison (influent vs. effluent) is critical in establishing PFAS transformation intermediates and products, their fates in the wastewater treatment plant, and assessing potential impact to the Bay water system.

Materials and methods

Materials. LC-MS grade methanol and water were purchased from VWR Scientific (Radnor, PA). PFAS analytical standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

Sample Preparation and Instrument Analysis. Wastewater sample collection and analysis were described elsewhere[3]. In brief, wastewater samples were collected in 2015 and extracted using solid phase extraction (SPE, Oasis WAX SPE cartridges, Waters, Milford, MA). The prepared samples were injected in triplicates to Agilent 1290 UPLC system with a Zorbax Extend-C18 column (2.1x50 mm, 1.8 um), and analyzed by Agilent 6550 QTOF operating in negative mode electrospray ionization (ESI). In each batch, solvent blanks and spiked water samples were analyzed together with the samples.
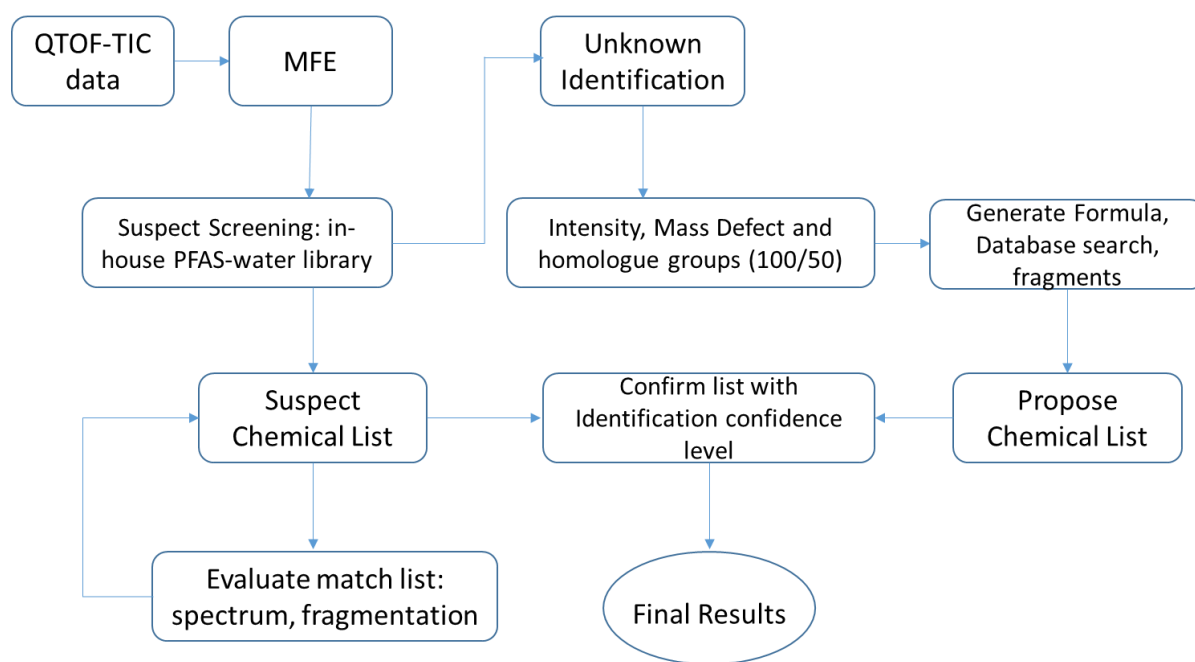
QTOF Data Analysis. Data were analyzed using the in-house developed workflow for PFAS chemicals. Briefly, TIC (total ion chromatography) were extracted using MFE (molecular feature extraction) algorithm with Agilent software package (Agilent MassHunter Qual and MPP). The resulted features were aligned across all samples within one batch, and blanks were subtracted. Features were then grouped as "significant in influent samples", "significant in effluent samples". Features were identified by combination of suspect screening and unknown identification, as shown in the workflow chart (Figure 1). An in-house PFAS-water library (with ~ 200 PFAS structures) was developed based on literature search [5-7]. Features were screened against this library, and matches were evaluated based on accurate mass, isotopic patterns and fragments identification. The remaining unknown features were prioritized and identified based on intensity and PFAS characteristics: mass defects (-0.1 to 0.15 Da), and homologous series with mass differences of 50 Da (-CF2-) and of 100 Da (-CF2-CF2-). The prioritized unknown features were identified using molecular formula generator and fragments identification.
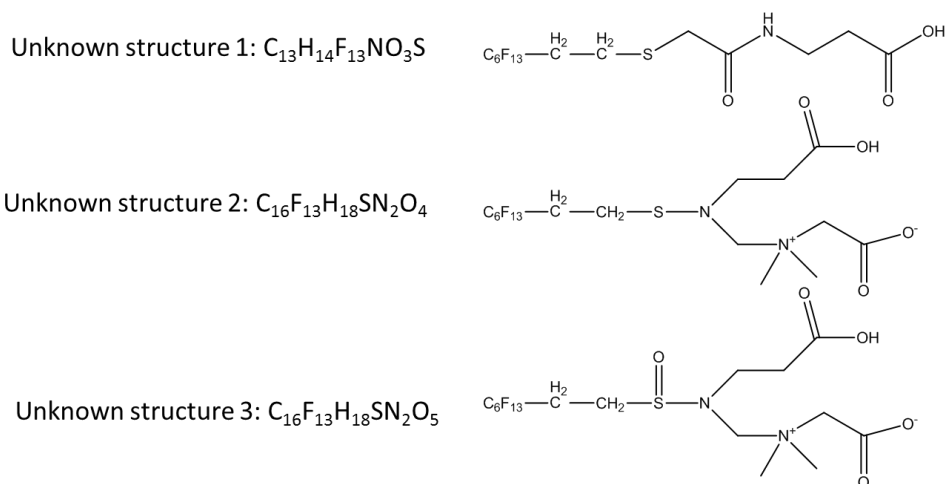

Results and discussion

Suspect Screening. Using the workflow as shown in Figure 1, extracted features were first searched against the in-house PFAS library. The library hits were evaluated with spectrum characteristics and fragments identification. ~ 40 PFAS compounds were identified with the confidence level of 2 or higher [8]. In addition to the perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs) groups, FTSAS, FTABs, and Perfluoralkylsulfonamido-Based Surfactants (PFASAC) homologue groups were also identified. 6:2 FTSAS were found to be the major compounds found in the wastewater influent, while its oxidation products, 6:2 FTSAS_O and 6:2 FTSAS_O2 were found with elevated levels in the effluent samples. 6:2 FTSAS and FTAB are major formulation of ANSUL and National Foam AFFF. The high presence of these chemicals in the influent samples confirmed the sources of attribution at this wastewater plant.

PFOS was also found to be the dominant PFSAs in the wastewater, suggesting that even after the phase-out efforts since the early 2000s, there are still historical residuals in AFFF impacted sites. PFCAs were only detected at very low levels, but for the short chain PFCAs such as PFHxA and PFPeA, there was an significant increasing in the effluent samples comparing with the influent, suggesting that short chain PFCAs are among the transformation products of PFAS precursors [9].

Unknown Identification. Features that were not matched in the PFAS library were further examined using the workflow in Figure 1. The top intensity features with mass defects of -0.1 to 0.15 were examined in priority. By combining efforts of formula generation, fragments identification and database search, novel PFAS formulation structures were proposed. We were able to identify homologues of two fluorotelomer based structures dominant in the influent and one structure in the effluent. Interestingly, the third structure in the effluent was also identified as the oxidation product of one of the novel structures, by the difference in mass of one oxygen atom (16 Da). The proposed formulations and structures were shown in Figure 2.

Figure 1. PFAS chemicals non-target analysis workflow

Unknown structure 1: $C_{13}H_{14}F_{13}NO_3S$

Unknown structure 2: $C_{16}F_{13}H_{18}SN_2O_4$

Unknown structure 3: $C_{16}F_{13}H_{18}SN_2O_5$

Figure 2. Proposed unknown identification structures.

Acknowledgements

References

1. Filipovic, M., A., W., Norstrom, K., Bibi, M., Lindberg, M., and Osteras, A. (2015). Chemosphere *129*, 39-45.
2. Moody, C.A., and Field, J.A. (2000). Environ. Sci. Technol. *34*, 3864-3870.
3. Houtz, E.F., Sutton, R., Park, J.S., and Sedlak, D.L. (2016). Water Research *95*, 143-149.
4. Houtz, E.F., Wang, M., and Park, J.S. (2017). manuscript in preparation.
5. D'Agostino, L.A., and Mabury, S.A. (2014). Environ. Sci. Technol. *48*, 121-129.
6. Place, B.J., and Field, J.A. (2012). Environ. Sci. Technol. *46*, 7120-7127.
7. Strynar, M., Dagnino, S., McMahen, R., Liang, S., Lindstrom, A., Andersen, E., McMillan, L., Thurman, M., I., F., and C., B. (2015). Environ. Sci. Technol. *49*, 11622-11630.
8. Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., and Hollender, J. (2014). Environ. Sci. Technol. *48*, 2097-2098.
9. Harding-Marjanovic, K.C., Houtz, E.F., Yi, S., Field, J.A., Sedlak, D.L., and Alvarez-Cohen, L. (2015). Environ. Sci. Technol. *49*, 7666-7674.