Environmental Forensic Investigation of the Manufacturing and Use of PFAS by Non-Targeted Analysis

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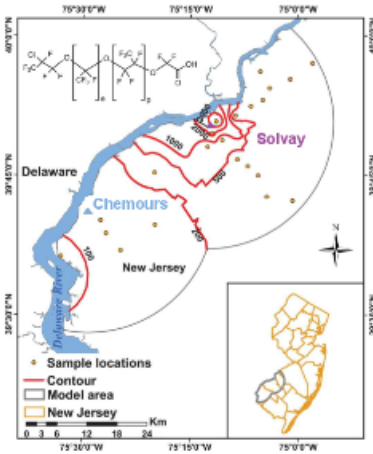
Abstract

Per- and polyfluoroalkyl substances (PFAS) are environmentally persistent and high interest class of chemical pollutants with a rapidly expanding roster. As manufacturing processes evolve, the number of PFAS in use in commerce has reached potentially hundreds of analytes, and new and emerging analytical techniques such as non-targeted analysis (NTA) are critical to identify and monitor the most environmentally relevant chemical pollutants.

High resolution mass spectrometry (HRMS) has been a workhorse technique supporting non-targeted approaches to sample analysis, compound discovery, and chemical characterization across a range of media and unique circumstances. Following the general phase-out of legacy PFAS such as PFOA/PFOS, industrial usage has shifted to alternative replacement PFAS, and it has been the domain of non-targeted analysis to identify the replacement species. New chemical species continue to be uncovered and described using a combination of computational tools; over the past several years we have investigated the presence of legacy and emerging PFAS chemistries in wide ranging samples collected by numerous state and regional EPA offices and to reveal a highly fragmented landscape of emerging PFAS chemicals. In contrast to the prior ubiquity of perfluorinated alkyl acids such as PFOS/PFOA, NTA investigations have revealed PFAS that are structurally diverse including: chlorinated perfluoropolyethers (ClPFPECAs) processing aids, polyfluorinated side products of polyfluorovinylidine (PVDF), as well as other novel PFAS fluoroether species exhibiting ether linkages and acid head groups, corresponding to their specialized applications. This poster details some general examples of the applications of non-targeted analysis to novel PFAS detection and monitoring in site characterization efforts.

Spatial Characterization of Novel Chlorinated PFAS



Sampling: Spatially disparate soil samples were collected along soil transects in the region surrounding two different PFAS production companies (blue + purple triangles) along with nearby surface water. (McCord 2020, Washington 2020)

Analysis: Surface water and soil extracts were analyzed by LC-MS. *De novo* structural assignment revealed a series of novel PFAS (Markush structure, top left), and MS abundances were used to estimate concentrations using PFNA as a surrogate calibration curve, plotted spatially with contours (pg/g).

Results : The geospatial distribution of the emerging PFAS compound was observed to center around a single plant as a point source, with peak concentrations of ~ 3000pg/g.

Figure 1. Estimated ∑ClPFPECAs from PFNA surrogate calibration in surface soils (picograms/gram). Contour lines were generated by inverse-square distance weighted values of the five nearest data points in ArcMAP 10.6.1.
Adapted from: DOI: 10.1126/science.aba7127

In Situ Generation of Vinylidene Polymer Processing Aids

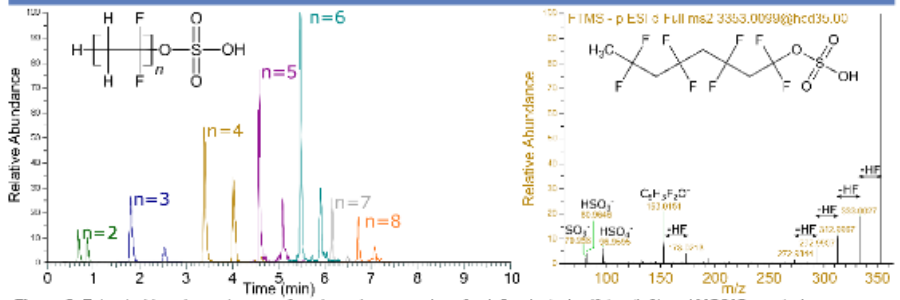


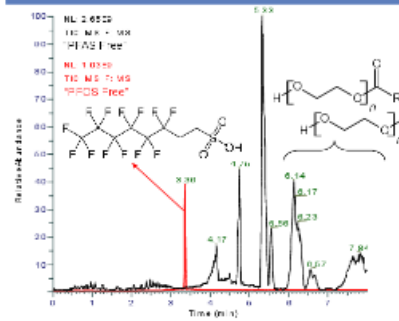
Figure 2. Extracted Ion chromatograms for a homologous series of polyfluorinated sulfates (left) and MS/MS spectral assignment of diagnostic fragments (right).

Sampling: Effluent and groundwater grab samples were collected from a fluorochemical manufacturer producing (poly)vinylidene fluoride products and using non-fluorosurfactant based polymer processing aids.

Analysis: Water was processed using WAX extraction as EPA Method 533 for targeted analysis, and non-targeted analysis using an Orbitrap Fusion was conducted on excess extracts following the targeted quantification. Novel compounds were manually investigated to assign chemical structures based on MS/MS interpretation.

Results: Homologous series of at least six polyfluorinated surfactants with repeating groups CH_2F_2, C_2F_4, and/or C_2H_4 and variable ionizable head groups CO_2, SO_3, and SO_4 were identified. Sulfate Markush structure and MS/MS shown in **Figure 2**. Even when non-fluorinated surfactants are used as polymer processing aid, low molecular weight polymer byproducts are generated and can be significant contributors to PFAS waste concentrations.

Replacement Chemicals for PFAS Based Products



Sampling: Fourteen fume suppressant products for metal treatment were sourced for analysis

Analysis: Liquid product samples were serially diluted in water and analyzed by large-volume aqueous injection by LC-MS

Results: NTA analysis of "PFOS Free" products identified 6:2 fluorotelomer sulfonate as the primary replacement compound, often at mg/mL concentrations. "PFAS Free" products used complex mixtures of organic, non-ionic surfactants.

Figure 3. Total Ion Chromatograms for two select fume suppressant products, one "PFOS Free" (red) the other "PFAS free" (black). 6:2 fluorotelomer sulfonate is annotated as the primary/only peak in fluorine containing PFOS free products, while non-fluorinated products contain mixtures of non-ionic ethylene glycol surfactants.

Gas Phase Emission of High Mass Fluoroethers

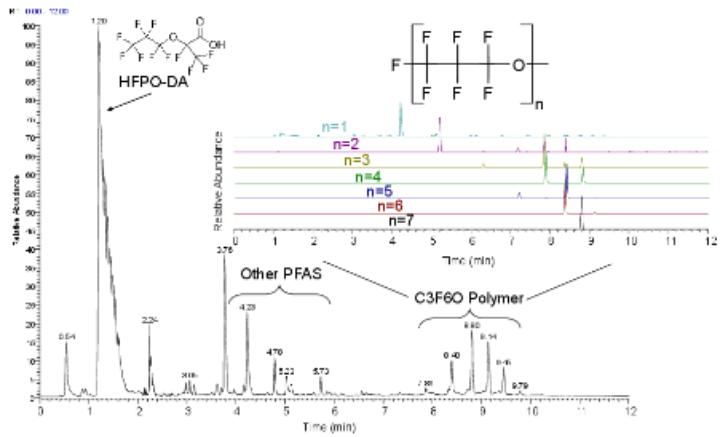


Figure 4. Chromatogram of extract prepared from stack sampling of PFA polymer use site. HFPO-DA and legacy PFAS such as PFHxA elute before a series of novel high-molecular weight polymers (inset, right).

Sampling: An EPA OTM-45 sampling train was used to collect stack emissions from a polymer production and use facility. Stack samples were collected associated with three fluoropolymers lines: polytetrafluoroethene (PTFE), fluorinated ethylene propylene (FEP), and (poly)perfluoroalkoxy alkanes (PFA)

Analysis: Methanolic traps and methanolic extracts from the XAD resin capture were characterized by UPLC-MS/MS with data dependent acquisition on an Orbitrap Fusion mass spectrometer.

Results: NTA examination found gas-phase emissions of low molecular weight PFAS, such as HFPO-DA, could be captured by the sampling method. High molecular weight fluoroethers >1kDa were also detected in the extracts, potentially from partial decomposition/volatilization of fluoropolymer or molecular growth reactions from excess short chain additives such as HFPO-DA

References

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