# Semiquantitative Suspect Screening to Assess Poly- and Perfluoroalkyl Substances (PFASs) in the Environment

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COLORADOSCHOOLOFMINES
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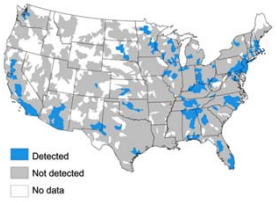
## Poly- and Perfluoroalkyl Substances (PFASs)

Since the 1960s, PFAS have entered the environment through the application of aqueous film-forming foams (AFFFs).


Highly persistent surfactants, PFAS are frequently detected in water supplies in watersheds that contain airports or military bases.

*Environ. Sci. Technol. Lett.* 2016, 3, 344–350

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## Poly- and Perfluoroalkyl Substances (PFASs)

PFAAs and sulfonamide-based PFAA-precursors

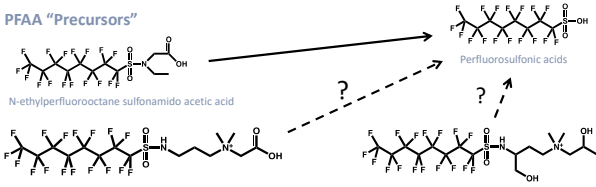
While numerous PFAS have been identified, some are of specific interest or subject to US EPA drinking water health advisories.

Perfluorooctanoic acid (PFOA)

Perfluorooctane sulfonic acid (PFOS)

Polyfluorinated, sulfonamide-based compounds can be environmentally transformed to perfluoroalkyl acids (PFAA).

PFAA "Precursors"




Zhang et al (2017) Environ Pollut *229*, 159–167.

Barzen-Hanson et al (2017) ES&T *51*(4), 2047–2057.

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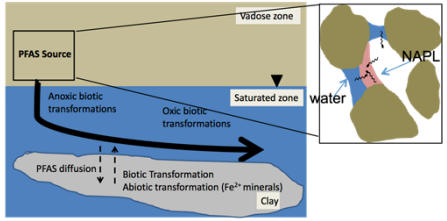
Key Fate and Transport Processes Impacting the Mass Discharge, Attenuation, and Treatment of Poly- and Perfluoroalkyl Substances and Comingled Chlorinated Solvents or Aromatic Hydrocarbons (SERDP ER-2720)

**Project goal** Determine the fundamental processes controlling PFAS fate and transport in AFFF-impacted soils.

**Experimental Objective** Evaluate the release of PFAS, especially sulfonamide-based PFAA precursors, from AFFF-impacted soils. *What happens to these "precursor" compounds?*



# PFAS release from AFFF-impacted soils

## Experimental

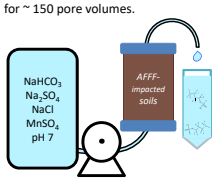
**Experimental Objective** Evaluate the release of PFAS, especially sulfonamide-based PFAA precursors, from AFFF-impacted soils.

- Which PFAS are present in and released from AFFF-impacted soils?
- Are sulfonamide-based potential PFAA precursors significant to the overall mass balance?

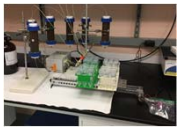
**Experimental Design**

Surface soils collected from fire-training grounds at two AFFF-impacted sites.


Artificial groundwater was pumped through soils with HRT of 12 hours for ~ 150 pore volumes.




Column effluents collected with fraction collector.



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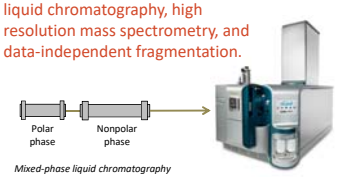
# Combined target/suspect/nontarget PFAS analysis

## LC-QToF-MS allows simultaneous combined analysis

LC-QToF-MS combines of mixed-mode liquid chromatography, high resolution mass spectrometry, and data-independent fragmentation.




*Mixed-phase liquid chromatography*

*SCIEX X500R QToF-MS*

**Target Analysis**

Quantification with reference standards and mass-labeled surrogates.

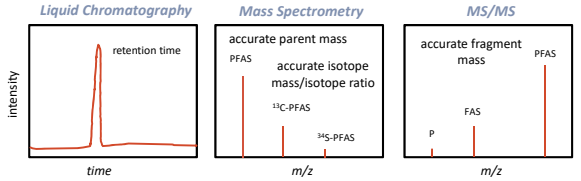
**Nontarget Analysis**

Identification of novel compounds.

**Suspect Screening**

Semi-quantitation of suspect compounds (previously identified compounds without reference standards)

Information associated with all MS features:

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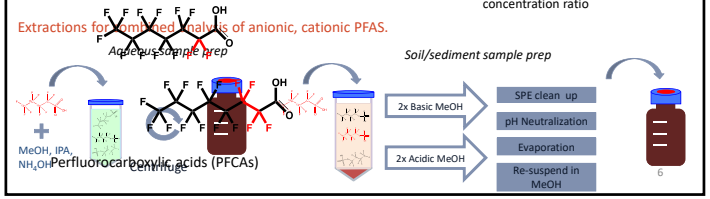
# Target PFAS analysis by LC-QToF-MS

## Quantitation based on external calibrations and mass-labeled surrogates

External calibrations determined for 47 compounds in 12 homologous series classes.

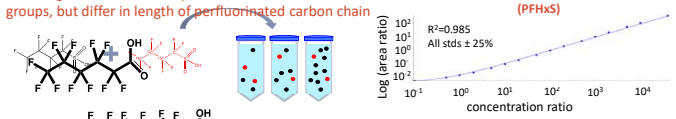
Perfluorocarboxylic acids (**PFCAs**, $C_4 - C_{18}$)
Perfluorosulfonic acids (**PFSAs**, $C_3 - C_8$)
X:2 Fluorotelomer sulfonic acids (**FTAs**, X = 4,6,8)
X:2 Fluorotelomer carboxylic acids (**FTCAs**, X = 4,6,8)
X:2 Fluorotelomer unsaturate carboxylic acids (**FTUCAs**, X = 6,8,10)ADONA, GenX, PFEtCHxS
Perfluorooctanesulfonamides (**FASA**, -, N-Me-, N-Et-)
Perfluorooctane sulfonamido acetic acids (**FASAA**, -, N-Me-, N-Et-)
F-53b ($C_9$, $C_{11}$)
Cl-PFOS

Extraction for combined analysis of anionic, cationic PFAS.




Perfluorocarboxylic acids (PFCAs)

Homologous series of compounds with common functional groups, but differ in length of perfluorinated carbon chain

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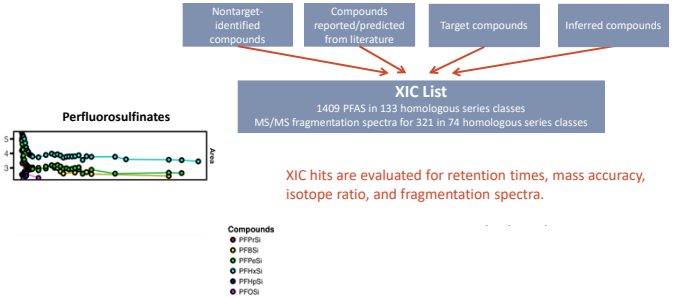
# Suspect PFAS Analysis

## Extracted Ion Chromatogram (XIC) Lists

Identified features are compared against an extracted ion chromatogram (XIC) list.




XIC hits are evaluated for retention times, mass accuracy, isotope ratio, and fragmentation spectra.

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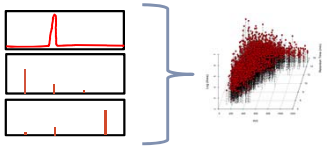
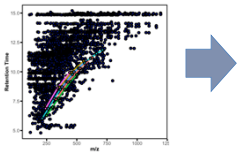
# Nontarget PFAS Analysis Workflow

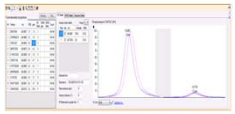
***Feature Identification***
Select features with S/N > 10, peak width < 2 min, peak height > 50 cps. Convert to list of m/z, intensity, RT.



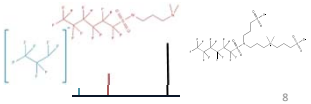
***Feature Prioritization***
Homologous series ($CF_2$, $C_2F_4$), low mass defect (>0.85, < 0.15)



***Formula Determination***
Formula ID determined with accurate mass, confirmed by isotope ratio



***Structure Determination***
Molecular structure determined by comparison of observed fragments with in-silico fragmentation of potential structures.



Barzen-Hanson, et al. (2017). ES&T *51*(4), 2047–2057.

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# PFAS release from AFFF-impacted soils

## Experimental

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- Which PFAS are present in and released from AFFF-impacted soils?
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**Experimental Design**

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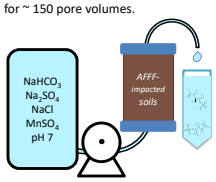


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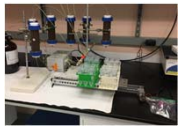

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# PFAS release from AFFF-impacted soils

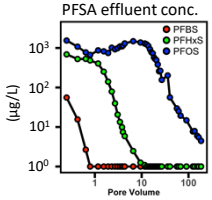
## PFSA concentrations in AFB 1 soil by target analysis

Short chain PFSA concentrations decrease monotonically in effluent, longer chain PFSAs show initial increase.

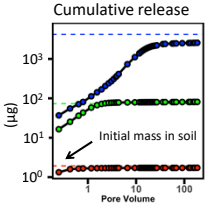
Cumulative masses released are similar to the initial PFAS mass.

After 150 pore volumes, > 95% of PFSA mass is in effluent (solid), < 5% remains in soils (white).

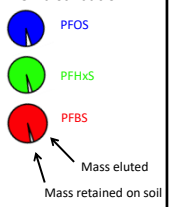
PFSA effluent conc.




Cumulative release




Final PFSA distribution

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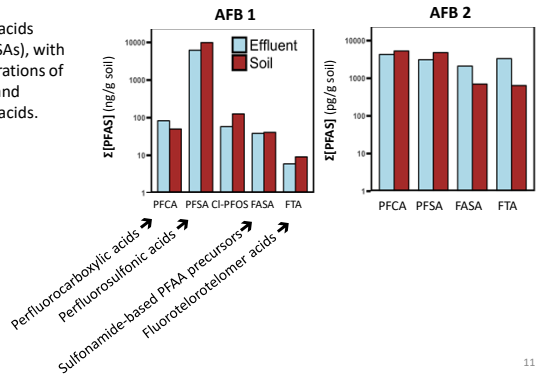
# PFAS release from AFFF-impacted soils

## PFAS concentrations in soils by target analysis

Target analysis suggests both soils contain predominantly perfluoroalkyl acids (PFCAs and PFSAs), with lower concentrations of sulfonamides and fluorotelomer acids.

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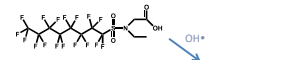
# Non-identified PFAS in AFFF-impacted soils

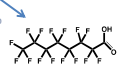
TOP, TOF assays identify presence of large "missing" PFAS fraction

**Total oxidizable precursor (TOP) assay converts precursor compounds to quantifiable PFAAs.**

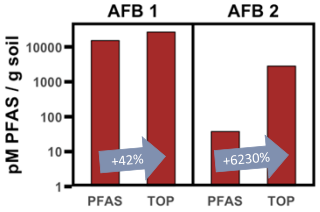


N-ethylperfluorooctane sulfonamido acetic acid

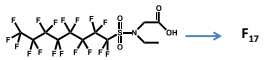
OH•



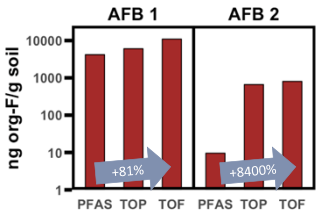
PFOA




**Total organofluorine (TOF) assay quantifies organofluorine concentrations**




N-ethylperfluorooctane sulfonamido acetic acid




# PFAS release from AFFF-impacted soils

Suspects screening hits: 167 compounds in 37 classes

**AFB 2 Soil**

**Target classes**
PFCA (C4-C8)
PFAS (C3-C10)
FASA (C4, C6, C8)
X:2 FTS (6:2, 8:2, 10:2)

**Substituted PFAAs**
H-PFAA (C8-C12)

**PFSA Derivatives**
PFASi (C8)

**Sulfonamide Precursors**
AmPr-FASA-PrA (C2-C6) – OR –
CEtAmPr-FASA (C2-C6)

**AFB 2 Effluent**

**Target classes**
PFCA (C4-C9)
PFAS (C2-C10)
FASA (C3-C8)
EtFASA (C6, C8)
FASAA (C4-C8)
X:2 FTS (2:2, 4:2, 6:2, 8:2)

**Substituted PFAAs**
UPFAS (C8)
X:2 UFTS (6:2)
X:2 FTOS (4:2, 6:2)

**FT Sulfonamides**
1-OH X:2 FTS (1OH-4:2,6:2) –OR-
X:2 FTSA (6:2, 8:2)
X:2 FTSO2PrAd-DiMeEtS (6;2, 8:2)

**AFB 1 Soil**

**Target Classes**
PFCA (C4-C8)
PFAS (C3-C10)
FASA (C3-C8)
MeFASA (C4-C8)
FASAA (C3-C6)
MeFASAA (C3-C8)

**Substituted PFAAs**
Cl-PFAS (C8)

**PFSA Derivatives**
PFASi (C4-C8)

**Sulfonamide Precursors**
AmPr-FASA (C3-C6)
CMeAmPr-FASA (C2-C6)

**FT Sulfonamides**
X:2 FTSA-PrAn (4:2,6:2)
X:2 FTSA-Pr-MeAA (4:2,6:2)

**AFB 1 Effluent**

**Target classes**
PFCA (C4-C9)
PFAS (C3-C10)
FASA (C2-C8)
MeFASA (C2-C8)
EtFASA (C8)
FASAA (C2-C8)
MeFASAA (C2-C12)
X:2 FTS (6:2,8:2)

**Subsituted PFAAs**
O-U-PFAA (C6-C10)
Cl-PFAS (C3-C8)
H-PFAS – (C3-C10)
H-UPFAS (C5, C6, C8)
K-PFAS (C4-C9)
O-PFAS (C4-C9) – OR – PFA-OS (C3–C8)
UPFAS – (C6-C10)
FSS-PFAS (C4-C8)
X:1 PFAS (6:1 PFHpS, 8:1 PFOS)
X:2 UFTS (4:2, 6:2, 7:2)

**PFSA Derivatives**
PFASi – (C3-C8)

**Sulfonamide Precursors**
AmPr-FASA (C3-C5)
CMeAmPr – FASA (C3-C6)
AmPr-FASA-PrA (C2-C6) - OR –
CEtAmPr-FASA (C2-C6)
SPrAmPr-FASA (C3-C6)
CMeAmPr-FASAPrA (C4, C6)
Am-CPr-FASA (C4-C6)
OAmPr-FASA (C3-C6)
SPr-FASA (C5,C6,C8)
SOHPrAmPr-FASA (C4-C6)
SPrAmPr-FASAA (C6)
SPrAmPr-FASAPrS (C6-C8)

**FT Sulfonamides**
X:2 FTSA (8:2)
X:2 FTSA-Pr-MeAA (2:2, 4:2, 6:2)
X:2 FTSA-PrAn (2:2, 4:2, 6:2)
X:2 FTS2PrAd-DiMeEtS (4:2, 6:2, 8:2)

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# Suspect Analysis of PFAS release from soils

Semi-quantitative suspect screening

**Semi-quantitation of suspect PFAS in soils and effluents is determined as a function of peak area, response factor of related target calibrant, and recovery of internal standard.**

$$"mass"_{suspect} = (response\ factor_{cal-IS}) \times \frac{molar\ mass_{suspect}}{molar\ mass_{cal}} \times \frac{area_{suspect}}{area_{IS}} \times nominal\ mass_{IS}$$

**Associate suspects with external calibrants and surrogates according to ESI- ionizable groups.**

| Example Suspect Class | ESI- Ionizable groups | External Calibrant | Internal Standard |
|---|---|---|---|
| H-PFAA | Carboxylic Acid | PFOA | $^{13}C_8$ - PFOA |
| FSS-PFAS | Sulfonic Acid | PFOS | $^{13}C_8$ - PFOS |
| AmPr-FOAd | Sulfonamide | FOSA | $^{13}C_8$ - FOSA |
| CMeAmPr-FOSA | Sulfonamido Acetic Acids | FOSAA | $D_3$ - FOSAA |

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$$"mass"_{suspect} = (response\ factor_{cal-IS}) \times \frac{molar\ mass_{suspect}}{molar\ mass_{cal}} \times \frac{area_{suspect}}{area_{IS}} \times nominal\ mass_{IS}$$

$$"mass"_{CMeAmPr\text{-}FBSA} = (response\ factor_{FOSAA\text{-}D_3\text{-}FOSAA}) \times \frac{molar\ mass_{CMeAMPr\text{-}FBSA}}{molar\ mass_{FOSAA}} \times \frac{area_{CMeAMPr\text{-}FBSA}}{area_{D_3\text{-}FOSAA}} \times nominal\ mass_{D_3\text{-}FOSAA}$$

$$"mass"_{CMeAmPr\text{-}FBSA} = (3.6705) \times \frac{422.06\ mu}{559.96\ mu} \times \frac{253220}{19011} \times 100\ pg$$

$$"mass"_{CMeAmPr\text{-}FBSA} = 3685\ pg$$

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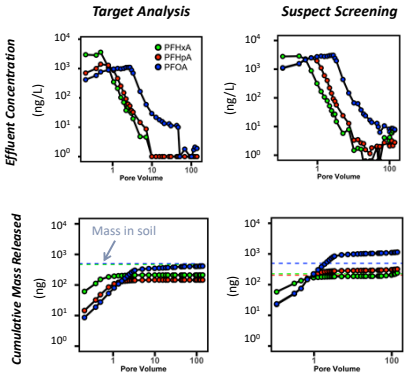
# Suspect Analysis of PFAS release from soils

## Comparison with target data – PFCAs in AFB 2 soil effluent




Similar trends are observed, but suspect concentrations are typically 1-3x higher than target in aqueous samples.

**PFHxA mass released in effluent:**
Target: 0.50 ng/g soil
Suspect 0.57 ng/g soil

**PFHxA concentration in soils**
Target: 1.11 ng/g
Suspect: 0.54 ng/g

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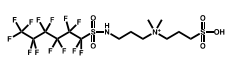
# Suspect Analysis of PFAS release from AFB 1

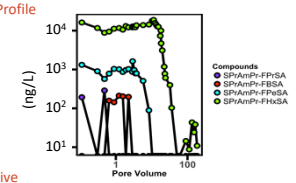
## Semi-quantitation of suspect sulfonamide-based PFAA precursor

SPrAmPr-FHxSA

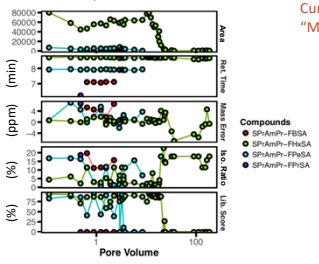


Calibrant = FOSA
Internal Standard = $^{13}C_8$ - FOSA

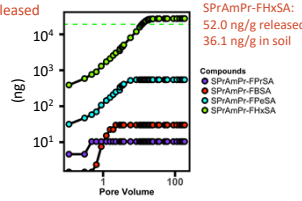
Elution Profile




Suspect Dashboard




Cumulative "Mass" Released




SPrAmPr-FHxSA: 52.0 ng/g released vs. 36.1 ng/g in soil

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# Suspect Analysis of PFAS release from soils

## Results – Mass of all eluted PFAS compared with mass in soil

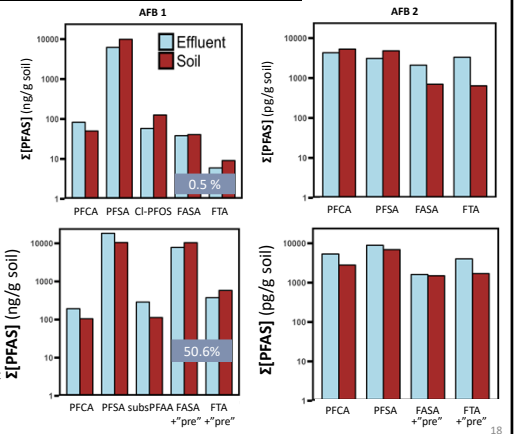
### Target PFAS analysis

PFAS mass is predominantly PFAAs in both soils, with lower concentrations of sulfonamides and fluorotelomer compounds.

### Suspect PFAS analysis

Contribution of sulfonamides and sulfonamide precursors becomes apparent with suspect screening.

Mass fraction of sulfonamides and likely PFAA precursors increases from **0.5% to 50.6%** with semi-quantitative suspect screening in AFB 1 soil.

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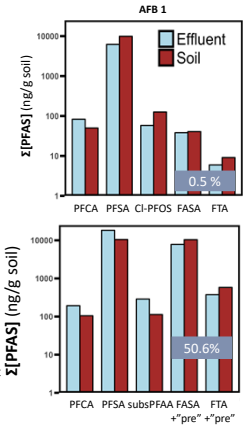
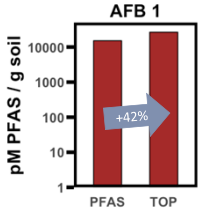
Contribution of sulfonamides and sulfonamide precursors becomes apparent with suspect screening.

Mass fraction of sulfonamides and likely PFAA precursors increases from **0.5% to 50.6%** with semi-quantitative suspect screening in AFB 1 soil.




### TOP assay




**The addition of sulfonamide-based precursors to the overall PFAS mass balance agrees well with "missing" PFAS identified by TOP assay.**

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## Summary

**Experimental Objective** Evaluate the release of PFAS, especially sulfonamide-based PFAA precursors, from AFFF-impacted soils.

- Which PFAS are present in and released from AFFF-impacted soils?
- Are sulfonamide-based potential PFAA precursors significant to the overall mass balance?

Suspect screening with LC-QToF-MS allows the semi-quantitation of suspect PFAS, while simultaneously performing target and nontarget analysis.

Suspect screening identified 167 PFASs from 37 classes in soils and soil effluents from two AFFF-impacted US Air Force base.

In AFB 1 soil, the mass fraction of sulfonamide-based precursors, identified only by suspect screening, agrees well with the "precursor" fraction identified by TOP assay.

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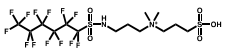
## Acknowledgments

- Megan Coney and Kayleen Chee
- Anastasia Maydanov

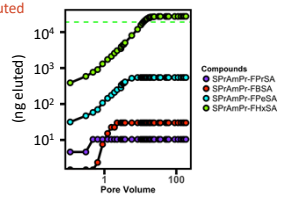
## Thanks, questions?

SPrAmPr-FHxSA



Calibrant = FOSA
Internal Standard = $^{13}C_8$ - FOSA

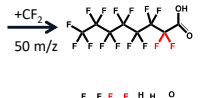
Cumulative "Mass" eluted

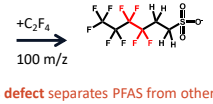


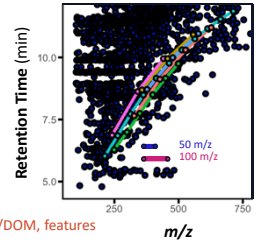

## Nontarget PFAS Analysis

Feature prioritization by homologous series, mass defect

Members of **homologous series** (-$CF_2$ or -$C_2F_4$) prioritized.

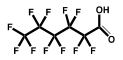



**$^{19}$F negative mass defect** separates PFAS from other analytes/DOM, features with mass defect > 0.85 or < 0.15 prioritized.

| Isotope | – | Mass |
|---|---|---|
| $^{12}$C | – | 12.0000 |
| $^{1}$H | – | 1.0073 |
| $^{19}$F | – | 18.9984 |
| $^{14}$N | – | 14.0031 |
| $^{16}$O | – | 15.99499 |
| $^{32}$S | – | 31.9721 |



PFHxA
(m/z 312.9724)

Barzen-Hanson, et al. (2017). ES&T *51*(4), 2047–2057.

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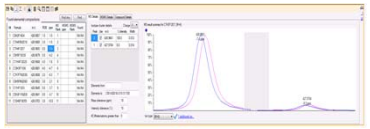
# Nontarget PFAS Analysis

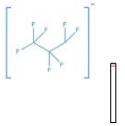
## Formula and structural determination

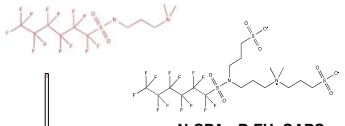
***Formulas determination*** by comparison of accurate mass to potential formulas, formula assignment confirmed by isotope ratio.

**Formulas assignment rules**
Charge = -1, +1
RDB = 0 – 5
Formula = $C_{0\text{-}50}H_{0\text{-}50}O_{0\text{-}12}N_{0\text{-}4}S_{0\text{-}4}P_{0\text{-}4}Cl_{0\text{-}4}F_{0\text{-}50}$
Mass Error < 5 ppm
Isotope Distribution Error < 5%
(Preference given to formulas with $F_{13}$, $F_{17}$



***Structure determination*** by fragmentation spectra of observed fragments and neutral losses, matched by variety of tools (e.g., Metfrag).





**N-SPAmP-FHxSAPS**
(727.049 m/z)

m/z

Barzen-Hanson, et al. (2017). ES&T *51*(4), 2047–2057.

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# PFAS release from AFFF-impacted soils

## Why suspect screening?

**Experimental Objective** Evaluate the release of PFAS, especially sulfonamide-based PFAA precursors, from AFFF-impacted soils.

**Target Analysis:**

- Provides quantitation for a limited number of analytes, especially few sulfonamides/sulfonamide-based PFAA precursors.

**Nontarget Analysis:**

- Identifies novel compounds, but high standards for compound identification limits causes very high “detection limits.”
- Difficult to compare results from different matrices, analytical days.

**Suspect Screening:**

- Semi-quantitate suspect PFAS, with identification based on parent mass, isotope ratio, fragmentation spectra, and retention time.

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