# PFAS and HRMS: What Will You Miss With Conventional LC-MS/MS?

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# Acknowledgements


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Bridget Ulrich, PhD
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*Northeastern*

John Kornuc
*U.S. Navy*

Dave Adamson
Poonam Kulkarni
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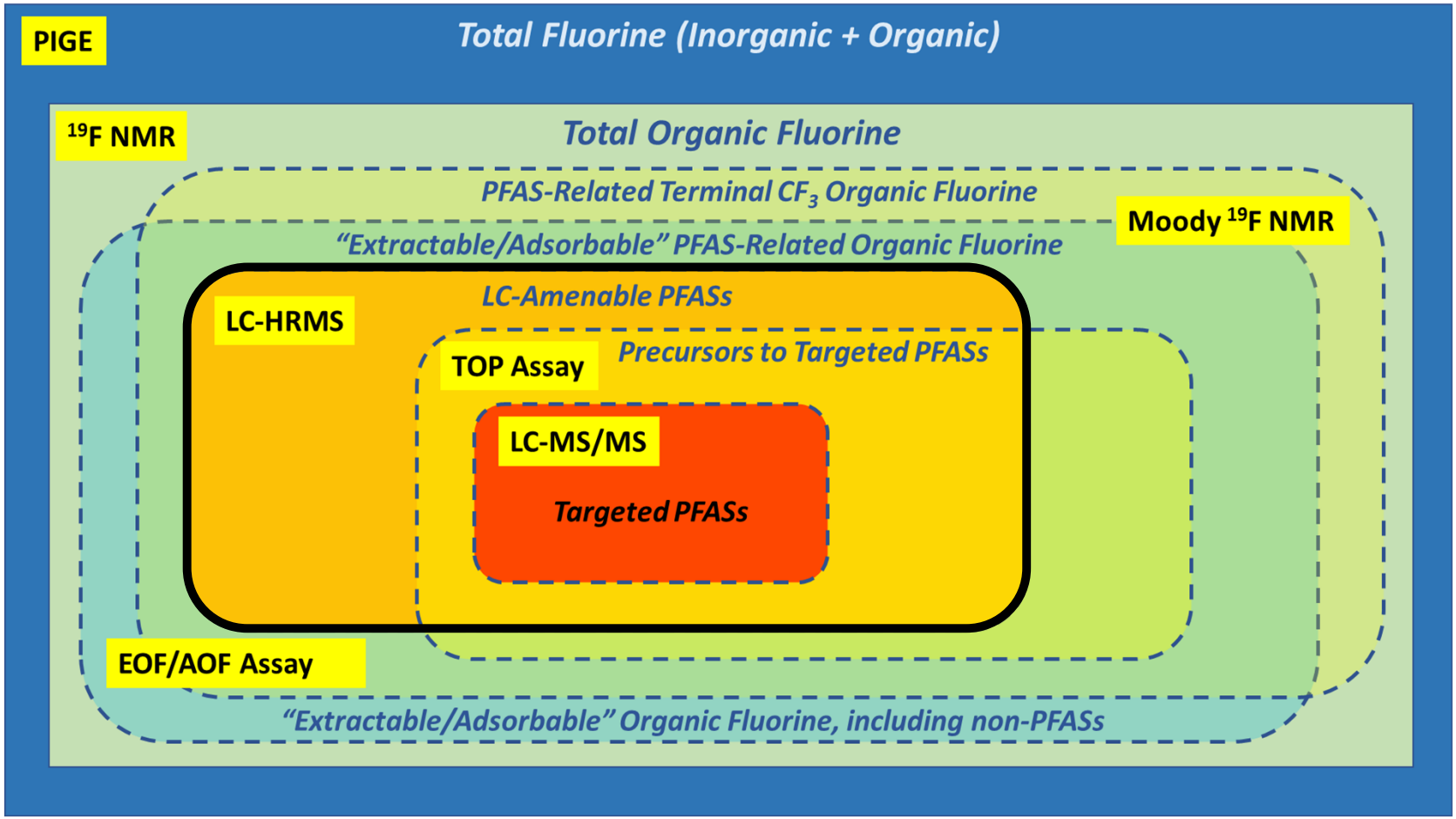
SERDP DOD • EPA • DOE | ESTCP | NIH NIEHS

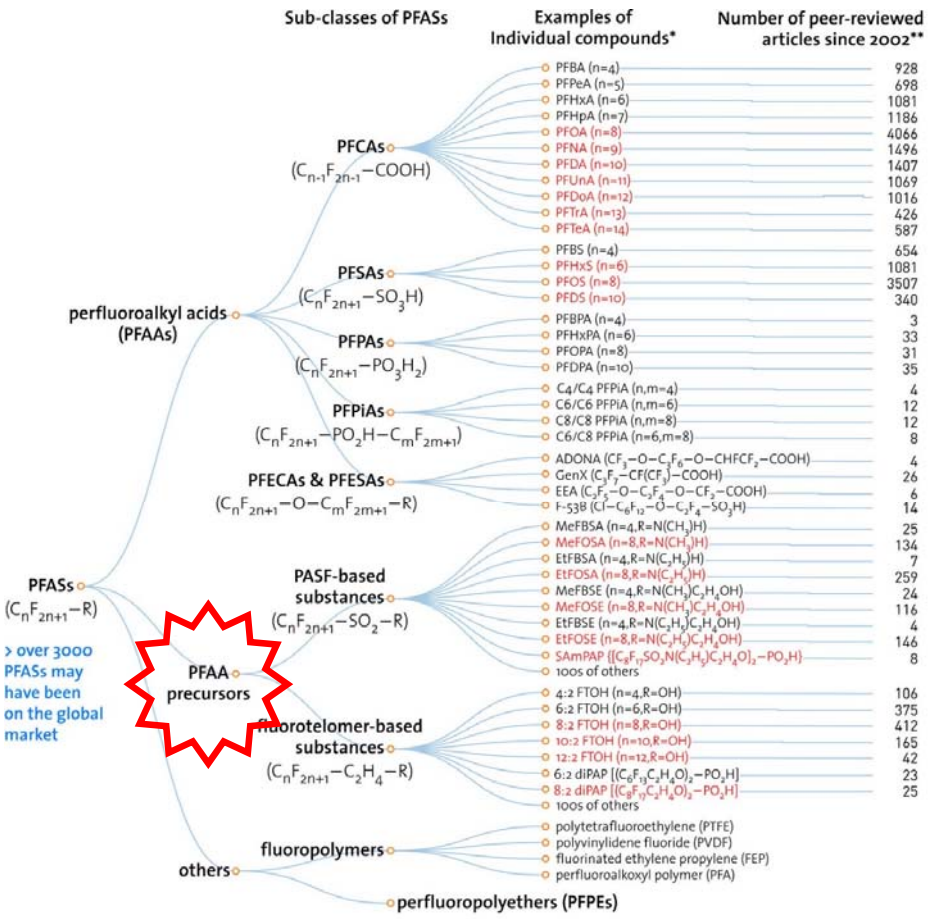
TESTING *for* PEASE

SEACOAST WOMEN'S GIVING CIRCLE




McDonough *et al.*, 2019, *Current Opinion in Environmental Science & Health.* https://doi.org/10.1016/j.coesh.2018.08.005

# PFAS Family Tree: It's not just PFOS and PFOA




THE FLUORINE

# DETECTIVES

RESEARCHERS ARE BATTLING TO IDENTIFY AND ASSESS A WORRYING CLASS OF PERSISTENT CHEMICALS.

BY XIAOZHI LIM

*Nature*, 566 (26) 2019

# But what's actually in AFFF-impacted samples?

Environmental Science & Technology

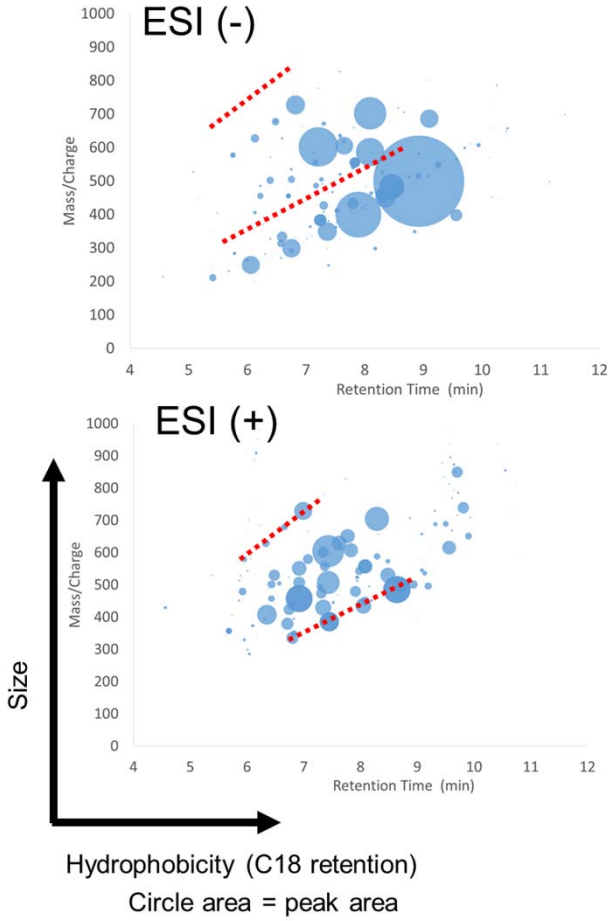
Article

pubs.acs.org/est

**Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater**

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[▽,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[∥] Nicole Riddell,[∥] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]

- Do we really need to look for >1400 PFASs in all samples?
- Some of these are just hypothetical, and others may never leave the source zone
- What is actually in samples impacted by AFFF?



# HRMS Suspect Criteria for PFAS

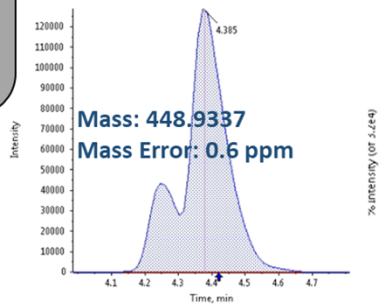
QToF-MS SWATH®:
Scan and fragment all ions in mass range

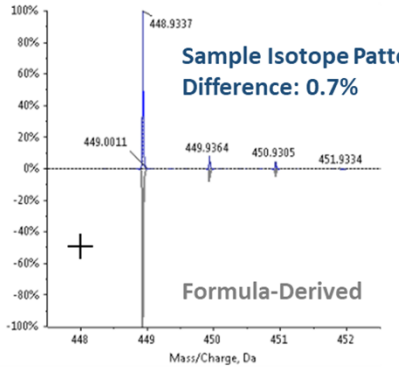
Screen for matches using extracted ion chromatograph (XIC) list:
List of mass and formula for 1432 characterized and theoretical PFASs

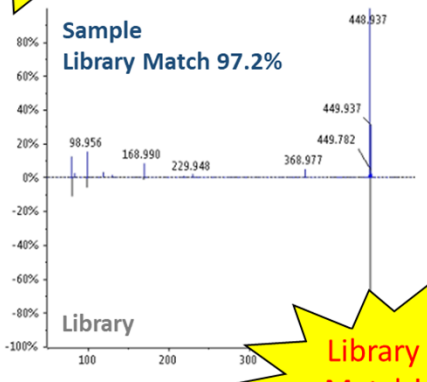
Precursor mass within 5 ppm of known value

Isotope pattern match within 10%

XIC Match!




Library Match!

Screen for peak ID matches using high-res spectral library:
Collection of fragmentation spectra for 323 PFASs

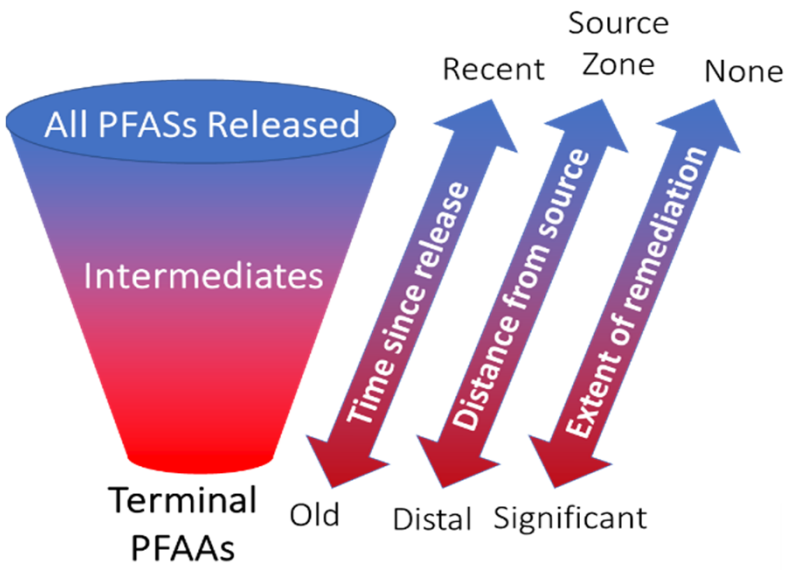
Precursor mass within 10 ppm of known value

Isotope pattern match within 20%

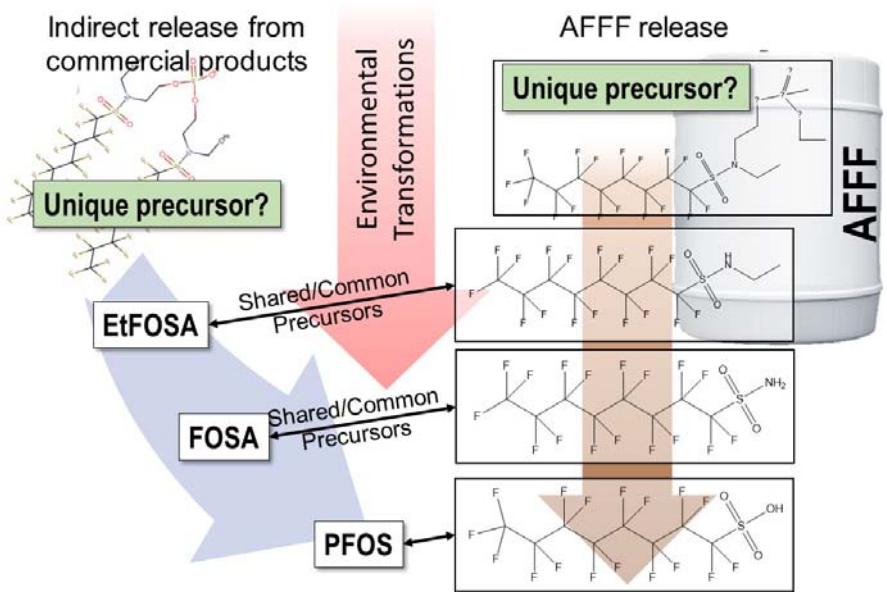
Fragments matching score ≥ 70%

# Transport and Transformation

Complexity varies with time, space, and remedial history

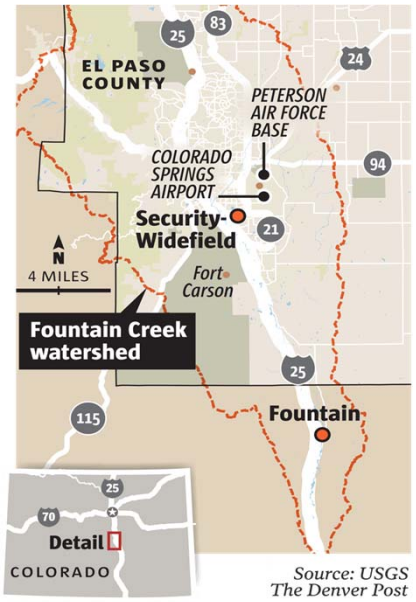



Some PFASs are known degradation intermediates of those in AFFF, but also consumer products

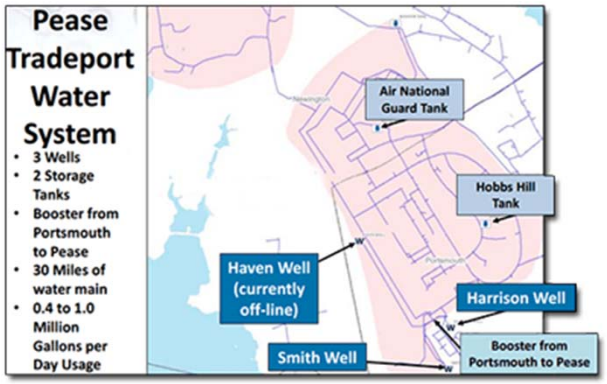


# A tale of two sites: Peterson and Pease

- Security, Fountain, and Widefield in Colorado
  - **Water** sampled (untreated public and private wells)as part of an NIH R21 co-hort analyses
  - Median serum levels of PFHxS are ~10x NHANES
  - Both private and public wells sampled




- Pease Tradeport in New Hampshire
  - **Water** sampled in Portsmouth, NH as part of a privately funded study of water
  - Both untreated and treated (carbon) water analyzed over time

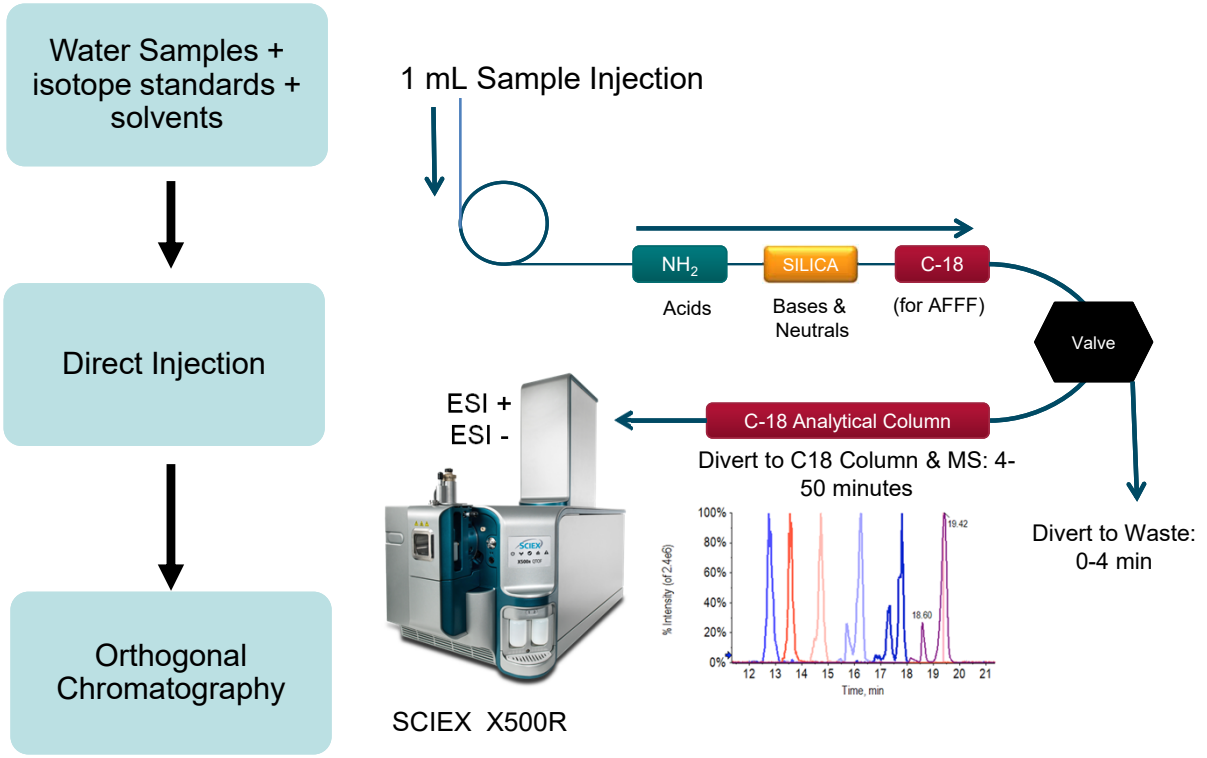



https://pfasproject.com

Barton *et al.*, 2020, *International Journal of Hygiene and Environmental Health.* https://doi.org/10.1016/j.ijheh.2019.07.012

# Water Analysis by LC-Q-ToF-MS

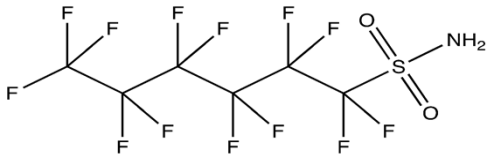
- To avoid bias, we prefer a “whole tube” direct injection approach
  - 7 mL of water in a 15 mL tube
  - Add stable isotopes and various solvents to minimize losses and ensure consistencies during transfers
  - Separate injections for ESI+ and ESI-
  - Data acquired in SWATH mode




Backe *et al.*, 2013, *ES&T;* Barzen-Hanson and Field, 2015, *ES&T Letters*. **Murray et al., 2019. *J. Haz. Mat*,** https://doi.org/10.1016/j.jhazmat.2018.11.050

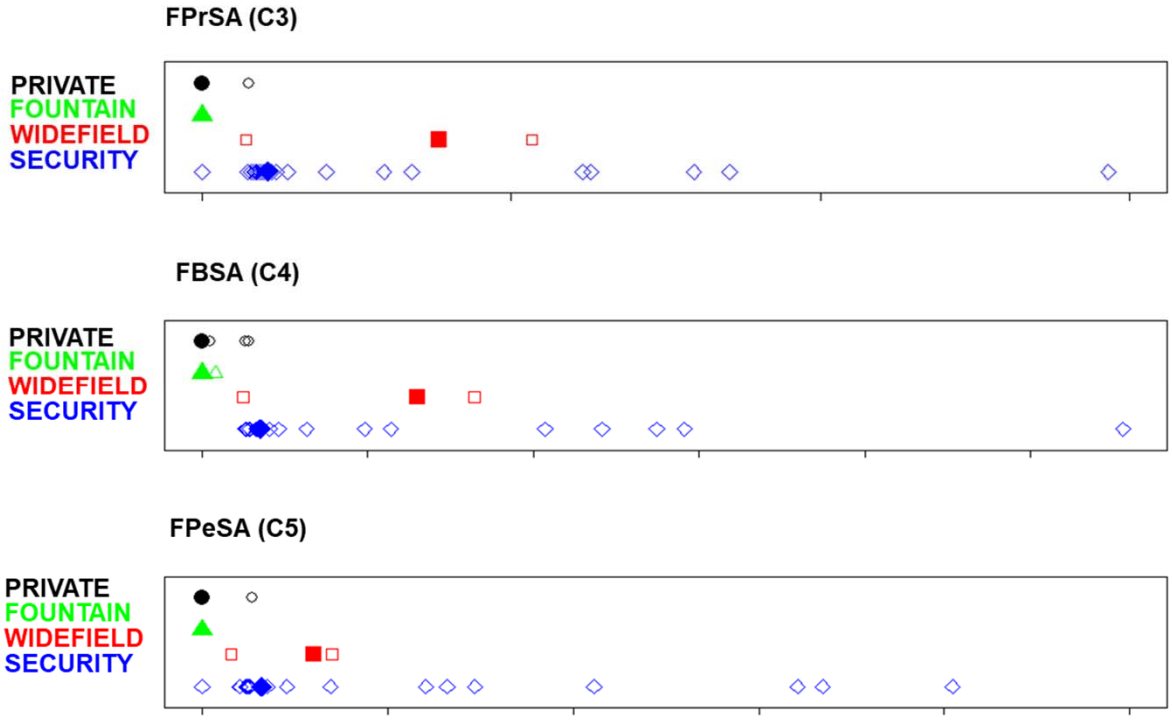
# Colorado Wells: Sulfonamides frequently detected

- Homologs of FOSA (C8) very frequently detected



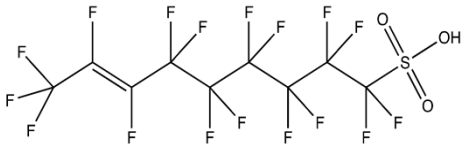

FHxSA (C6)

- Generally, **Private wells ~ Fountain < Widefield < Security**



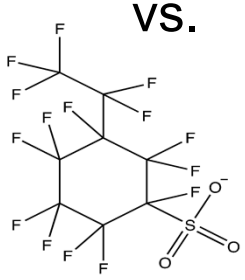

**Private wells:** circles; **Fountain:** triangles; **Widefield:** squares; **Security:** diamonds
**All quantities are relative – no concentrations (yet) available*
Filled Shapes are **Median**: 50% of values are lower, 50% are greater, than this value

# Colorado Wells: UPFOS or PFEtCHxS?

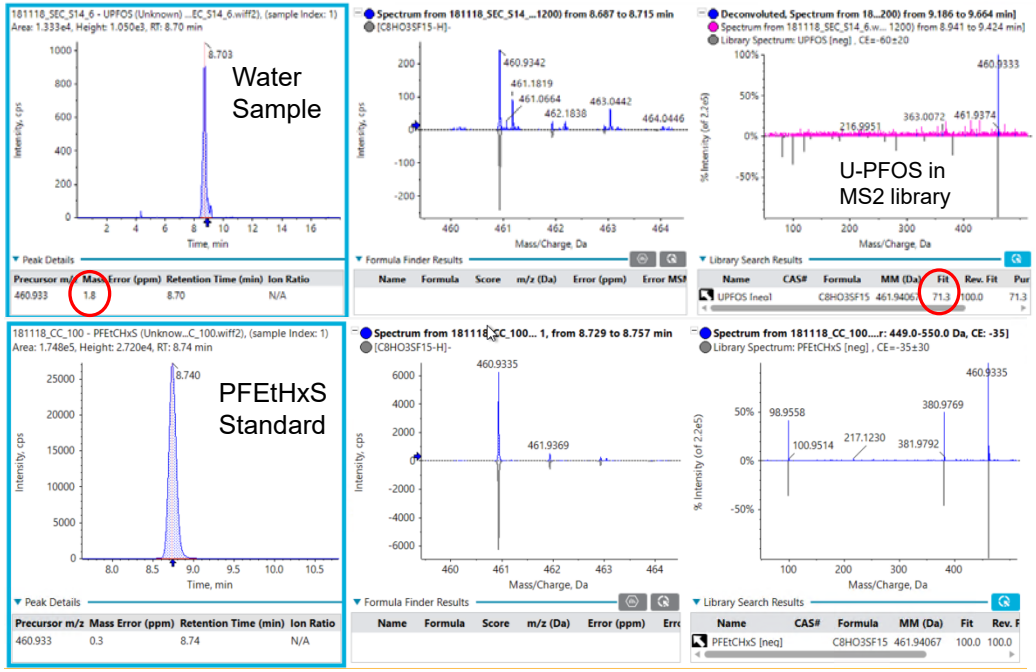


U-PFOS
(no standard)

vs.

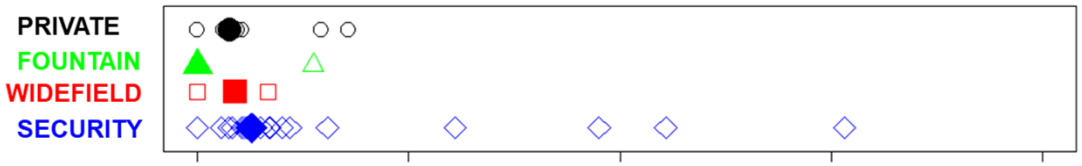


PFEtHxS
(has standard)




- Retention time, parent ion mass (<5 ppm), and isotope patterns consistent with both
- MS2 data somewhat ambiguous

**Private wells:** circles; **Fountain:** triangles; **Widefield:** squares; **Security:** diamonds
**All quantities are relative – no concentrations (yet) available*
Filled Shapes are **Median**: 50% of values are lower, 50% are greater, than this value



# PFASs in Untreated Colorado Well Water

**In summary, four PFASs frequently detected (found in > 70% of Colorado well samples):**

- C3-C5 perfluoroalkyl sulfonamides (FASAs) – FPrSA, FBSA, FPeSA
- One cyclic and/or unsaturated sulfonate – PFEtCHxS/U-PFOS

**What was sporadically detected?**

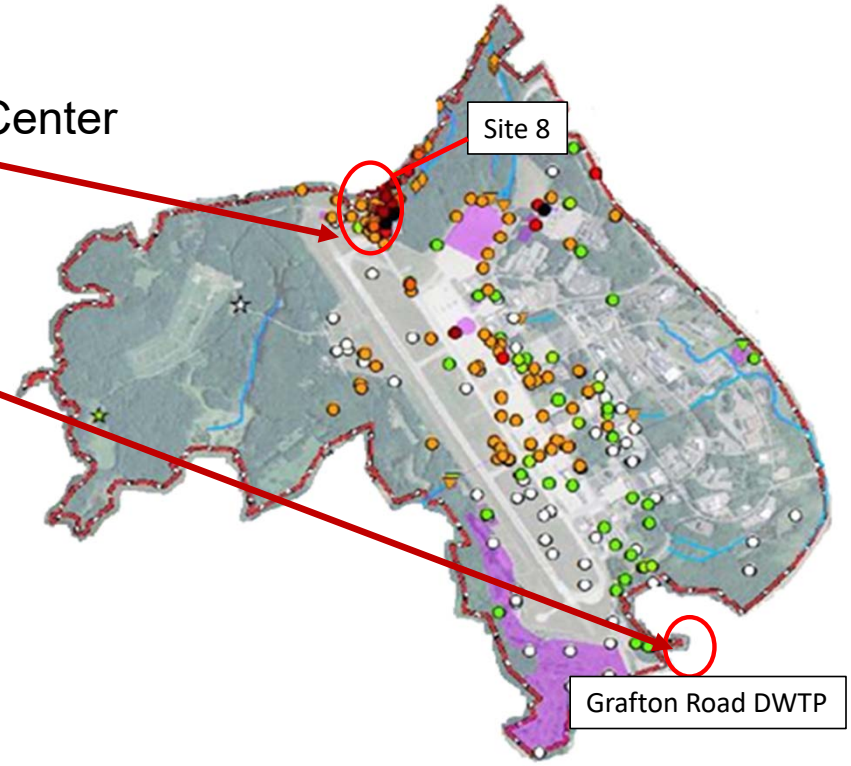
| Compounds | Percent Detection |
|---|---|
| C6 FASA (FHxSA) | 32% |
| C5, C6 Sulfinates (PFHxSi, PFPeSi) | 3%; 13% |
| Keto-sulfonates (K-PFOS; K-PFHxS) | 8%; 3% |
| Various substituted sulfonamides | 3-45% |

# Pease Tradeport, New Hampshire

## Site 8 - Fire Training Center

## Grafton Road

Harrison and Smith Well Granular Activated Carbon (GAC) Treatment System




Target Analyte List

| Perfluorosulfonates | Perfluorocarboxylates |
|---|---|
| PFPrS | PFBA |
| PFBS | PFPeA |
| PFPeS | PFHxA |
| PFHxS | PFHpA |
| PFHpS | PFOA |
| PFOS | PFNA |
| PFNS | PFDA |
| PFDS | PFUdA |
| PFUdS | PFDoA |
| PFDoS | PFTrDA |
| **Chlorinated perfluoroalkane sulfonates** | PFTeDA |
| Cl-PFOS | PFHxDA |
| Cl-O-PFNS | PFODA |
| Cl-O-PFUdS | **Fluorotelomer Sulfonates** |
| **Perfluoroalkane sulfonamides** | 4:2 FTS |
| FOSA | 6:2 FTS |
| MeFOSA | 8:2 FTS |
| EtFOSA | 10:2 FTS |
| **Perfluoroalkane sulfonamido acetic acids** | **Fluorotelomer Alkanoic Acids** |
| FOSAA | 3:3 FTA |
| MeFOSAA | 5:3 FTA |
| EtFOSAA | 7:3 FTA |
| | 6:2 FTA |
| | 8:2 FTA |
| | 10:2 FTA |
| | 6:2 FTUA |
| | 8:2 FTUA |
| | 10:2 FTUA |

# Pease Water Results: Site 8

## 48 PFASs detected on suspect list

PFAA derivatives
ECF precursors
FT precursors

| | |
|---|---|
| PFEtCHxS | O-perfluorosulfonates (i.e., O-PFHxS; C6-C10) |
| H-PFDS | U-perfluorosulfonates (i.e., UPFHxS; C6, C9) |
| H-UPFOS | K-perfluorosulfonates (i.e., K-PFHxS; C5, C6, C8) |
| F5S-PFOS | Perfluorosulfinates (i.e., PFPeSi; C5-C6) |
| PeH-FHpOS | H-perfluorocarboxylates (i.e., H-PFHpA; C7, C8, C10) |
| SPrAmPr-FHxSAA | Perfluoroalkane sulfonamides (i.e., FHxSA; C3-C6) |
| CMeAmPr-FHxSA | SPr perfluoroalkane sulfonamides (i.e., SPr-FHxSA; C4-C6) |
| 6:2 UFTS | SPrAmPr perfluoroalkane sulfonamides (i.e., SPrAmPr-FHxSA; C4-C6) |
| 6:2 FTSO2PrA | SPrAmPr perfluoroalkane sulfonamide PrS's (i.e., SPrAmPr-FHxSAPrS; C5-C6) |
| 8:2 FTSO2PrAd-DiMeEtS | S-OHPrAmPr-perfluoroalkane sulfonamides (i.e., S-OHPrAmPr-FHxSA; C5-C6) |

S-OHPrAmPr perfluoroalkane sulfonamido OHPrS's (i.e., S-OHPrAmPr-FHxSA-OHPrS; C5-C6)
diOHPrAm-MeOHPr perfuoroalkane sulfonamido PrS's (i.e., diOHPrAm-MeOHPr-FHxSAPrS; C4-C6)
X:2 fluorotelomer SO2PrAd-DiMeEtS's (i.e., 6:2 FTSO2PrAd-DiMeEtS; 4:2, 6:2, 8:2)
X:2 fluorotelomer SO-PrAd-DiMePrS's(i.e., 6:2 FTSO-PrAd-DiMePrS; 6:2, 8:2)

# Pease Water Results: Grafton Influent

5 PFASs detected on suspect list

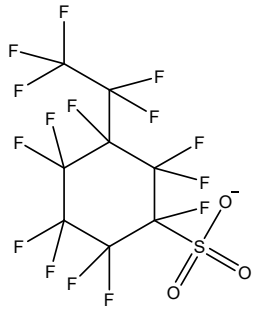
PFAA derivatives
ECF precursors
FT precursors

| | |
|---|---|
| PFEtCHxS | O-perfluorosulfonates (i.e., O-PFHxS; C6-C10) |
| H-PFDS | U-perfluorosulfonates (i.e., UPFHxS; C6, C9) |
| H-UPFOS | K-perfluorosulfonates (i.e., K-PFHxS; C5, C6, C8) |
| F5S-PFOS | Perfluorosulfinates (i.e., PFPeSi; C5-C6) |
| PeH-FHpOS | H-perfluorocarboxylates (i.e,, H-PFHpA; C7, C8, C10) |
| SPrAmPr-FHxSAA | Perfluoroalkane sulfonamides (i.e., FHxSA; C3-C6) |
| CMeAmPr-FHxSA | SPr perfluoroalkane sulfonamides (i.e., SPr-FHxSA; C4-C6) |
| 6:2 UFTS | SPrAmPr perfluoroalkane sulfonamides (i.e., SPrAmPr-FHxSA; C4-C6) |
| 6:2 FTSO2PrA | SPrAmPr perfluoroalkane sulfonamide PrS's (i.e., SPrAmPr-FHxSAPrS; C5-C6) |
| 8:2 FTSO2PrAd-DiMeEtS | S-OHPrAmPr-perfluoroalkane sulfonamides (i.e., S-OHPrAmPr-FHxSA; C5-C6) |

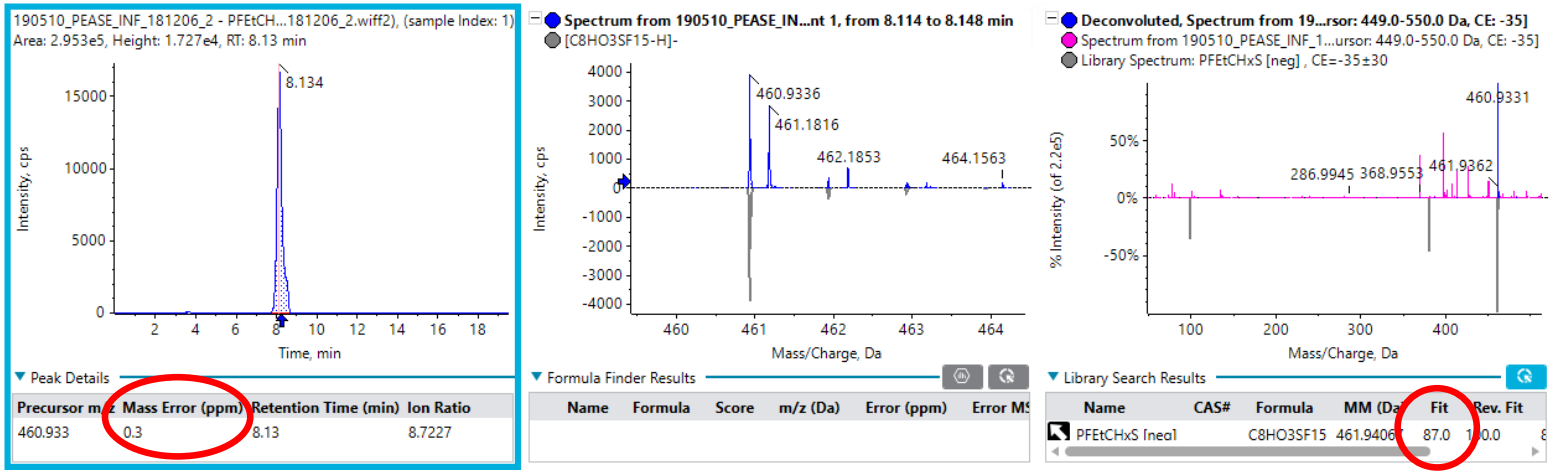
S-OHPrAmPr perfluoroalkane sulfonamido OHPrS's (i.e., S-OHPrAmPr-FHxSA-OHPrS; C5-C6)
diOHPrAm-MeOHPr perfuoroalkane sulfonamido PrS's (i.e., diOHPrAm-MeOHPr-FHxSAPrS; C4-C6)
X:2 fluorotelomer SO2PrAd-DiMeEtS's (i.e., 6:2 FTSO2PrAd-DiMeEtS; 4:2, 6:2, 8:2)
X:2 fluorotelomer SO-PrAd-DiMePrS's(i.e., 6:2 FTSO-PrAd-DiMePrS; 6:2, 8:2)

All 5 PFASs also detected in untreated Colorado wells

# Pease Grafton Influent: PFEtCHxS



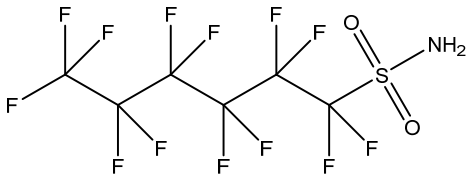

- Detected in 4 of 10 influent samples

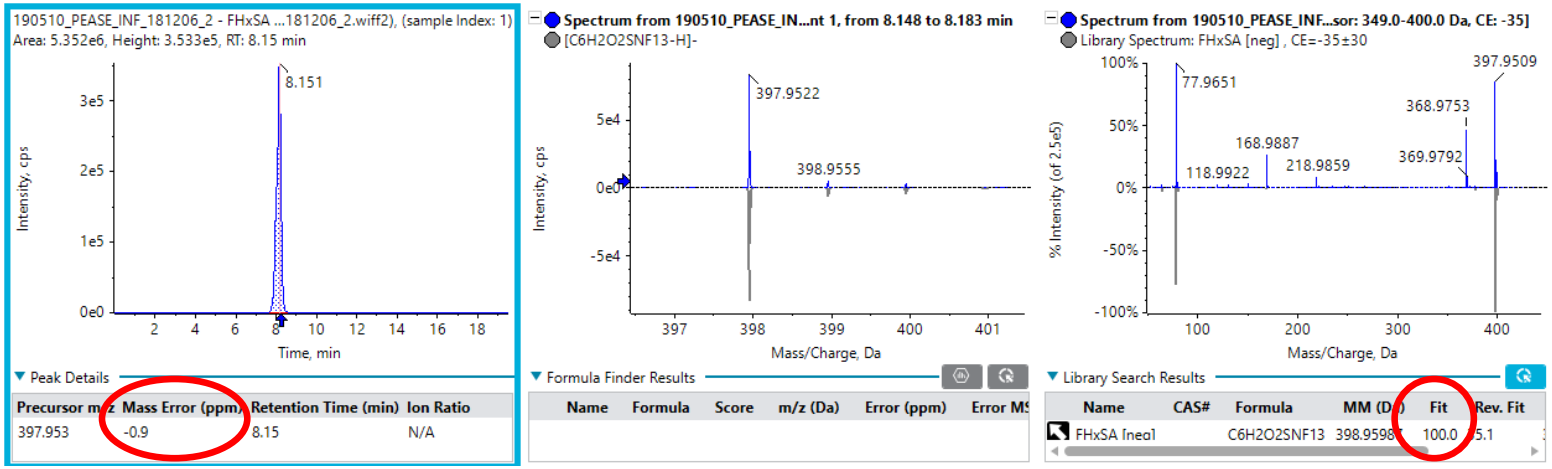



- Not detected at “25%” point in carbon vessel or in lag vessel effluent

# Pease Grafton Influent: FHxSA

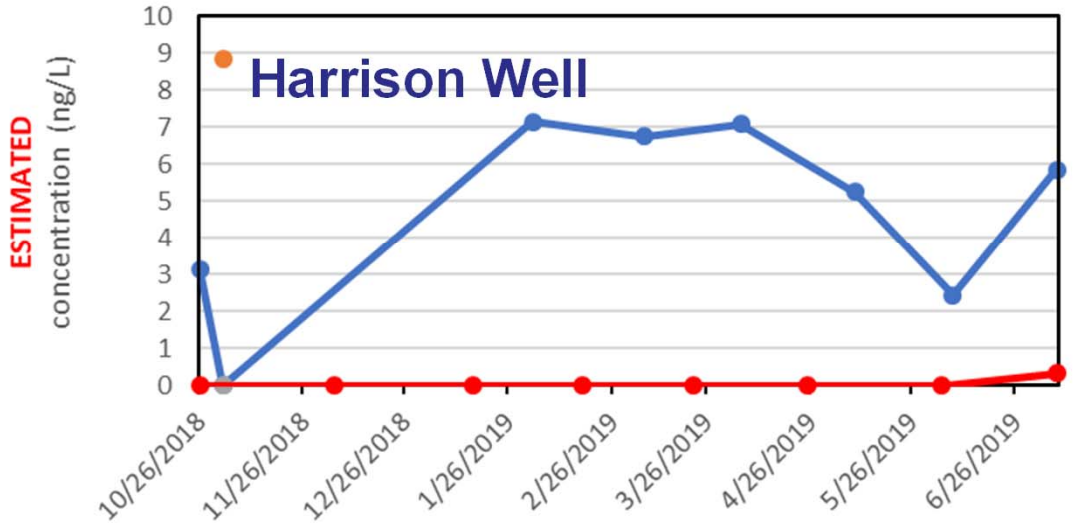
- Detected in 8 of 10 influent samples




- Not detected in lag vessel effluent

# Pease Water: Grafton FHxSA Profile




Influent ~ 3-7 ng/L (estimated)

94% reduction at ¼ through lead carbon vessel

- FHxSA not detected in effluent
- Analytical standard now available for FHxSA
  - Can be added to targeted LC-MS/MS analyte list

# And soils?

Existing AFFF-impacted site data suggests that **soils** may be a major repository of PFAS mass

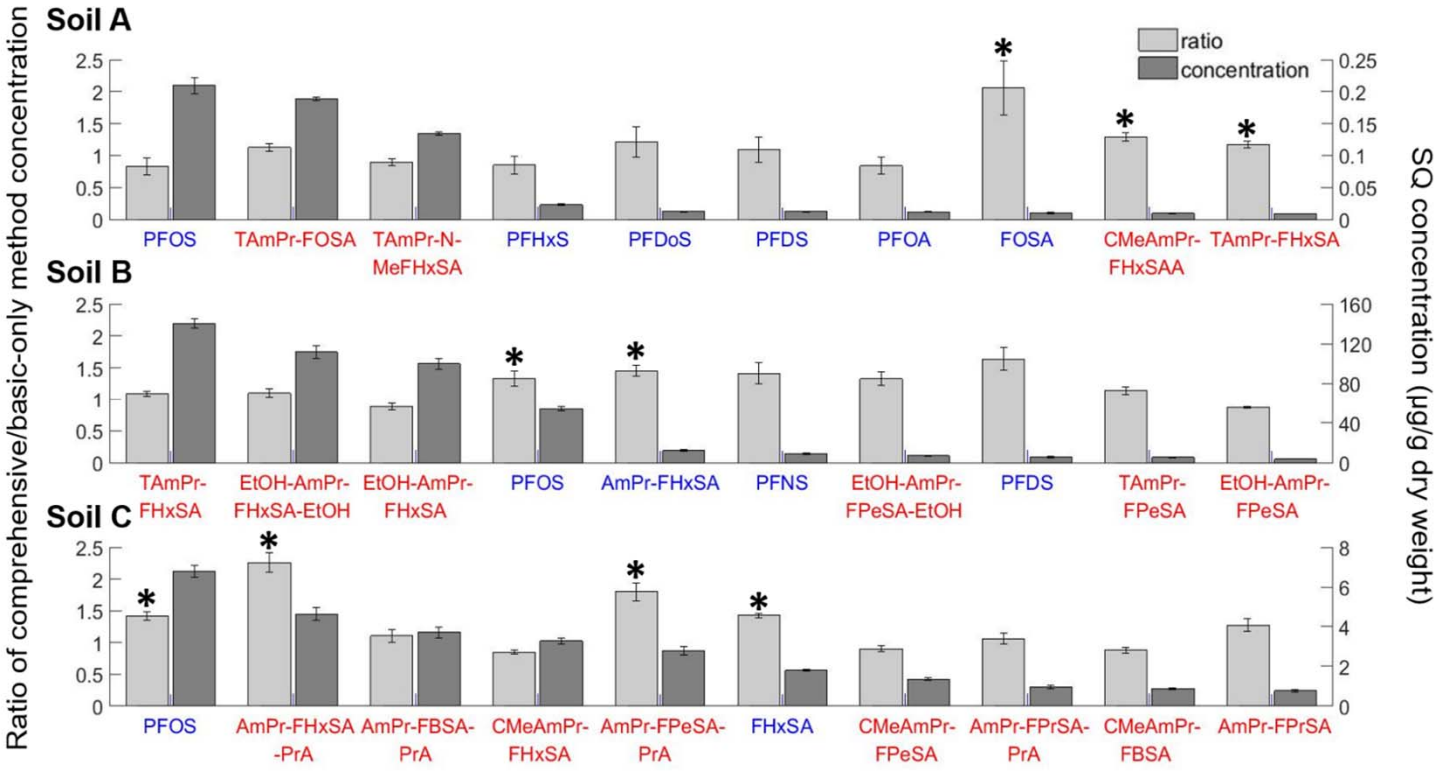
- A novel **soil extraction method** was used to enhance extraction of cationic and zwitterionic PFASs and analyze the extracts by LC-QToF-MS in both ESI+ and ESI- modes


(Older methods were only basic methanol extraction with ESI-)

Nickerson et al. 2020, *ES&T.* https://doi.org/10.1021/acs.est.0c00792

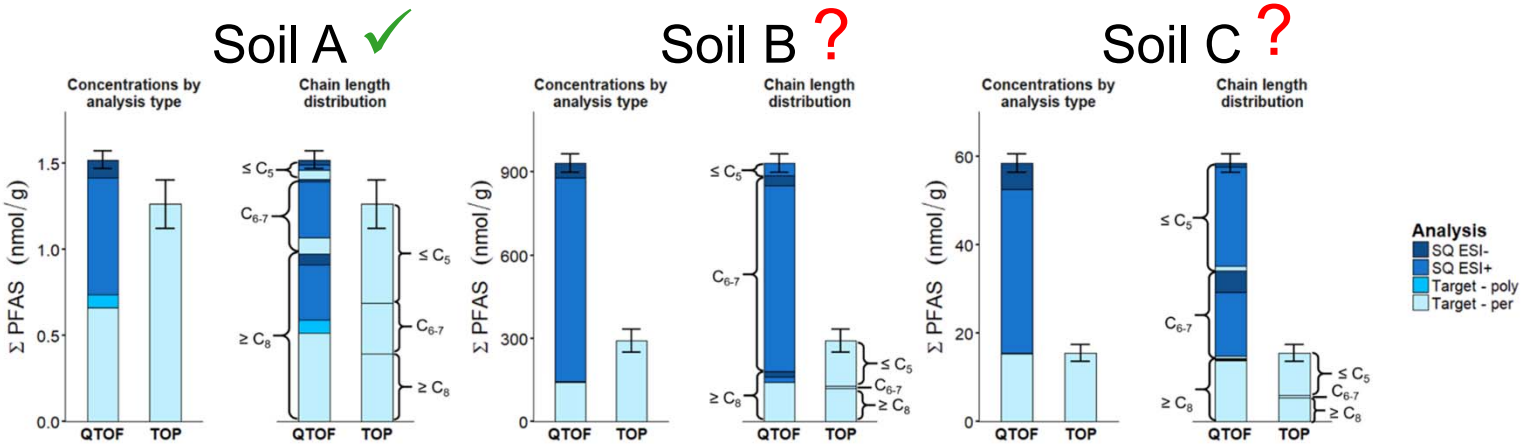
# ESI+ PFASs are abundant in AFFF-impacted soils

- ESI- PFASs (vs. ESI+ PFASs) not always the most abundant (semi quantitative estimates)
- Our novel method generally enhanced* extraction of PFASs



# HRMS Suspect Semi-quantitation

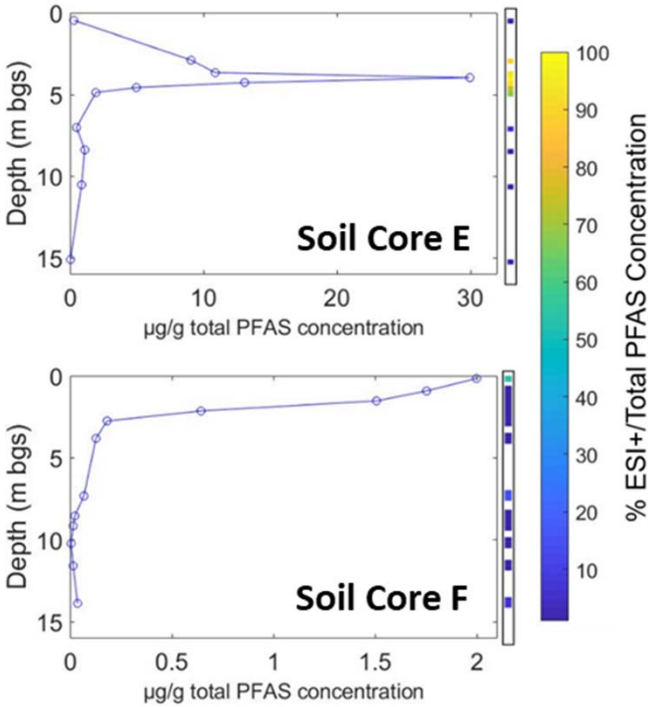
Final characterization of soils by QTOF vs. the total oxidizable precursor (TOP) assay suggests some precursors not adequately captured via TOP (as currently employed)



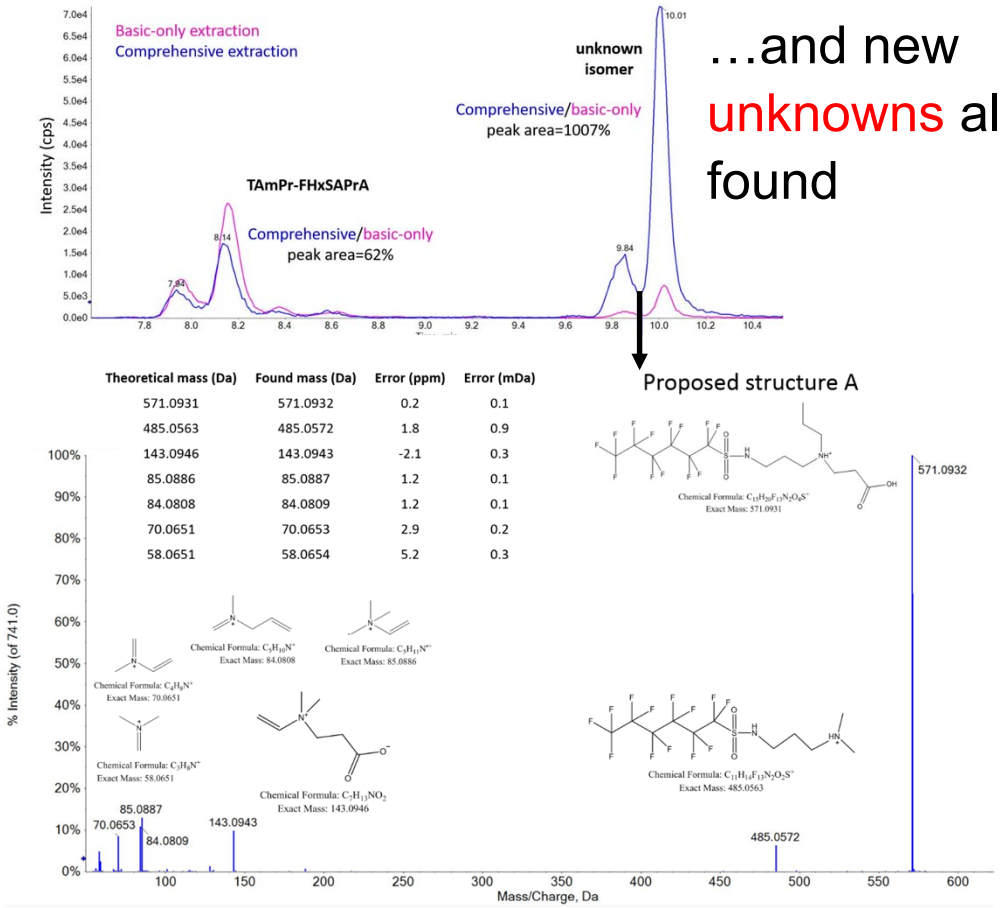

- When compared to the LC-MS/MS based TOP assay, our SQ approach either agrees or is more conservative
- Importantly, chemical characteristics are maintained when using LC-QToF-MS (unlike TOP)

Nickerson et al. 2020, *ES&T.* https://doi.org/10.1021/acs.est.0c00792

# ESI+ PFASs are important in source zone soils




Depth profiles of total PFAS concentration (SQ) and % ESI+ concentration (SQ) soil cores from two former FTAs




…and new unknowns also found

# Conclusions

- HRMS for PFASs in water samples
  - Several compounds (perfluoroalkyl sulfonamides, cyclic sulfonates) appear to be present in multiple AFFF-impacted waters
  - Mainly ESI- compounds observed in water
  - **Good news:** analytical standards for some are now available
  - **Bad news:** many “standard” analytical LC-MSMS lists do not include them
- HRMS for PFASs in soil samples
  - Many compounds (particularly ECF-derived zwitterions) appear to be present in multiple AFFF-impacted soils in source zones
  - Both ESI- and ESI+ compounds observed
  - **Good news:** analytical standards for some are now available
  - **Bad news:** “Standard” analytical LC-MSMS lists do not include them