

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

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EARTH  ENERGY  ENVIRONMENT



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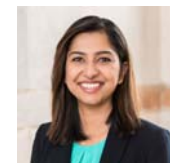
Jennifer Field  
*Oregon State*

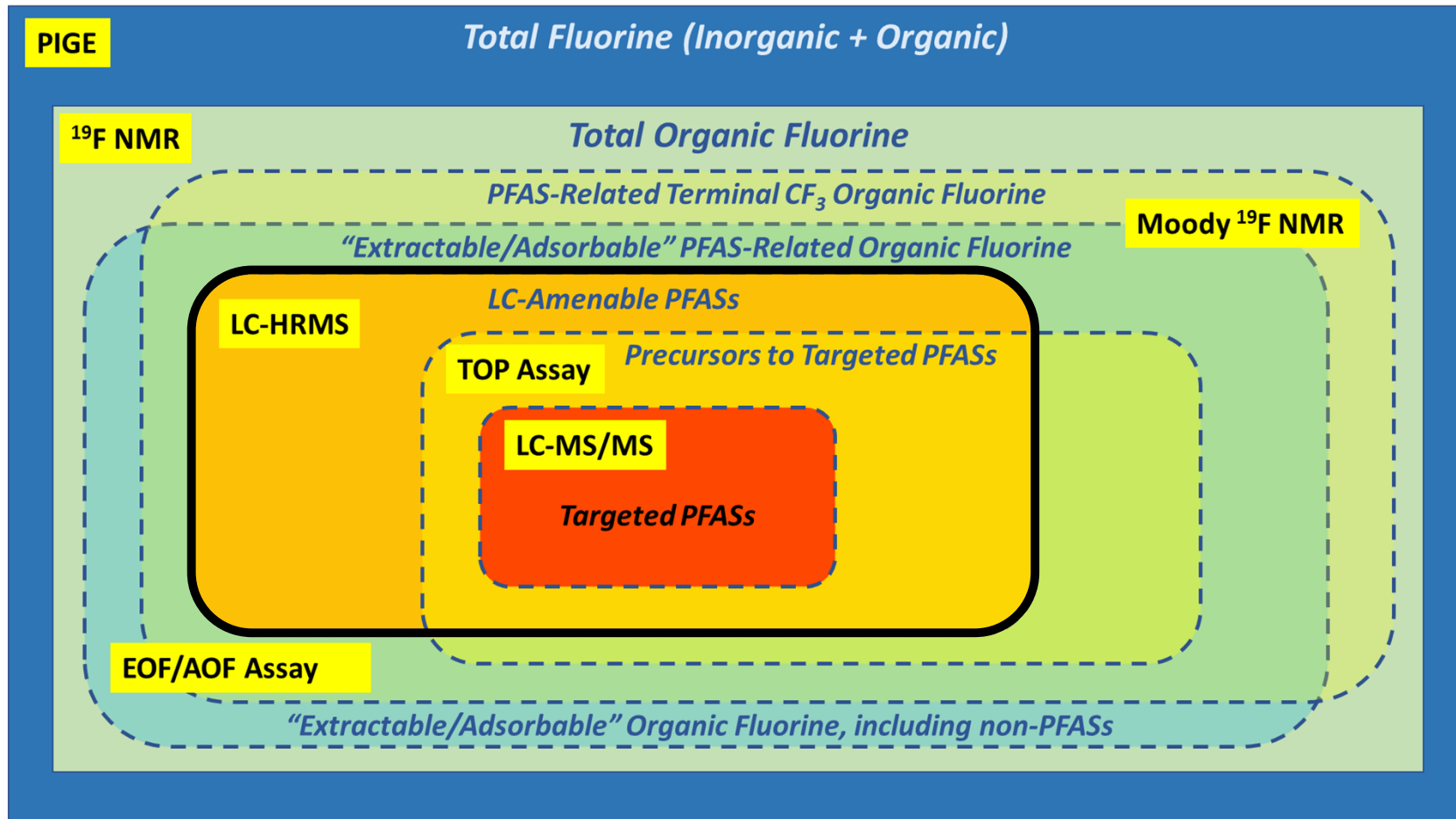
John Adgate  
Anne Starling  
Kelsey Barton  
*CoSPH*

Loretta Fernandez  
*Northeastern*

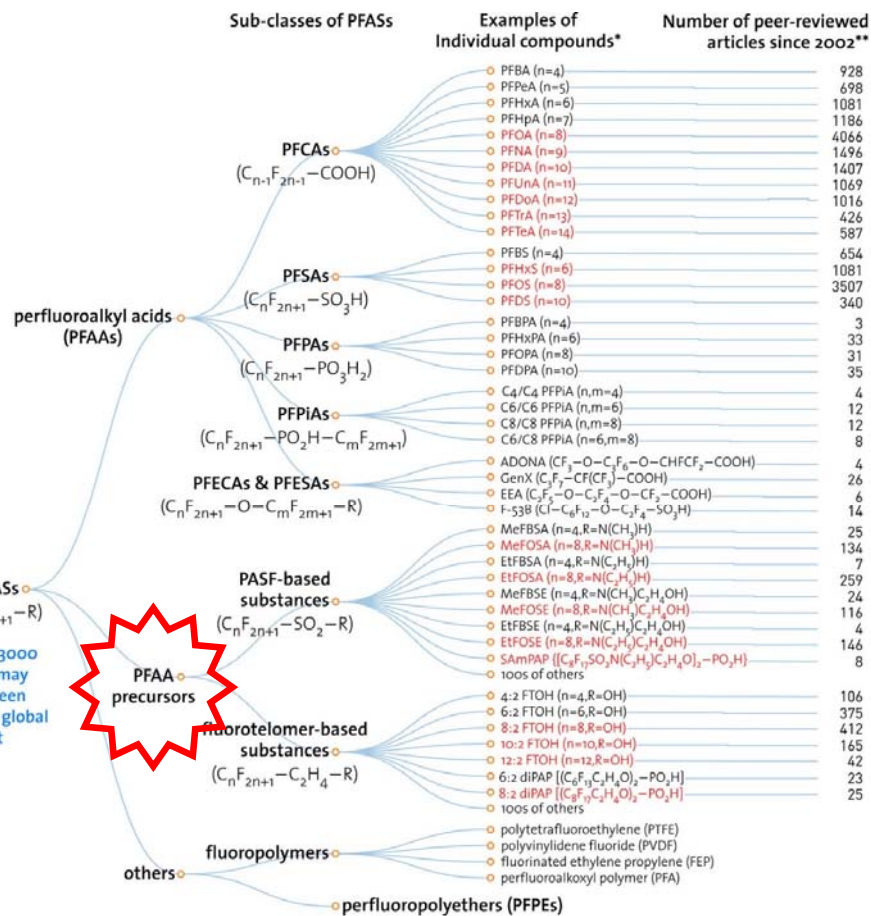
John Kornuc  
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Dave Adamson  
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*GSI*





# 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

\* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs, <http://oe.cd/1AN>).  
 \*\* The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

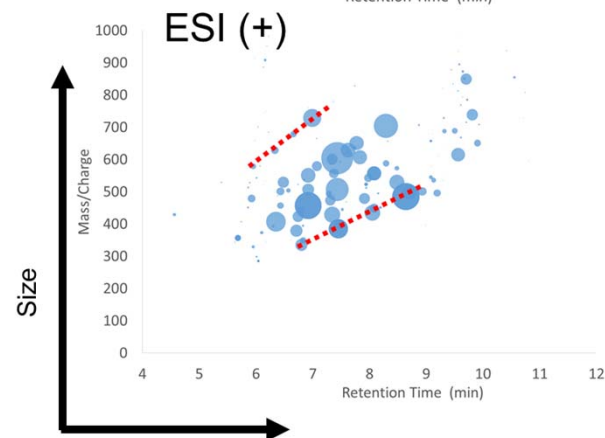
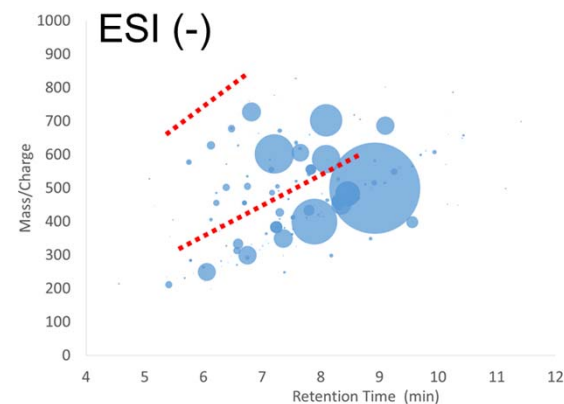


# But what's actually in AFFF-impacted samples?

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

Krista A. Barzen-Hanson,<sup>†</sup> Simon C. Roberts,<sup>∇,‡</sup> Sarah Choyke,<sup>§</sup> Karl Oetjen,<sup>‡</sup> Alan McAlees,<sup>||</sup> Nicole Riddell,<sup>||</sup> Robert McCrindle,<sup>⊥</sup> P. Lee Ferguson,<sup>§</sup> Christopher P. Higgins,<sup>\*,‡</sup> and Jennifer A. Field<sup>\*,#</sup>

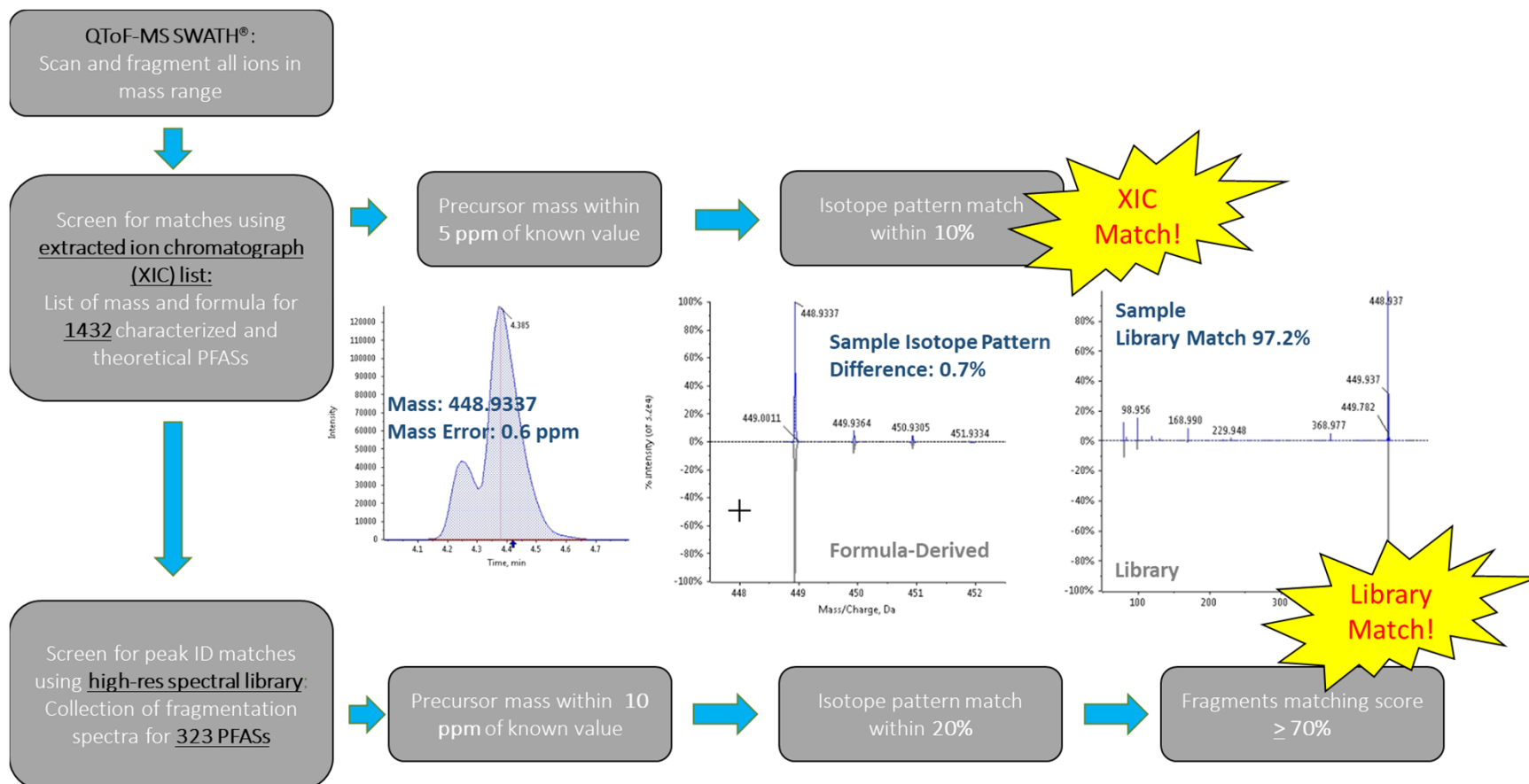
- Do we really need to look for >1400 PFASs in all samples?
- Some of these are just hypothetical, and others may never leave the source zone
- What is actually in samples impacted by AFFF?



Hydrophobicity (C18 retention)

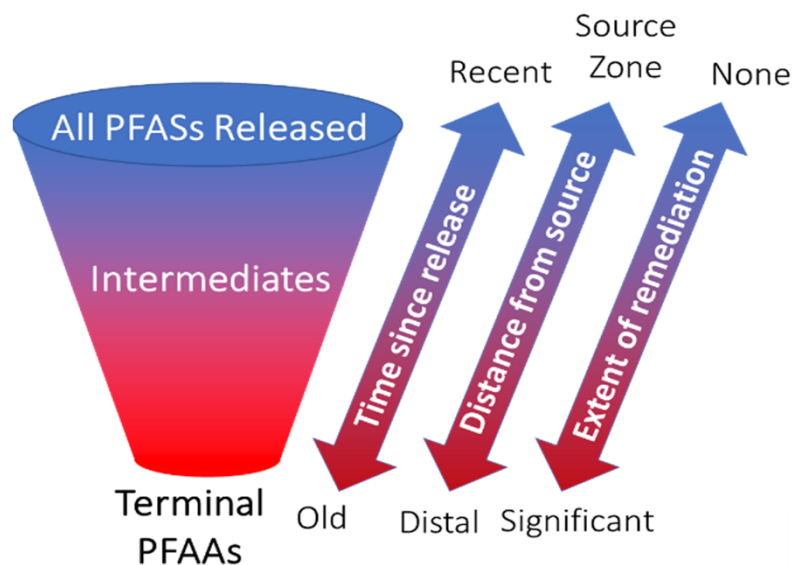
Circle area = peak area

# HRMS Suspect Criteria for PFASs

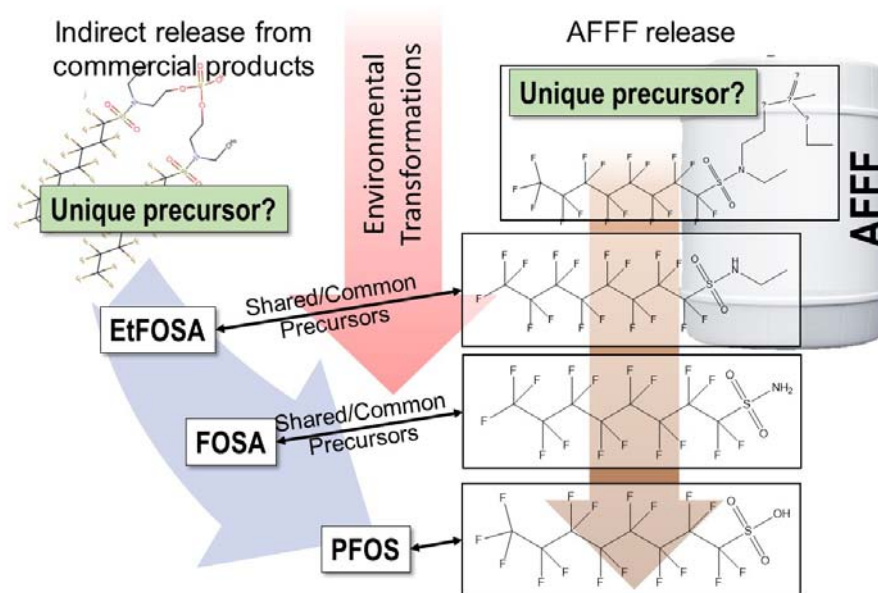


# Transport and Transformation

Complexity varies with time, space, and remedial history



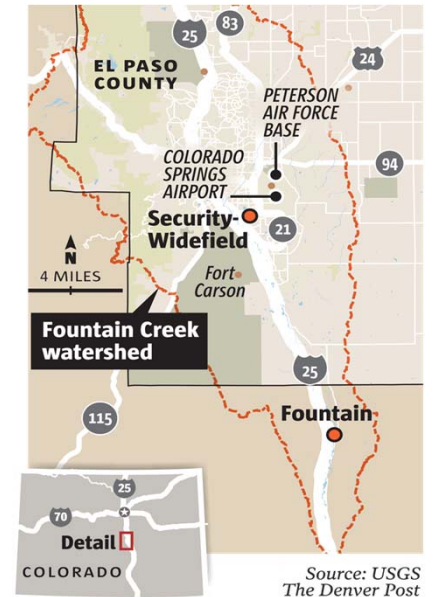
Some PFASs are known degradation intermediates of those in AFFF, but also consumer products



# A tale of two sites: Peterson and Pease

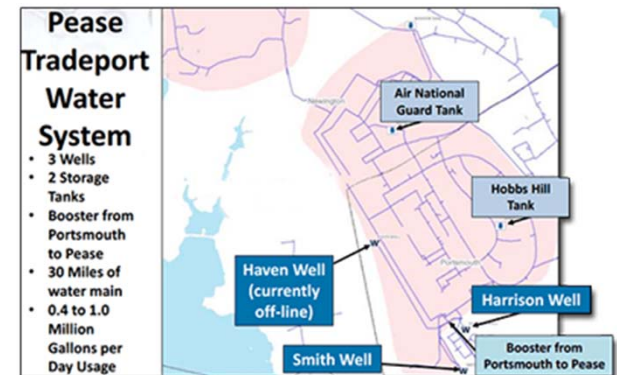
- Security, Fountain, and Widefield in Colorado

- **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

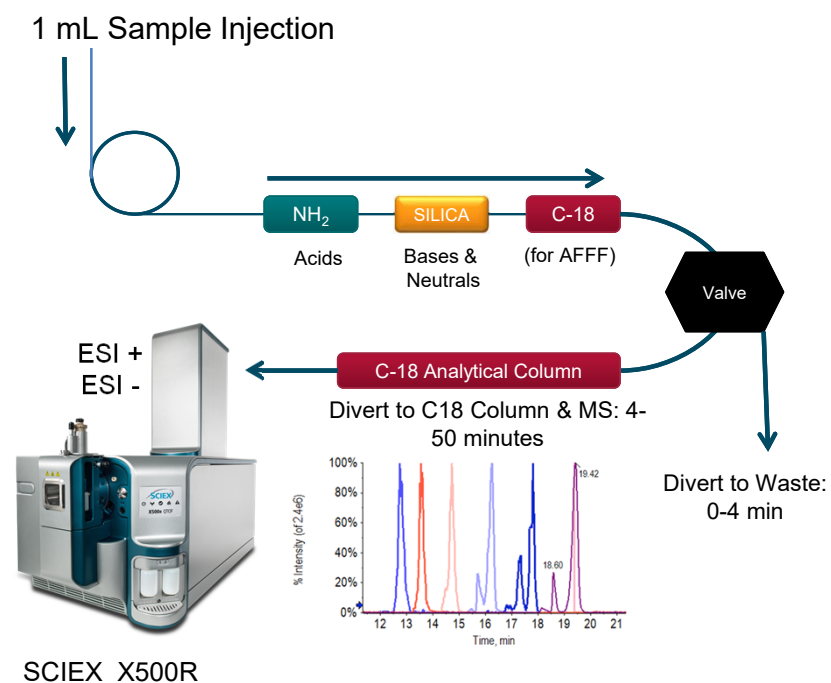
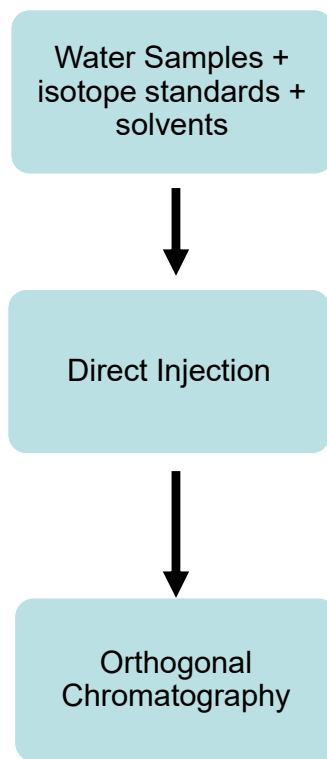


<https://pfasproject.com>



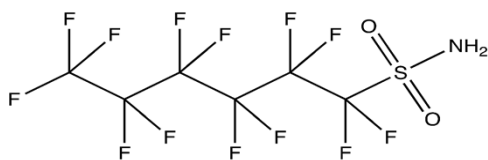
# Water Analysis by LC-Q-ToF-MS

- 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



# Colorado Wells: Sulfonamides frequently detected

- Homologs of FOSA (C8) very frequently detected



FHxSA (C6)

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

FPrSA (C3)

PRIVATE  
FOUNTAIN  
WIDEFIELD  
SECURITY



FBSA (C4)

PRIVATE  
FOUNTAIN  
WIDEFIELD  
SECURITY



FPeSA (C5)

PRIVATE  
FOUNTAIN  
WIDEFIELD  
SECURITY

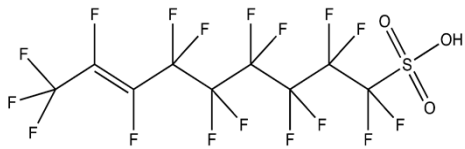


**Private wells:** circles; **Fountain:** triangles; **Widefield:** squares; **Security:** diamonds

*\*All quantities are relative – no concentrations (yet) available*

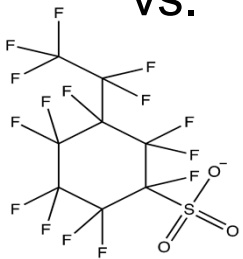
Filled Shapes are **Median:** 50% of values are lower, 50% are greater, than this value

# Colorado Wells: UPFOS or PFEtCHxS?



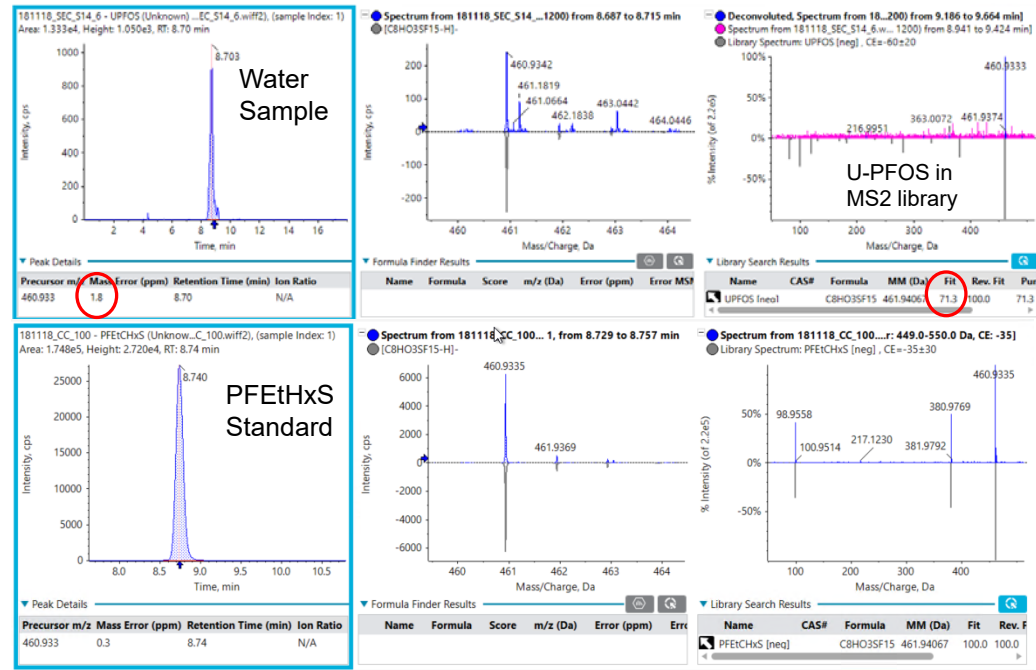
U-PFOS  
(no standard)

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?**

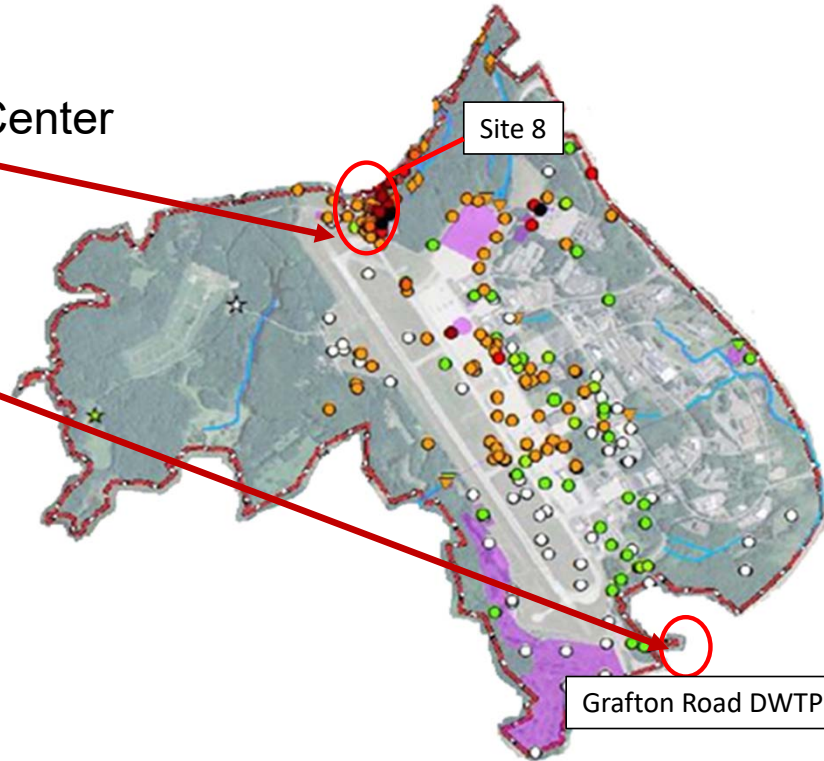
<b>Compounds</b>	<b>Percent Detection</b>
C6 FASA (FHxSA)	32%
C5, C6 Sulfinates (PFHxSi, PFPeSi)	3%; 13%
Keto-sulfonates (K-PFOS; K-PFHxS)	8%; 3%
Various substituted sulfonamides	3-45%

# 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
<b>Chlorinated perfluoroalkane sulfonates</b>	PFTeDA
Cl-PFOS	PFHxDA
Cl-O-PFNS	PFODA
Cl-O-PFUdS	<b>Fluorotelomer Sulfonates</b>
<b>Perfluoroalkane sulfonamides</b>	4:2 FTS
FOSA	6:2 FTS
MeFOSA	8:2 FTS
EtFOSA	10:2 FTS
<b>Perfluoroalkane sulfonamido acetic acids</b>	<b>Fluorotelomer Alkanoic Acids</b>
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	Perfluorosulfonates (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 OHPPrS's (i.e., S-OHPrAmPr-FHxSA-OHPPrS; C5-C6)
	diOHPrAm-MeOHPr perfluoroalkane 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

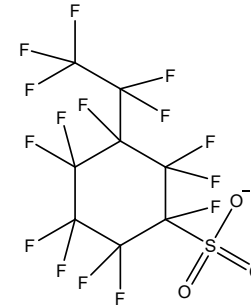
5 PFASs detected on suspect list

PFAA derivatives  
ECF precursors  
FT precursors

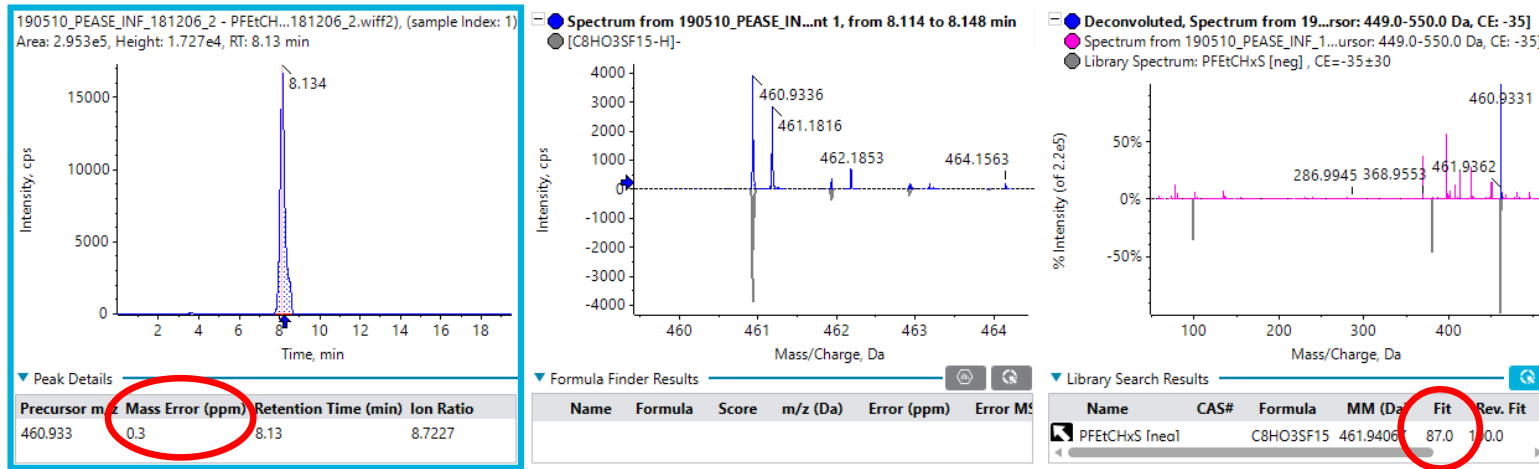
PFEtCHxS	O-perfluorosulfonates (i.e., O-PFHxS; C6-C10)
H-PFDS	U-perfluorosulfonates (i.e., UPFHxS; C6, C9)
H-UPFOS	K-perfluorosulfonates (i.e., K-PFHxS; C5, C6, C8)
F5S-PFOS	Perfluorosulfinates (i.e., PFPeSi; C5-C6)
PeH-FHpOS	H-perfluorocarboxylates (i.e., H-PFHpA; C7, C8, C10)
SPrAmPr-FHxSAA	<b>Perfluoroalkane sulfonamides (i.e., FHxSA; C3-C6)</b>
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 Pr'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 OHPr's (i.e., S-OHPrAmPr-FHxSA-OHPrS; C5-C6)
	diOHPrAm-MeOHPr perfluoroalkane sulfonamido Pr'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: PF<sub>6</sub>EtCH<sub>2</sub>S



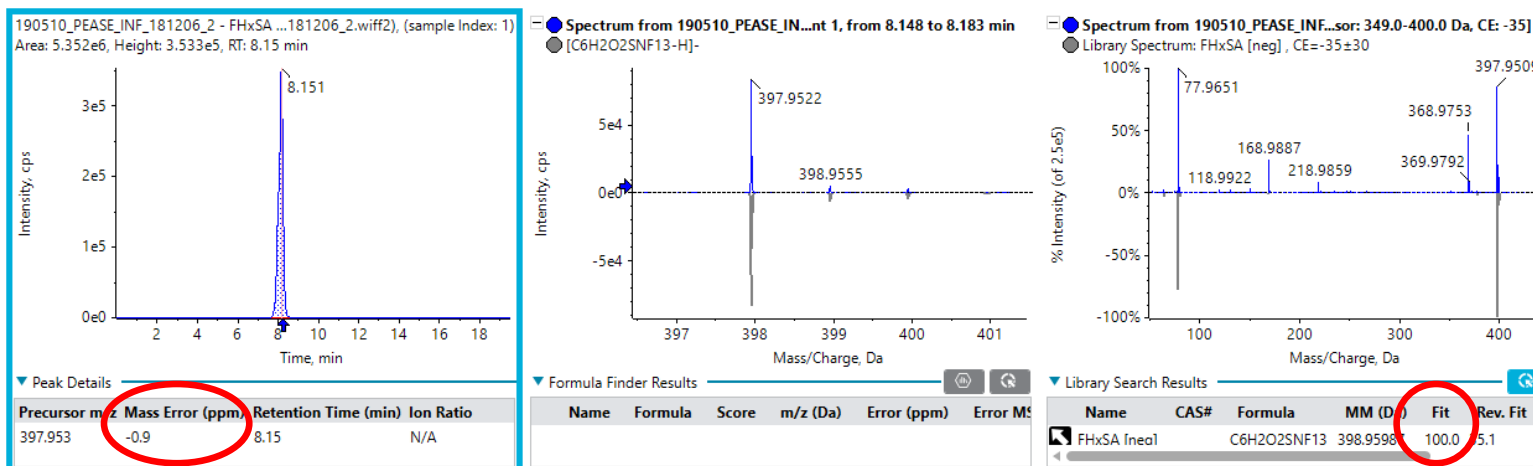
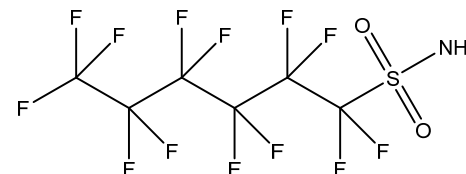
- Detected in 4 of 10 influent samples



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

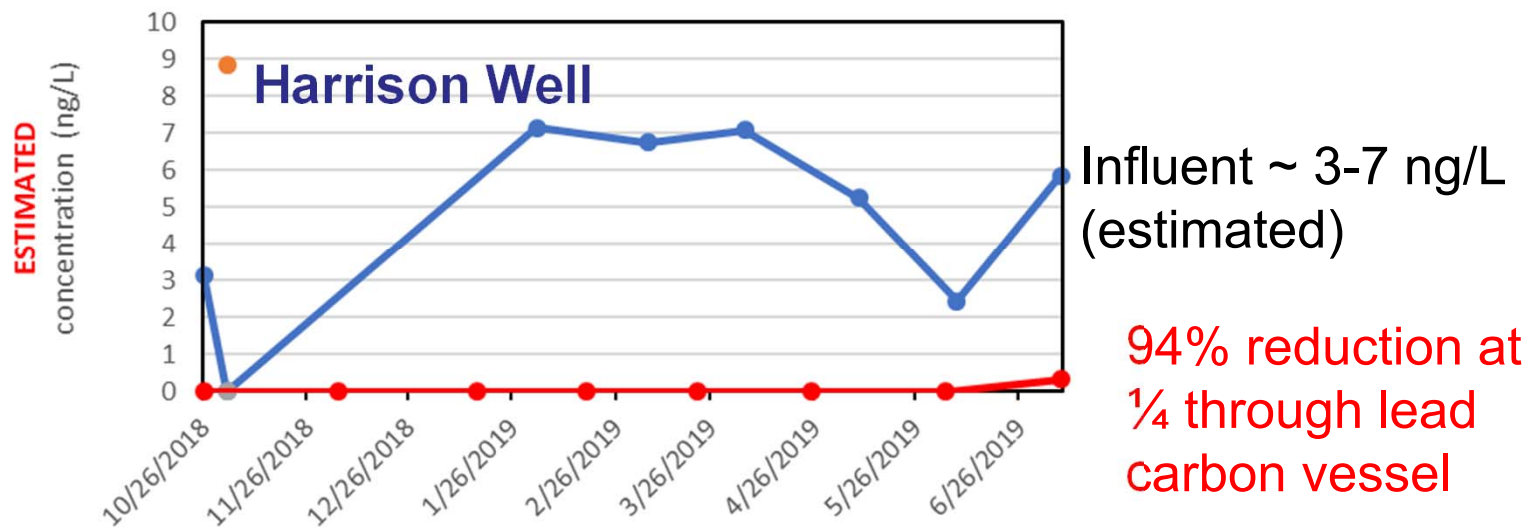
# Pease Grafton Influent: FHxSA

- Detected in 8 of 10 influent samples



- Not detected in lag vessel effluent

## Pease Water: Grafton FHxSA Profile



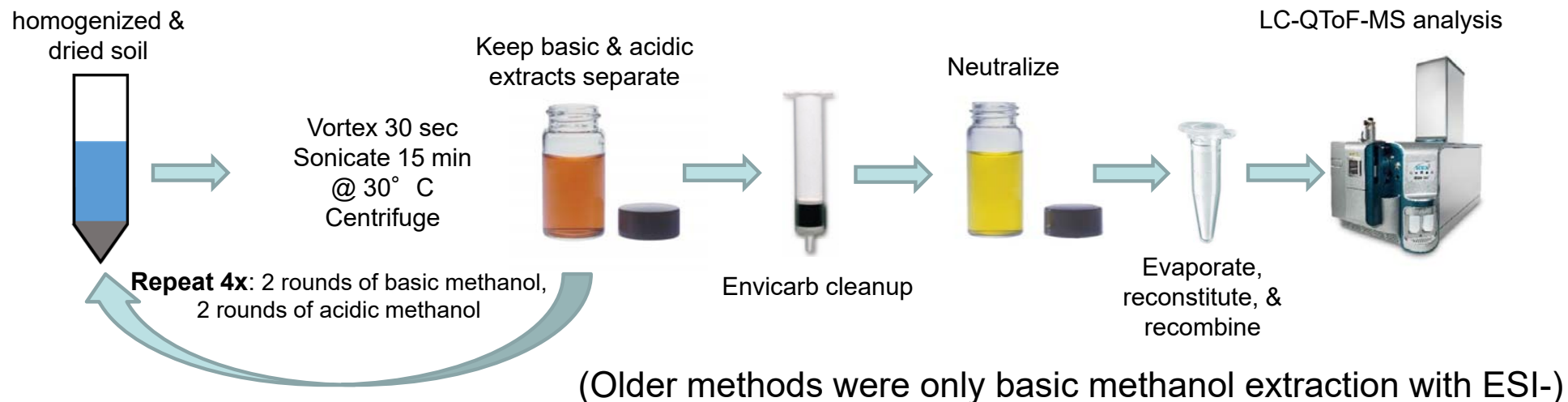
- FHxSA not detected in effluent
- Analytical standard now available for FHxSA
  - Can be added to targeted LC-MS/MS analyte list



## And soils?

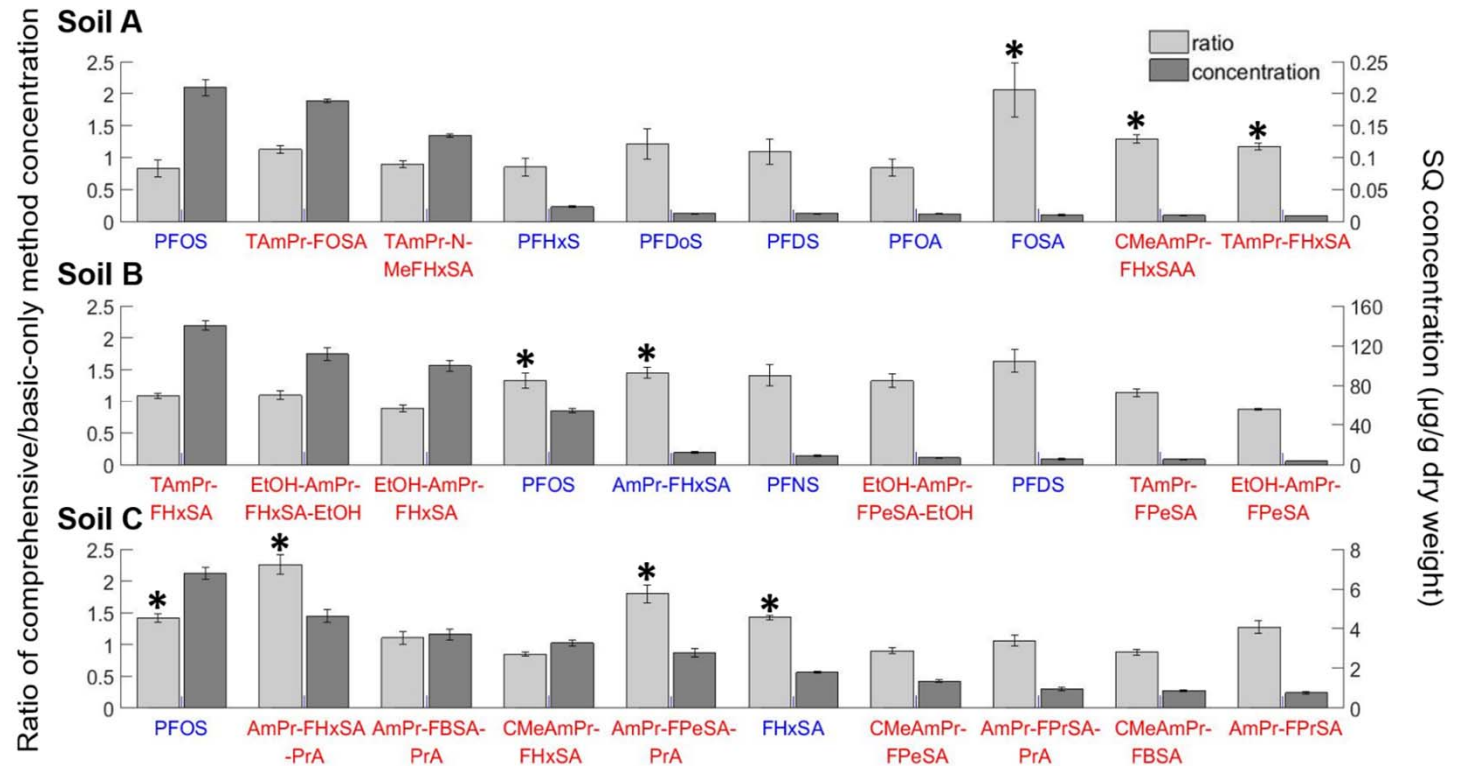
Existing AFFF-impacted site data suggests that **soils** may be a major repository of PFAS mass

- 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



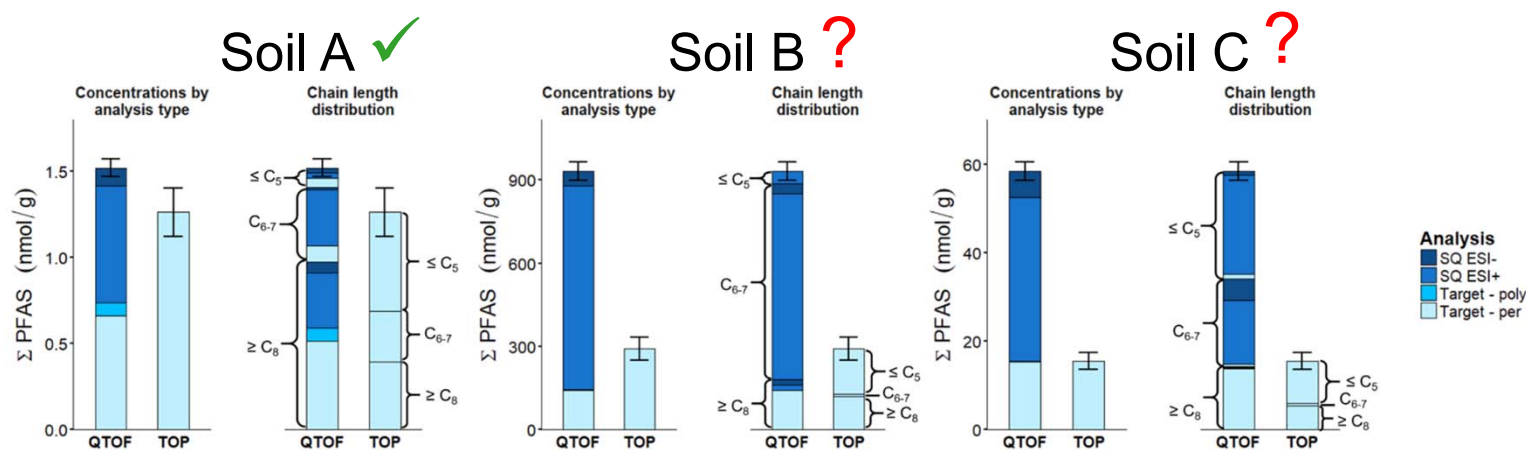
# ESI+ PFASs are abundant in AFFF-impacted soils

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



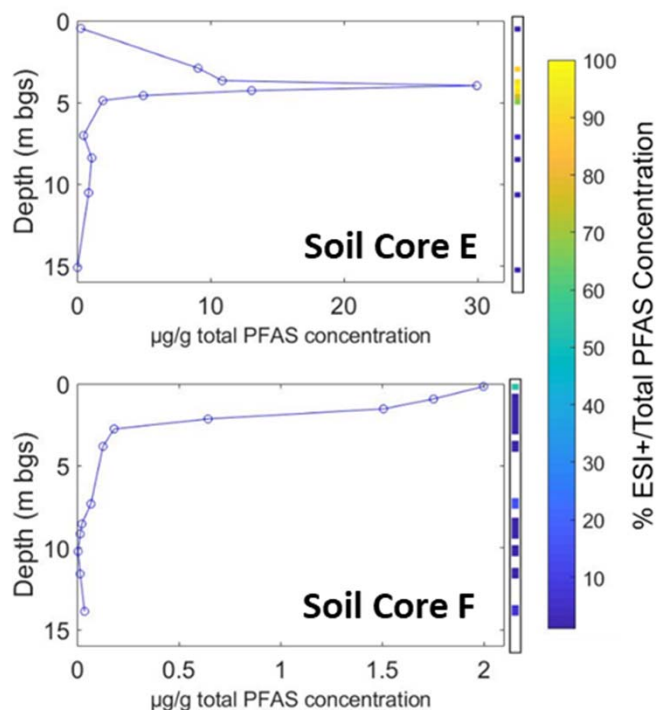
# HRMS Suspect Semi-quantitation

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

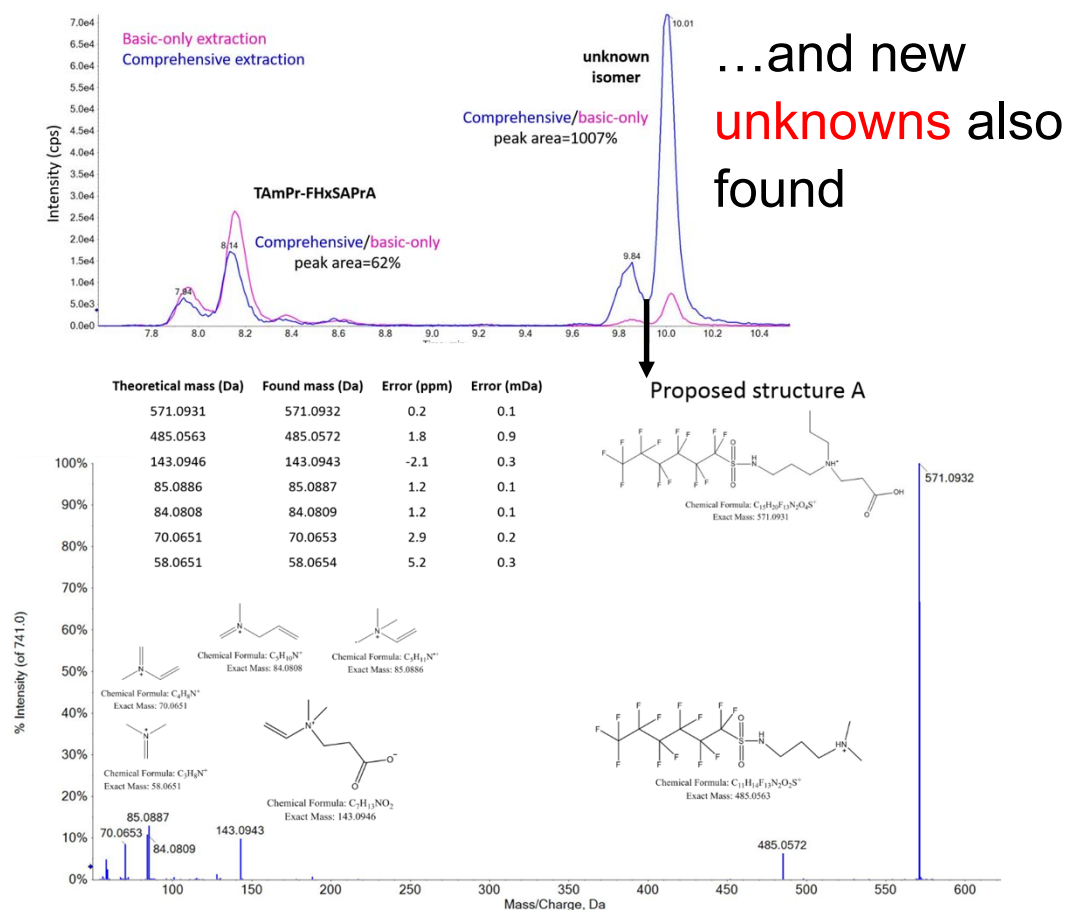


- When compared to the LC-MS/MS based TOP assay, our SQ approach either agrees or is more conservative
- Importantly, chemical characteristics are maintained when using LC-QToF-MS (unlike TOP)

# 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



# 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