Per- and Polyfluoroalkyl Substances (PFAS) in AFFF Formulations and Groundwater

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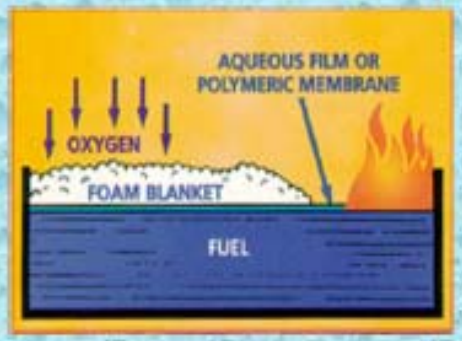
Outline

- Per- and polyfluoroalkyl substances (PFAS) in aqueous film forming foams (AFFF)
- Current and alternative PFAS method based on micro liquid-liquid extraction, large-volume injection, orthogonal LC-MS/MS
- Data quality tiers and quality control
- Groundwater data for US military sites
- Mass balance: total fluorine (TOP assay & PIGE)
- Conclusions
- Acknowledgments

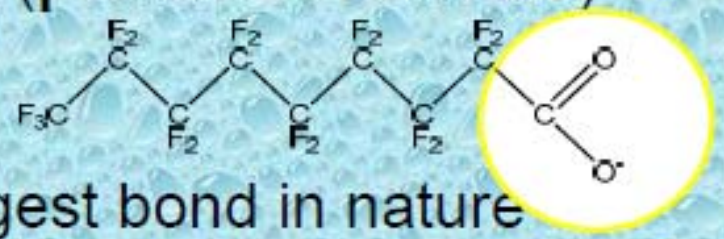
Fire-Fighter Training Areas

- AFFF blankets fuel, cools the fuel surface, prevents re-ignition by suppressing release of flammable vapors
- Aqueous film-forming foams (AFFF) routinely used for fire fighter training at municipal and military fire training areas
- AFFF waste discharged from military fire-training area until 2000
- U.S. military accounts for 75% of all the AFFF used in the United States
- AFFF formulations must meet specifications (Mil Spec) to be used by the U.S. military

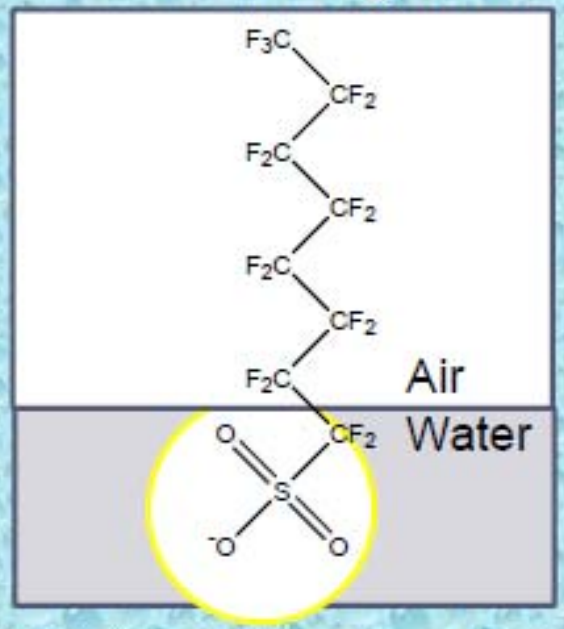


Unique Chemistry

PFOA (**per**fluorooctanoate)

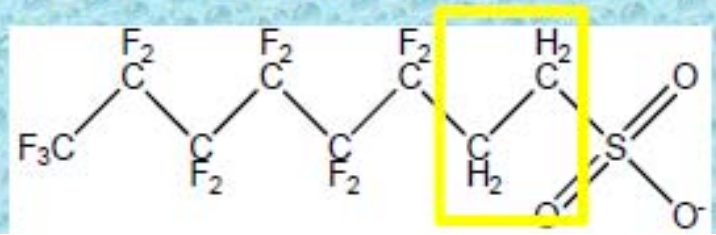


- C-F bond is the shortest and strongest bond in nature
- Less tendency to associate with other phases – oil, water
- Few degradation processes: too much energy to break bonds
  - stable in acids, bases, (most) oxidants, heat
  - microorganisms cannot gain energy from breaking the



***Per*fluorinated** = all carbon atoms fully fluorinated (no hydrogen atoms)

***Poly*fluorinated =** some carbons are not fully fluorinated (have H)

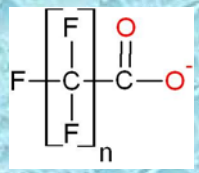


PFOS (**per**fluorooctane sulfonate)

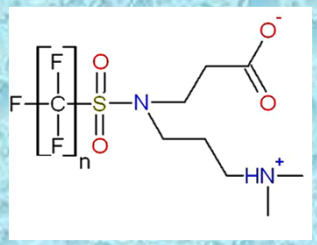
3M AFFF: 3 & 6% Lightwater

Perfluoroalkyl Sulfonates (n = 2-10)

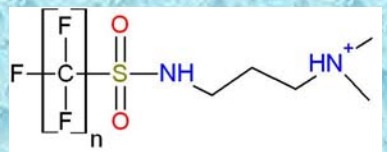
Perfluoroalkyl Carboxylates (n = 2-13)



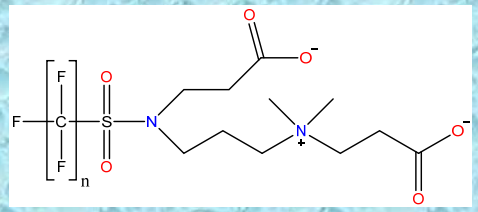
Perfluoroalkyl Sulfonamide Amino Carboxylates (n = 3-8)



Perfluoroalkyl Sulfonamido Amines (n = 3-8)

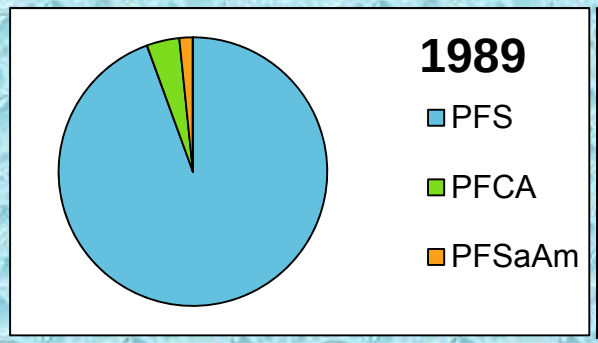


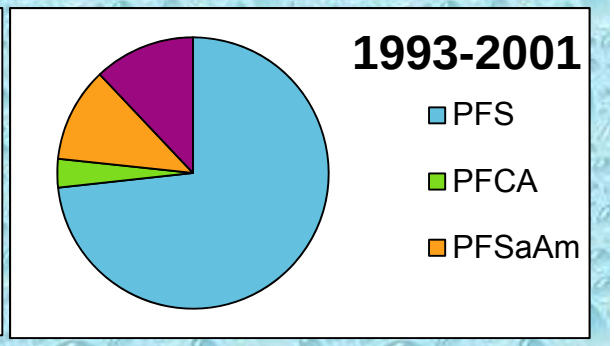
Unnamed (n = 3-6)



Five 3M AFFFs (1989-2001)

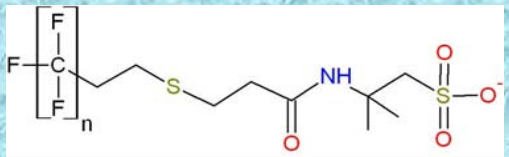
- ✓ PFOS>>cationic/zwitterionic>carboxylates
- ✓ Cationic/zwitterionic added by 1993
- ✓ All contain ultra-short C2-C3 sulfonates



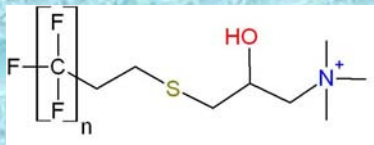


Telomer-Based AFFFs (as of 2013)

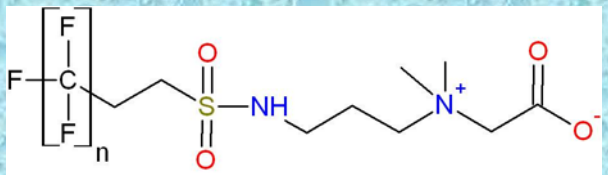
Fluorotelomer Thio Amido Sulfonates (n = 4,6,8,10,12,14)



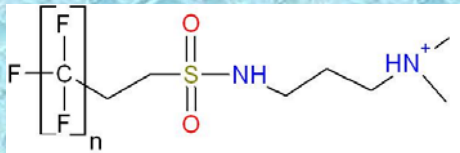
Fluorotelomer Thio Hydroxy Ammonium (n= 4,6,8,10)



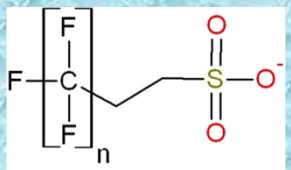
Fluorotelomer Sulfonamido Betaines (n= 4,6,8,10,12)



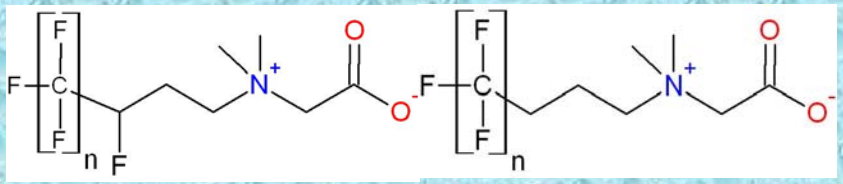
Fluorotelomer Sulfonamido Amines (n= 4,6,8,10,12)



Fluorotelomer Sulfonates



Fluorotelomer Betaines (n = 5,7,9)



Ansul
Chemguard

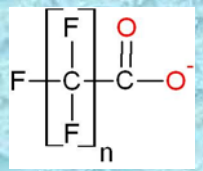
Angus (Tridol)

National Foam (Aer-O-Water)
Fire Service Plus

Buckeye

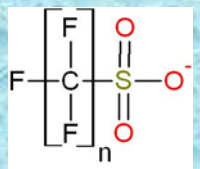
PFAS Analytes

Perfluoroalkyl Carboxylates



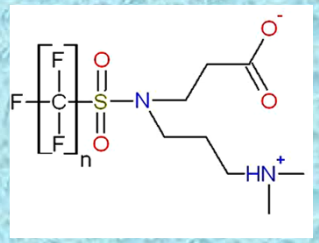
PFEtA	n = 2	PFNA	n = 9
PFPrA	n = 3	PFDA	n = 10
PFBA	n = 4	PFUdA	n = 11
PFPeA	n = 5	PFDoA	n = 12
PFHxA	n = 6	PFTrA	n = 13
PFHpA	n = 7	PFTeA	n = 14
PFOA	n = 8		

Perfluoroalkyl Sulfonates



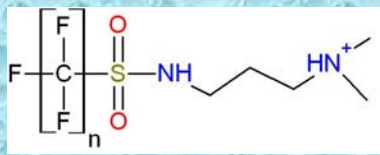
PFEtS	n = 2
PFPrS	n = 3
PFBS	n = 4
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFDS	n = 10

Perfluoroalkyl Sulfonamide Amino Carboxylates



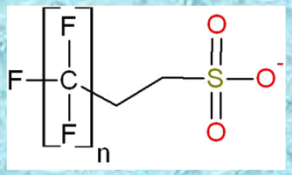
PFPrSaAmA	n = 3
PFBSaAmA	n = 4
PFPeSaAmA	n = 5
PFHxSaAmA	n = 6
PFOSaAmA	n = 8

Perfluoroalkyl Sulfonamido Amines



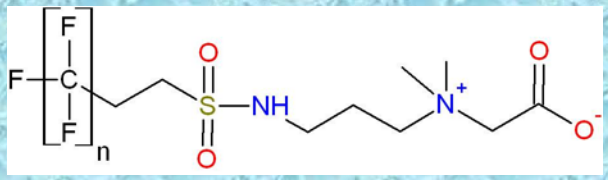
PFBSaAm	n = 4
PFPeSaAm	n = 5
PFHxSaAm	n = 6
PFOSaAm	n = 8

Fluorotelomer Sulfonates



4-2 FtS	n = 4
6-2 FtS	n = 6
8-2 FtS	n = 8

Fluorotelomer Sulfonamido Betaines

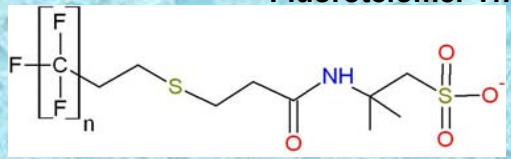


6-2 FtSaB	n = 6
8-2 FtSaB	n = 8
10-2 FtSaB	n = 10
12-2 FtSaB	n = 12

Fluorotelomer Sulfonamido Amines

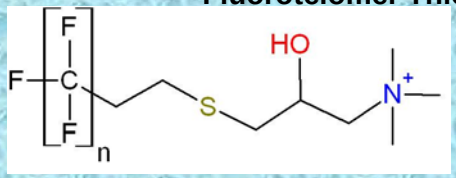
6-2 FtSaAm	n = 6
8-2 FtSaAm	n = 8

Fluorotelomer Thio Amido Sulfonates



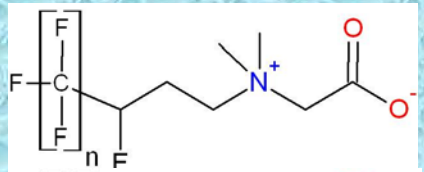
4-2 FtTAoS	n = 4
6-2 FtTAoS	n = 6
8-2 FtTAoS	n = 8

Fluorotelomer Thio Hydroxy Ammonium

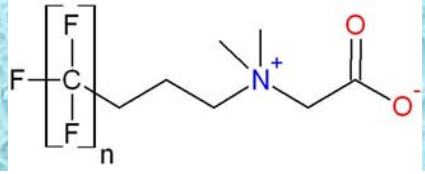


6-2 FtTHN$^+$	n = 6

Fluorotelomer Betaines



5-1-2 FtB	n = 5
7-1-2 FtB	n = 7
9-1-2 FtB	n = 9



5-3 FtB	n = 5
7-3 FtB	n = 7
9-3 FtB	n = 9

Solid Phase Extraction (EPA Method 537)

- 9 perfluoroalkyl carboxylates (4, 6-13)
- 3 perfluoroalkyl sulfonates (4,6,8)
- 2 sulfonamido acetic acids
- Cost (>$300/sample)/expertise required
- Does not include fluorotelomer sulfonates
- **Artifacts**: contamination/loss due to filtration/sample concentration

- SPE materials are sources of +ve (seals, o-rings, tubing, septa) and –ve artifacts)
- Organic solvent & solid waste
- Tedious, slow, expensive (labor, materials)
- Only fraction of extract/analyte/effort utilized (10 µL /1 mL)
- Does not reduce matrix effects

Alternative PFAS Method

- 12 perfluoroalkyl carboxylates (C2-C14); LOQ 10 ng/L
- 9 perfluoroalkyl sulfonates (C2-C10); LOQ 10 ng/L
- 3 telomer sulfonates (4:2, 6:2, 8:2); LOQ 10 ng/L
- 16 additional 3M AFFF and 26 additional fluorotelomer-based chemicals; LOQ: 2-50 ng/L

- Micro liquid-liquid extraction: 1.2 mL extract
- Efficient use of extract/labor/$: 0.9 mL (900 μL) injected
- No positive/negative artifacts due to filters or SPE media
- No SPE solid waste & only 0.3 mL organic solvent waste

Backe et al. ES&T, 2013; Barzen-Hanson and Field, 2015

Micro Liquid-Liquid Extraction

1) Add 10 µL 6 N HCl to 3mL groundwater sample

2) Saturate groundwater with NaCl (~ 1 g)

3) Spike internal standards

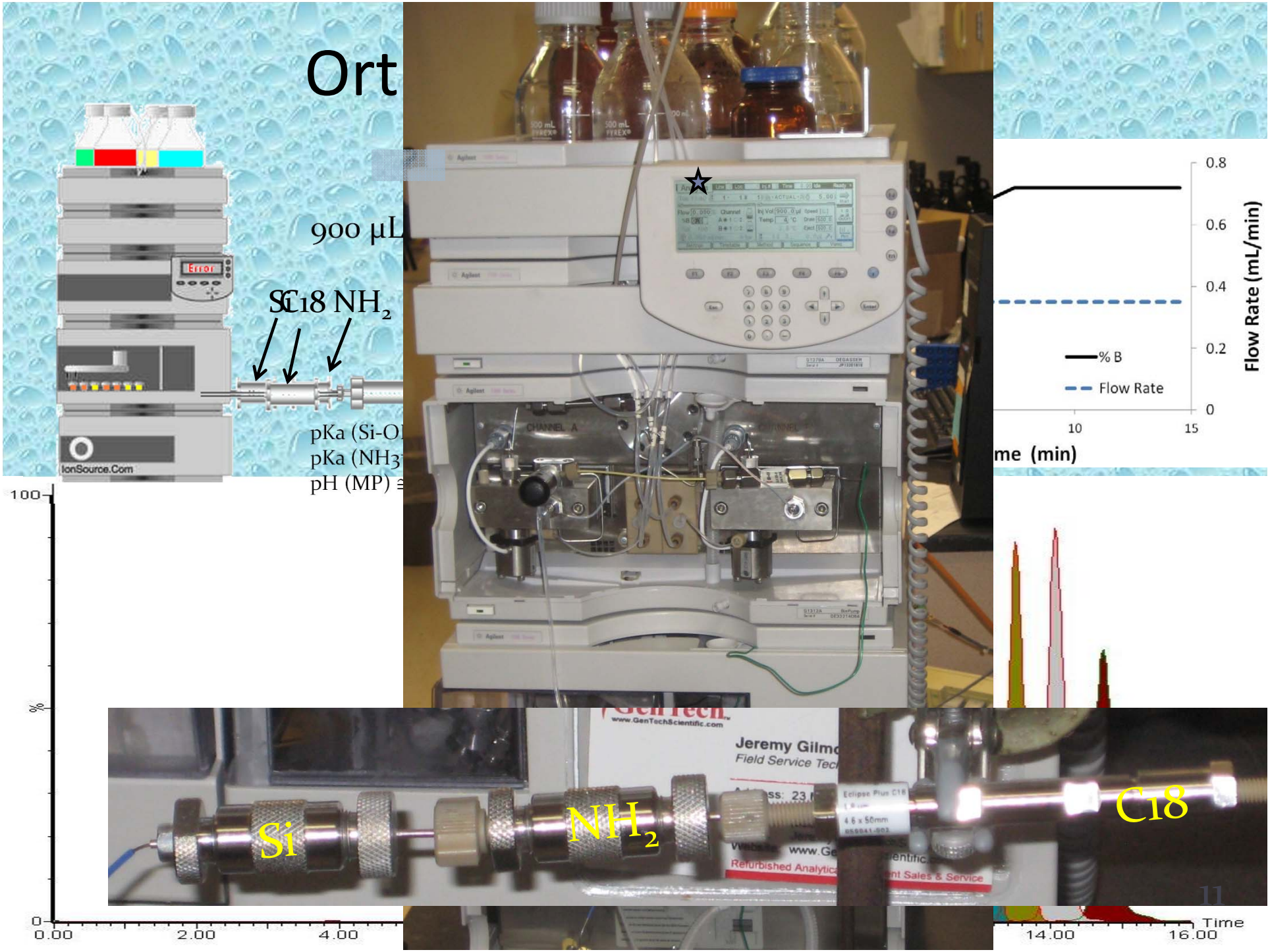
4) Extract sample 3x
Total volume: 1.0 mL 10% TFE/90% EtOAc

4) Bring to 1.5 mL with MeOH

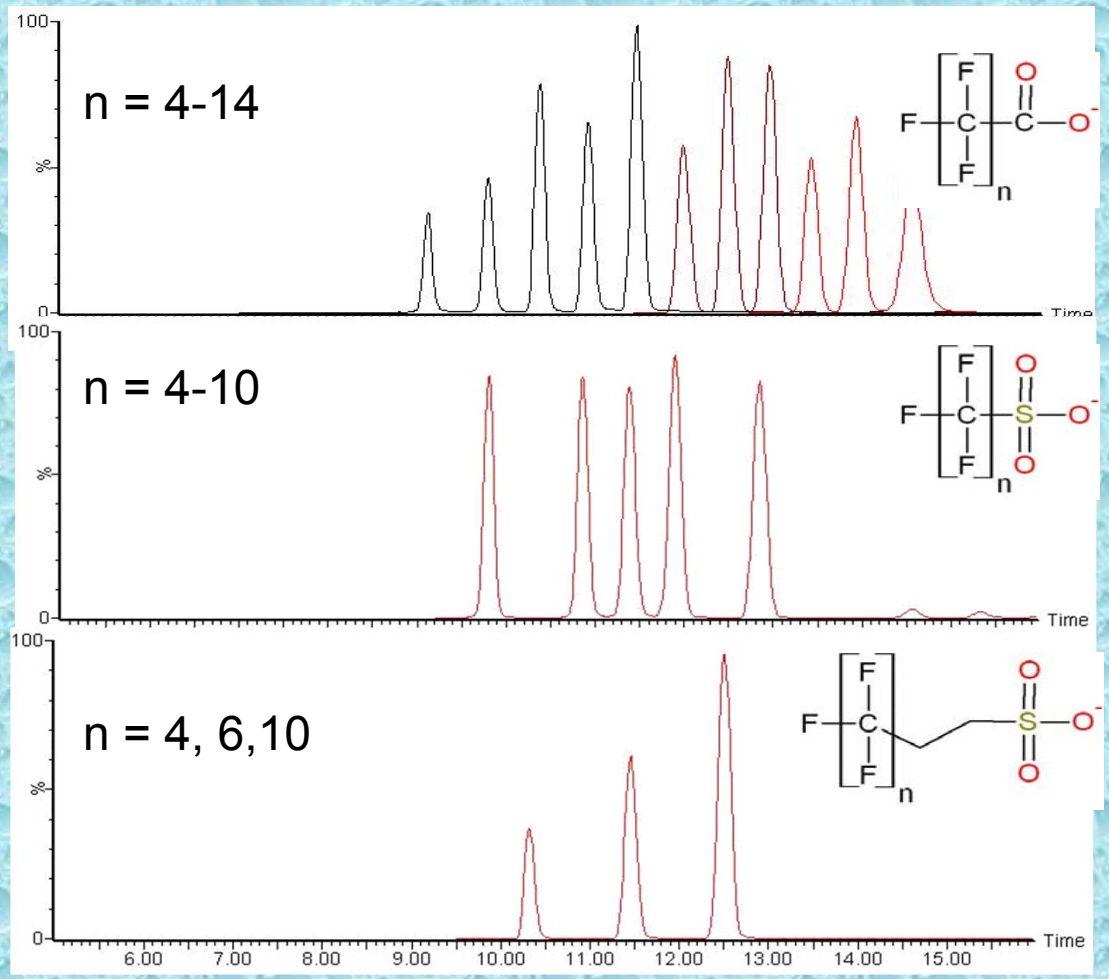
5) Inject 900 µL onto HPLC

Backe et al. ES&T, 2013

Ort

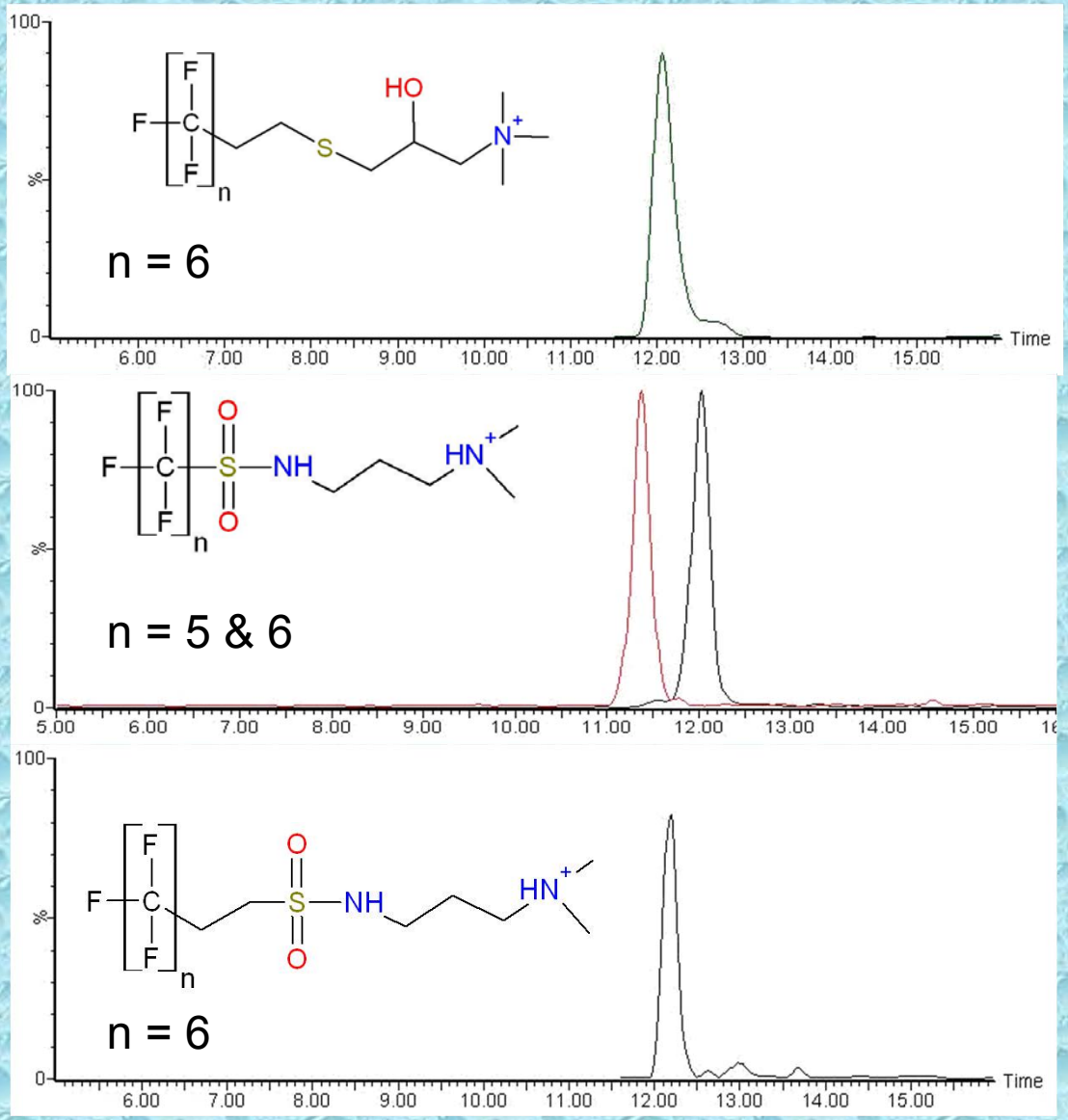

900 µL
Si C18 NH2
pKa (Si-O
pKa (NH3
pH (MP) ≅
Error
IonSource.Com
0.8
0.6
0.4
0.2
0
Flow Rate (mL/min)
% B
Flow Rate
10
15
me (min)
100
%
0
0.00
2.00
4.00
14.00
16.00
Time
Si
NH2
C18
Jeremy Gilmo
Field Service Tech
Eclipse Plus C18
4.6 x 50mm
Refurbished Analytica
nt Sales & Service

Anionic



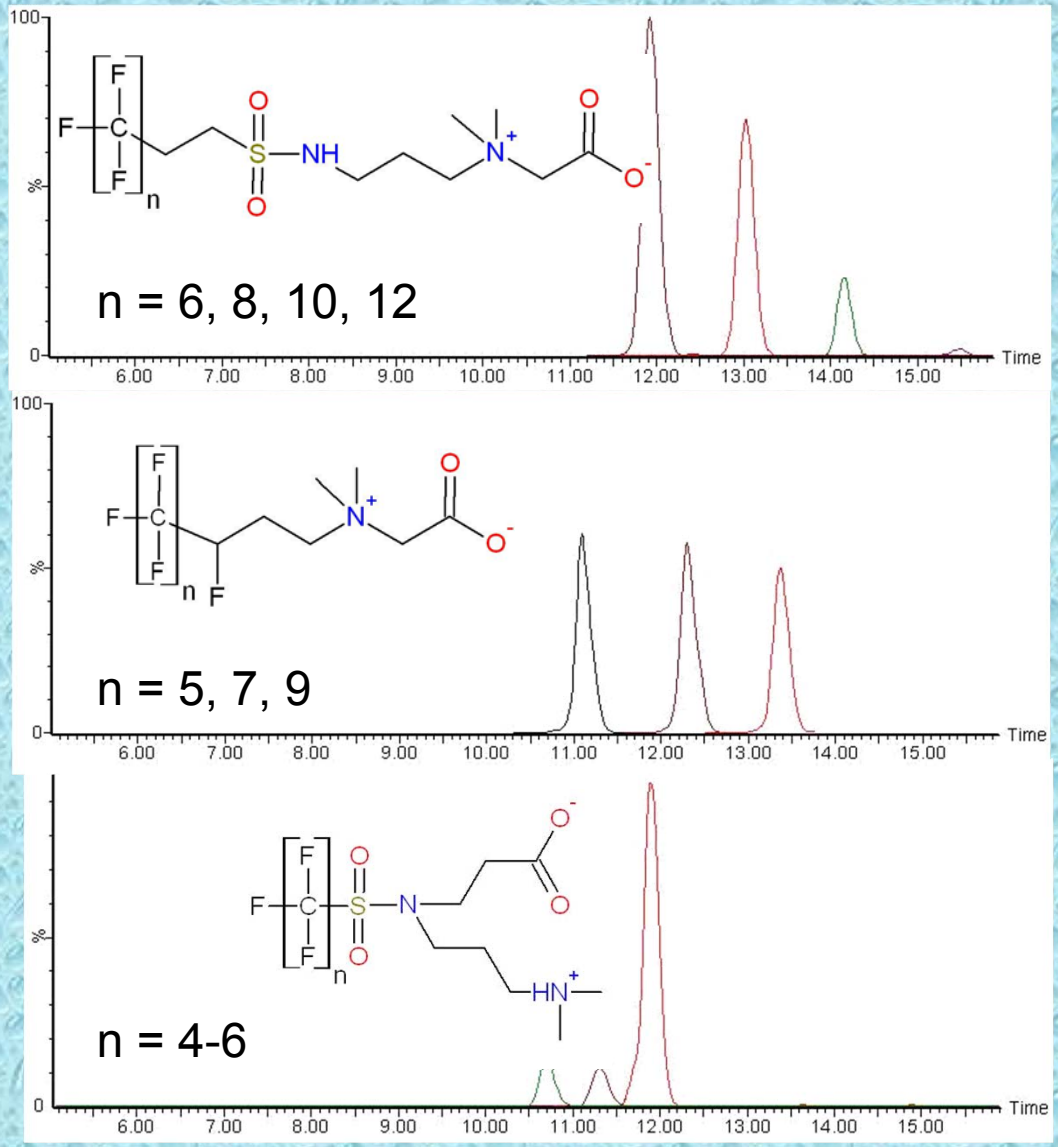
Backe et al. ES&T, 2013

Cationic



Backe et al. ES&T, 2013

Zwitterionic



Backe et al. ES&T, 2013

Method Performance

Analyte	Accuracy (%)	Precision (% RSD)	LOD (ng/L)
Perfluoroalkyl sulfonates (-) (e.g., PFOS)	96 – 104	3.7 – 11	0.71 - 1.7
Perfluoroalkyl carboxylates (-) (e.g., PFOA)	99 - 107	4.2 - 11	0.93 - 1.8
Fluorotelomer sulfonates (-)	99 – 106	10 – 12	0.84 - 1.9
Fluorotelomer thioamidosulfonates (-)	107	9.1	2.6
Fluorotelomer betaines (+)	78 - 144	8.2 - 15	3.6 – 23
Fluorotelomer thio hydroxy ammounium (+/-)	101	5.6	5.0

Backe et al. ES&T, 2013

Data Quality Tiers

Quantitative

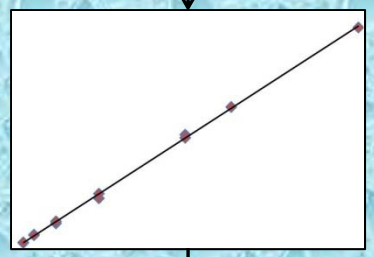
↓

Authentic analytical standards

↓

Known chemical concentration

↓



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Calculated concentrations ± 20 %

Semi-Quantitative

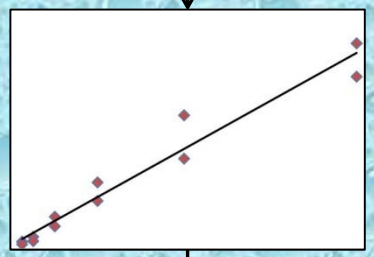
↓

Commercial source materials

↓

Estimated chemical concentration

↓



↓

Calculated concentrations ± order of magnitude

Qualitative

↓

No analytical standard or commercial sources available

↓

Assume equal molar response

Backe et al. ES&T, 2013

Quality Control

- Extreme range in PFAS groundwater concentrations requires dilution for
  - 1:200 dilution to estimate dilution factor
  - Samples then run undilute for low concentrations
  - Samples diluted and reanalyzed to bring high concentrations onto calibration scale (<3,000 ng/L)
- High concentrations of PFOS suppress labeled PFOS internal standard, used for Sq and QI analytes
- Sequences contain ~20-30% QC including solvent and extraction blanks, overspikes, and recovery samples
- Must be vigilant for contamination, background contamination on HPLC pump

Typical Groundwater Data

Red = UCMR3	Field Site 1 ng/L	Field Site 2[a] ng/L
4:2 FtTAoS	990	210
6:2 FtTAoS	53,000	6,900
4:2 FtS	230	7,500
6:2 FtS	5,700	220,000
8:2 FtS	11,000	370
PFBS*	64,000	43,000
PFPeS	49,000	NA
PFHxS*	380,000	240,000
PFHpS	60,000	11,000
PFOS*	1,100,000	78,000
PFNS	3,000	NA
PFDS	<LOD	<LOD
PFBA	6,100	24,000
PFPeA	39,000	69,000
PFHxA*	27,000	130,000
PFHpA*	55,000	15,000
PFOA*	63,000	51,000
PFNA*	1,000	220
PFDA*	290	<LOD

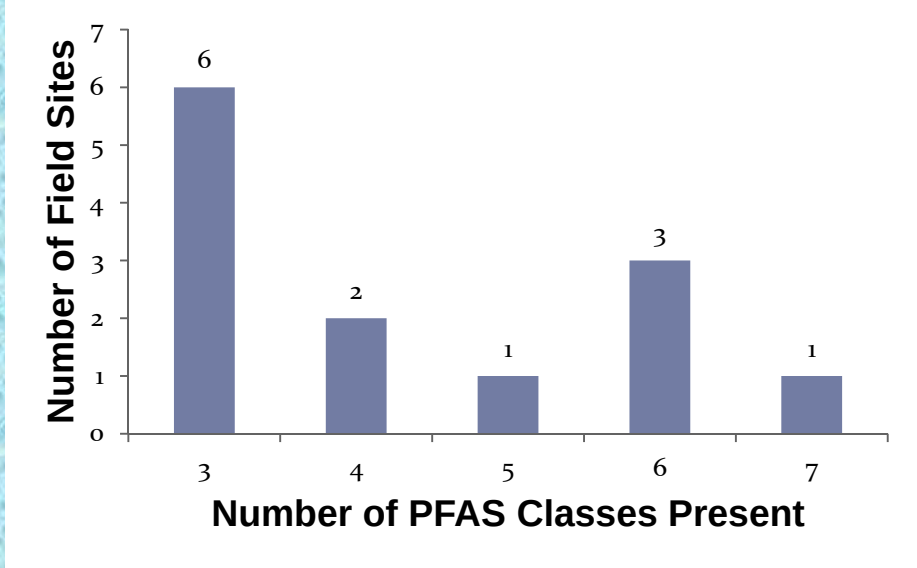
- Only 6 on UCMR3 (red)
- Only (*) in EPA Method 537
- Wide range in concentrations (ng/L to mg/L)
- FtTAoS (precursor) @ 53,000 ng/L
- 6:2 FtS > PFOS and PFOA
- PFOS and PFOA exceed EPA health advisory levels (200 and 400 ng/L)
- Carboxylates and telomer sulfonates minor components in AFFF (1980s-present)

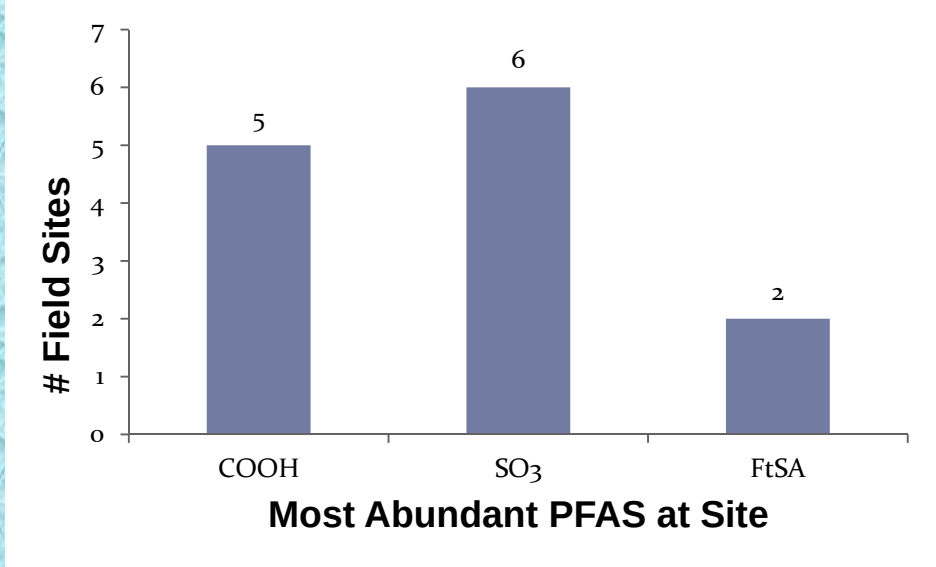
[a] Backe 2013, ES&T
UCMR3 =Unregulated Contaminant Monitoring Regulation 3
.

Groundwater at US Military Sites

- ✓ 13 sites tested
- ✓ Up to 7 PFAS classes present
- ✓ Highest concentrations for carboxylates, sulfonates, and telomer sulfonates
  - 14.6 mg/L 6:2 FtS
  - 6.6 mg/L PFOA
  - 1.0 mg/L PFOS
- Telomer sulfonates: 100% detection frequency

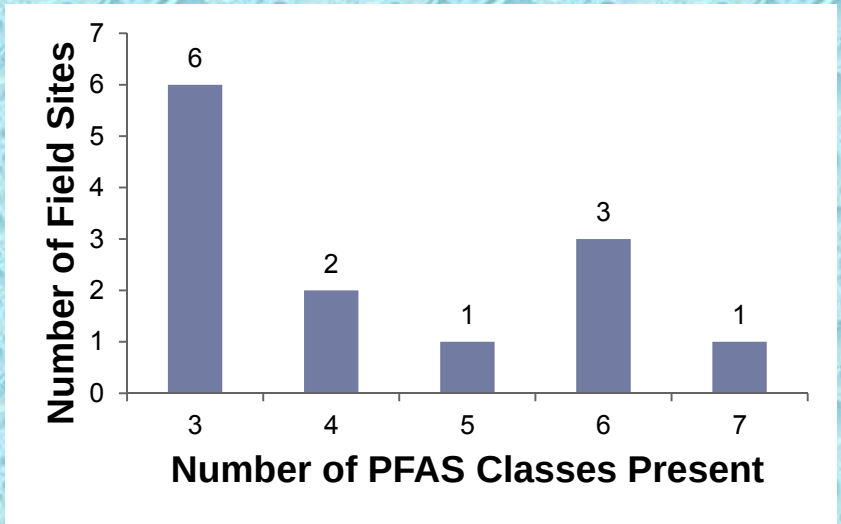
Backe et al. ES&T 2013; Schultz et al. ES&T 2004

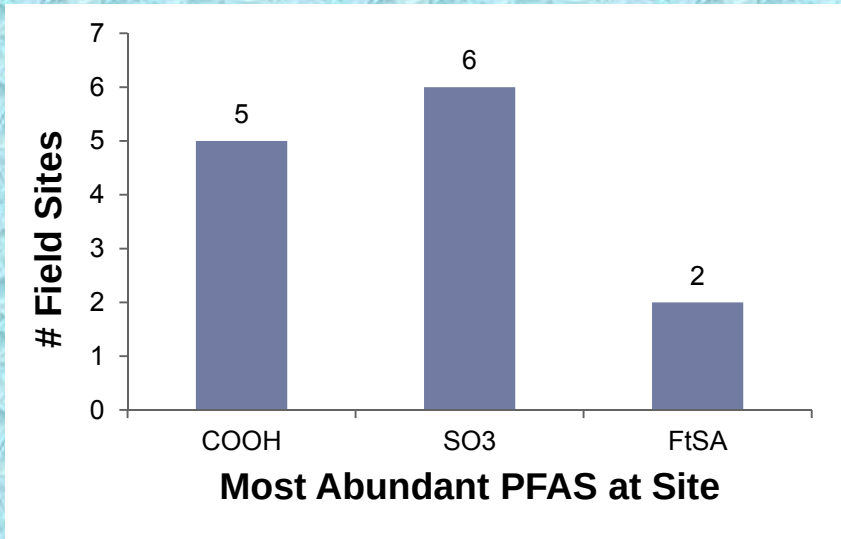




Groundwater at US Military Sites

- ✓ 13 sites tested
- ✓ Up to 7 PFAS classes present
- ✓ Highest concentrations for carboxylates, sulfonates, and telomer sulfonates to date:
  - 14.6 mg/L 6:2 FtS
  - 6.6 mg/L PFOA
  - 1.0 mg/L PFOS
- Telomer sulfonates: 100% detection frequency

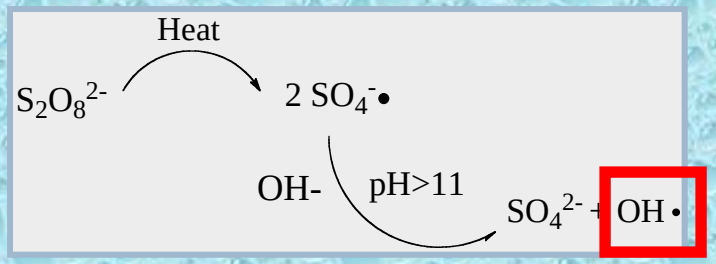


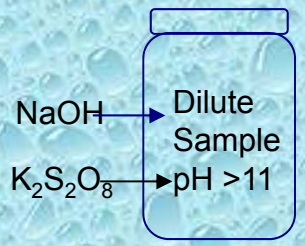


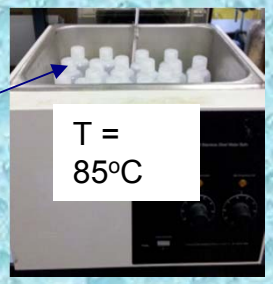
Backe et al. ES&T 2013; Schultz et al. ES&T 2004

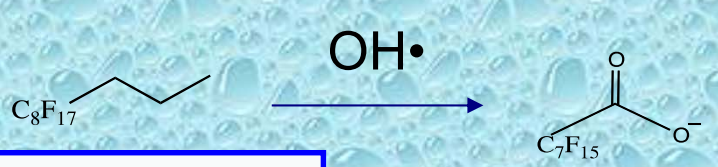
Mass Balance: Total Oxidizable Precursor (TOP) Assay

- ✓ Reaction with hydroxyl radicals reveals precursors with the potential to form 'dead-end' fluorochemicals
- ✓ Applied to AFFF formulations and field samples
- ✓ 50% of PFASs not yet identified in AFFF-contaminated groundwater, sediment, and soil









C8 Fluorotelomer Precursor

PFOA

+ $C_nF_{2n+1}COO^-$ n= 3 -6

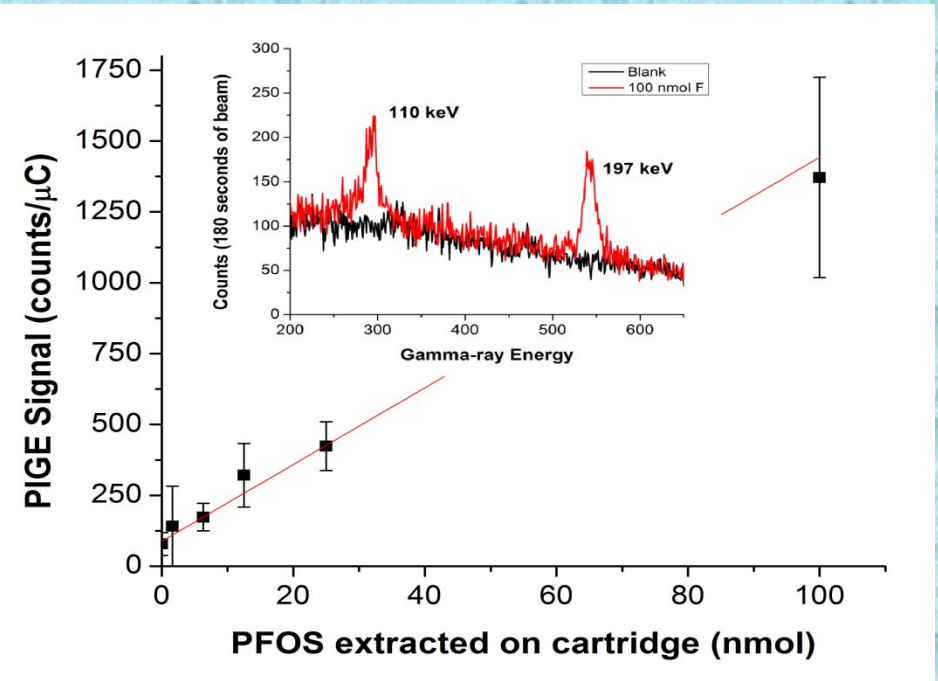
C7 and shorter PFCAs

Houtz et al. ES&T 2013

Mass Balance: Total Fluorine

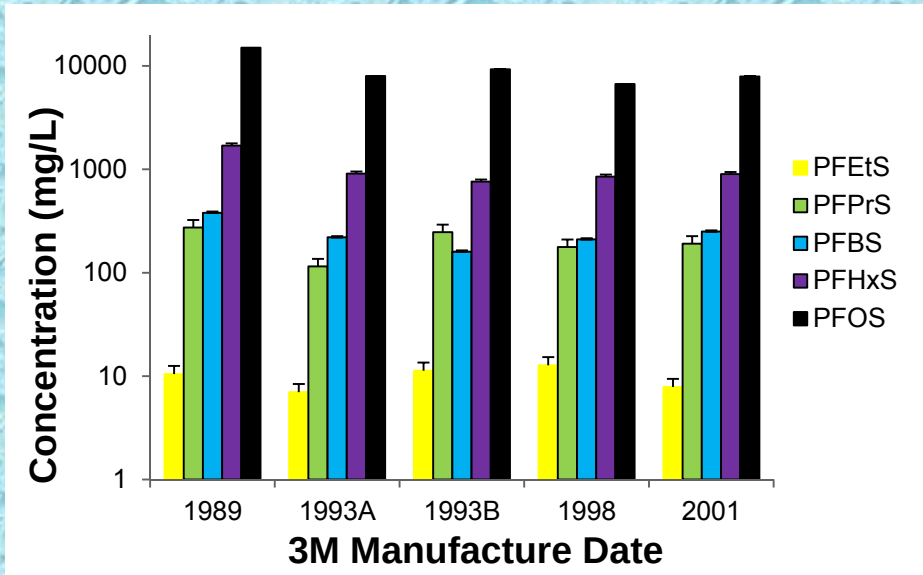
Particle Induced Gamma-Ray Emission (PIGE) Spectroscopy by Graham Peaslee (Hope College)[a]

- ✓ PFAS adsorbed onto a OASIS WAX SPE cartridge
- ✓ SPE dried, frit removed, superglued into solid target
- ✓ Target analyzed with 10 nA of 3.4 MeV protons for 180 s
- ✓ Simple, fast, inexpensive (few $/sample) compared to TOP assay
- ✓ Quantitative screening tool
- ✓ Currently being validated for groundwater

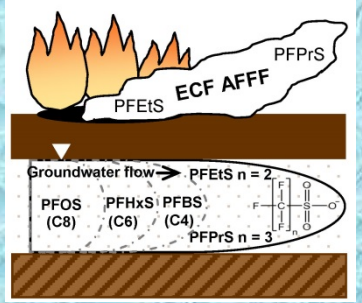


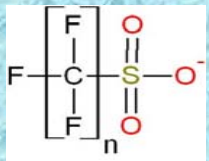
[a]Peaslee's contact email: Peaslee@Hope.edu

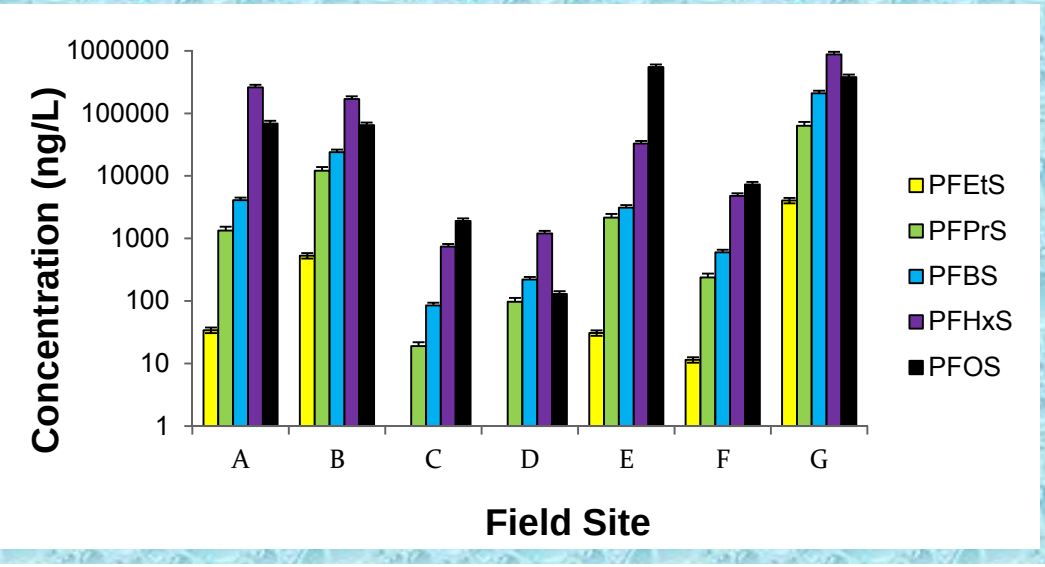
Ultra-Short (C2&3) Sulfonates



- C2 & C3 in 3M AFFFs and in field site groundwater
- Concentrations at some sites exceed PFBS MN state health risk limit (7,000 ng/L)
- Likely at leading edge of plumes (conservative transport)
- Challenging to remove by GAC
- Production may increase if PFBS production up







[a] Barzen-Hanson and Field, 2015
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Conclusions

- Liquid-liquid extraction with large volume extraction and orthogonal LC-MS/MS
  - robust, cost-efficient alternative to SPE
  - suitable for the wide range of PFAS classes and concentrations in AFFF-contaminated groundwater
  - artifact free
- Up to 7 PFAS classes quantified in groundwater at US military AFFF-contaminated sites at up to mg/L levels
- Data quality requires constant attention
- Mass balance not closed: TOP assay indicates presence of unidentified PFAS in groundwater, sediment, soil
- PIGE likely to be a rapid, quantitative, cost effective screening tool for determining total F

Acknowledgments

- Strategic Environmental Research and Development Program (SERDP ER-2128)
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- Graham Peaslee at Hope College
- Erika Houtz and David Sedlak, UC Berkeley
- In Memoriam: Dr. Melissa Schultz