

Environmental Fate and Transport of Poly- and Perfluoroalkyl Substances at Aqueous Film- Forming Foam Impacted Sites

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COLORADO SCHOOL OF MINES

EARTH  ENERGY  ENVIRONMENT



A Team Effort



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Former Firefighter Training Areas (FTAs)

What do we *really* know about poly- and perfluoroalkyl substances (PFASs) at these sites?



Likely present at *all* sites where aqueous film forming foam (AFFF) was used

- Composition?
- Spatial distribution?

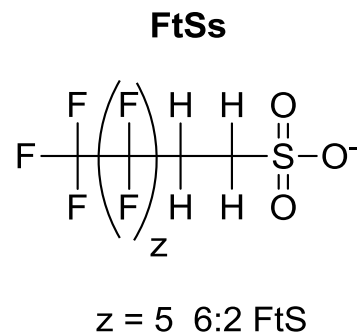
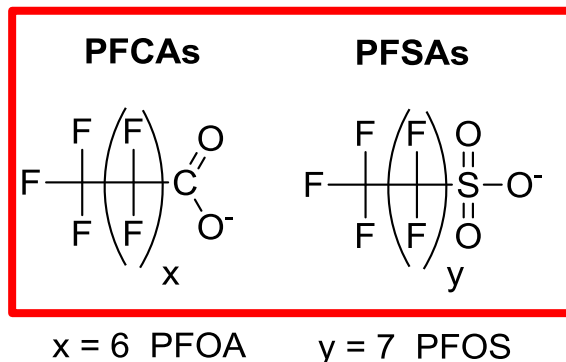
To what extent have remediation efforts aimed at co-contaminants altered the composition and distribution of PFASs?



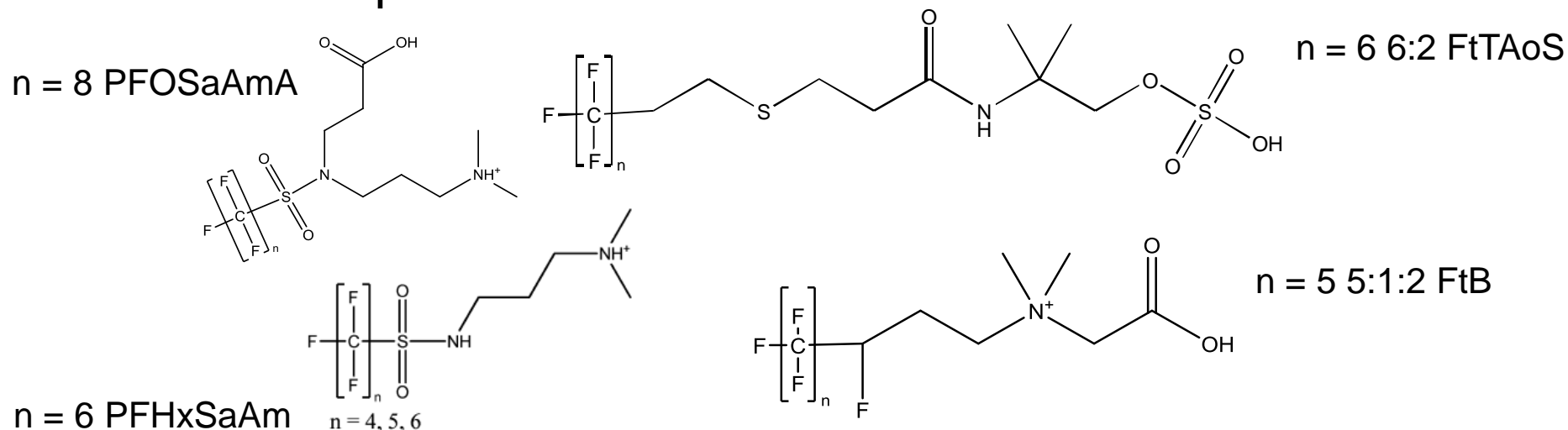
Composition at AFFF-impacted Sites

Perfluoroalkyl acids
(PFAAs) present

- Some presumed PFAA precursors

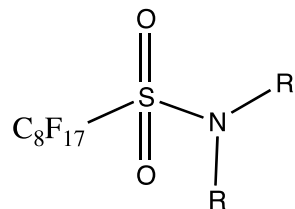


Presumptive PFAA precursors identified in AFFF and/or at AFFF-impacted sites:

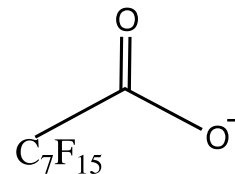


The Total Oxidizable Precursor (TOP) Assay

Polyfluorinated
Sulfonate
Precursors

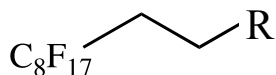


$\text{OH}\cdot$

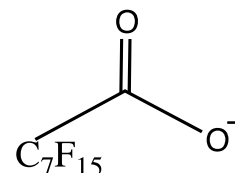


PFOA

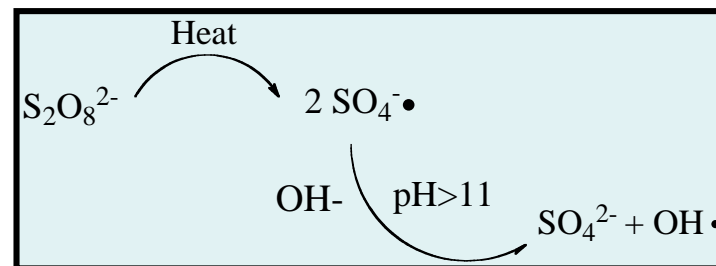
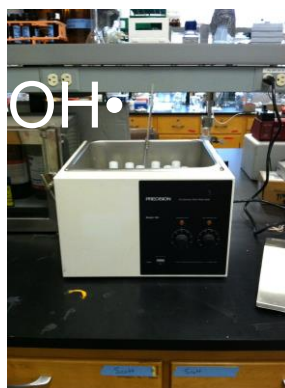
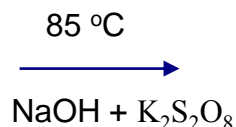
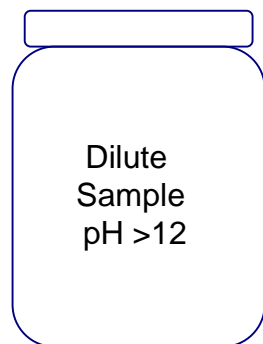
Polyfluorinated
Carboxylate
Precursors



$\text{OH}\cdot$

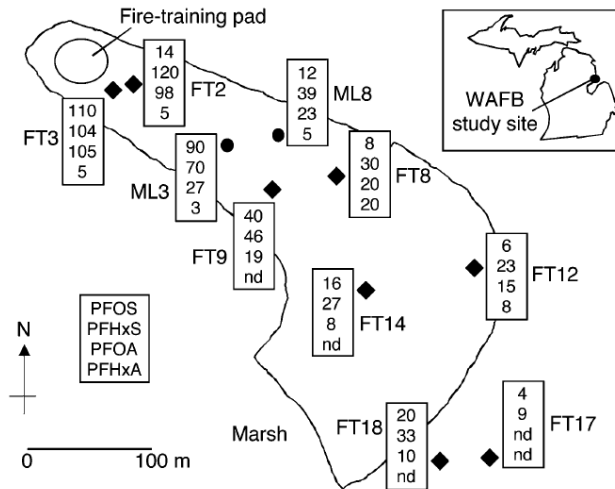


+ shorter
products

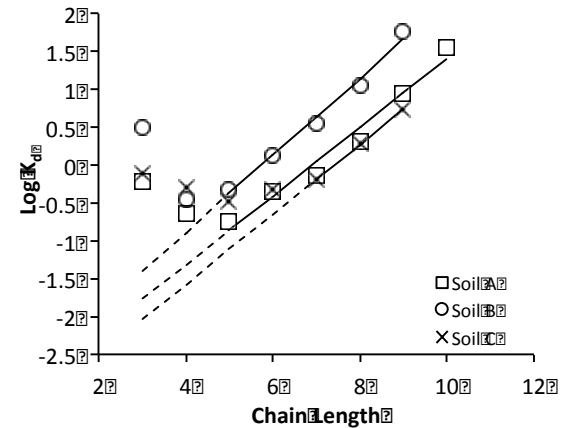


PFAS Transport Potential

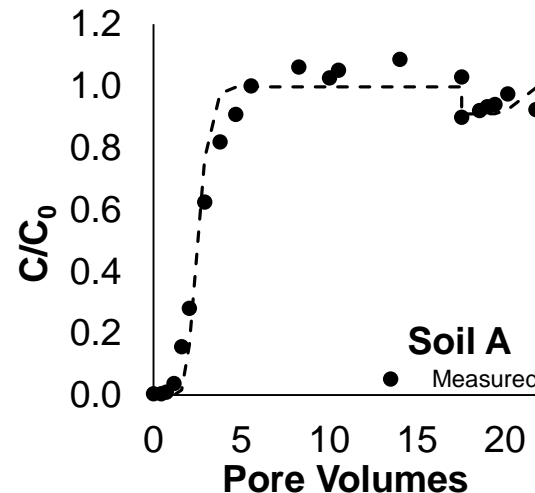
PFASs are transported in groundwater...



but not at the same rates...



and there may be kinetic limitations.



Former Firefighter Training Areas

What do we *really* know about PFASs at these sites?

One might expect:

1. PFASs to be present in and around historical fuel plumes
2. Depending on site activities, *some* conversion of presumed PFAA precursors to PFAAs
3. Depending on release, *some* differential transport of PFAAs
 - Shorter chain PFAAs > longer chain PFAAs



Ellsworth Air Force Base, South Dakota

Investigated former firefighter training area (OU-1)

- “Bermed pit” in use from 1942-1990
- VOCs, SVOCs, pesticides, and chlorinated solvents in groundwater

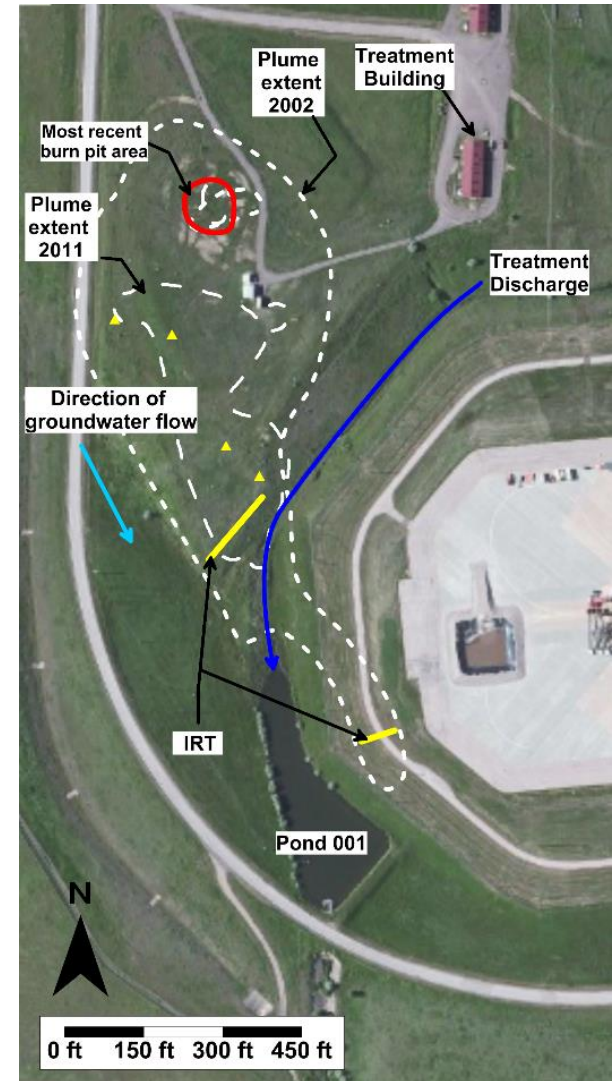
Remediation (1996-2011)

- Soil Vapor Extraction
- Groundwater Pump and Treat
- Oxygen Infusion Wells



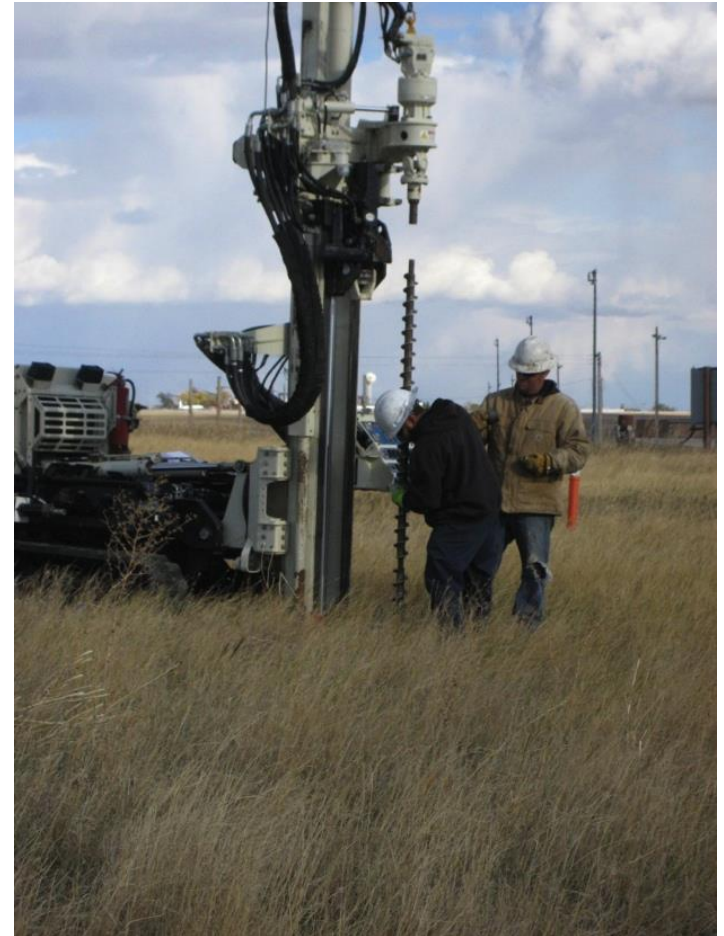
Site Overview

- Typical depth to groundwater ~ 5 m
 - Clay loam and gravely sandy loam
- Fairly extensive pump-and-treat followed by bioparging

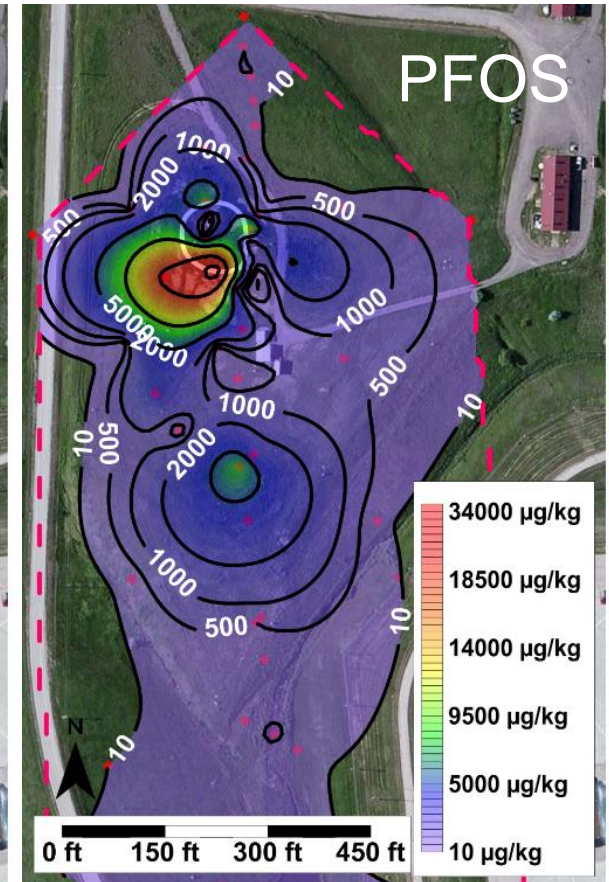
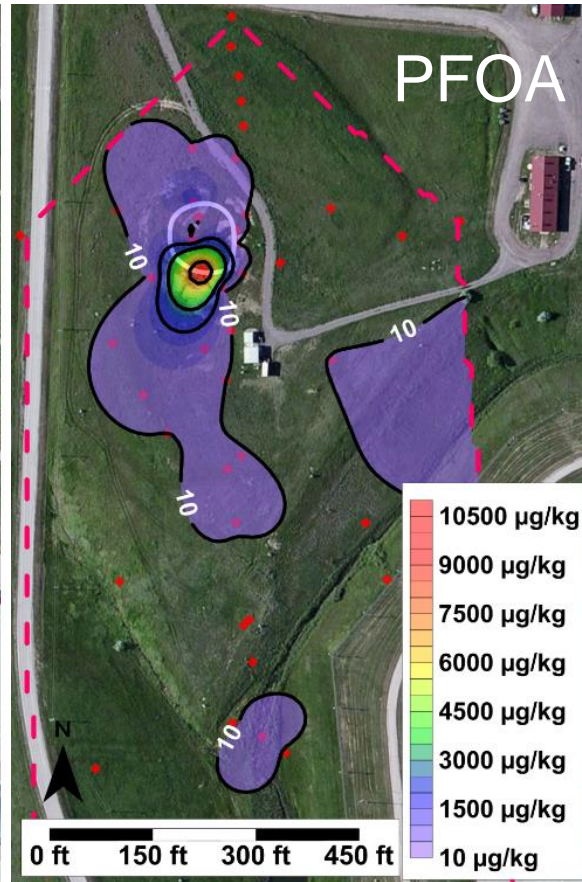
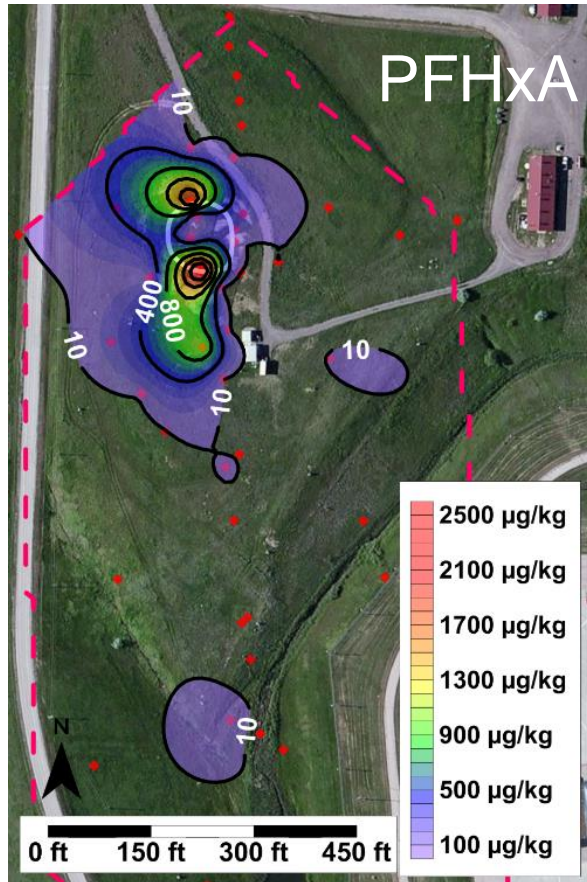


Field Sampling and Analysis

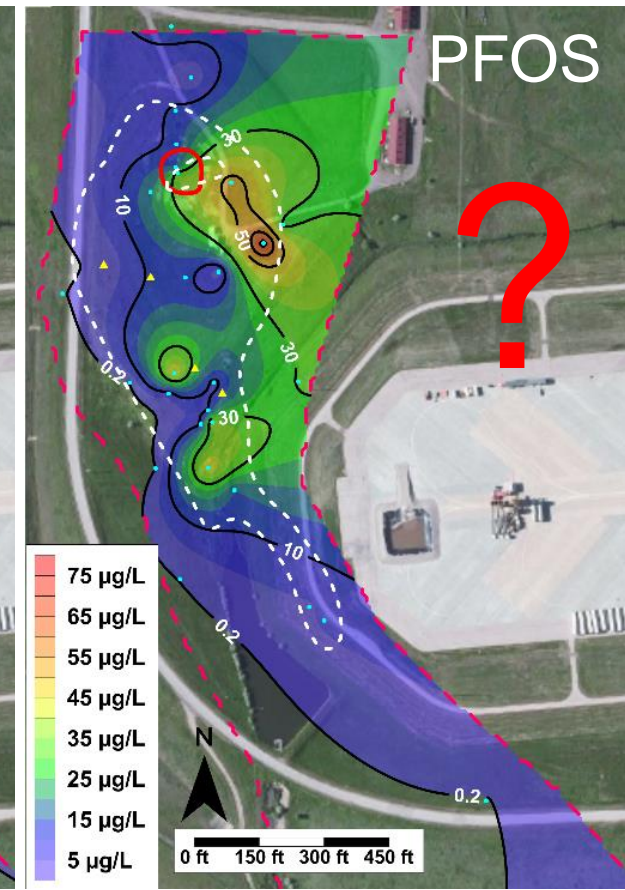
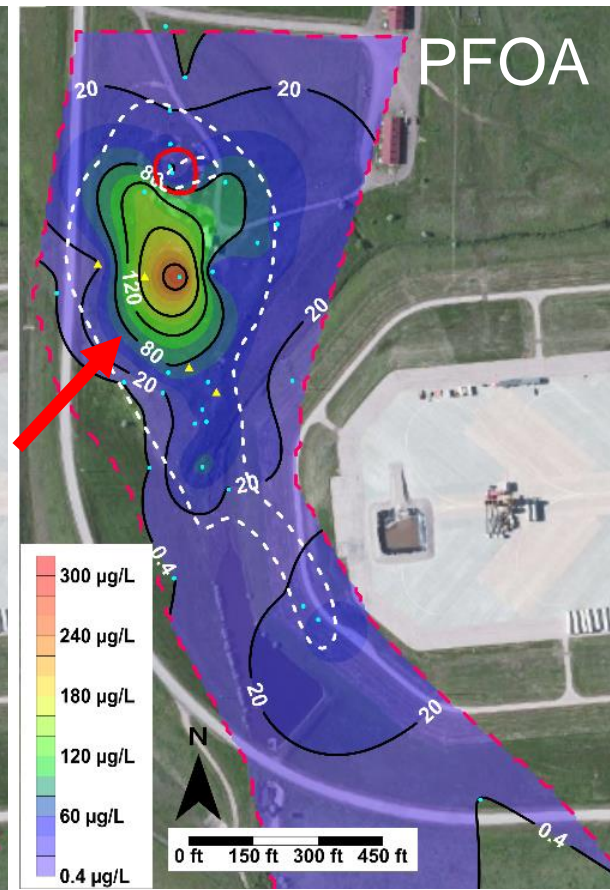
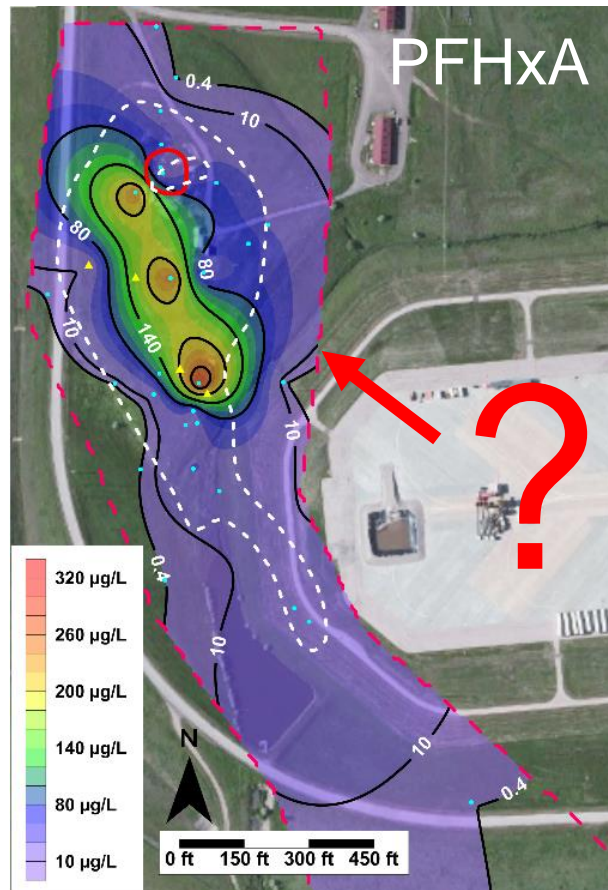
- Samples collected October 2011 and August 2012:
 - 2011: 17 temporary wells drilled (soil, aquifer solids, groundwater)
 - 2012: 22 additional groundwater samples and 34 additional soils
- Analyzed for PFAAs at CSM
 - All groundwater samples analyzed for PFAAs and known AFFF components or suspected transformation products at UCB
- All groundwater samples also subjected to TOP assay at UCB
- Spatial analysis at CSM using Surfer (Golden Software)



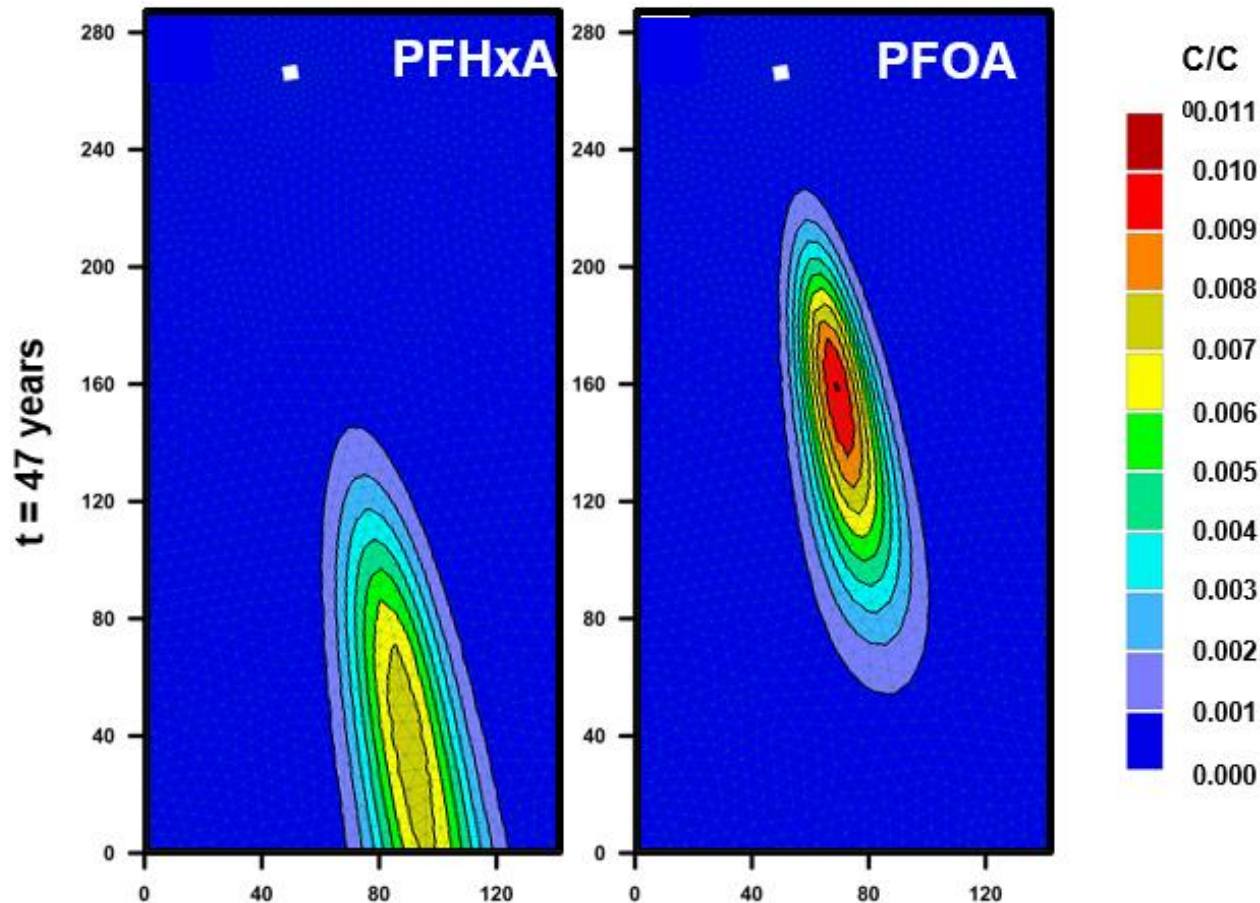
Surface Soil Contamination



Groundwater Contamination



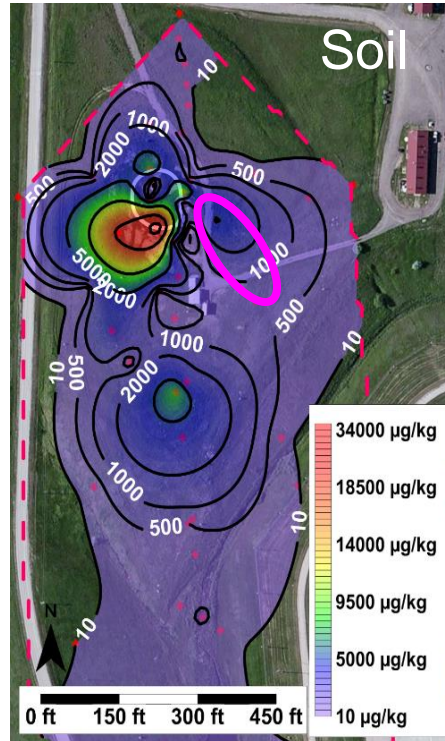
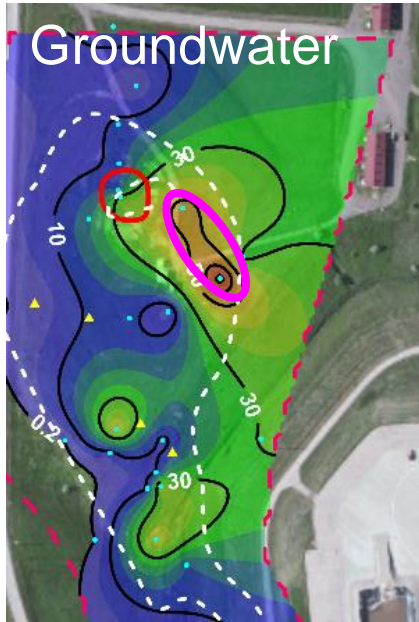
HYDRUS 2-D Model



- Much greater differential transport would be expected
 - Release ongoing?



What's up with PFOS?



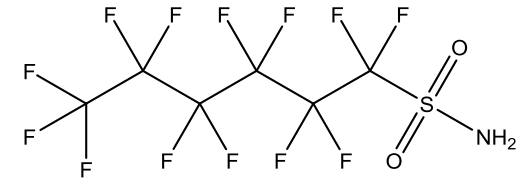
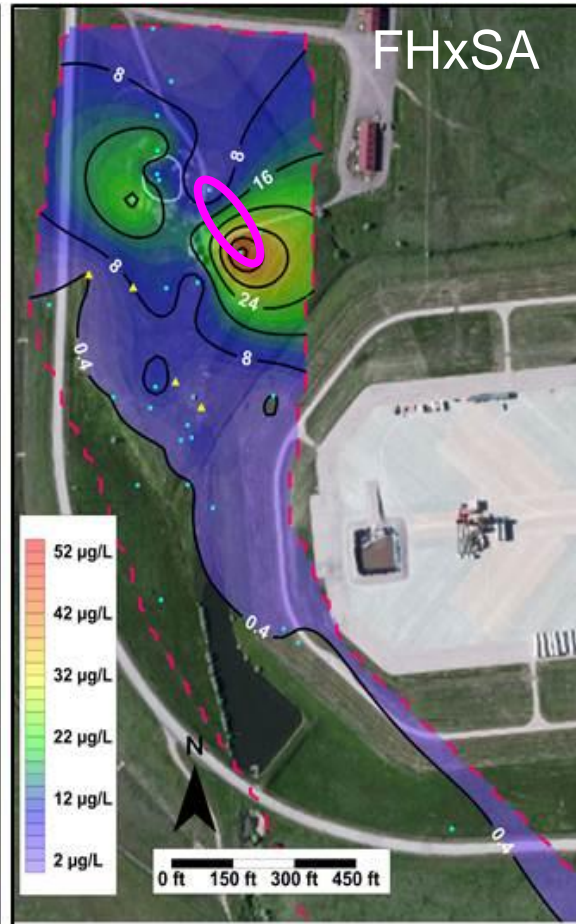
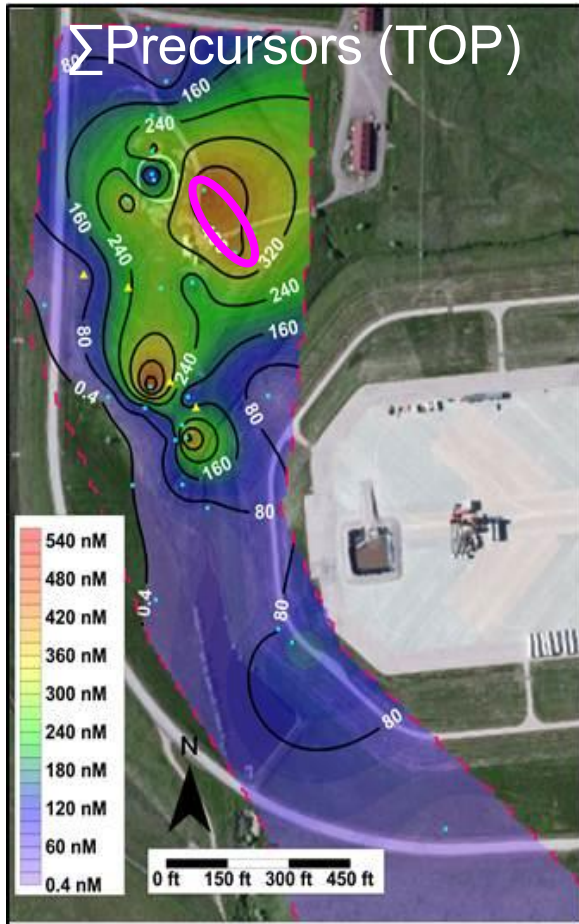
Additional surface source?

Groundwater pumping?

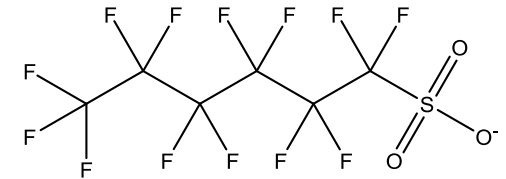


...but why then are shorter chain PFAAs still present in “historical” plume?

Precursors?



↓ O₂, microbes?

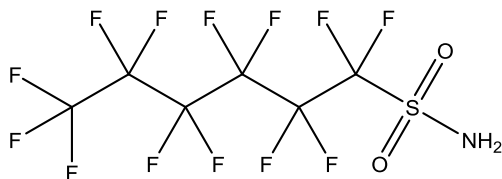


- TOP assay and directly-measured precursors elevated in this zone

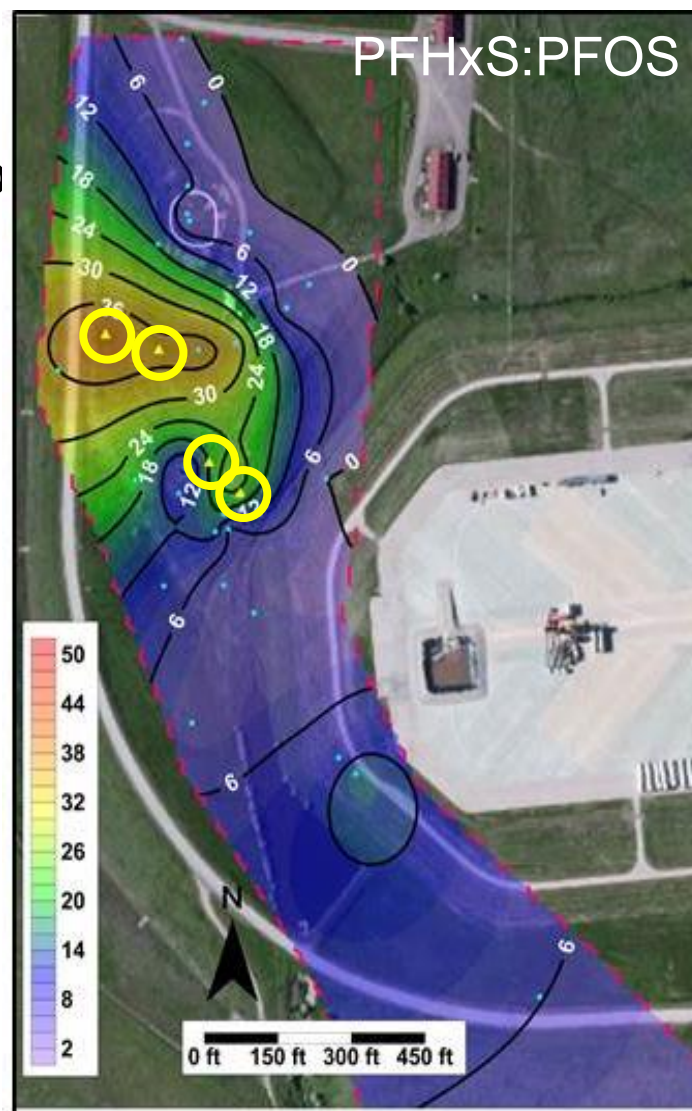
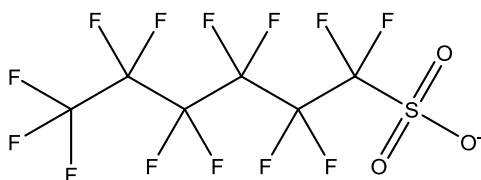


Effect of biosparging?

- PFHxS: PFOS ratio ~ 0.1 in AFFF[†]
- If co-released, would expect ratio to ↑ (continually) downgradient
- PFHxS produced in situ?
 - Highest ratios (~ 50) near biosparging wells



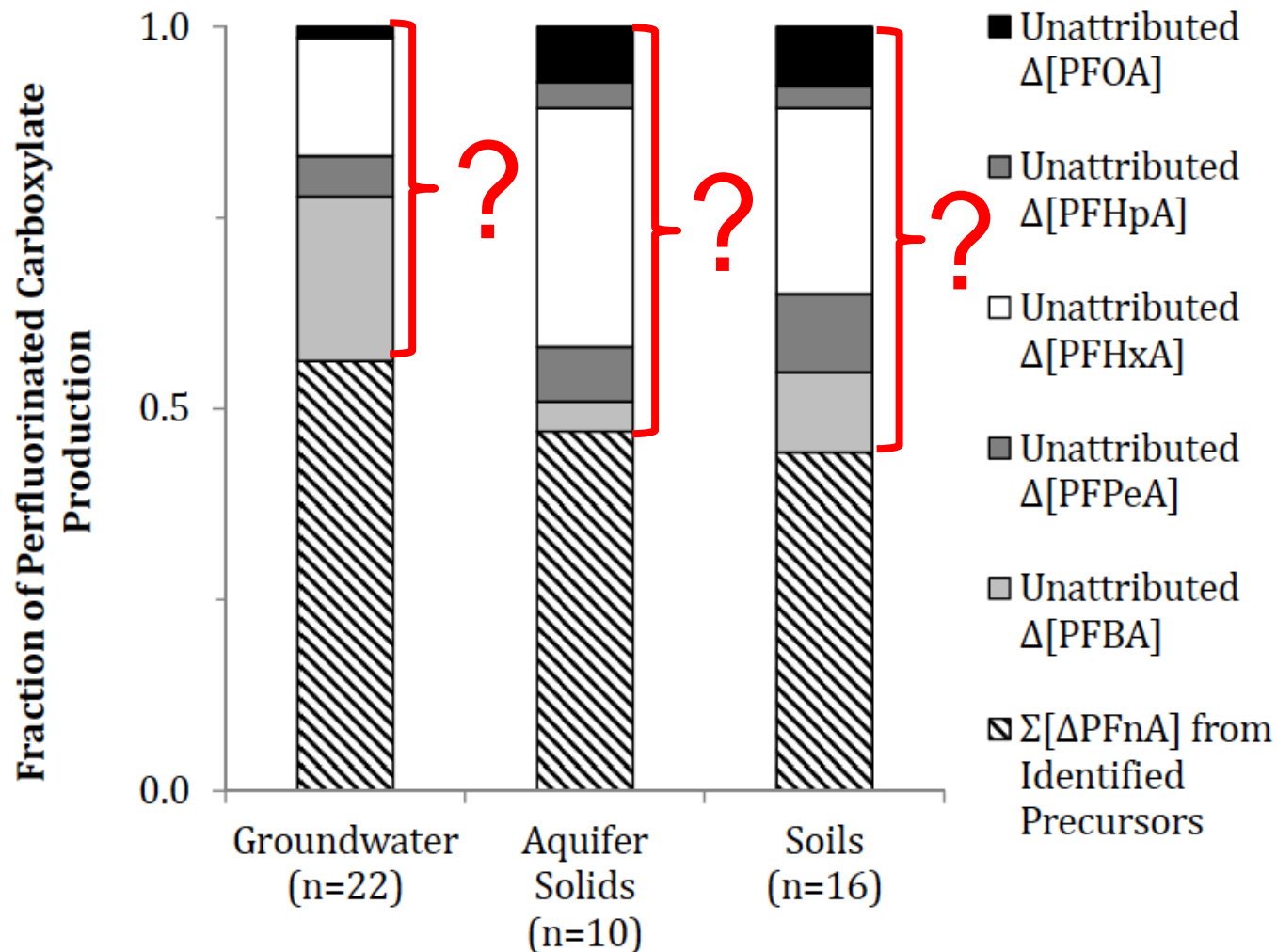
↓ **biosparging?**



[†]Houtz *et al.*, 2013 *ES&T*.



We still have a long way to go....



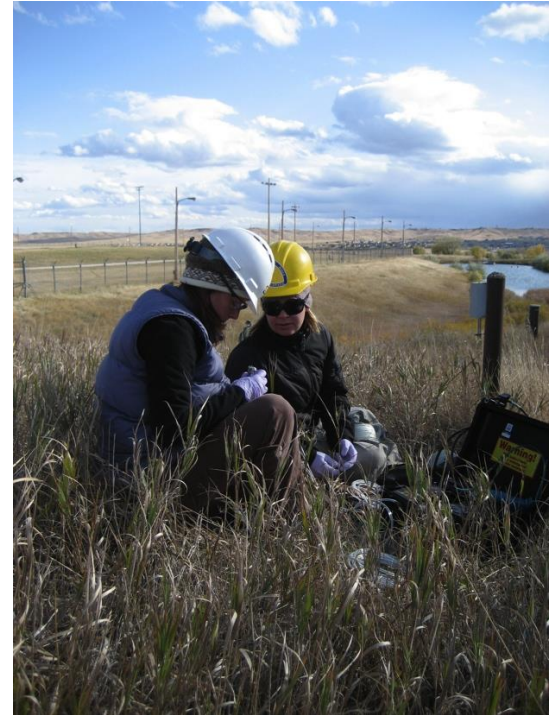
We still don't know what comprises ~50% of the mass of precursors



Field Study Implications

PFAS levels and distribution at Ellsworth AFB suggest **significant impacts of remediation** on PFAS **composition** and **distribution**

- “Eastern” source zone may represent original composition?
- “Main” PFAA plume primarily a result of precursor transformation?
- Source zone issue or dilute plume issue?



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