Per- and Polyfluoroalkyl Substances (PFASs): Analytical and Characterization Frontiers

January 28, 2016

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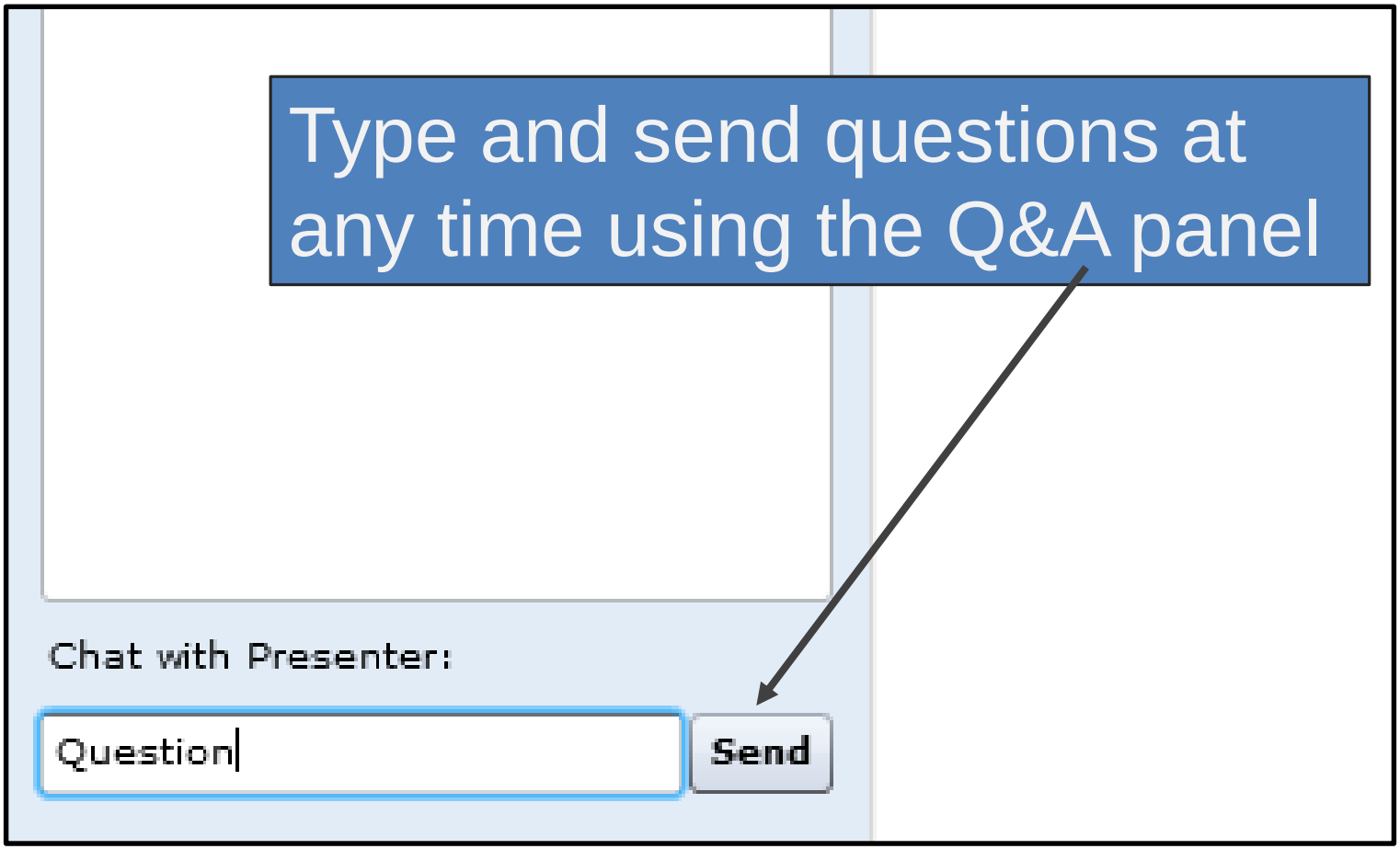
Welcome and Introductions

Rula A. Deeb, Ph.D.
Webinar Coordinator

Agenda

- **Webinar Logistics**
  Dr. Rula Deeb, Geosyntec Consultants (5 minutes)
- **Overview of SERDP and ESTCP**
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)
- **PFAS: An Air Force Perspective**
  Dr. Stephen TerMaath, Air Force Civil Engineer Center (10 minutes + Q&A)
- **Characterizing Fluorochemicals in AFFF-Contaminated Groundwater at Military Sites**
  Dr. Jennifer Field, Oregon State University (20 minutes + Q&A)
- **Understanding the Transport of Perfluorochemicals in Groundwater at AFFF-Impacted Sites**
  Dr. Christopher Higgins, Colorado School of Mines (20 minutes + Q&A)
- **Final Q&A session**

How to Ask Questions



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    - U.S./Canada: 1-877-776-3503
    - International: 330-871-6014
    - Required conference ID: 1602402
- Submit a question using the chat box

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Environmental Restoration Program Manager

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SERDP

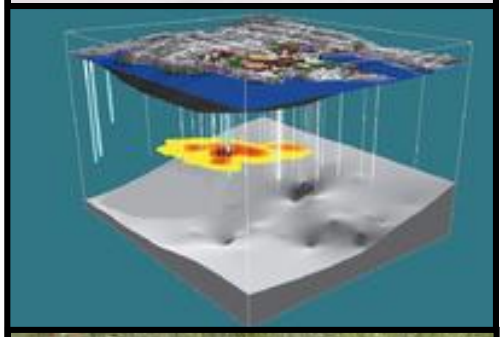
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

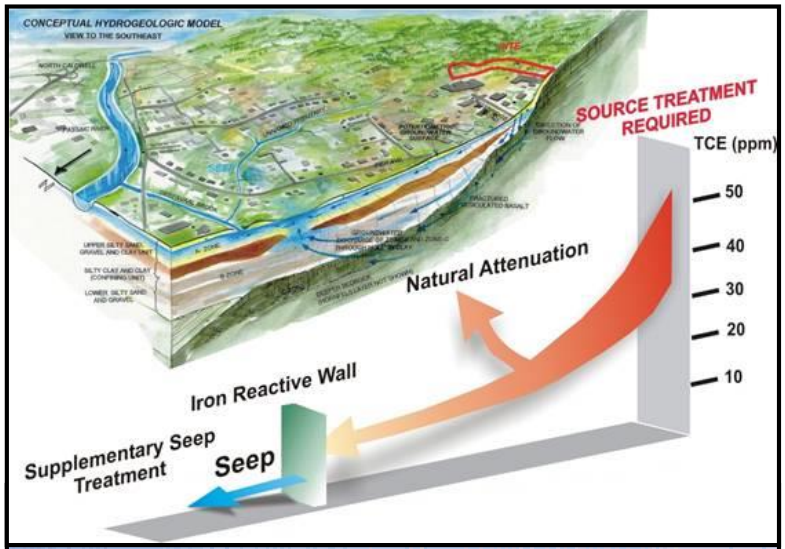
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms



Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



SERDP and ESTCP Webinar Series

DATE	Topics
February 11, 2016	Chromate/Hazardous Material Free Coating Systems for Military Aircraft and Ground Support Equipment
February 25, 2016	Recent Advances in the Classification of Underwater Munitions Near a Water-Sediment Boundary
March 10, 2016	Fate, Transport and Effects of Insensitive Munitions
March 24, 2016	Cadmium and Chromate Elimination Efforts: Implementation Plans and Strategic Roadmaps for Three DoD Depots
April 7, 2016	Resource Conservation and Climate Change
April 21, 2016	Long Term Monitoring Issues at Chlorinated Solvent Sites

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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PFAS: Air Force Perspective

Stephen TerMaath, Ph.D., P.E.
BRAC Program Management, AFCEC

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Air Force Use

- PFOS and PFOA principle active ingredient in aqueous film forming foam (AFFF)
- AFFF usage dates to 1970
- Hundreds of potential release sites

Emerging Contaminants

- Provisional Health Advisories (PHA) for PFOA and PFOS
  - Used as allowable levels in drinking water
- Air Force initiated program to identify potential release sites
- Third Unregulated Contaminant Monitoring Rule (UCMR 3) requires analysis of public water systems for PFOA and PFOS

Air Force Approach

- Identify release areas
  - Fight petroleum fires
  - Fire training areas
  - Dispensing equipment calibration and testing
- Use hydrogeology knowledge for potential pathway to water supply wells
- If pathway complete, determine if levels above PHA

Air Force Approach

- Take immediate action to mitigate water supply exposures above PHA in pathway from Air Force source
- Mitigations include use of alternate water supplies, treatment of the water supply, and interrupting pathway to water supply
  - Currently, granular activated carbon is only acceptable treatment method

Observations

- Have data from a limited number of locations
- PFOA and PFOS move slowly through groundwater
- At sites with petroleum contamination in groundwater, PFOA and PFOS plumes are more expansive than the petroleum plume

Knowledge Gaps

- Alternatives to GAC treatment systems
- Alternatives for groundwater restoration
- Fate and transport
- Consensus on human health effects

For additional information, please visit
http://www.afcec.af.mil/environment/perfluorinated compounds/index.asp

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Q&A Session 1

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State of Knowledge on Per- and Polyfluoroalkyl Substances (PFASs) at Military Sites

Jennifer Field, Ph.D.
Oregon State University

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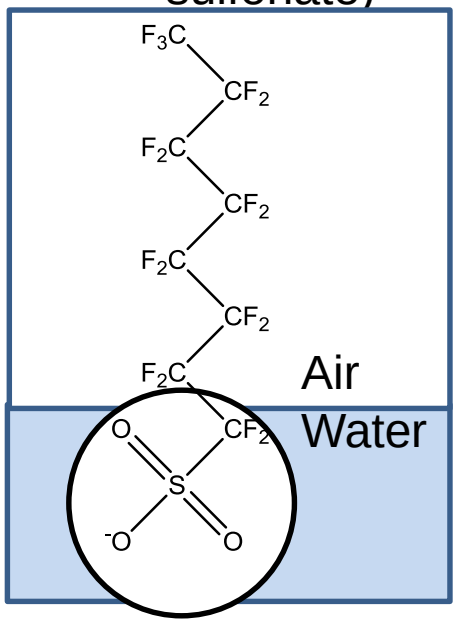
Agenda

- Unique chemistry of PFASs
- Technical objectives and approach
- Results and significance
- Conclusions and benefits to DoD
- Acknowledgments

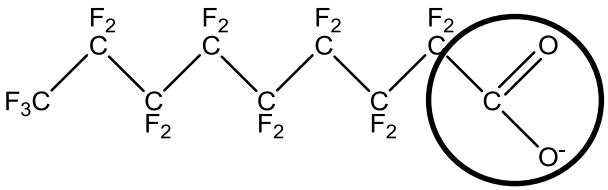
Unique Chemistry of PFASs

- C-F bond is the shortest and strongest bond in nature
- Less tendency to associate with oil and water compared to hydrocarbons (hydrophobic and oleophobic)
  - Few engineered or environmental degradation processes
  - Stable in acids, bases, oxidants, heat
  - Too much energy to break bonds
  - Microorganisms cannot gain energy from breaking the bond

PFOS (**per**fluorooctane sulfonate)

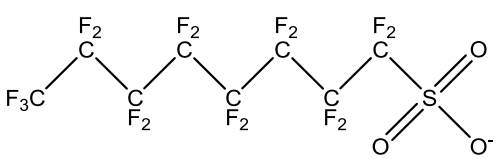


PFOA perfluorooctanoate)



Nomenclature

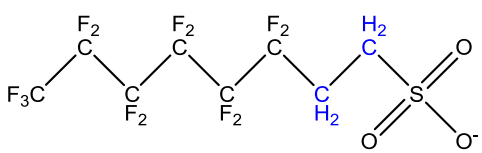
- Need to unify the nomenclature and acronyms
  - Internationally-accepted nomenclature
  - Communicate accurately inside and outside DoD
- P in PFC means perfluorinated chemical
  - Per = all carbons in aliphatic chain bonded only to F
  - Few chemicals fit this category (e.g., PFOS and PFOA)



PFOS (perfluorooctane sulfonate)

- Branched/linear isomers and odd/even chain lengths
- Persistent

- Polyfluorinated



6:2 FTSA (*poly*fluorotelomer sulfonate)

- -CH2- linkages = 'weakness' in molecule, susceptible to biodegradation and abiotic degradation (oxidation)

Technical Objectives

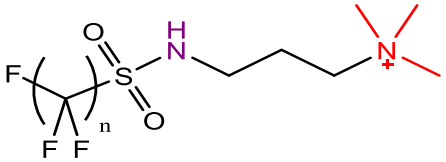
- Characterize per- and polyfluoroalkyl substances (PFAS) composition of aqueous film-forming foam (AFFF) formulations
- Characterize PFAS and precursor composition of AFFF-contaminated groundwater, sediment and soil
- Characterize PFAS biodegradation under aerobic and anaerobic conditions
- Characterize the sorption of the newly-identified anionic, cationic and zwitterionic PFASs

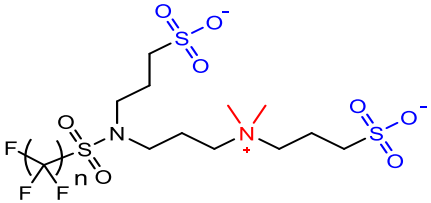
Approach

- Analytical characterization
  - Mass spectrometry and oxidation-based assays
  - PIGE (particle-induced gamma ray emission) spectroscopy for total fluorine
- Microcosm biodegradation experiments
  - Aerobic and anaerobic conditions
- Batch sorption experiments

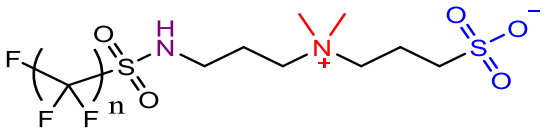
AFFF Characterization
(U.S. 'MilSpec' Formulations)

- 3M AFFF
  - PFOS was a major component of 3M AFFF
  - PFHxS (C6) > PFOS in 3M AFFF
  - PFOA minor component in AFFF
  - Ultra-short sulfonates as well as cationic and zwitterionic structures
  - Many PFOS-like structures due to 'messy' chemistry





- Telomer-based AFFF
  - PFOS not present in telomer-based AFFF
  - Fluorotelomer sulfonates (FTSAs) minor component
  - Anionic, cationic and zwitterionic structures



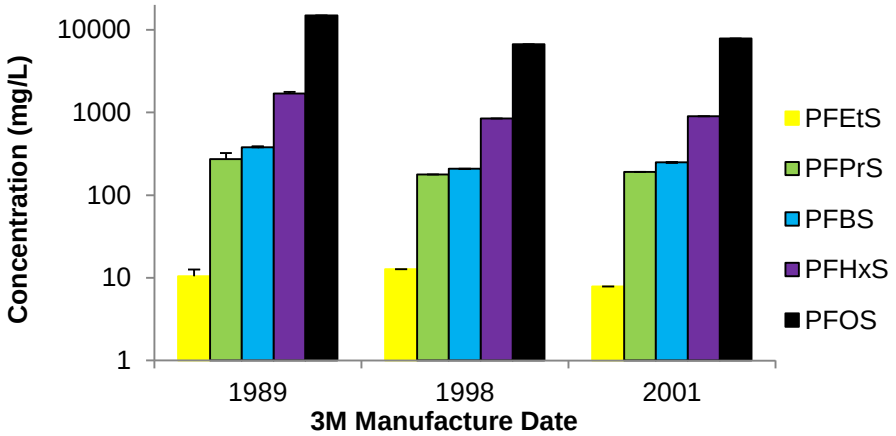
Site Characterization

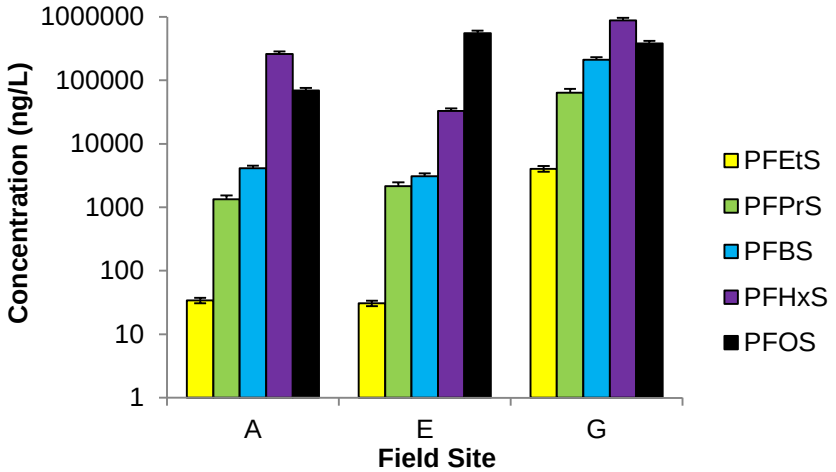
	PFAS	Site 1 (µg/L)	Site 2 (µg/L)
FTSA	6:2 FtTAoS	18	6.9
	6:2 FTSA	230	220
C4-C8 PFSAs	PFBS	65	43
	PFPeS	49	NA
	PFHxS	380	240
	PFHpS	5.9	11
	PFOS	1,000	78
C4-C8 PFCAs	PFBA	28	24
	PFPeA	66	69
	PFHxA	140	130
	PFHpA	26	15
	PFOA	94	51

- Only 5 on UCMR3 (in red) and EPA Method 537, and 6 not in listed in EPA Method 537 (in **purple**)
- PFOS and PFOA >> EPA provisional health advisory levels (0.2 and 0.4 µg/L)
- PFBS and PFBA >> State of MN chronic noncancer health risk limits (7 µg/L)
- World records (for water)
  - PFOS = 1 mg/L
  - PFOA = 6.6 mg/L
  - 6:2 FTSA = 14.6 mg/L

Site Characterization

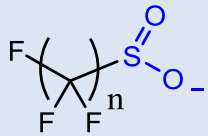
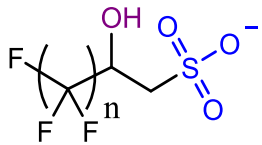
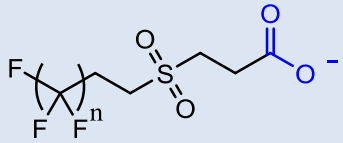
- Ultra-short sulfonates
  - C2 (PFEtS) and C3 (PFPrS) in groundwater and 3M AFFF (source)
  - Concentrations > MN health risk limit (7 µg/L) for PFBS
  - Highly mobile - likely at leading edge of plumes
  - Challenging to remove by GAC





Site Characterization

- Identify indicators of in situ (bio)transformation
- Identify remedial targets
- Prioritize PFASs that pose higher risk

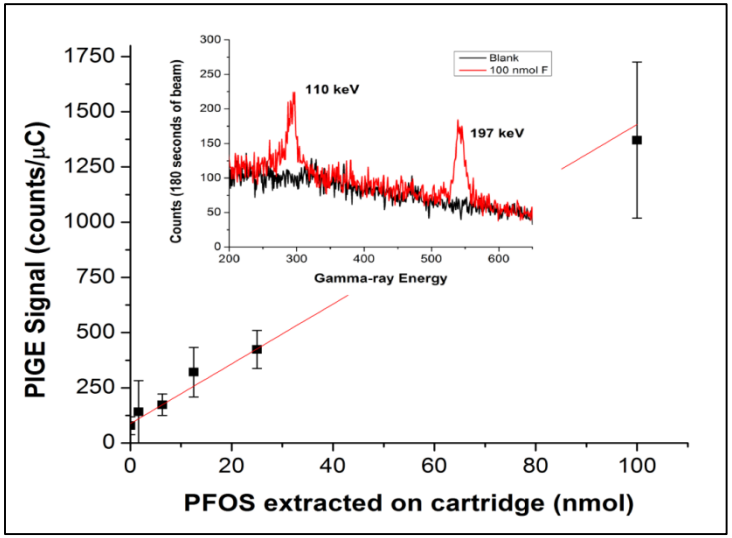
Structure	Frequency of Detection (13 sites)	Charged State Source
	9 sites	**Anion** 3M
	6 sites	**Zwitterion** Ansul
	3 sites	**Anion** Ansul

Significance: Structure Determines Properties, Fate and Transport

- Properties
  - High aqueous solubility and low vapor pressure
  - Low Henry's Law (not removed by air sparging)
- Transport potential
  - Anionic > zwitterionic > cationic
  - Cation exchange may create immobile source zones
- Biodegradation
  - Few data for anions
  - No data for zwitterions and cations
- Toxicity
  - Data for PFOS/PFOA/PFBS
  - No data on zwitterions/cations

Site Characterization

- Total oxidizable precursor (TOP) assay
  - Quantifies precursor (total PFASs) in groundwater, sediment, soil
  - Closes mass balance in microcosm studies
- Total fluorine by PIGE
  - PFAS in groundwater sorbed onto media to create 'target'
  - 10 nA of 3.4 MeV protons for 180 s
  - Quantitative, high-throughput
  - Inexpensive screening tool

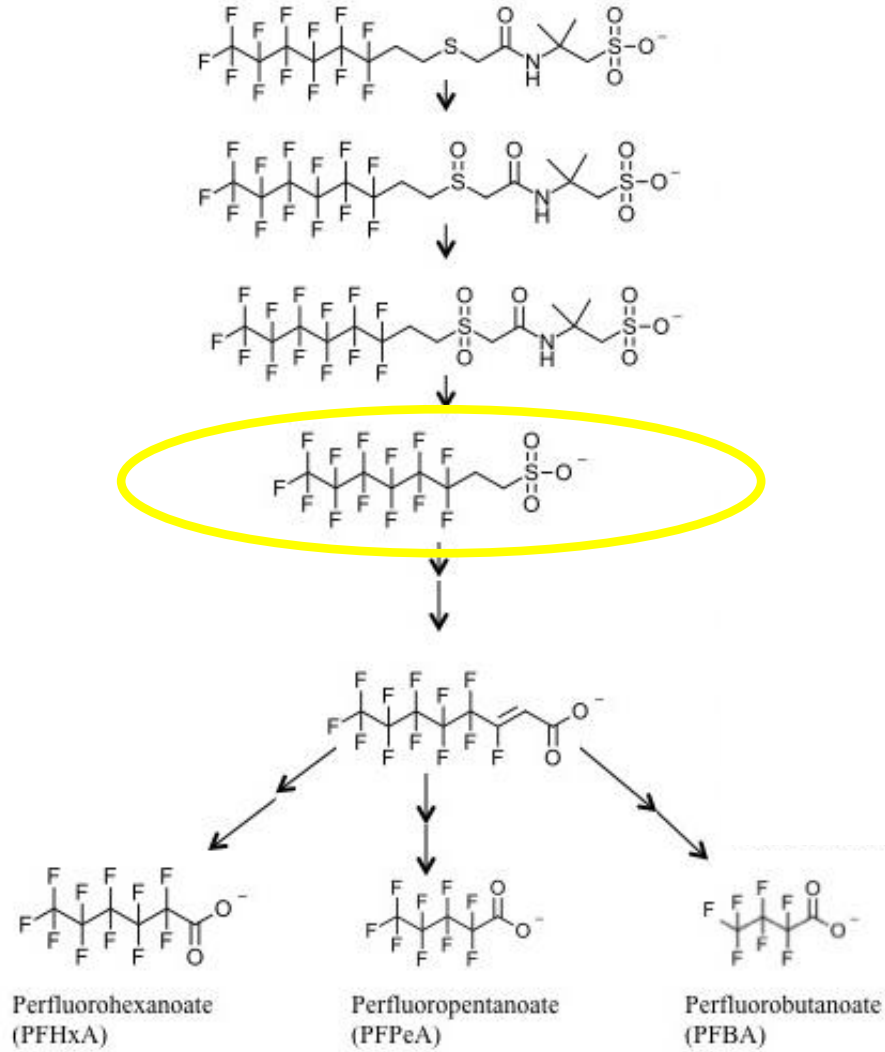


Significance for Site Characterization

- Close the mass balance
- Differentiate AFFF sources from landfill leachate, wastewater effluent, atmospheric deposition
- Develop conceptual site models
- Understand potential human and wildlife exposure
- Design remedial treatment strategies
- Close data gaps on transport, biodegradation and toxicity

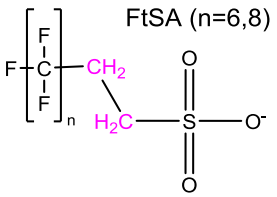
Biotransformation

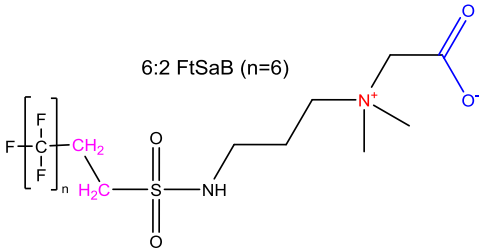
- Telomer sulfonates are biodegradation products
- Telomer sulfonates >> precursors in site groundwater
- Stable under anoxic conditions
- Aerobically degraded to short-chain carboxylates

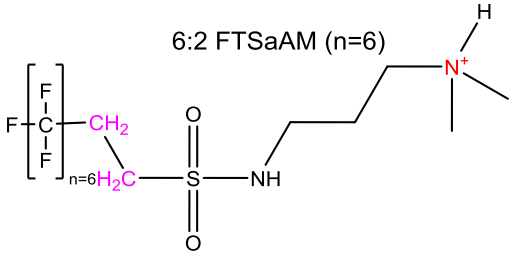


Sorption to Sediment

- Longer chain lengths = greater affinity for sediment
- Sorption of 6:2 FTSA (same C number) < PFOS (more mobile)
- Zwitterionic FTSAB (+/-) sorb less than anions (same chain length)
- Cationic (FtSaAm) sorbs strongly to sediment, mobility low, may form source zones
- pH will impact mobility in subsurface







Conclusions

- PFOS and PFOA are important but not the only major PFASs at AFFF-contaminated sites
- Telomer-based substances biodegrade to metastable intermediates but not PFOS
- Mobility in groundwater anions > zwitterions > cations
- Anion mobility depends on chain length
- Mobility of many substances influenced by sediment, soil and water geochemistry

Benefits to DoD

- Hundreds of fire/crash testing (mixed waste) sites
- Full characterization of PFAS contamination
  - More accurate conceptual site models
  - Identify remedial approaches that decrease time and cost
  - Optimized monitoring
  - Fingerprinting to differentiate AFFF from other sources
  - Source zone identification
  - Accurate predictions of transport
  - Indicators of in situ biotransformation
- Groundwater contaminated by PFAS used as drinking water source is a potential exposure pathway for humans and wildlife
  - Attention to short-chain PFAS highly mobile, difficult to remove from water

Acknowledgments

Project Team Members

- Dr. David L. Sedlak, UC Berkeley
  - Advanced oxidation and contaminant fate expert
- Dr. Lisa Alvarez-Cohen UC Berkeley
  - Environmental microbiologist/engineer
- Dr. Markus Kleber, Oregon State University
  - Soil scientist

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2128

Speaker Contact Information

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Q&A Session 2

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Understanding the Transport of Perfluorochemicals in Groundwater at AFFF-Impacted Sites

Christopher P. Higgins, Ph.D.
Colorado School of Mines

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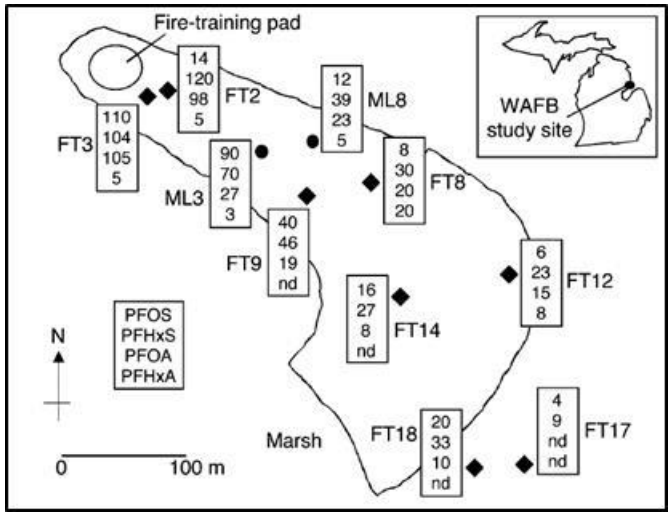
Agenda

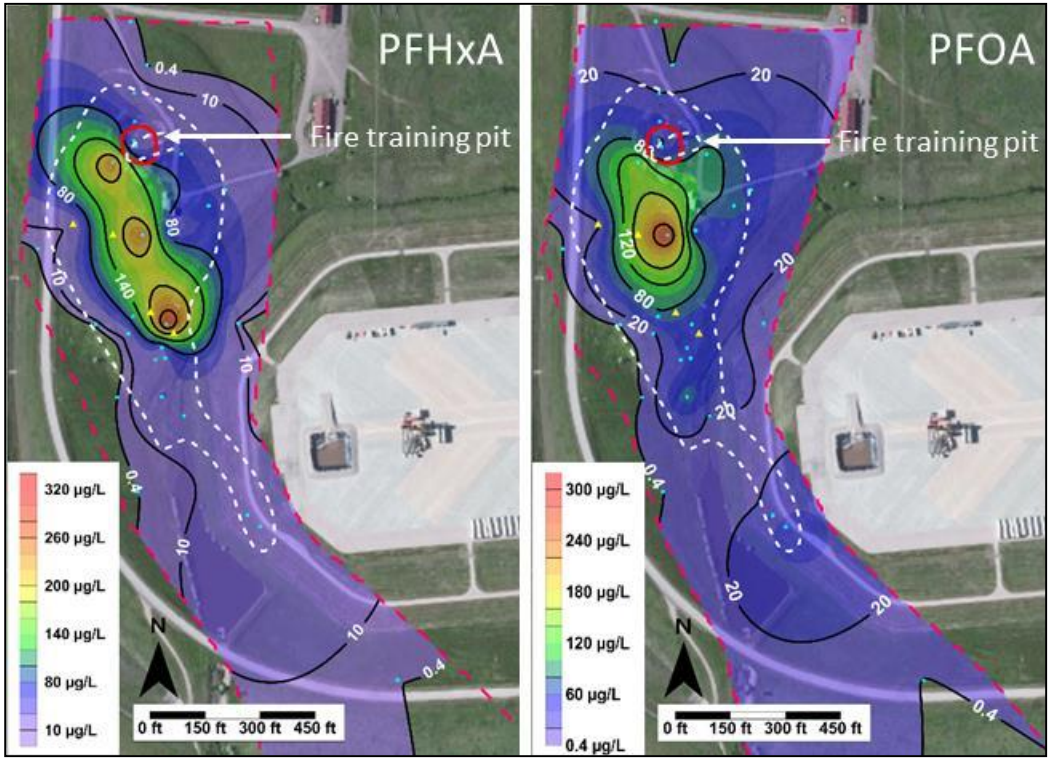
- Motivation
- Technical objectives and approach
- Results
- Conclusions
- Acknowledgments

Motivation

Perfluoroalkyl acids (PFAAs) are transported in groundwater…



Wurtsmith AFB



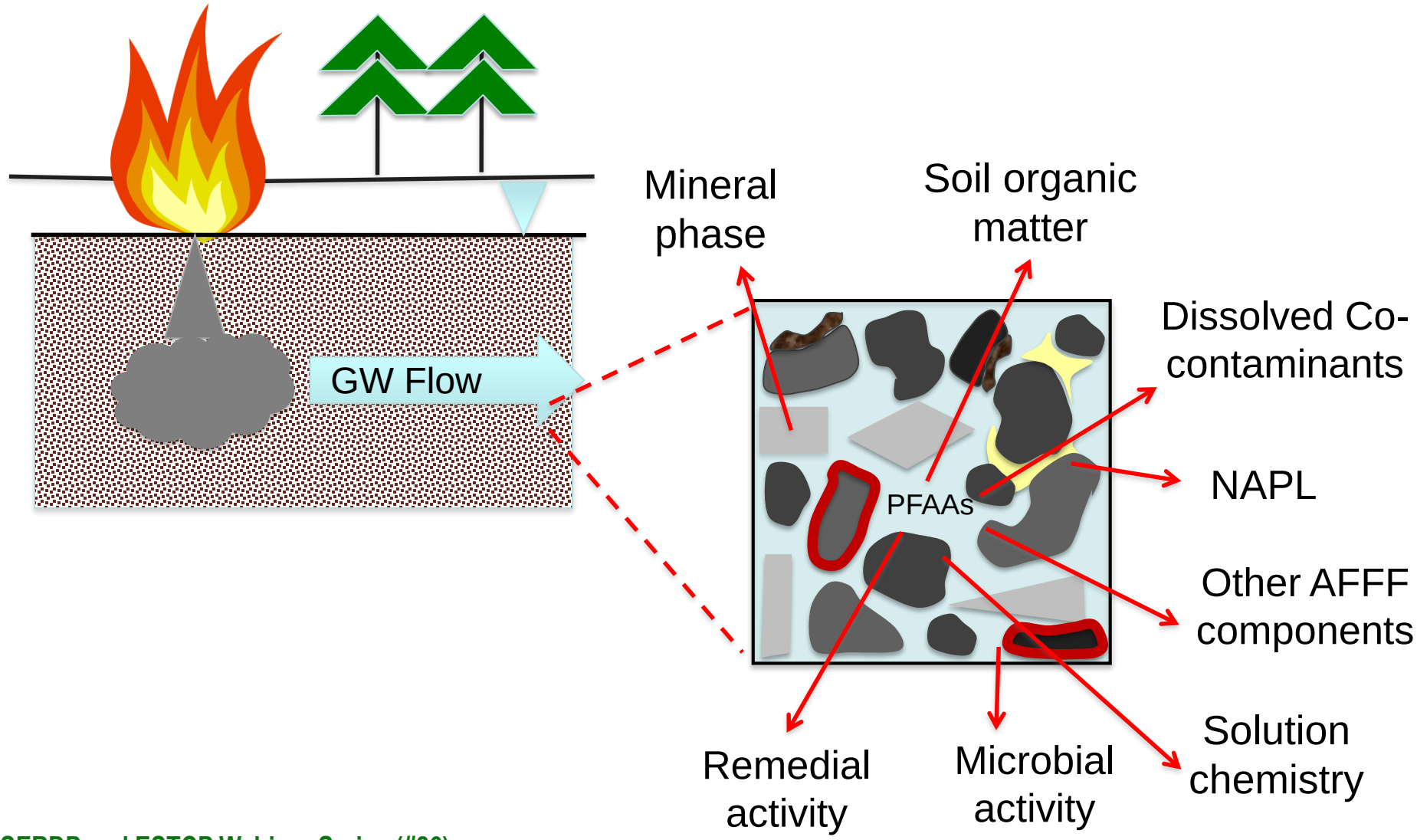
Ellsworth AFB

…but fundamental transport parameters were lacking for many PFAAs

Technical Objectives

- Determine the effects of physicochemical and biological parameters on PFAA fate and transport in groundwater in the presence of co-contaminants and during co-contaminant remediation
- Key research questions addressed
  - What are the effects of co-contaminants on PFAA transport?
  - How do biogeochemical conditions PFAA transport?
  - What are the impacts of co-contaminant remediation on PFAA fate and transport?

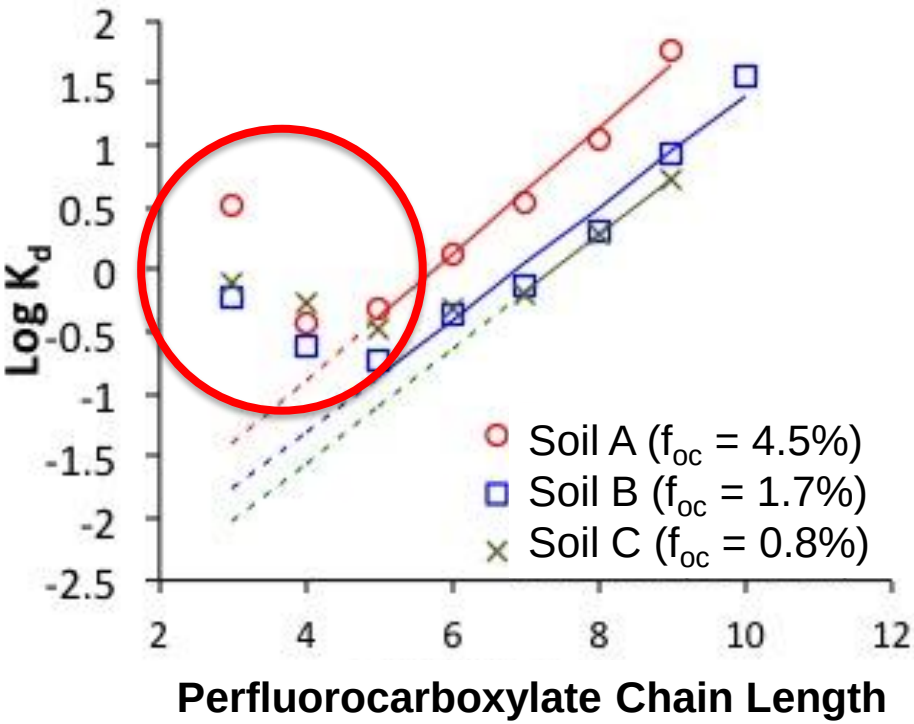
Conceptual Model

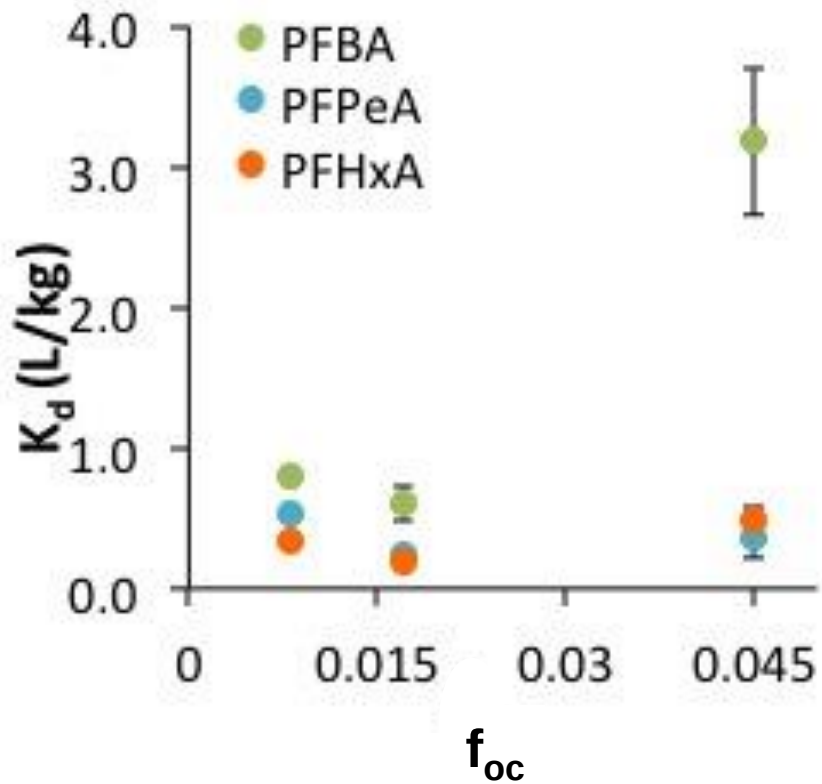


Approach

- Conducted a series of PFAA sorption batch and column experiments
  - Batch experiments for equilibrium assessment
    - With and without co-contaminants
  - Column experiments to mimic advective conditions
    - Unaltered conditions
    - Examined impacts of in situ chemical oxidation (ISCO), with and without NAPL

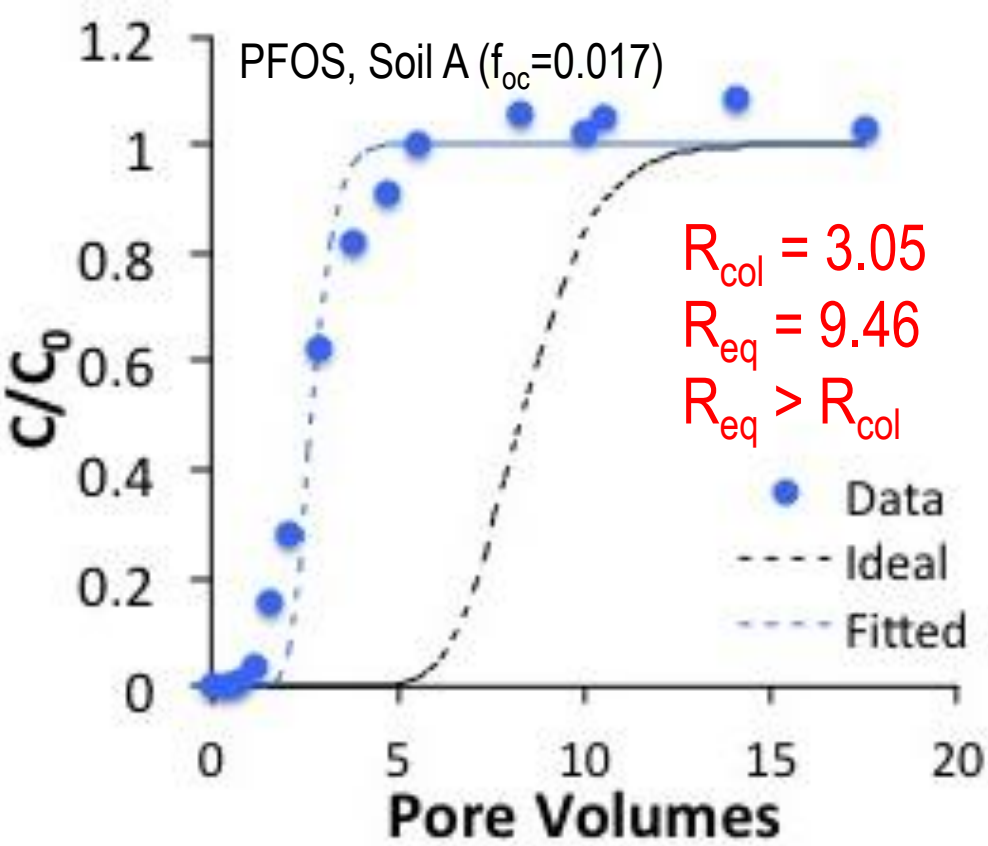
Stronger Sorption than Expected for Short-Chain PFAAs





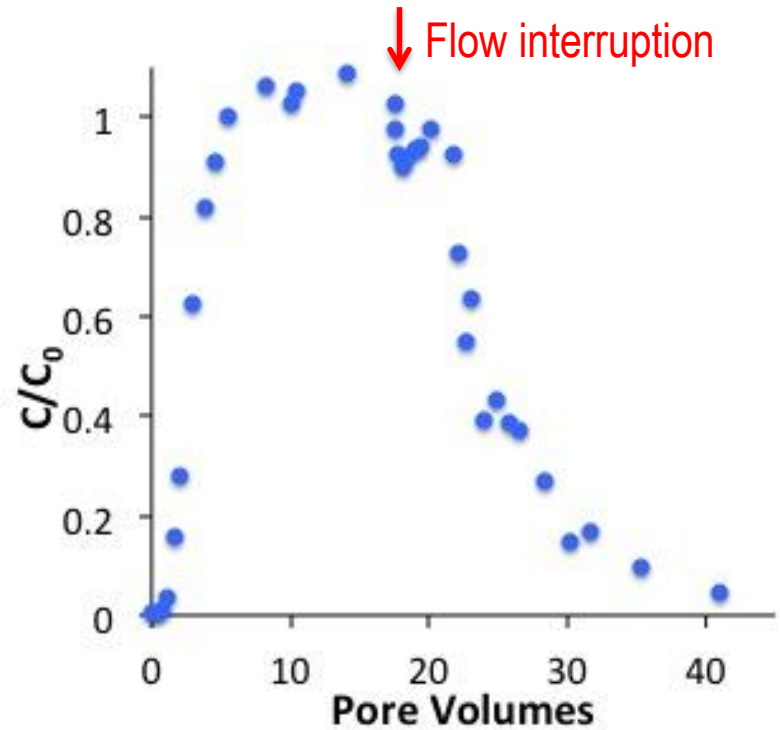
Organic carbon important, but may not be only driver for sorption

Non-Equilibrium Transport in Columns

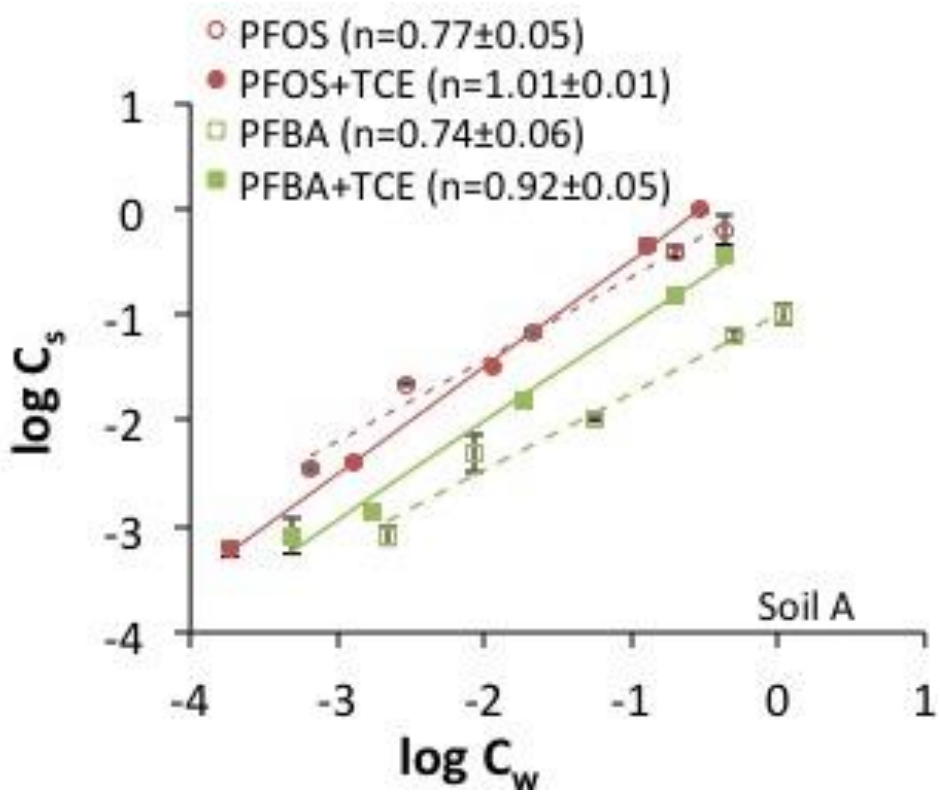


Breakthrough curves don't match equilibrium predictions

- Rate-limited sorption likely



NAPL Impacts PFAA Sorption



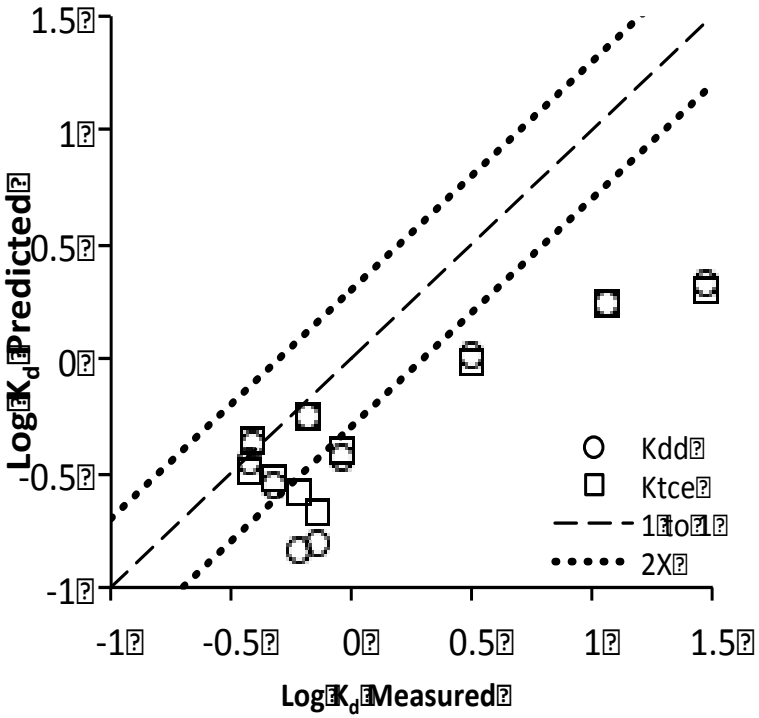
- NAPL impacts on K_d greater in low f_{oc} material
  - ↑ K_d for short-chain PFAAs
  - ↓ K_d for long-chain PFAAs
  - Isotherms generally more linear when NAPL present

…But NAPL Interactions Very Complex

K_{NAPL} values measured for dodecane (DD) and trichlorethene (TCE) NAPLs				
Analyte	K_{DD} (L/kg)	±	K_{TCE} (L/kg)	±
PFBA	0.23	0.24	0.86	0.60
PFPeA	0.50	0.34	1.72	0.72
PFHxA	2.20	0.60	1.85	0.37
PFHpA	1.32	0.35	1.50	0.59
PFOA	1.53	0.32	1.58	0.84
PFNA	2.66	0.81	1.98	1.73
PFDA	3.16	2.39	2.00	1.62
PFUnA	14.52	4.71	20.85	1.70
PFBS	NM	NM	0.19	0.17
PFHxS	NM	NM	0.22	0.22
PFOS	0.24	0.16	0.67	0.64

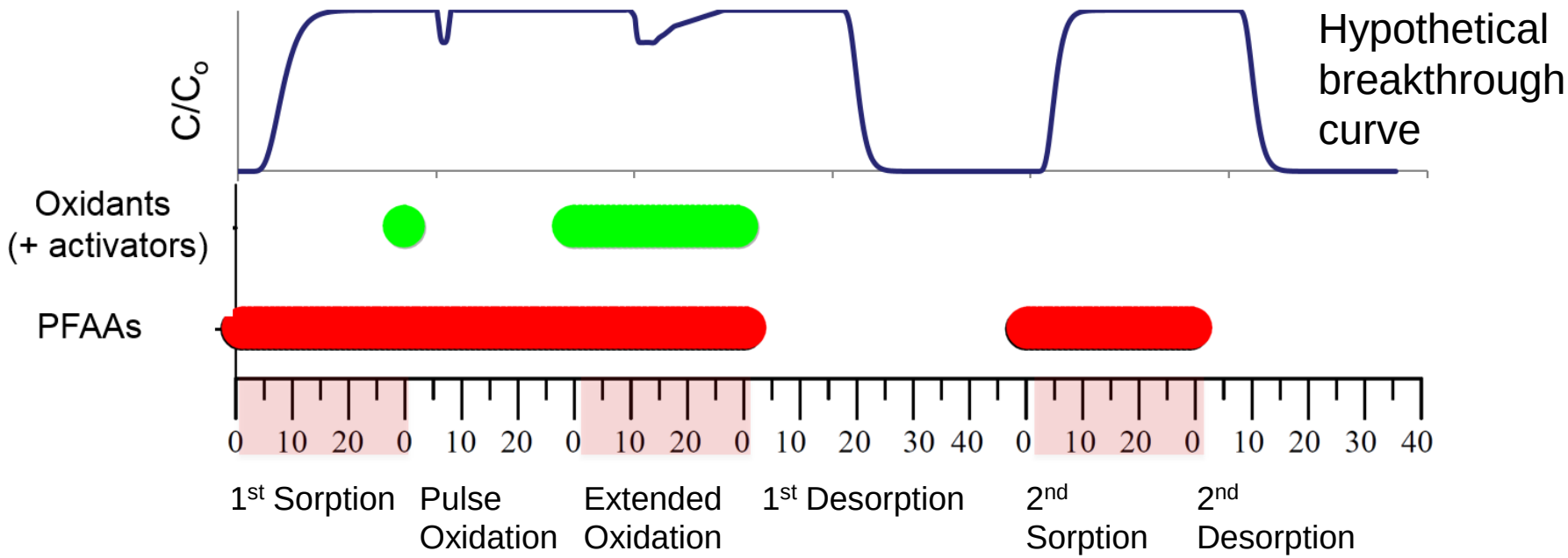
NM = no aqueous loss was measured

Measured sorption **greater** than predicted assuming *only* absorption into NAPL



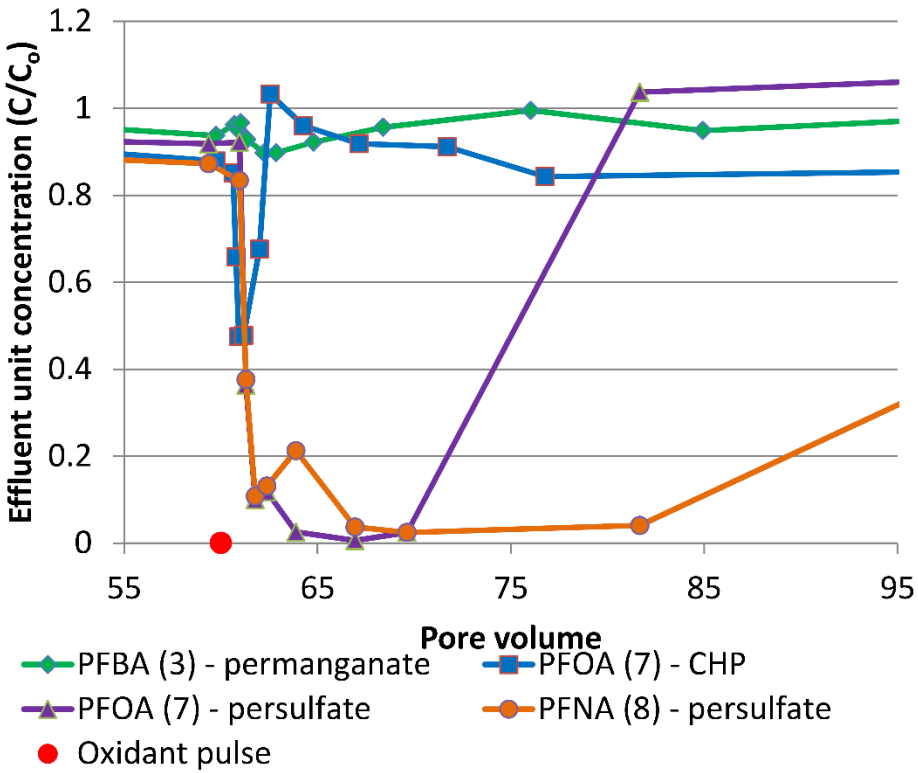
Column Transport with ISCO

- Experiments to mimic application of ISCO (with and without NAPL)
  - Activated persulfate: 10 g/L $S_2O_8^{2-}$ ($FeCl_2$/citric acid activation)
  - Permanganate: 1 g/L MnO_4^-
  - Catalyzed hydrogen peroxide: 0.5 g/L H_2O_2 ($FeSO_4$ activation)
  - TCE residual saturation (when present): 15 – 30%



Phase and phase-specific pore volumes

ISCO Can Impact PFAA Retardation

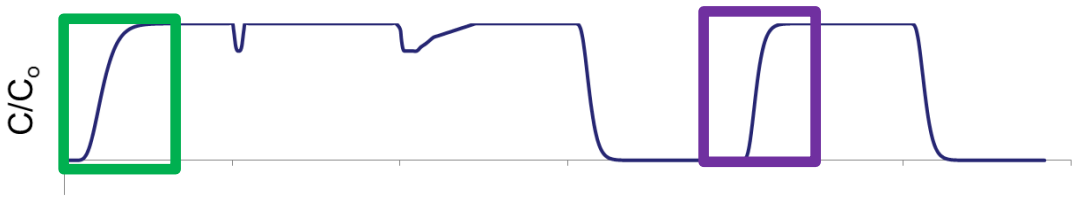


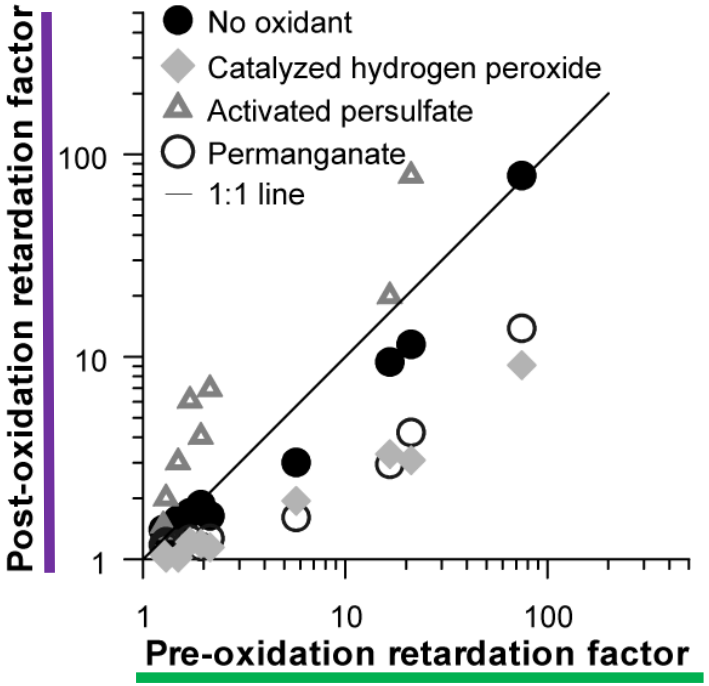
	Activated persulfate	Permanganate	Catalyzed hydrogen peroxide
	No TCE	No TCE	No TCE
PFBA (3)			
PFPeA (4)			
PFHxA (5)			
PFHpA (6)			
PFOA (7)			
PFNA (8)			
PFDA (9)			
PFUdA (10)			
PFBS (4)			
PFHxS (6)			
PFOS (8)			

- No effect
- Small dip -> recover
- Large dip -> recover
- Large dip -> not recover

- Persulfate greatest effect
- Effect ↑ with ↑ chain length

Variable Impacts of Prolonged ISCO on PFAA Transport

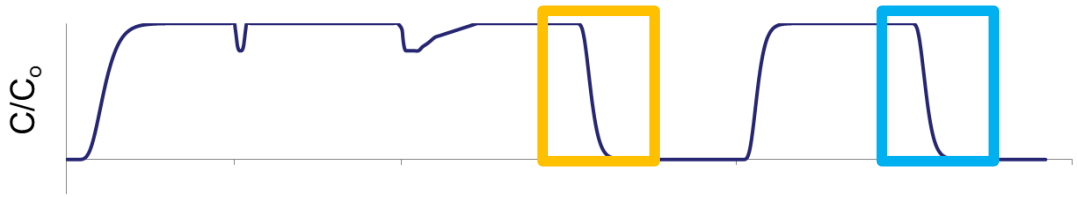




Breakthrough curves fit for retardation factors (*R* values)

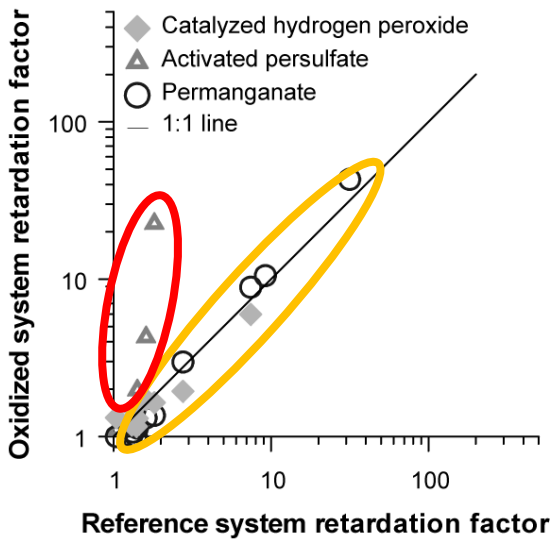
- Comparing pre- vs. post-oxidation effects
  - Persulfate *increased* retardation
  - Catalyzed hydrogen peroxide and permanganate *decreased* retardation
- Strong dependence on aqueous chemistry

ISCO Impacts PFAA Desorption

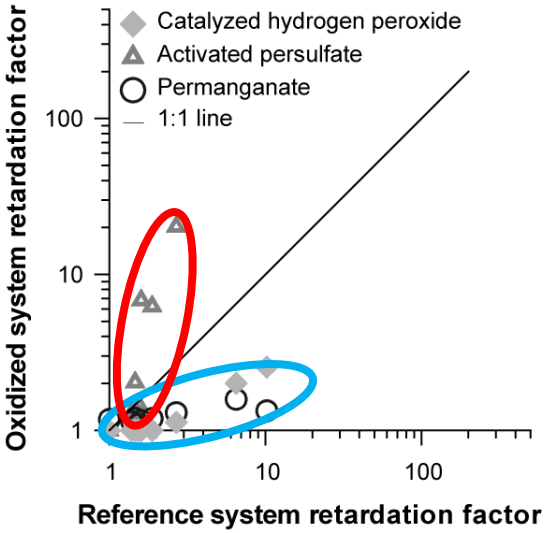


***Desorption* profiles also fit for retardation factors**

- **MUCH slower** desorption with **persulfate**
- **Minimal to no impact** of permanganate and hydrogen peroxide immediately following oxidant application, but **significantly faster** desorption over time

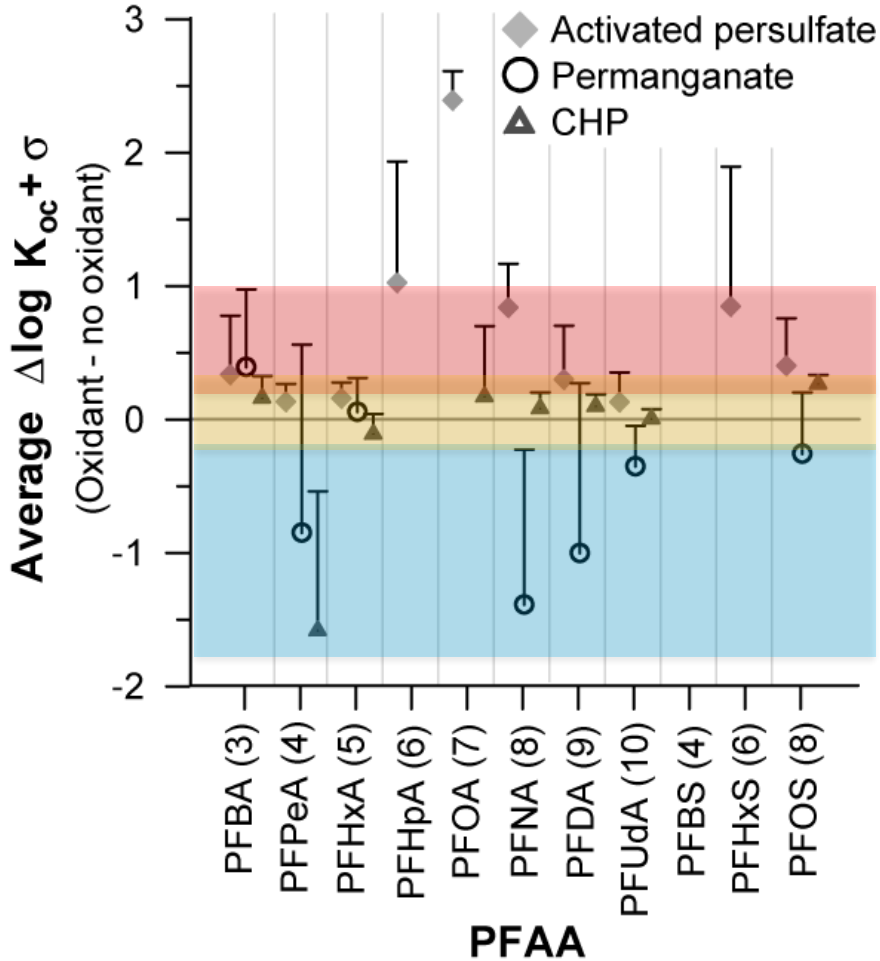


Fitted desorption during 1st Desorption Phase



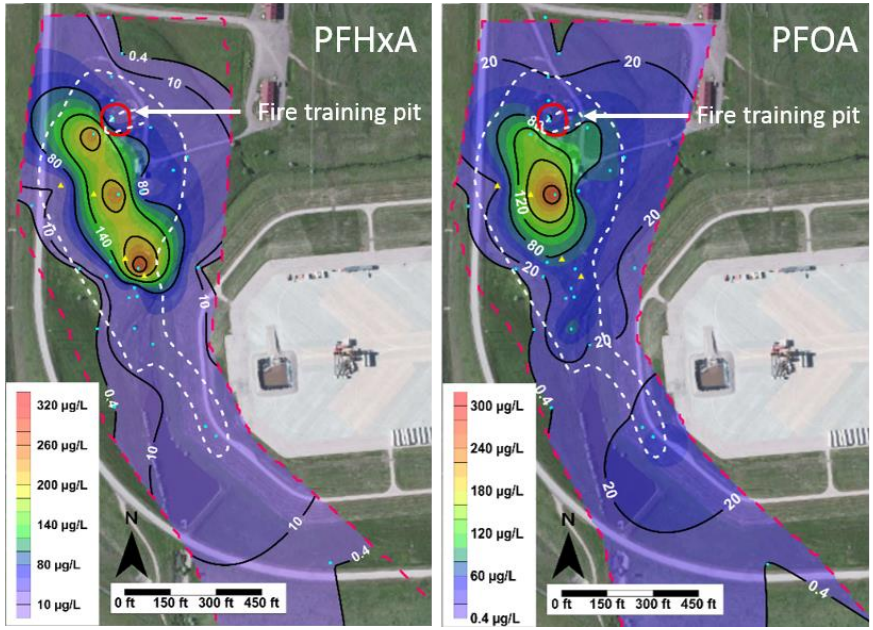
Fitted desorption during 2nd Desorption Phase

Column Dissections Confirm Results

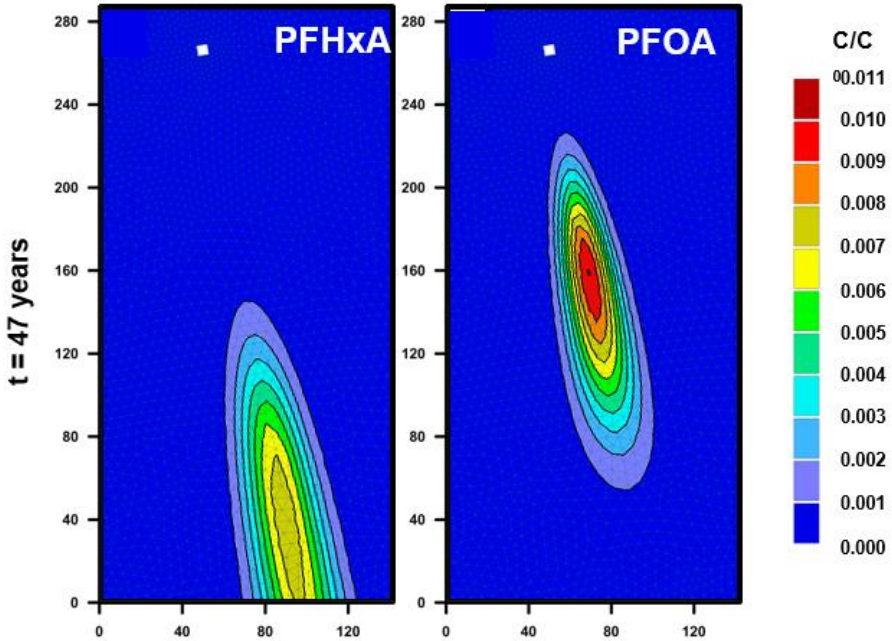


- Up to ~1.0 *increase* in log K_{oc} with persulfate
- Generally little impact with CHP
- Up to ~1.5 *decrease* in log K_{oc} with permanganate

Relevance



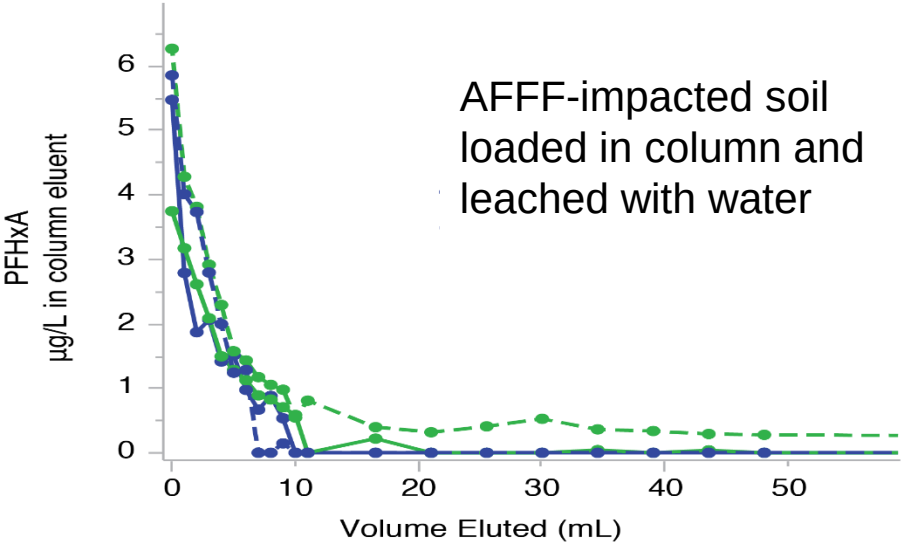
Ellsworth AFB



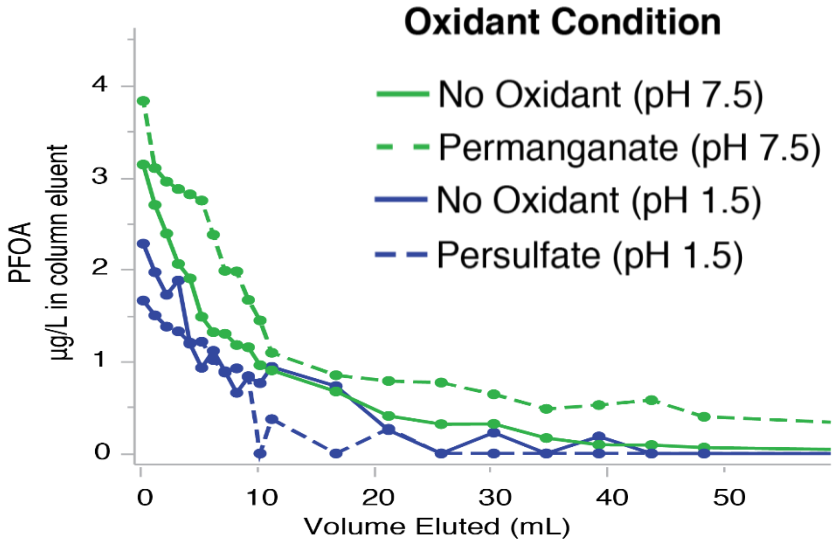
Ellsworth release scenario modeled in 2-D Hydrus

The *lack* of differential transport in the field suggests ongoing PFAA release from **source zones**

PFAA Release from AFFF-Impacted Soils

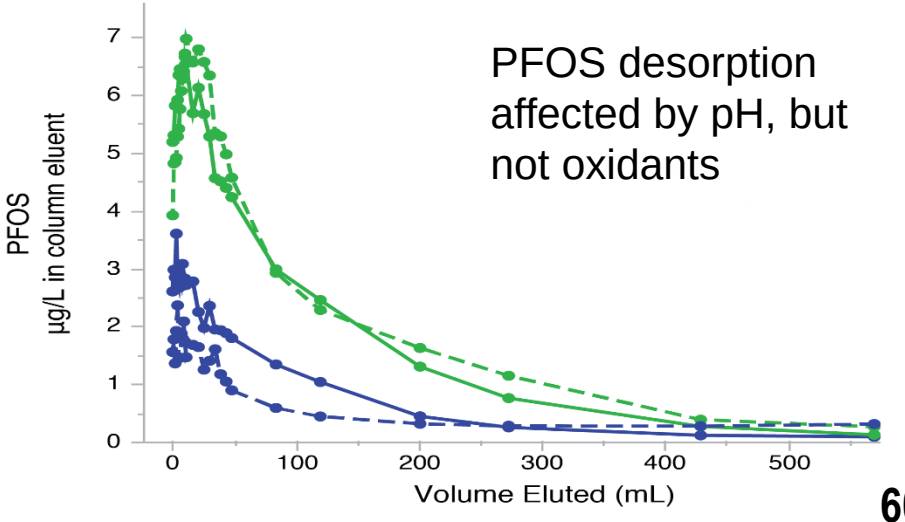


AFFF-impacted soil loaded in column and leached with water



Total Mass Released in 570 mL

	PFHxA	PFOA	PFOS
No Oxidant (pH 7.5)	94%	65%	56%
Permanganate (pH 7.5)	1060%	122%	66%
No Oxidant (pH 1.5)	79%	47%	24%
Persulfate (pH 1.5)	92%	33%	22%



PFOS desorption affected by pH, but not oxidants

Conclusions

- Transport of PFAAs generally depends on perfluoroalkyl chain length
- PFAAs likely both adsorb and absorb to NAPLs
- ISCO alters PFAA transport primarily through geochemical changes
- Research emphasizes need for source zone characterization

Next Steps

- SERDP Project ER-2424
  - "Investigating Electrocatalytic and Catalytic Approaches for In Situ Treatment of Perfluoroalkyl Contaminants in Groundwater" CB&I (C. Schaefer)
- ESTCP Project ER-201574-T2
  - "Catalyzing Rapid Information Transfer Among Key Stakeholders on Per- and Polyfluoroalkyl Substances (PFASs) at Contaminated Military Sites" OSU (J. Field)
- ESTCP Project ER-201633
  - "Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substance (PFASs) in Environmental Media at DoD Sites for Informed Decision-Making" Navy lead (J. Kornuc)

Acknowledgments

Project Team Members

- Dr. John E. McCray
  - Contaminant hydrologist
- Dr. Robert L. Siegrist
  - Environmental engineer
- Dr. Jonathan O. Sharp
  - Environmental microbiologist

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2126

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Q&A Session 3

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Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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