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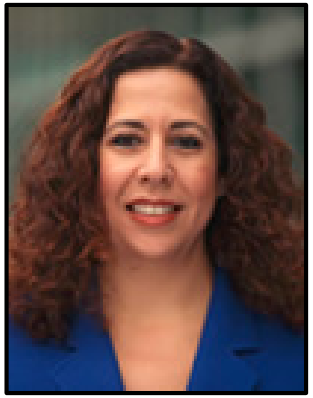
PFAS Fate, Transport and Treatment

July 23, 2020

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Coordinator

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Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Laboratory and Modeling Investigation of PFAS Transformation, Transport, and Retention in AFFF Source Areas** (25 minutes + Q&A)
  Dr. Linda Abriola, Tufts University
- ***H*ydrothermal *AL*kaline *T*reatment (HALT): An Innovative Technology for Complete Destruction of PFAS** (25 minutes + Q&A)
  Dr. Timothy Strathmann, Colorado School of Mines
- **Final Q&A session**

Zoom Instructions

- Download Zoom
  - https://zoom.us/download
- If you cannot download Zoom, you can view the slides using an internet browser
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- Find the Q&A button on your control bar and type in your question(s)
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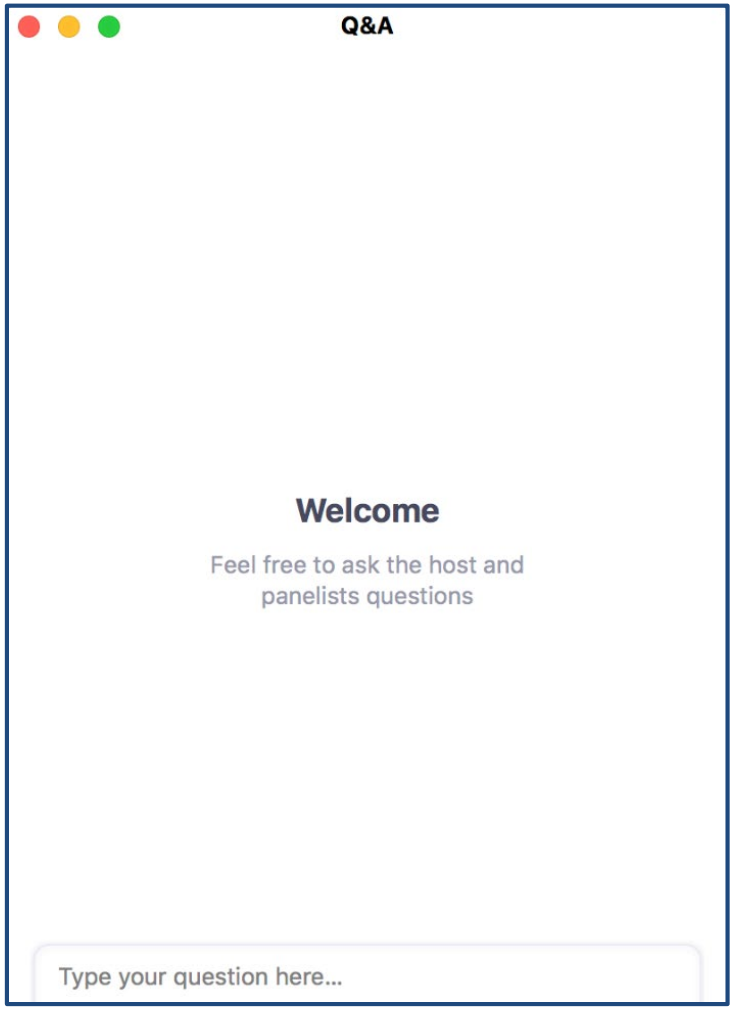

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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DoD's Environmental Technology Programs

Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

Environmental Drivers

Sustaining Ranges, Facilities and Operations

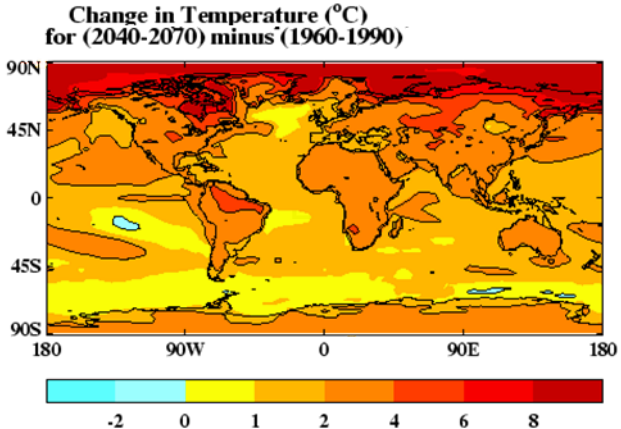
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

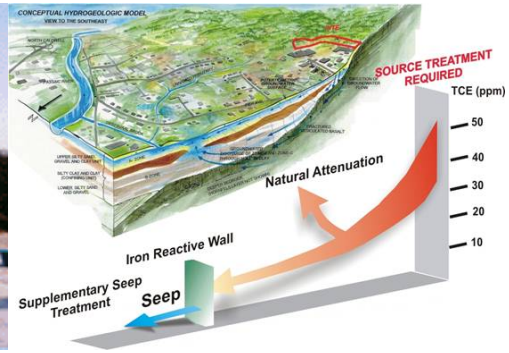
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



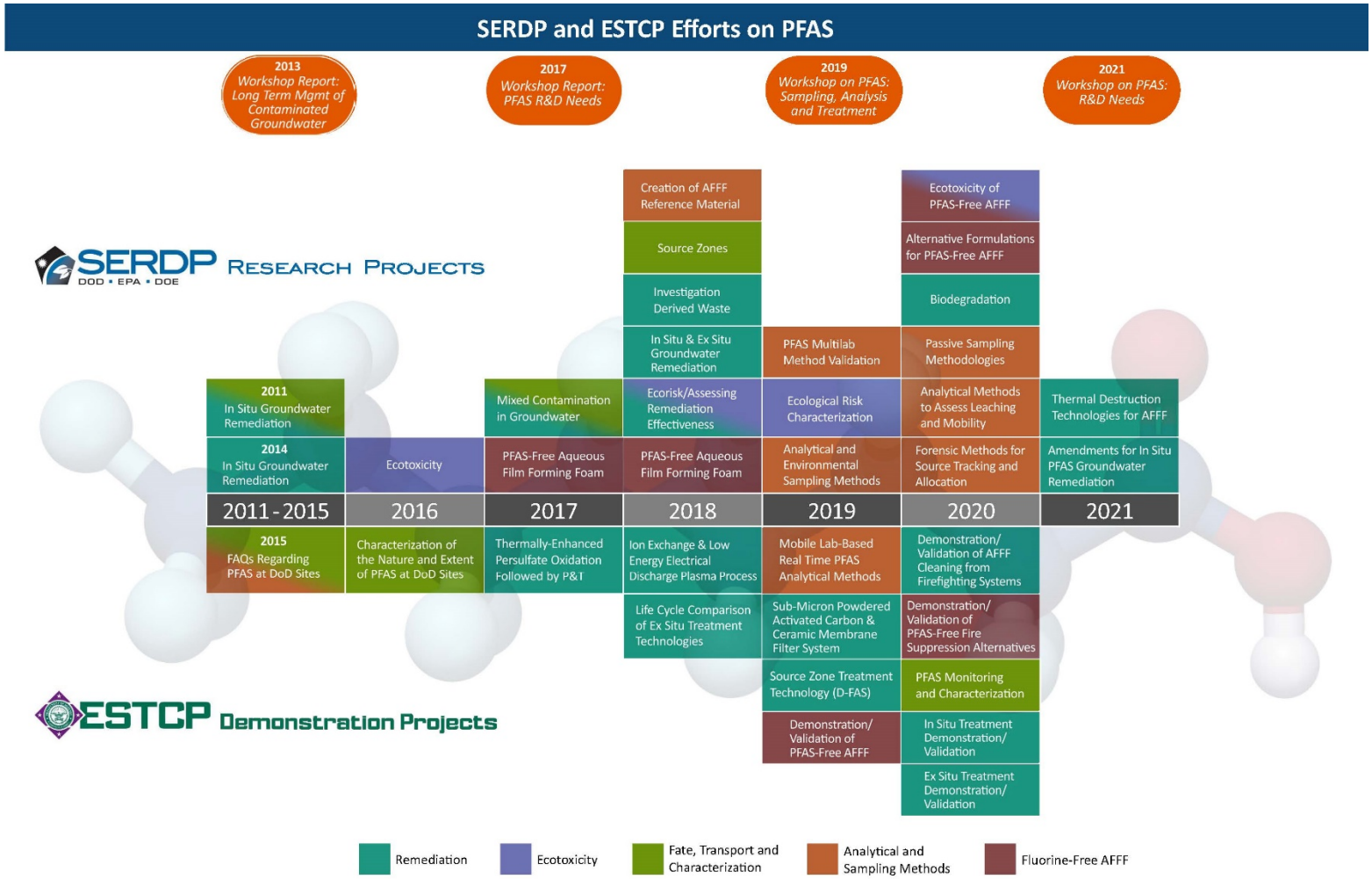
- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

PFAS Online Resource

https://map.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/pfas_efforts.pdf



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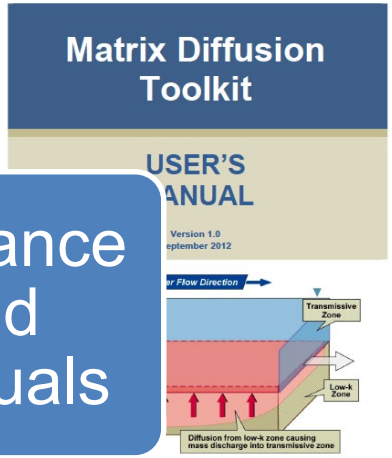

Webinars

In Person Training

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Technology Transfer

Guidance and Manuals

SERDP and ESTCP Webinar Series

Date	Topic
July 23, 2020	Predicting PFAS Fate and Transport in Subsurface Environments, and Treatment
August 20, 2020	Addressing Threatened and Endangered Species on DoD Lands
September 10, 2020	Reducing Hazardous Materials in Weapons Systems: Advances in Waterjet Applications and Cold Spray Technologies
September 24, 2020	Munitions Mobility and Burial in Underwater Environments
October 8, 2020	Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available Fluorine-Free Foams (**Part 1**)
October 22, 2020	Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available Fluorine-Free Foams (**Part 2**)

For upcoming webinars, please visit

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Save the Date

SERDP • ESTCP
SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

December 1-3, 2020
Washington, DC

Poster abstracts due August 14

Registration for virtual symposium is open

Laboratory and Modeling Investigation of PFAS Transformation, Transport, and Retention in AFFF Source Areas

Linda M. Abriola, Ph.D., NAE
Tufts University

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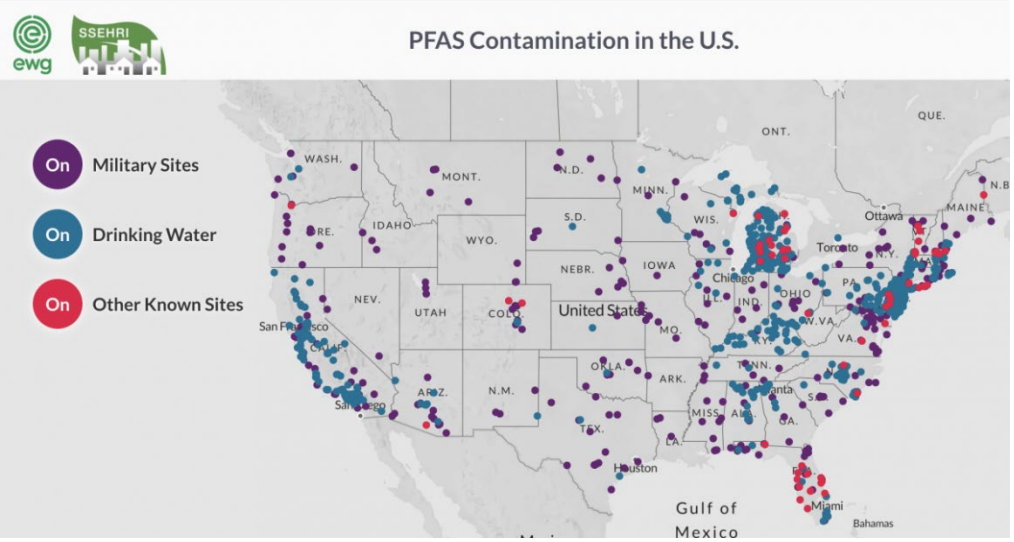
Outline

- Project overview
- Interface accumulation studies
- Sorption studies
- Implications for transport and retention
- Preliminary microcosm results
- Key findings

Research Objectives

Integrated experimental and modeling study



- Develop and validate mathematical models and decision tools that capture key processes

- Improve understanding of processes governing PFAS transport and persistence in complex AFFF source areas

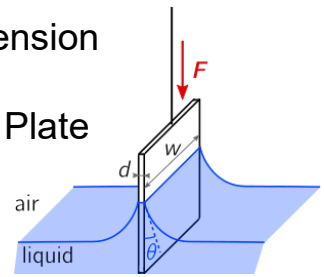
Studies on Interfacial Accumulation

Interfacial Tension (IFT) Measurement

Sigma T700 Tensiometer

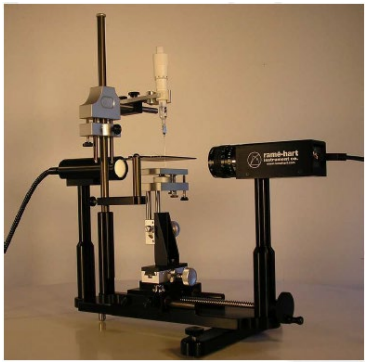
Resolution of 0.01 mN/m

Surface Tension by Wilhelmy Plate

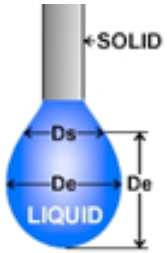


mN/m = dyne/cm = g/s²

Ramé-Hart Goniometer



Interfacial Tension by Pendant Drop

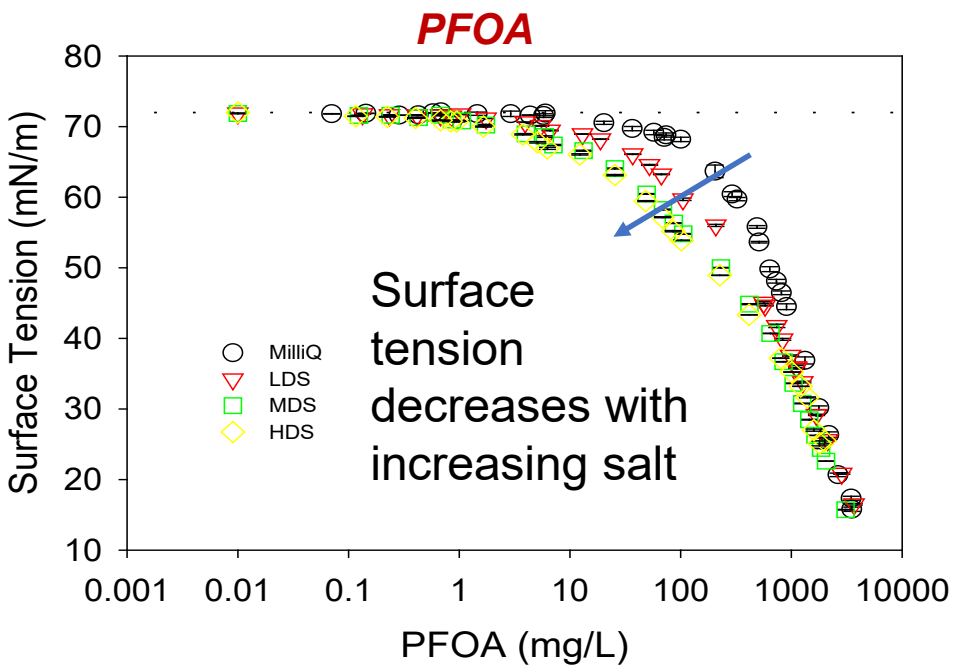


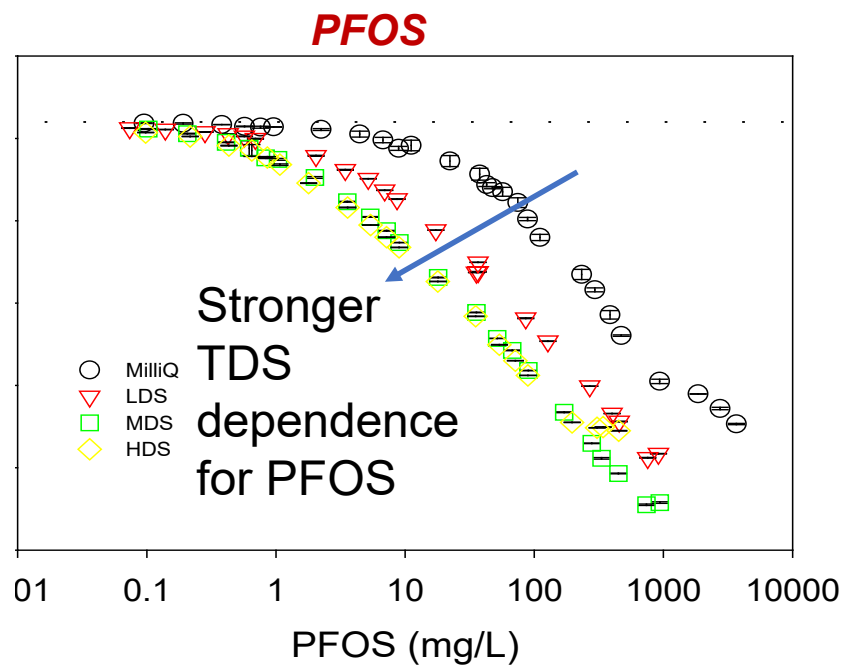
- IFT interfaces studied
  - Air-Water
  - Dodecane-Water
  - Tetrachloroethene (PCE)-Water
  - JP4-Water
- PFAS compounds
  - Perfluorooctanoate (PFOA)
  - Perfluorooctane sulfonate (PFOS)
  - Perfluorooctane sulfonamide (FOSA)
  - 3M and Ansul AFFF

Air-Water Interfacial Tension (IFT)

Effect of Dissolved Solids

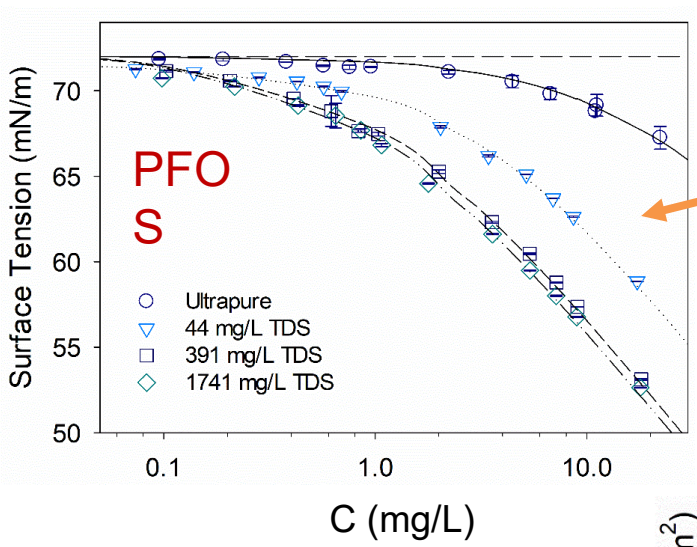
- Low Dissolved Solids (LDS) ca. 40 mg/L (high purity drinking water)
- Mid Dissolved Solids (MDS) ca. 400 mg/L (secondary drinking water)
- High Dissolved Solids (HDS) ca. 1,700 mg/L (unpleasant drinking water)





Estimating Surface Excess

- Interfacial tension is a measure of surface concentration (Γ)



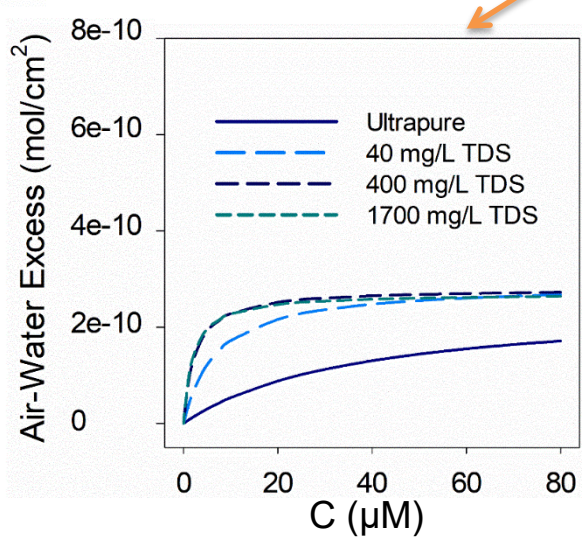
Szyszkowski Eq. Fit of Surface Tension:

$$\gamma = \gamma_0 \left[1 - aLn\left(\frac{C}{b} + 1\right)\right]$$

Gibb's Eq.: $\Gamma = -\frac{C}{RT}\left(\frac{\partial \gamma}{\partial C}\right)_T$

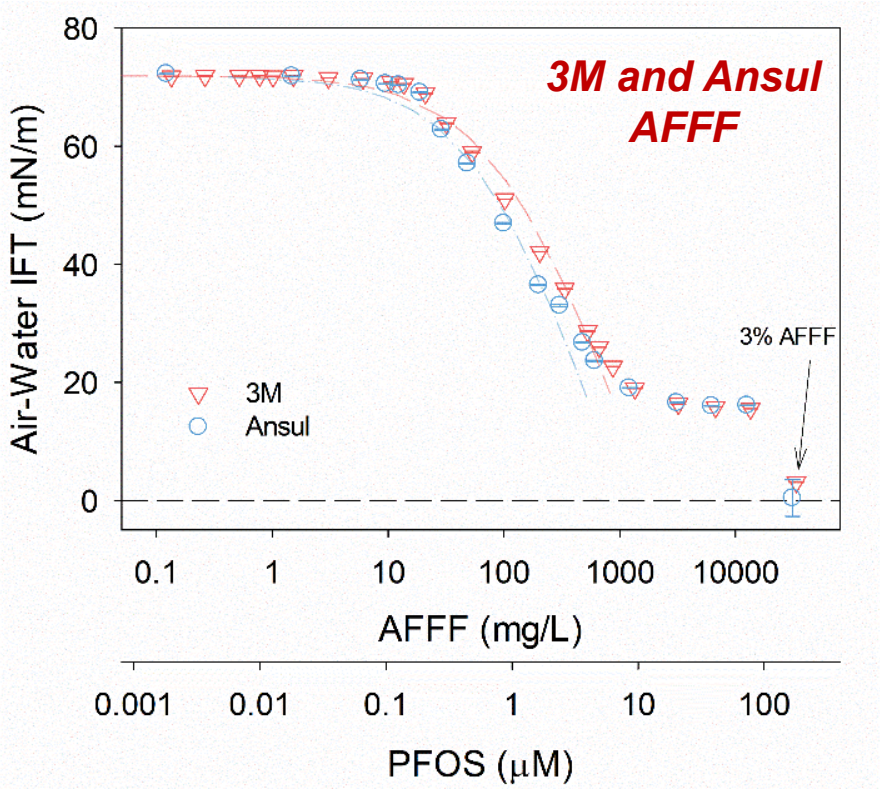
Langmuir/Szyszkowski Eq.

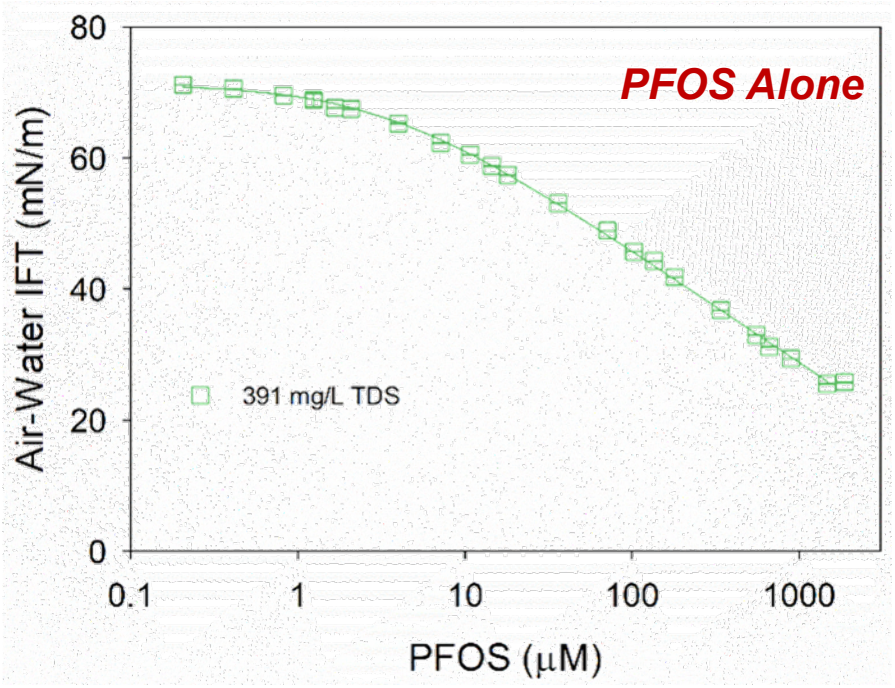
$$\Gamma = \frac{a\gamma_0}{RT}\frac{C}{C+b}$$



- PFOA and PFOS behave like anionic surfactants
- Increase in TDS increases interfacial accumulation (salting out)

Air-Water IFT (AFFF vs. PFOS)

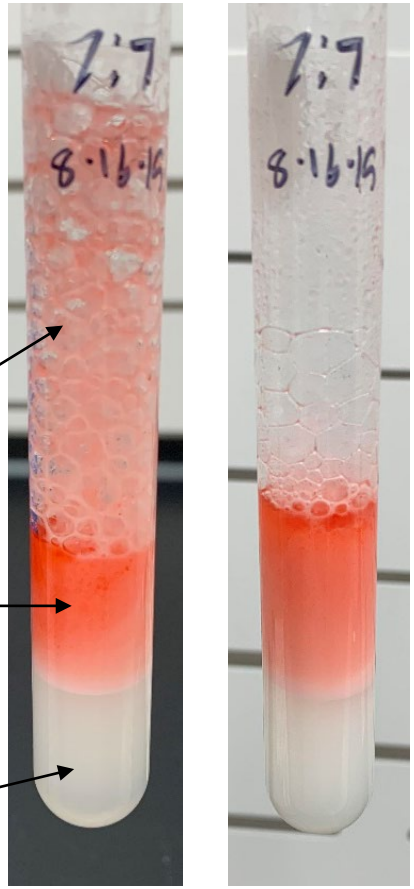




- PFOS is the predominant (>80%) perfluoroalkyl substance in AFFF
- Air-water AFFF IFT (400 mg/L TDS) decreased to less than 4 mN/m at 3% AFFF
- Other components, such as sodium dodecyl sulfate, contributed to the surface activity of AFFF solutions

NAPL-Water IFT Evaluation

3M

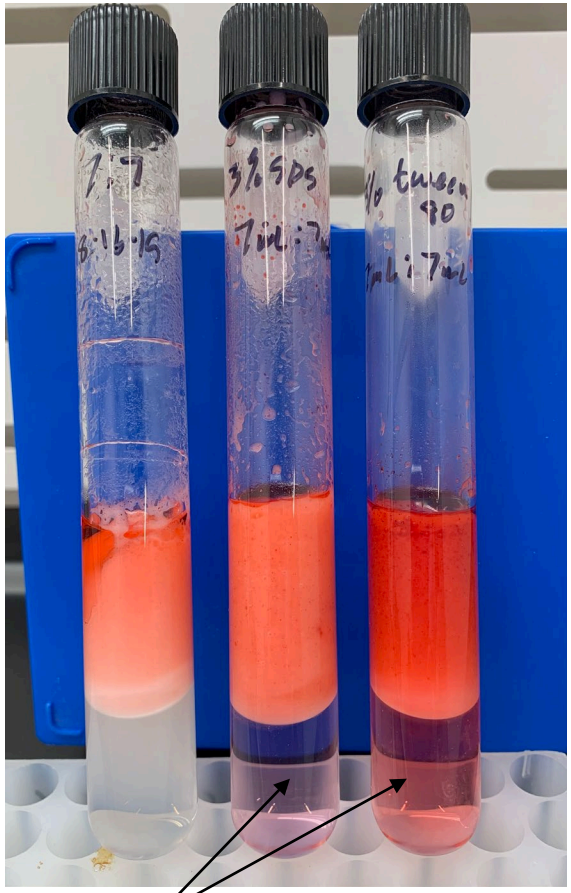


Foam

JP4
Macroemulsion

Aqueous Phase

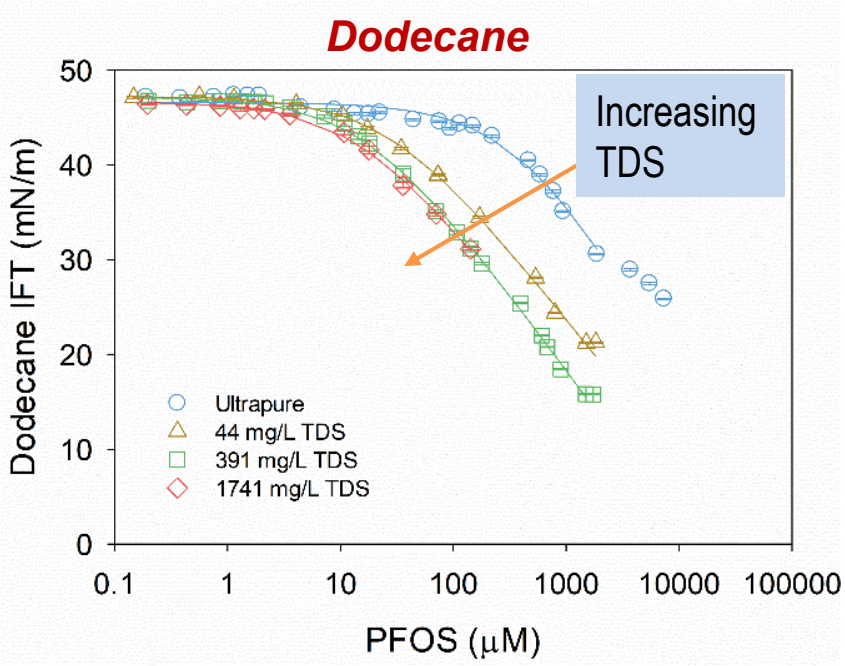
3M SDS Tween 80



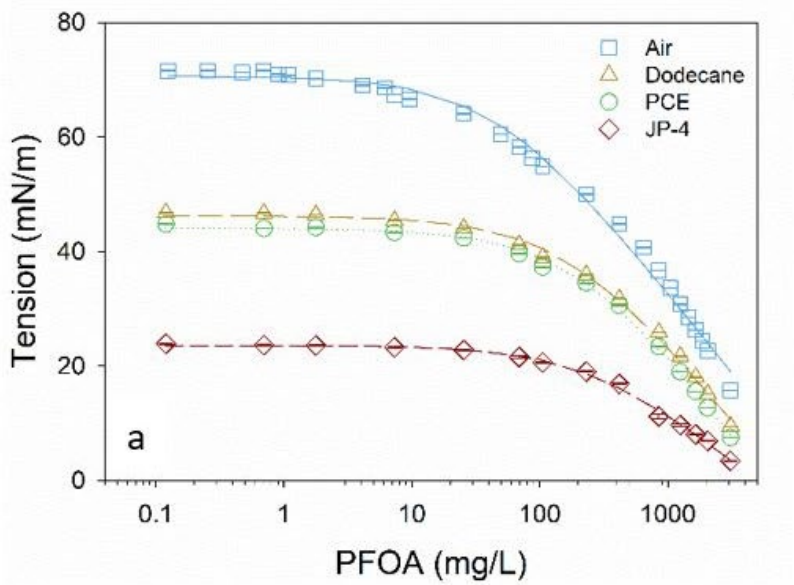
Micellar Solubilization

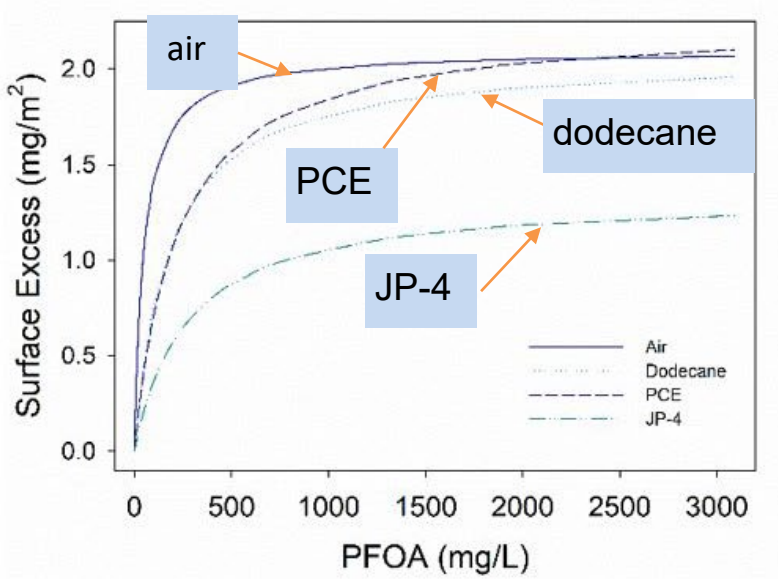
NAPL-Water IFT: PFOS

- Significant NAPL-water IFT reduction at elevated PFOS concentrations (>0.1 g/L)
- Confirms suggestion by Moody and Field (2000) that PFAS are oleophilic
- Significant NAPL mobilization by PFOA or PFOS not expected at typical field concentrations (<0.1 g/L)



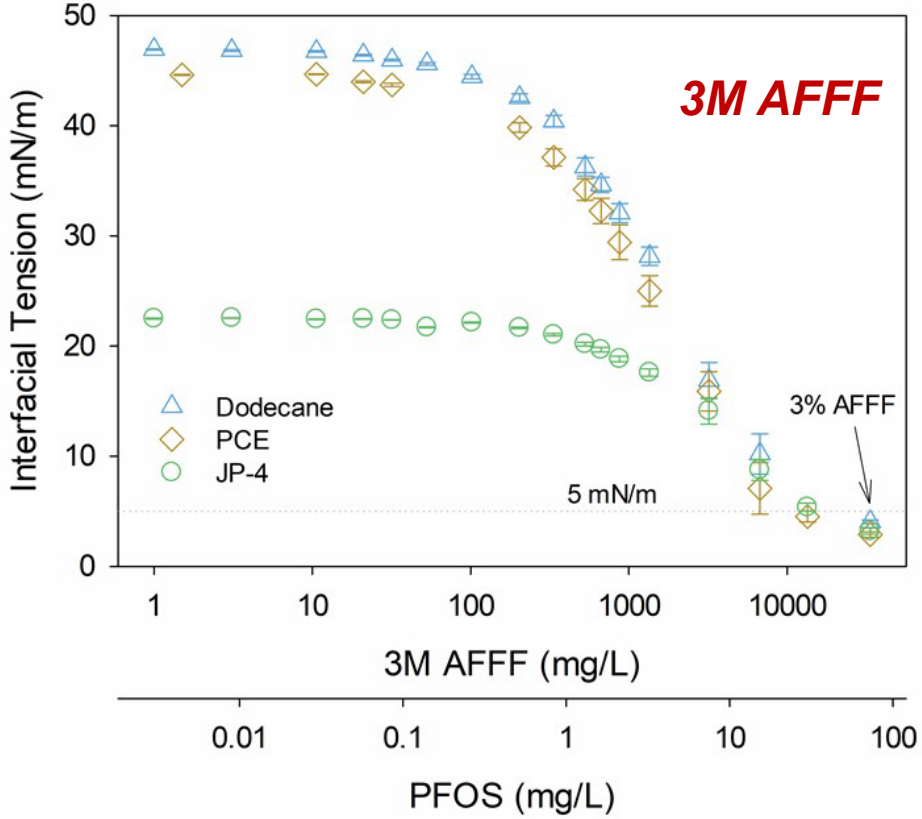
Estimated Surface Excess at NAPL-Water Interface (PFOA)





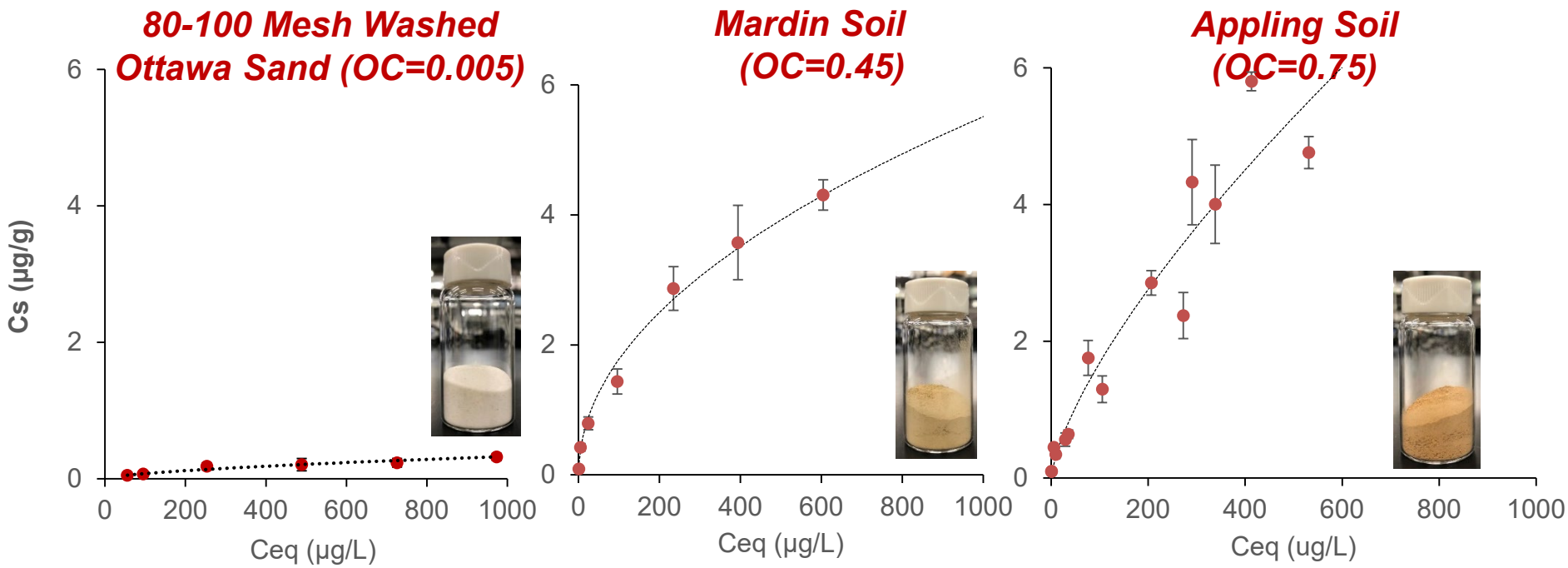
- PFAS accumulation at NAPL-water interface is smaller than at air-water interface
- PFAS exhibits significant accumulation at dodecane- and PCE- water interfaces
- Could form long- term PFAS source if NAPL is present in source zone

NAPL-Water Interfacial Tension (AFFF)



- NAPL IFTs decreased to <4 mN/m at AFFF concentrations >12 g/L
- Potential for mobilization of NAPL in regions where AFFF was applied

Batch Sorption Data (PFOS)

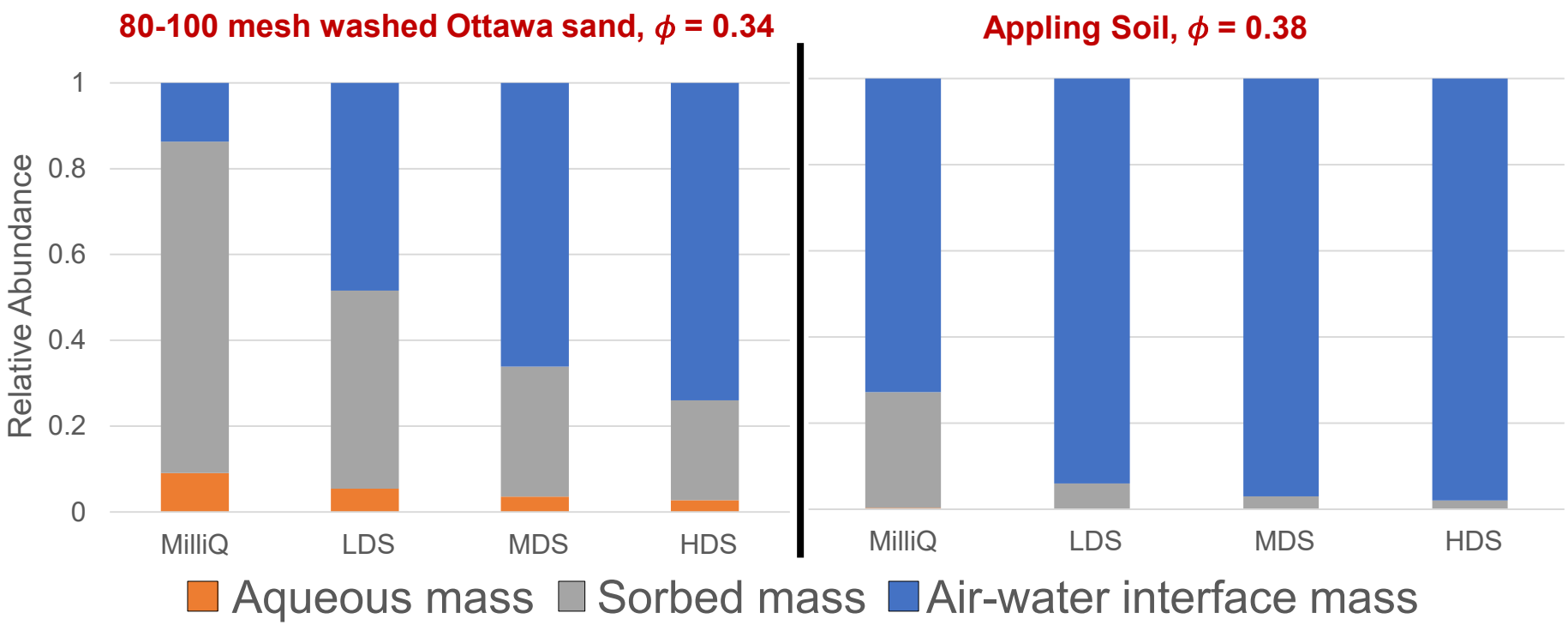


- Higher surface area and higher organic carbon (OC) soils exhibit larger sorption capacity
- Sorption is nonlinear and well-characterized by Freundlich isotherm

Implications: Estimated PFOS Phase Distribution in Two Unsaturated Soils

Total PFOS Mass = Mass in Water + Mass on Solids + Mass at Air-Water Interface

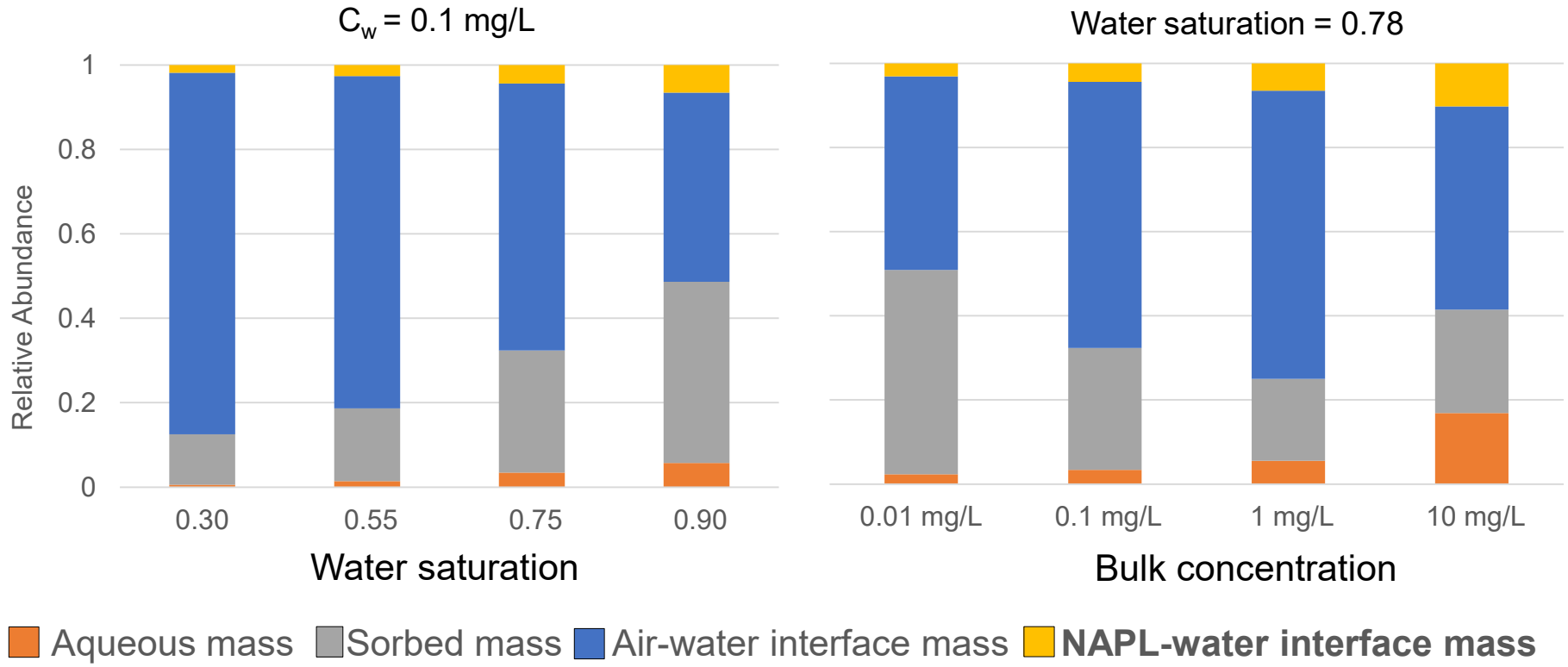
$$M_{Total} = V_T(C_w\,\theta_w + K_f\,(C_w)^n\,\rho_b + \Gamma_{aw}A_{aw})$$



C_w= 0.1 mg/L, Water saturation = 0.78

Implications: PFOS Phase Distribution

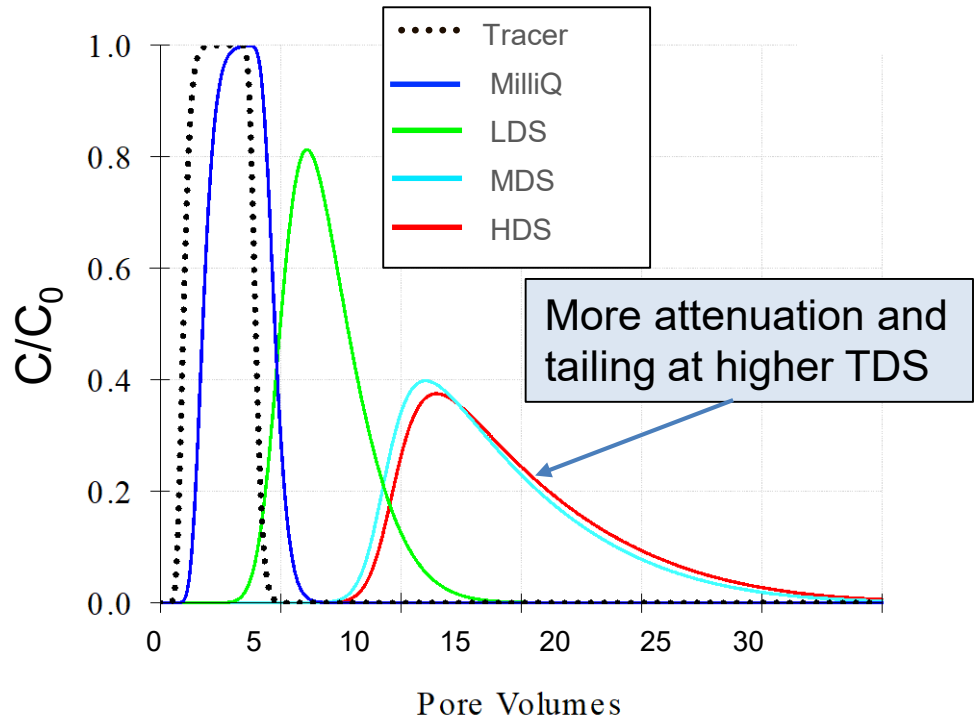
Varying Moisture Content and Concentration

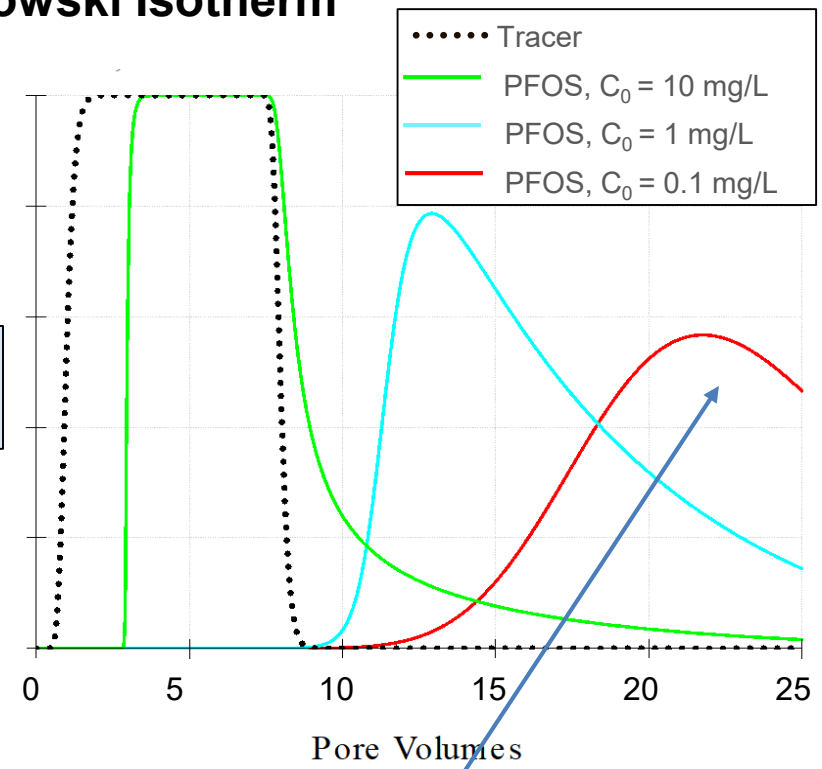


80-100 mesh washed Ottawa sand, ϕ = 0.34, NAPL (Dodecane) saturation = 0.02

Simulations: Effect of TDS and Concentration on PFOS Breakthrough

Langmuir/Szyszkowski Isotherm



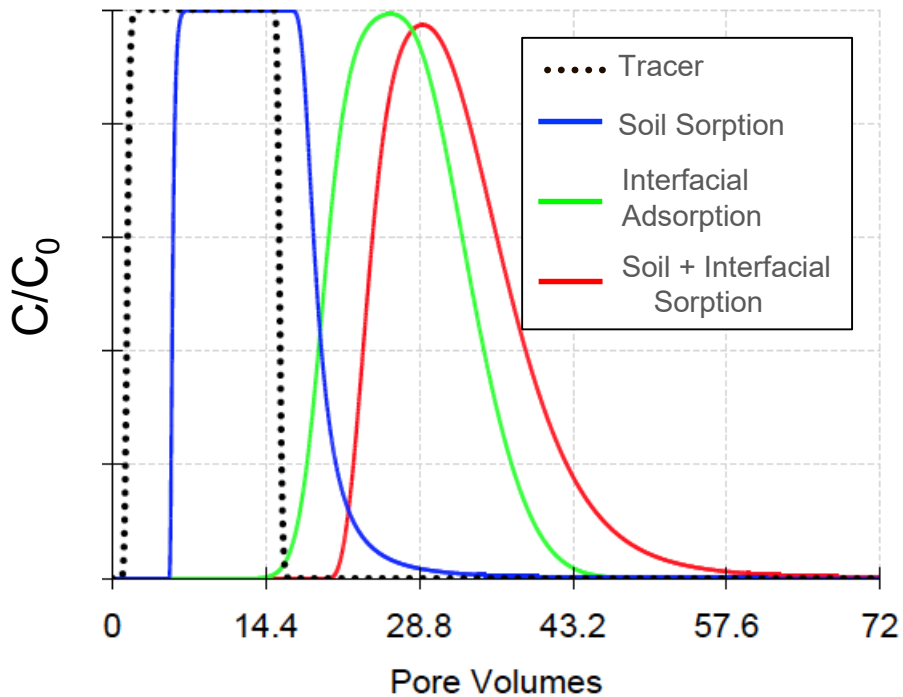


Greater proportion retained at lower concentrations (influence of non-linearity)

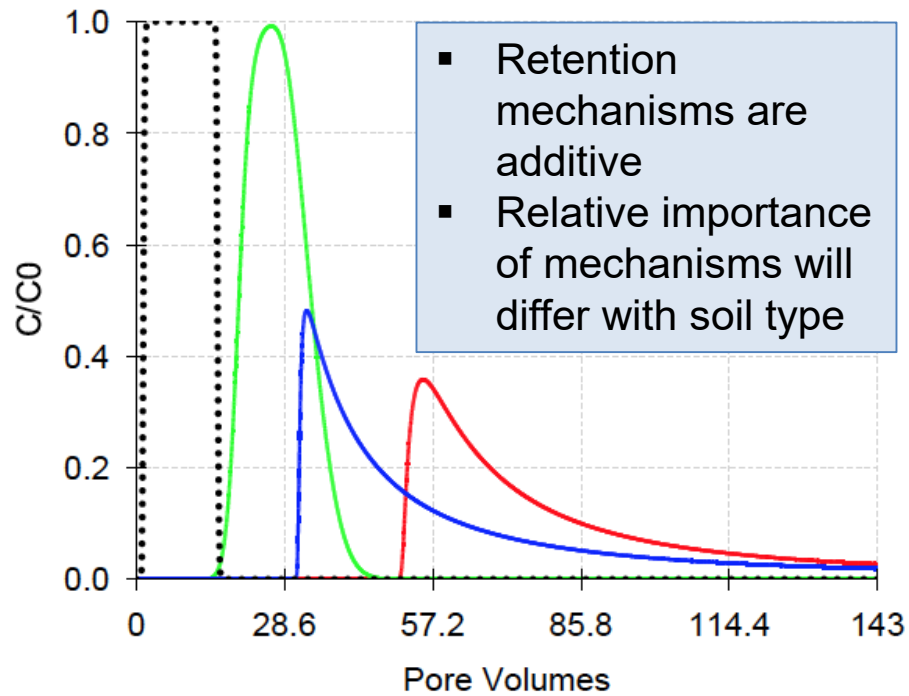
- No sorption
- Pulse injection (3 PV or 7 PV) of PFOS
- F-70 Ottawa sand (40-270 mesh), $\theta_w = 0.27$

Simulations: Coupled Sorption and Air-Water Interfacial Accumulation

Washed Ottawa Sand



Unwashed Ottawa Sand



- Retention mechanisms are additive
- Relative importance of mechanisms will differ with soil type

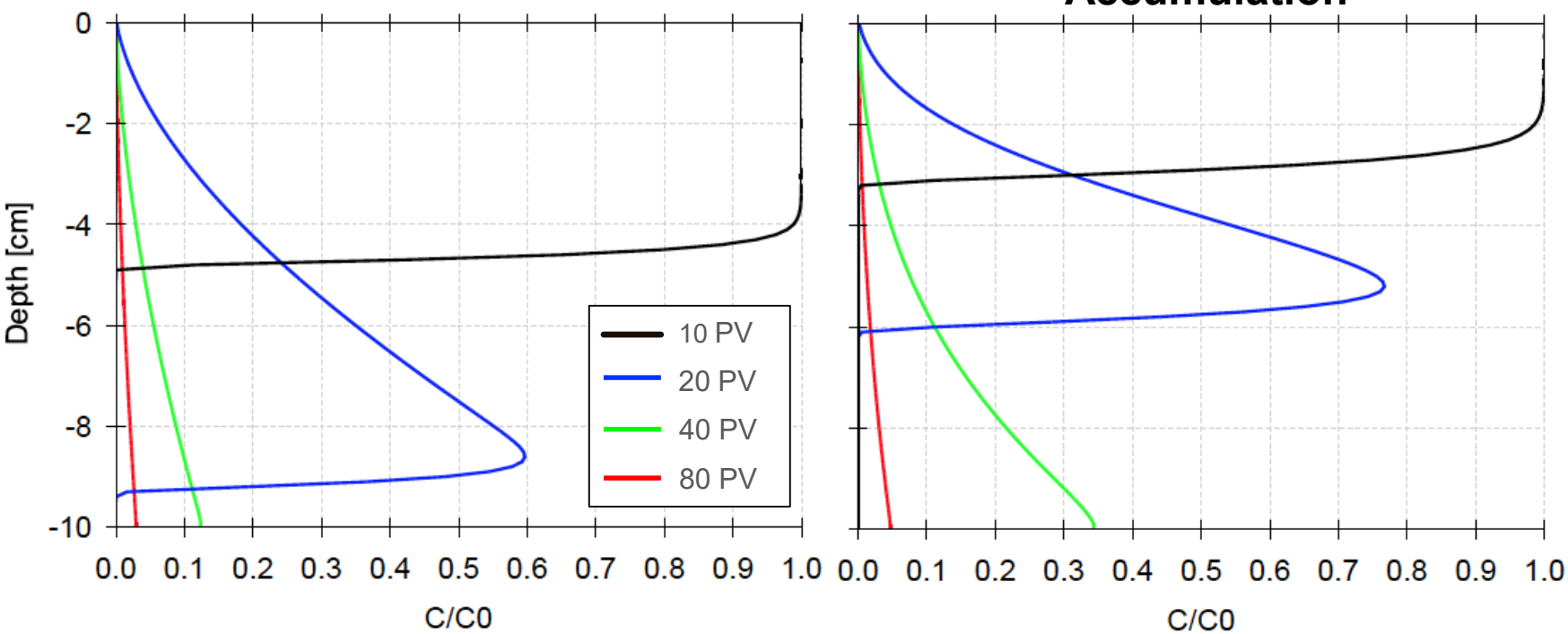
- Pulse injection (10 PV) of PFOS, C0=0.5 mg/L
- 80-100 mesh Ottawa sand, 10 mM NaCl
- $\theta_w = 0.22$, $\phi = 0.34$

- Sorption more important retention mechanism in higher OC soils

Simulations: Infiltration Profiles

80-100 mesh unwashed Ottawa sand

Soil Sorption Only | **Soil Sorption + Air-Water Accumulation**



- Pulse injection (10 PV) of PFOS, **C_0 = 0.5 mg/L**
- 10 mM NaCl
- θ_w **= 0.22**, ϕ = 0.34

- Much of mass is retained on air-water interfaces in profile

Microcosm Experiments

- Using materials from Robins AFB with native microbial community
- PFAS precursor transformation products and rates resulting from natural attenuation (abiotic and biotic) being measured

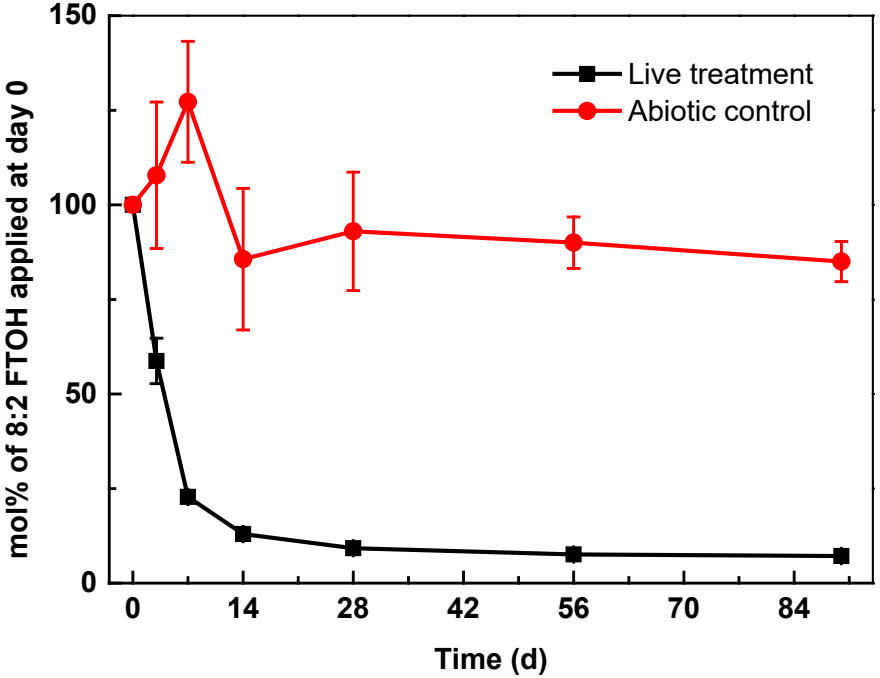
***Example**: 8:2 FTOH [$F(CF_2)_8CH_2CH_2OH$] (PFAA precursor widely used in the manufacturing of fluorotelomer-based products)*

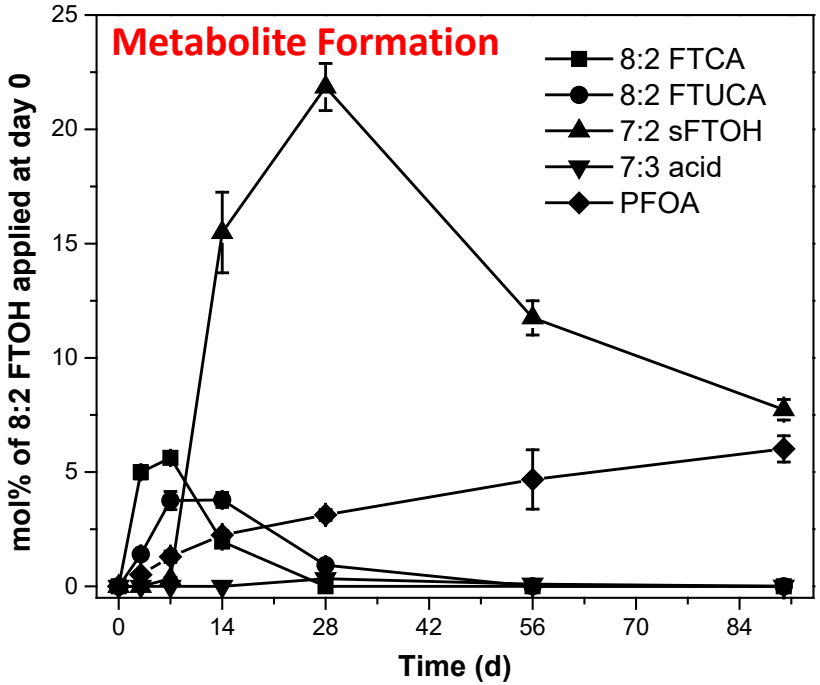
Reactor Set	Microcosms Components
Live treatment	10 g soil + 100 mL medium + 170 µg/L 8:2 FTOH in DGBE
Abiotic control	10 g soil + 100 mL medium + 170 µg/L 8:2 FTOH in DGBE+ 1 g/L of NaN_3
Live control	10 g soil + 100 mL medium + 85 µL of DGBE
Medium - only control	100 mL medium (no soil) + 170 µg/L 8:2 FTOH in DGBE

- First study of 8:2 FTOH fluorotelomer biotransformation potential and mechanisms in AFFF-impacted soil

Aerobic Biotransformation of 8:2 FTOH

Preliminary Results





- 8:2 FTOH was rapidly biotransformed in aerobic AFFF-impacted soil with a half-life less than 5 days

- 8:2 FTOH was initially biotransformed to 8:2 FTCA and 8:2 FTUCA
- 7:2 sFTOH was not detected until day 7, then accumulated rapidly
- PFOA yield reached 6.0% at day 90

Key Findings

- PFAS accumulate at air-water and NAPL-water interfaces
  - They are oleophilic and have surfactant-like properties
- Air-water surface accumulation will:
  - Significantly retard PFAS transport
  - Lead to substantial mass retention in unsaturated soils
- PFAS sorption and interfacial accumulation are nonlinear functions of concentration
- TDS substantially influences interfacial accumulation of PFOA and PFOS at air- and NAPL-water interfaces
  - Greater accumulation at higher TDS

Key Findings (Cont'd)

- NAPL mobilization by PFOA or PFOS not expected at typical field concentrations (<0.1 g/L)
  - However, could occur with AFFF formulations at high concentrations
- PFOS and PFOA could serve as long-term PFAS source if NAPL is present in the source zone
- 8:2 FTOH was rapidly biotransformed to poly- and perfluorinated metabolites in aerobic AFFF-impacted surface soil
  - Half-life <5 days

Benefits to DoD

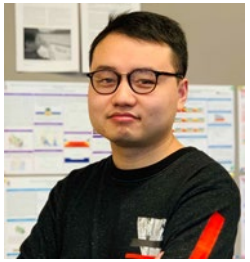
- Increased understanding of key PFAS retention/retardation mechanisms controlling elution and transport from AFFF source zone areas (vadose and saturated zone)
  - Improve site evaluation and risk assessment
- Database of retention properties for representative PFAS and field soils
- Fill key data gaps regarding PFAS biotransformation in AFFF-impacted soils and aquifer materials
- Mathematical modeling tools for:
  - Prediction of the distribution and fate of PFAS in source zones
  - Potential for continuing releases to groundwater plumes
  - Likely success of natural or enhanced attenuation

Acknowledgments

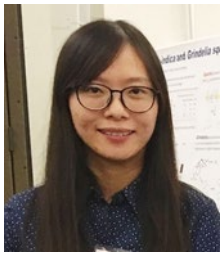
Dr. Kurt Pennell
Brown University

Dr. John Christ
S&B Christ Consulting

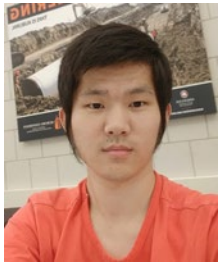
Dr. Masoud Arshadi
Tufts University



Chen Liu



Sheng Dong



Pengfei Yan

Dr. Natalie Cápiro
Auburn University

Dr. Tom Phelan
U.S. Air Force Academy

Dr. Jed Costanza
U.S. EPA

Ana Guedes

Additional Resources

- Costanza, J., M. Arshadi, **L. M. Abriola**, and K. D. Pennell. 2019. Accumulation of PFOA and PFOS at the air-water interface, Environ Sci and Technol Letters, 6(8), 487-491; https://pubs.acs.org/doi/full/10.1021/acs.estlett.9b00355.
- Arshadi, M., J. Costanza, **L. M. Abriola**, and K. D. Pennell. 2020. Comment on "Uptake of Poly- and Perfluoroalkyl Substances at the Air−Water Interface" by Schaefer et al. (2019), Environmental Science & Technology, https://dx.doi.org/10.1021/acs.est.0c01838.
- Costanza, J., **L. M. Abriola**, and K. D. Pennell. 2020. Aqueous film-forming foams exhibit greater interfacial activity than perfluorooctane substances, submitted to Environmental Science & Technology.

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER18-1149

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Q&A Session 1

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*H*ydrothermal *AL*kaline *T*reatment (***HALT***): An Innovative Technology for Complete Destruction of PFAS

Timothy Strathmann, Ph.D.
Colorado School of Mines

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Agenda

- Need for destructive PFAS treatment technologies
- Hydrothermal processes
- Demonstration of PFAS degradation and defluorination
- Technology outlook and opportunities

Current PFAS Treatment Approaches

- Focus on removal, not destruction
- Costly treatment due to frequent absorbent replacement

Granular Activated Carbon (GAC)

Ion Exchange (IX)

PFAS Destruction Challenging Due to Strength of C-F Bonds

- Few claims of slow biodegradation
- Unreactive with common drinking water chemicals
- More intensive interventions required for destruction

PFAS Destruction Challenging Due to Strength of C-F Bonds

Voice of the Rocky Mountain Empire

THE DENVER POST

TUESDAY, SEPTEMBER 10, 2019 MOSTLY SUNNY SKIES ▲87° ▼55° »14A • © THE DENVER POST • $2 PRICE MAY VARY OUTSIDE METRO DENVER ★★

PFAS ACROSS METRO DENVER

"Forever chemicals" found

FIRST LOOK

Groundwater is contaminated at levels thousands of times higher than advised

By Bruce Finley
The Denver Post

Groundwater tests over the past year have detected high levels of toxic "forever chemicals" across the Denver metro area, contamination that's both wider and more severe than previously known.

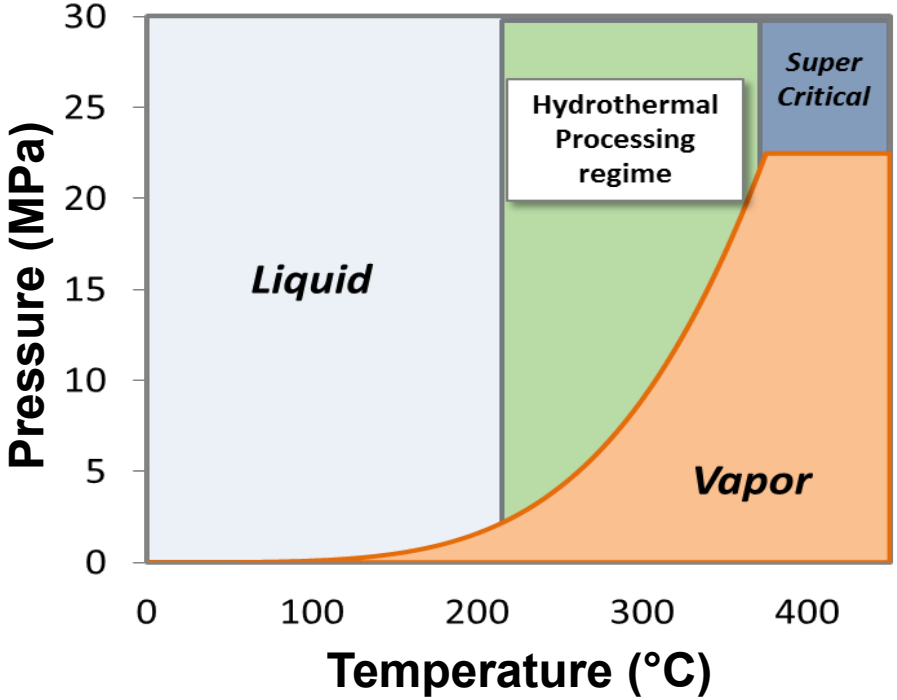
The discovery of these fluorochemicals, known as PFAS, at Buckley Air Force Base, along Sand Creek and at the Suncor oil refinery — as well as at new sites west of Boulder and around Colorado Springs — compelled state health officials this month to ramp up Colorado's response.

Tests have measured PFAS contamination in metro Denver at levels up to 2,928 times higher than a federal health advisory limit, offi-

- Few claims of slow biodegradation
- Unreactive with common drinking water chemicals
- More intensive interventions required for destruction

Effectiveness of Hydrothermal Technologies for PFAS Destruction

- Properties of water change as near critical temperature
- Hydrothermal processing exploited for biomass conversion to fuel
- Efficient for thermal processing of "wet" feeds



H_2O: $\Delta H_{25 \rightarrow 350}$ = 1.1 MJ/kg
ΔH_{vap} = 2.6 MJ/kg

Technical Approach

Amendments

H_2O

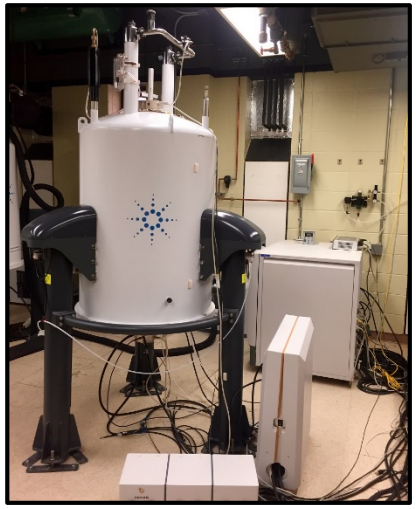
PFAS

Heat

200-350°C

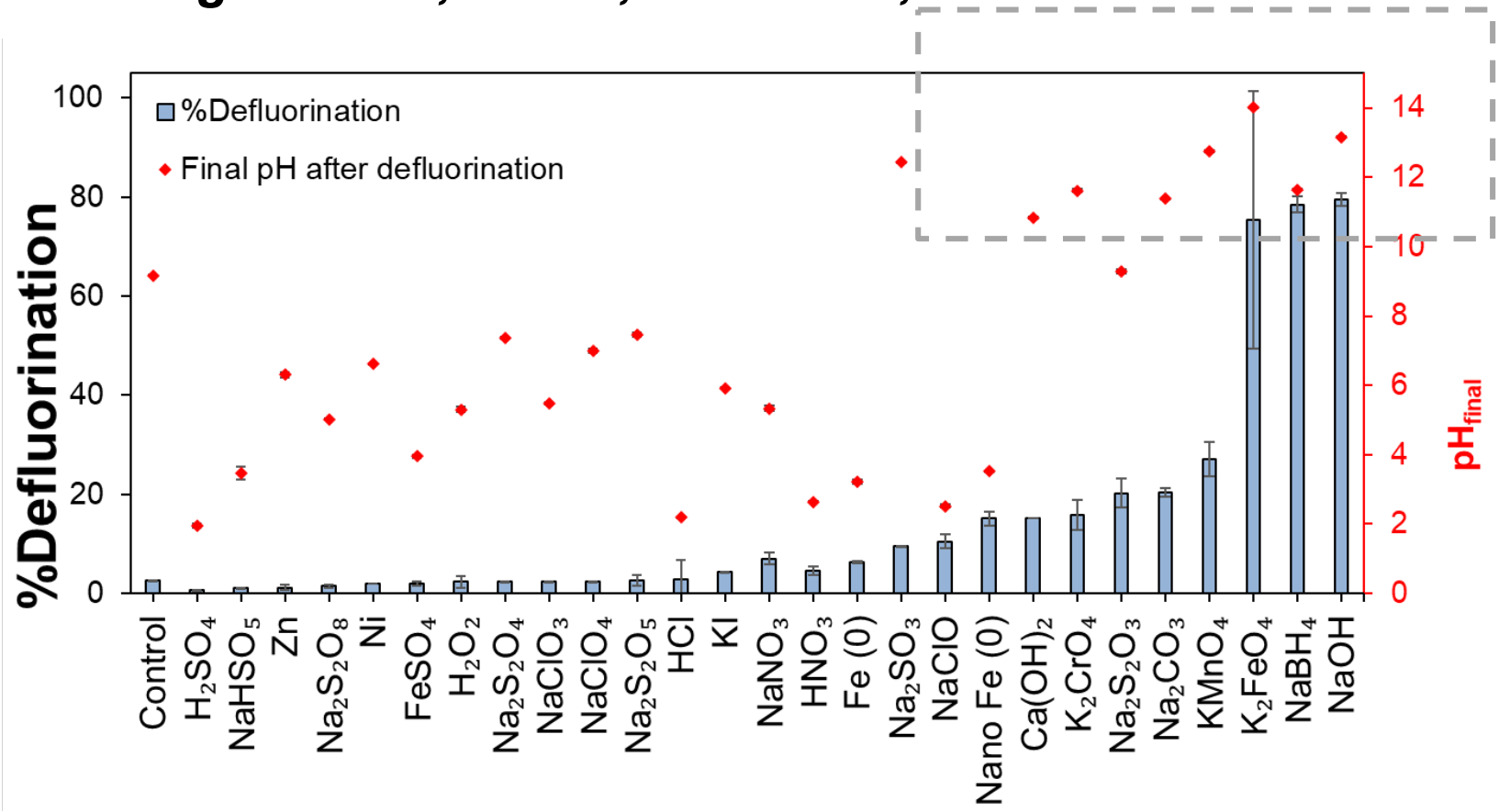
LC-QToF-MS,
LC-MS/MS
(*% Degradation*)

F^- ISE
(*% Defluorination*)



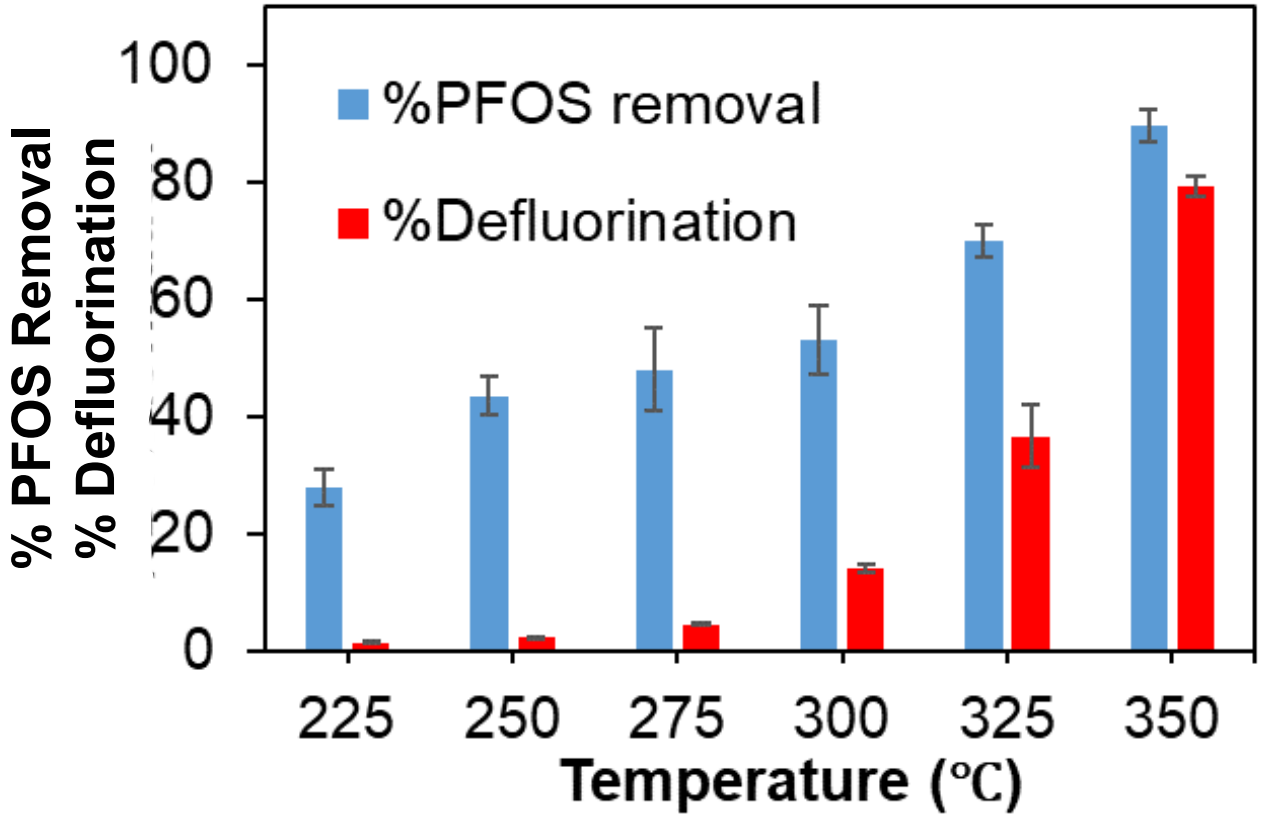
Alkali Amendments Promote PFOS Destruction

50 mg/L PFOS, 350°C, t = 90 min,1 mol/L amendment

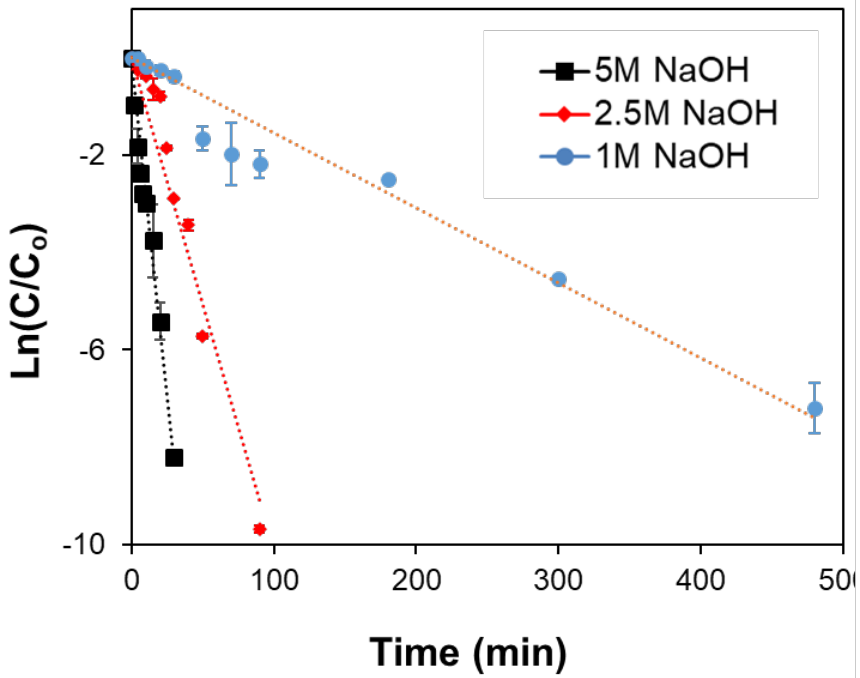


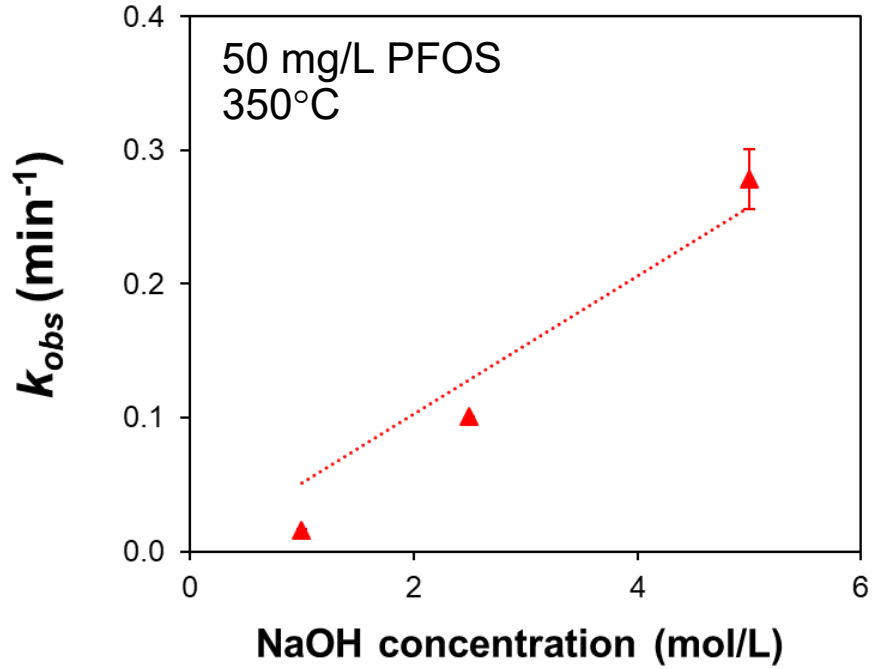
PFOS Destruction Rate Depends on Temperature and Alkali Concentration

50 mg/L PFOS, t = 90 min, 1 mol/L NaOH

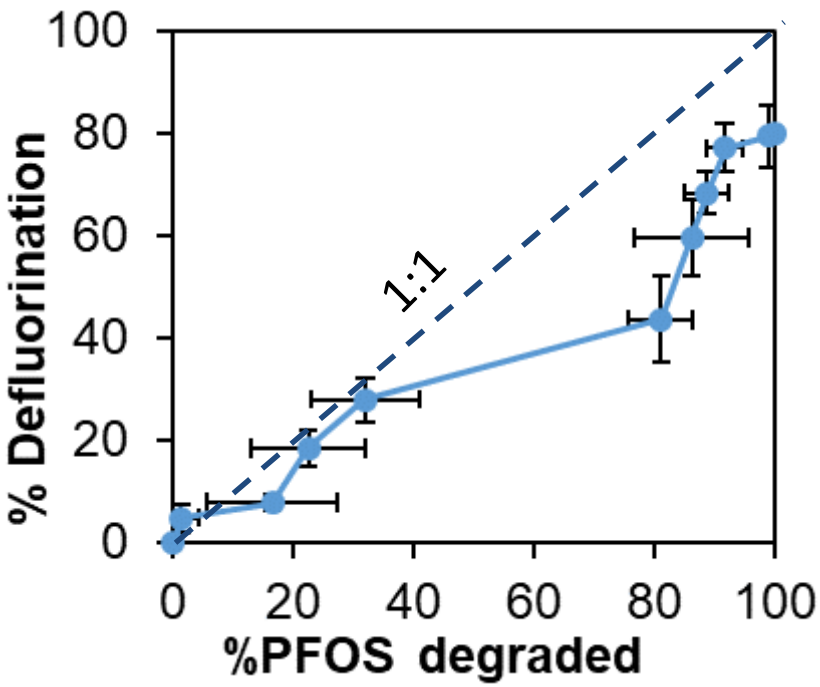


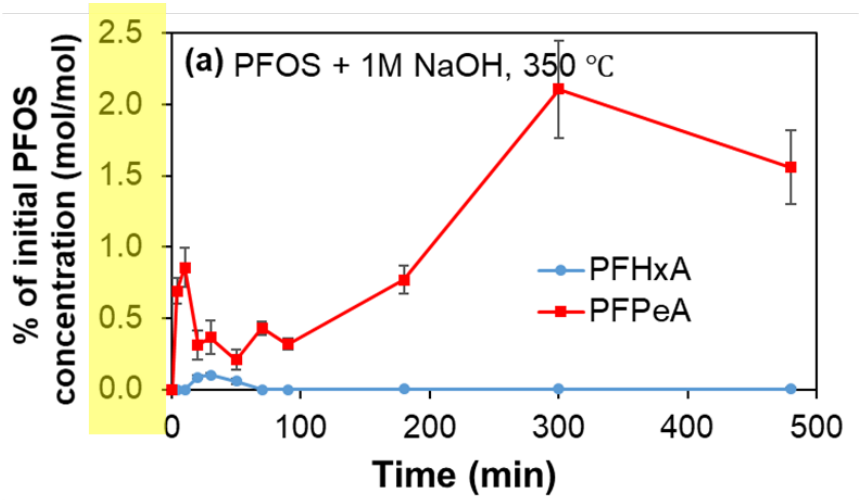
PFOS Destruction Rate Depends on Temperature and Alkali Concentration

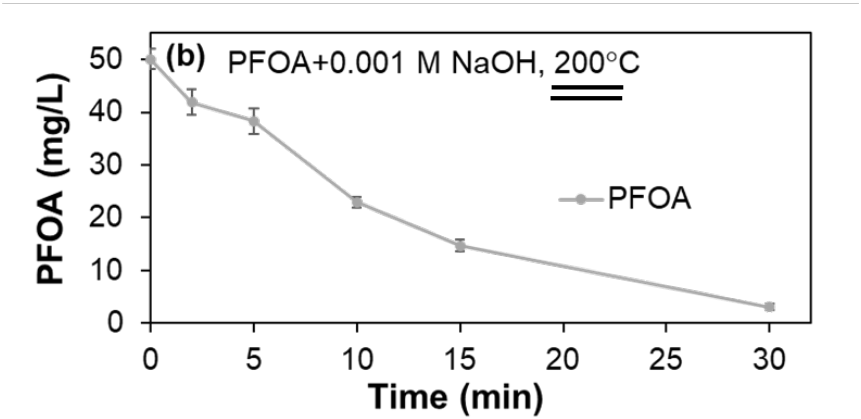




Complete Defluorination and Limited Organic Intermediates





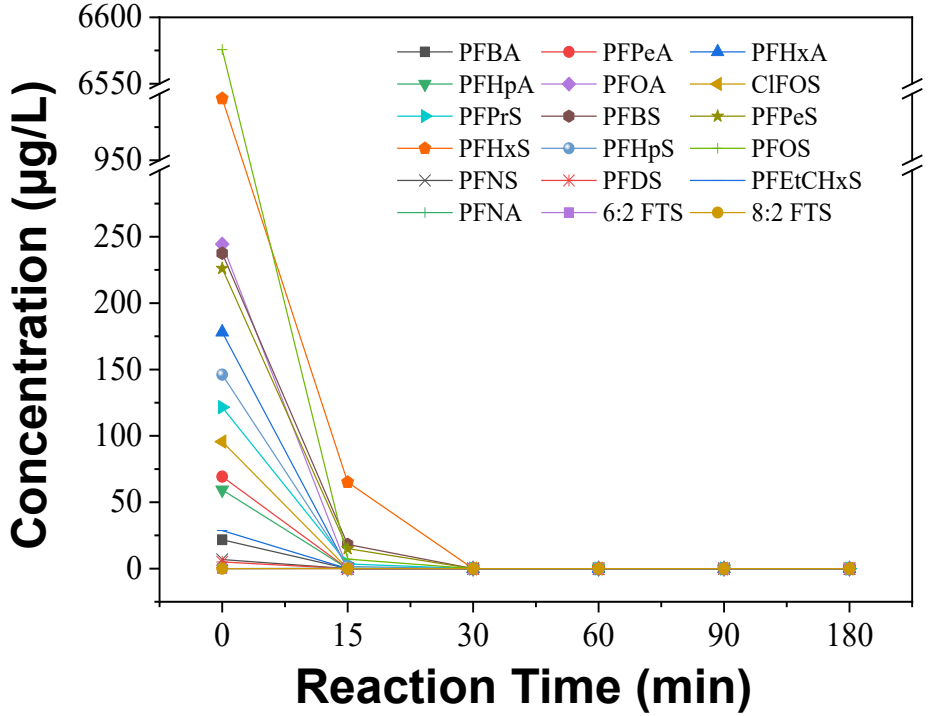


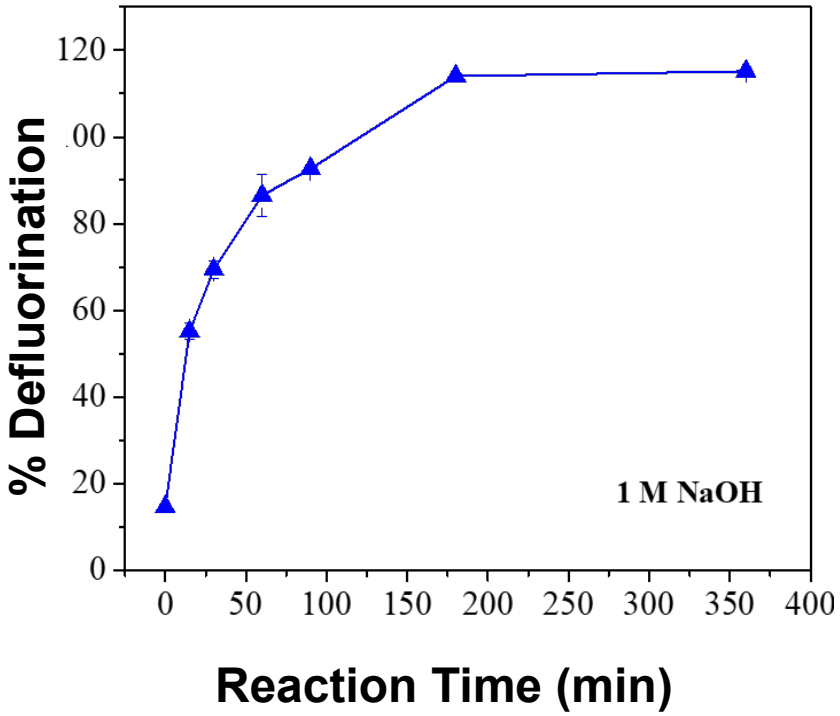
- *PFOA destruction occurs rapidly without amendments*

All PFAS Detected in AFFF Degraded and Defluorinated by *HALT*

***Image source**: U.S. Fire Administration*

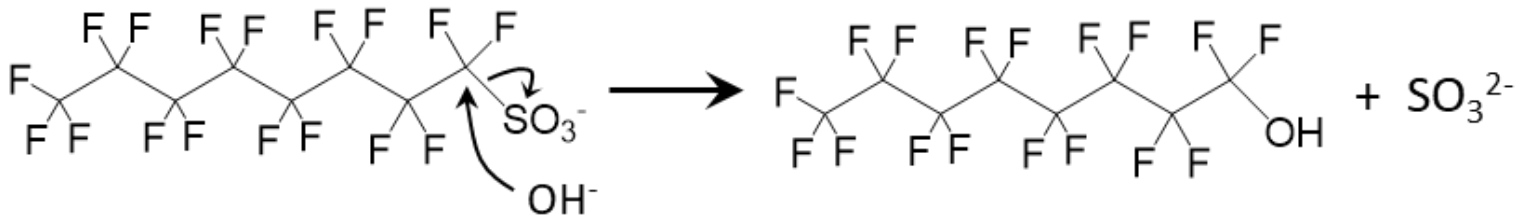
All PFAS Detected in AFFF Degraded and Defluorinated by *HALT*



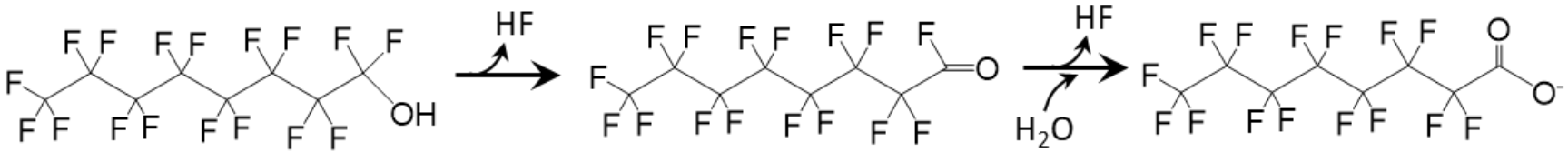


Findings Support a Tentative Reaction Mechanism

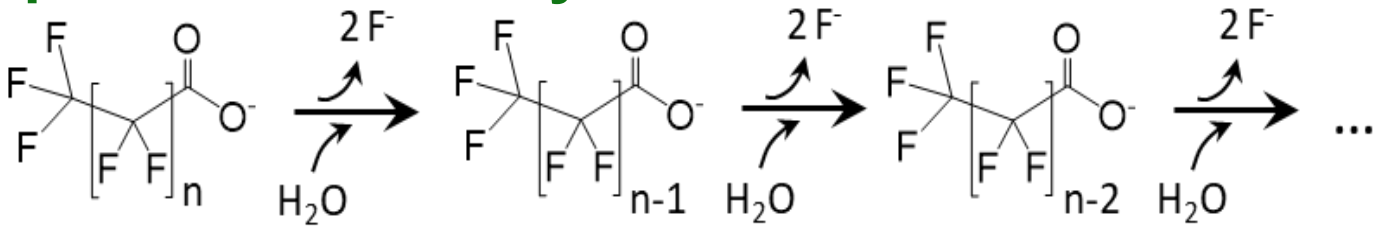
1) Nucleophilic attack



2) Hydrolysis



3) Sequential decarboxylation



Demonstrated PFAS Destruction in Contaminated Soil from DoD Sites

350°C, t = 90 min,
20% solids, 5 M NaOH

PFAS	Concentration (ng g^{-1})	Destruction %
PFOA	150	>99%
PFOS	22,900	94%
PFHxA	340	>99%
PFHxS	3,960	93%
FOSA	223	>99%
MeFOSAA	619	>99%
6:2 FTS	215	>99%
PFNS	1,894	>99%
PFDS	1,388	>99%

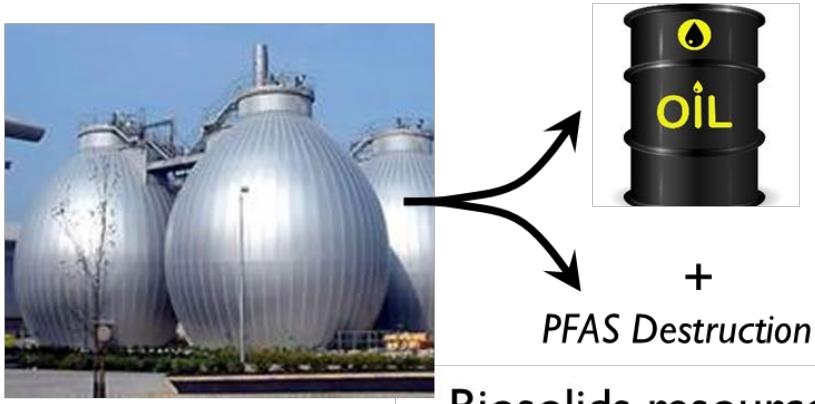
Less Energy Required to Treat Wet PFAS Waste Compared to Incineration

Treatment Process	Input Heat (kWh/m^3)
HALT	
Reaction at 350°C (no heat recovery)	317
Reaction at 350°C (60% heat recovery)	127
Incineration	
Combustion at 1,100°C (no heat recovery)	1,336
Combustion at 1,100°C (60% heat recovery)	534

Potential for Many Applications

Industrial waste

Destruction of AFFF stockpiles



Biosolids resource recovery

Conclusions

- Results demonstrate an innovative technology for PFAS destruction
- Hydrothermal conditions + low-cost alkalis (e.g., NaOH) promote PFAS destruction
- Full suite of PFAS detected in AFFF and degraded and defluorinated
- Successful tests with PFAS-containing soil and water from DoD sites

Benefits to DoD

- Technology uniquely suited for treatment of wet PFAS-containing wastes
  - Source zone soil/sediments
  - Liquid IDW
  - Unused AFFF stockpiles
- Lower-energy alternative to off-site incineration
- Potential development of mobile on-site treatment units

Additional Resources

- B. Wu, S. Hao, Y. Choi, C.P. Higgins, R. Deeb, and **T.J. Strathmann**. (2019). Rapid Destruction and Defluorination of Perfluorooctanesulfonate by Alkaline Hydrothermal Reaction. *Environmental Science & Technology Letters.* 6, 630-636. DOI: https://doi.org/10.1021/acs.estlett.9b00506
- Yu, A. Nickerson, Y. Li, Y. Fang, and **T.J. Strathmann** (2020). Fate of Per- and Polyfluoroalkyl Substances (PFAS) during Hydrothermal Liquefaction of Municipal Wastewater Treatment Sludge. *Environmental Science: Water Research and Technology*. 6, 1388-1399. DOI: https://doi.org/10.1039/C9EW01139K

For additional information, please visit https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1501

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Q&A Session 2

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The next webinar is on August 20, 2020

Addressing Threatened and Endangered Species on DoD Lands

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Survey Reminder

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

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