Transport and Remediation of Per- and Polyfluoroalkyl Substances (PFAS) in the Subsurface

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ADELAIDE 2019

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Research Objectives

- Improve our understanding of mechanisms governing the transport and persistence of PFAS in unsaturated soils and aquifer formations
- Develop and validate mathematical models that account for key processes controlling the transport and retention of PFAS in complex AFFF release areas
- Develop and test *in situ* remediation strategies to treat PFAS-impacted soils and groundwater

SERDP DOD ▪ EPA ▪ DOE

Projects ER18-1149 and ER-2714

Surface Active Agents (Surfactants)

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Properties and Nomenclature:

- Amphiphilic (polar and nonpolar moieties): Hydrophilic "head" group + Hydrophobic "tail" group
- Strong tendency to accumulate at interfaces (air-water, NAPL-water)
- Individual molecules (monomers) self assemble to form micelles as the aqueous phase concentration increases
- Classification based on the polar head group:

  Anionic, Cationic, Nonionic, Amphoteric, Zwitterionic

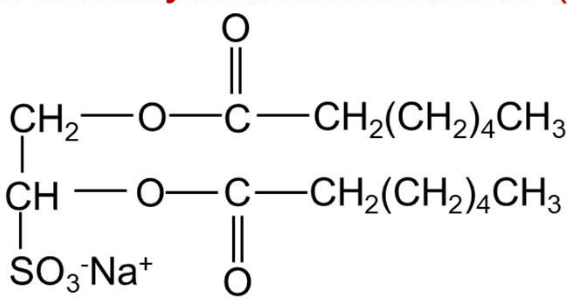
Examples of Anionic Surfactants

Sodium dodecyl sulfate (SDS):

$C_{12}H_{25}OSO_3^{-}Na^{+}$

MW = 288 g/mole
CMC = 2,100 mg/L

Sodium dihexylsuflosuccinate (SDHSS, Aerosol MA-100):



MW = 388 g/mole
CMC = 5,360 mg/L

- Anionic surfactants are sensitive to salt!!
- Salts can impact the CMC, IFT, phase behavior and aqueous solubility

Perfluorooctane sulfonic acid (PFOS)

$C_8HF_{17}SO_3$ — MW = 500 g/mole

$C_8F_{17}SO_3^{-}K^{+}$ — MW = 538 g/mole

CMC = 4,000-5,000 mg/L

....Aqueous solubility has been reported to be less than 1,000 mg/L

Critical Micelle Concentration (CMC)

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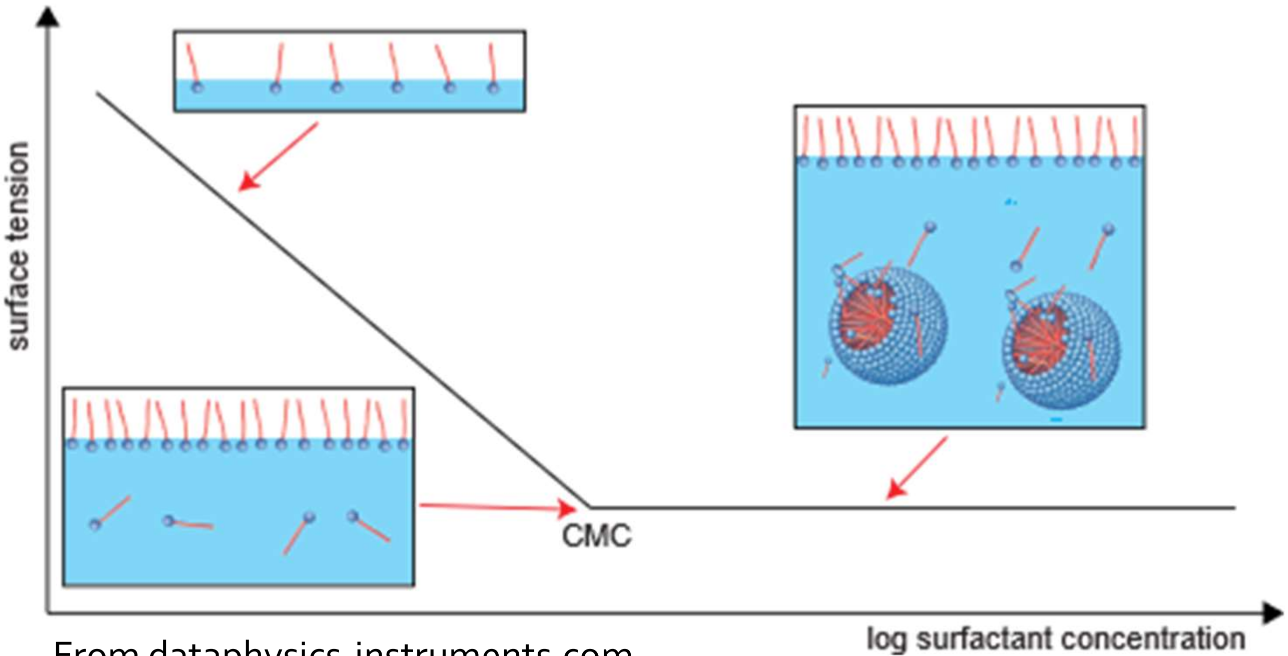

From dataphysics-instruments.com

- Above the CMC, the number of monomers remains constant, while the number of micelles continues to increase
- Surface tension remains constant above the CMC because the air-water interface is saturated

Interfacial Tension Instrumentation

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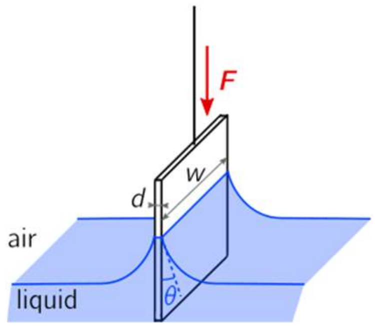
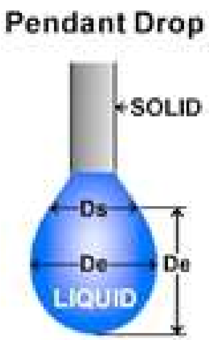
Sigma T700 Tensiometer

Resolution of
0.01 mN/m



Surface Tension by
Wilhelmy Plate

Ramé-Hart Goniometer



Interfacial Tension by
Pendant Drop

Note: mN/m = dyne/cm = g/s^2

Solutions for IFT Measurements

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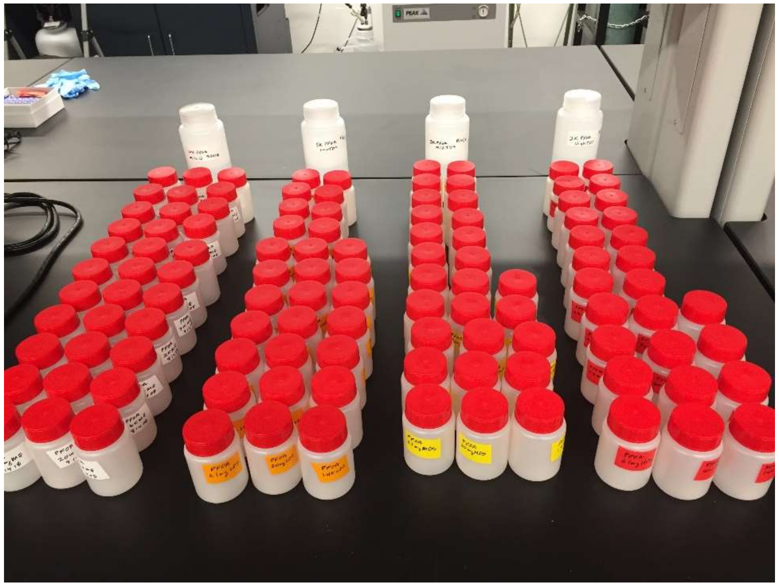
- Stock solutions ranged from 50 to 10,000 mg/L
  - PFOA or KPFOS solids using analytical balance
  - Sonicating for 30 min and heating overnight at 40 ^{o}C to dissolve
- Concentrations from 0.1 to 50 mg/L prepared by serial dilution from stock
- Concentrations verified by LC-MS/MS
- To simulate principal aquifers in US, aqueous solutions contained $MgSO_4$, $NaHCO_3$, KCl, and $CaCl_2$
  - **Low Dissolved Solids (LDS)** ~40 mg/L (high purity drinking water) ~9 mM
  - **Mid Dissolved Solids (MDS) ~**400 mg/L (secondary drinking water standard) ~90 mM
  - **High Dissolved Solids (HDS)** ~1,700 mg/L (unpleasant drinking water) ~380 mM



PFOA and PFOS working solutions from 0.1 to 10,000 mg/L in 100-mL HDPE bottles

Check for Solubility Issues

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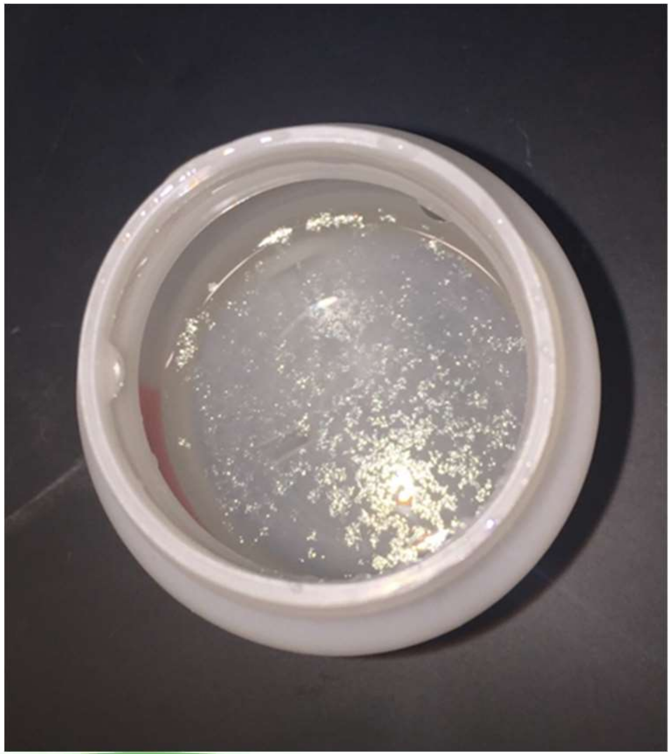
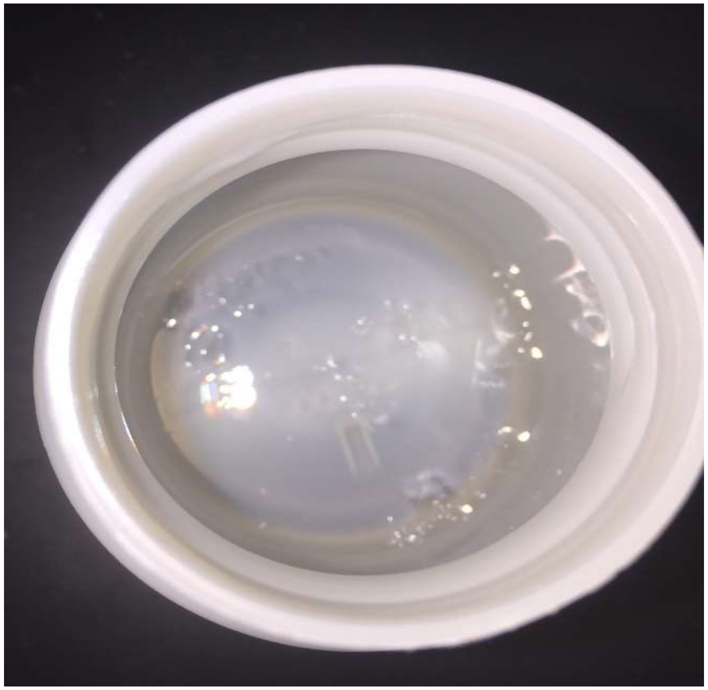
500 mg/L KPFOS in 1,700 mg/L TDS

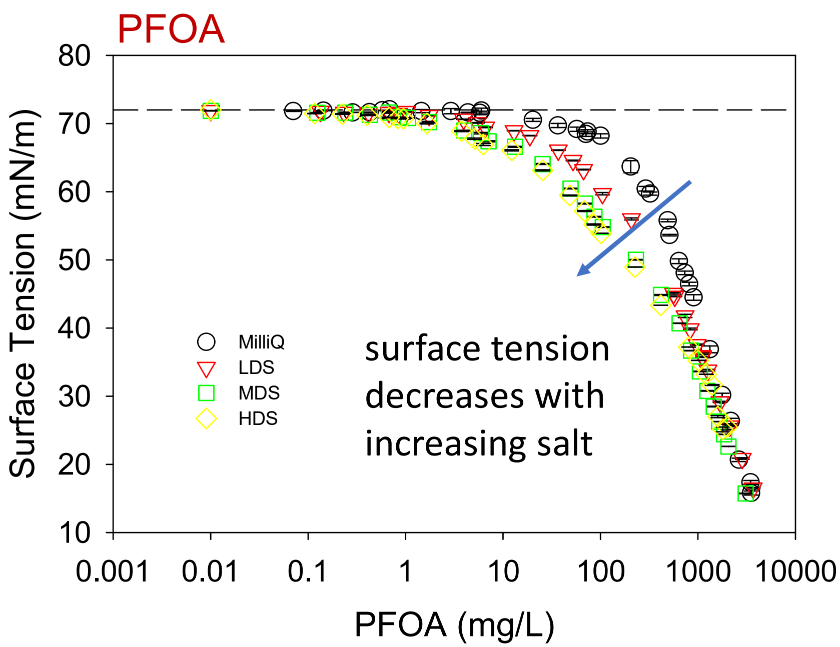


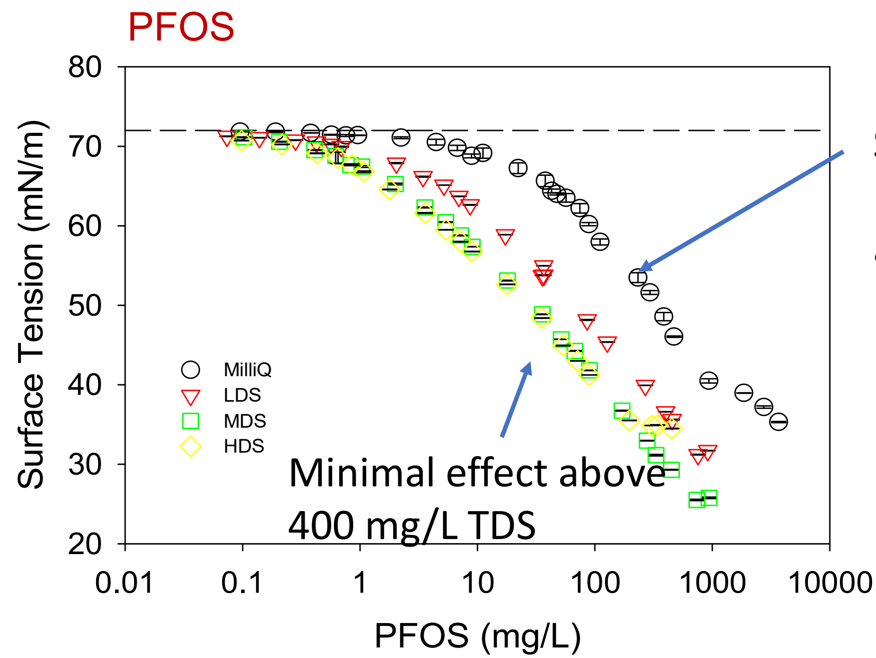
5,000 mg/L PFOA in ultrapure water



Air-Water Interfacial (Surface) Tension:

Effect of Salt Concentration





Similar decrease, but more apparent for PFOS

Costanza et al., 2019, *ES&T Letters*

Fitting Surface Tension Data:
Gibb's Surface Excess Equation

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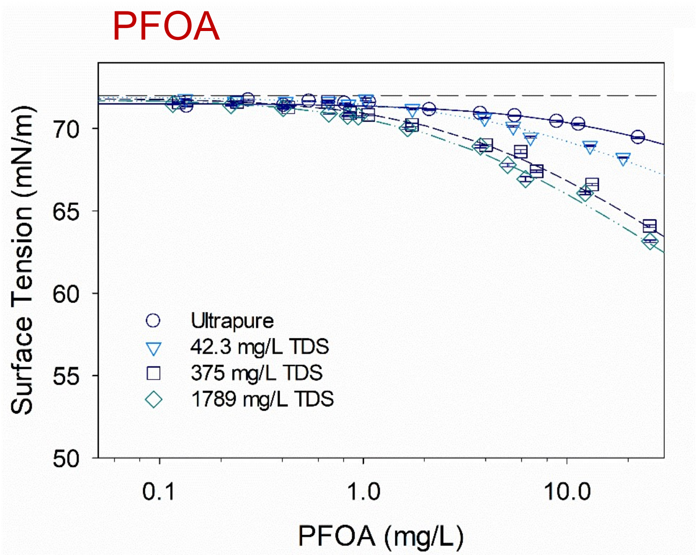

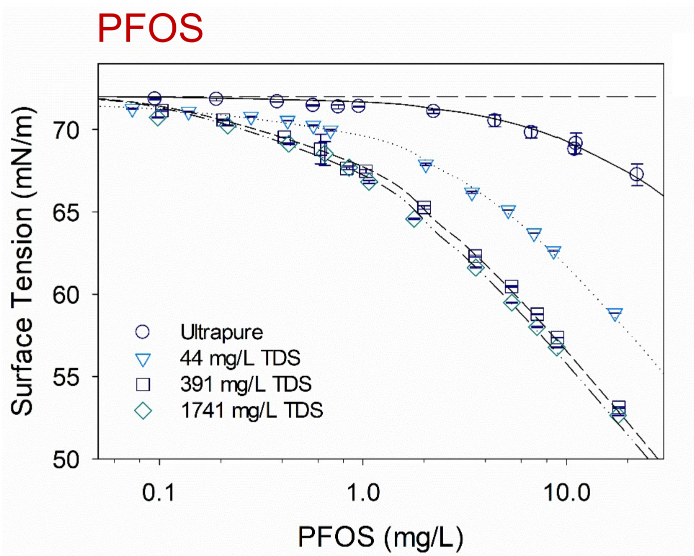

Interfacial tension is a measure of surface concentration or "excess" (Γ)

[Langmuir, 1917]

$$\Gamma = -\frac{C}{RT}\left(\frac{\partial \gamma}{\partial C}\right)_T \longrightarrow \gamma = \gamma_0\left[1 - a * ln\left(\frac{C}{b} + 1\right)\right] \longrightarrow \Gamma = \frac{a\gamma_0}{RT}\frac{C}{C + b}$$

Gibb's Equation Szyszkowski Equation Langmuir/Szyszkowski Eq.

Calculation of Surface Excess:
Equation Development

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Linear Form

$$\Gamma = -\frac{C}{RT}\left(\frac{\partial \gamma}{\partial C}\right)_T \longrightarrow K_i = \frac{1}{RT}\frac{\partial \gamma}{\partial \mathrm{C}} \longrightarrow \Gamma = K_i C_w$$

K_i = Linear Partition Coefficient (L/m^2)

Natural Log Form

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_T \longrightarrow K_i = \frac{1}{RT}\frac{\partial \gamma}{\partial \ln \mathrm{C}} \longrightarrow \Gamma = K_i \frac{C_w}{C_{ref}}$$

K_i = Natural Log Partition Coefficient (mg/m^2)

requires an arbitrary reference conc.

(e.g., Lyu et al., 2018, C_{ref}= 1 mg/L)

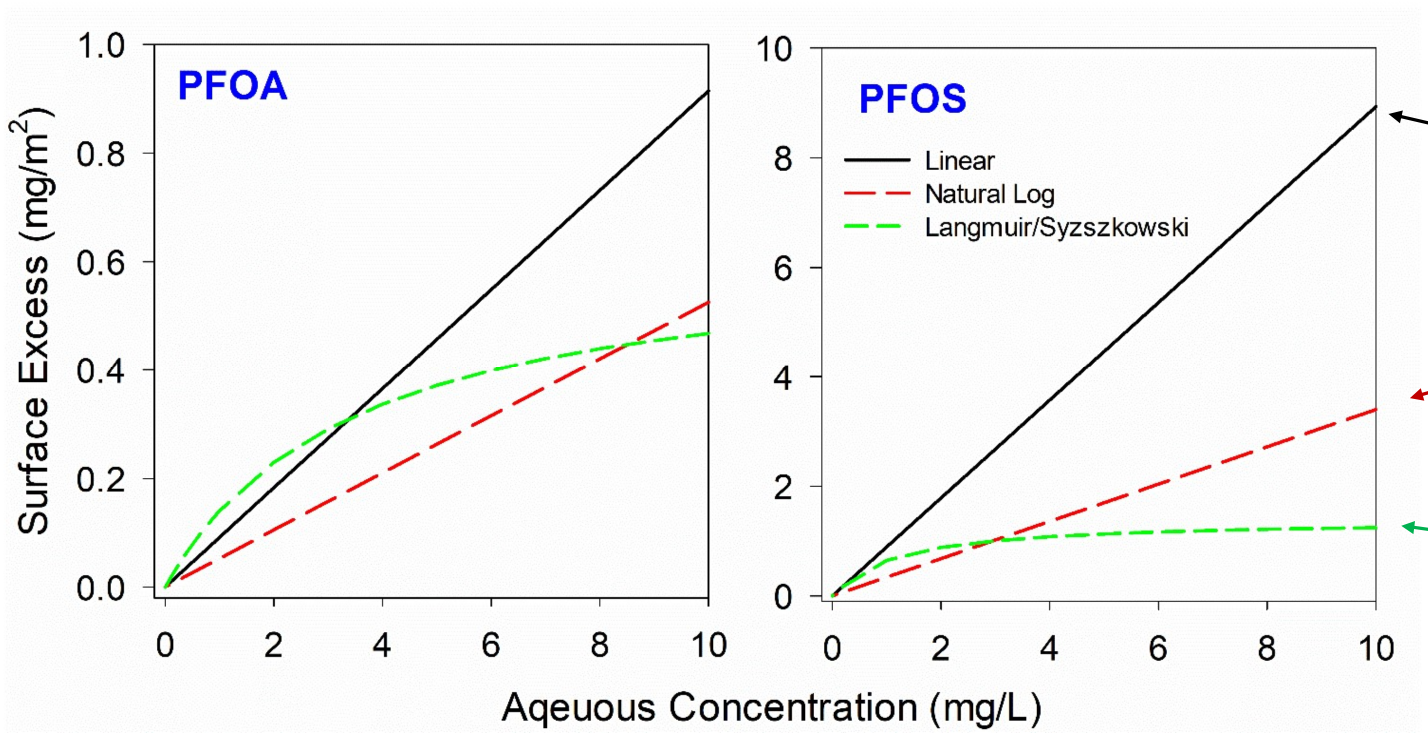
Nonlinear Form (Langmuir/Szyszkowski)

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

No partition coefficient, calculate directly from fit to surface tension data

Surface Excess Calculations:

Comparison of Different Approaches



Note: different y-axis scale

Linear

$$\Gamma = K_i C_w$$

Natural Log

$$\Gamma = K_i \frac{C_w}{C_{ref}}$$

Langmuir/Szyszkowski

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

Phase Distribution in Unsaturated Soils:
Langmuir/Szyszkowski Equation

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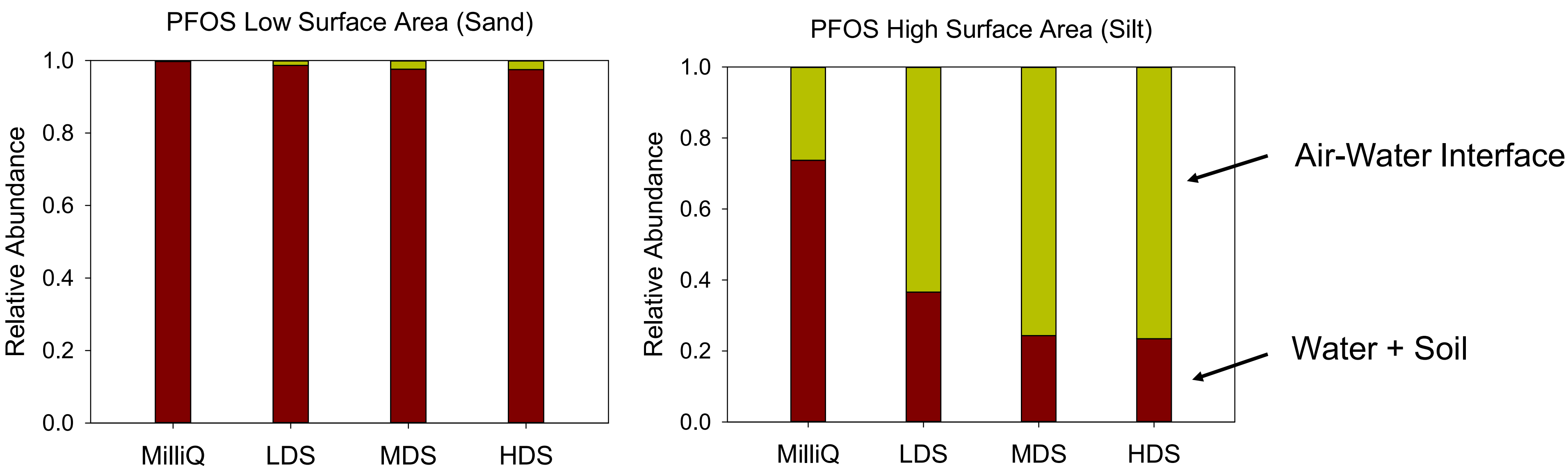

Total PFOS Mass = Mass in Water + Mass on Solids + Mass at Air-Water Interface

$$M_{Total} = V_T(C_w S_w + C_w K_D \rho_b + S_a \frac{a\gamma_0}{RT} \frac{C}{C+b})$$

Modeling PFAS Adsorption at Air-Water Interface

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Incorporate PFAS adsorption at air-water interface using a modified version of Hydrus

Richards Equation: $\frac{\partial \theta}{\partial t} = \nabla \cdot (k.\nabla h) + \frac{\partial k}{\partial z} + S$

$$\frac{\partial}{\partial t}\left(\varphi s_\alpha C_i^\alpha\right) + \nabla \cdot \varphi s_\alpha \left(C_i^\alpha V^\alpha - D_i^{h^\alpha} \nabla C_i^\alpha\right) = \varphi \sum_\beta E_{\alpha\beta_i} + R_i^\alpha$$

$$E_{ai}^i = -A_{ai}\frac{\partial \Gamma^i}{\partial t}$$

Langmuir Isotherm: $\Gamma^i = \frac{a\gamma_0}{RT}\frac{C^i}{C^i + b}$

a and *b*: Szyszkowski eq. parameters fitted using batch experimental results

Linear Isotherm: $\Gamma^i = K_i C^i$

K_i : linear partitioning coefficient

Specific Interfacial Area $[\mathrm{L}^{-1}]$, $A_{ai} = \mathrm{SA}\left(0.9031 - 0.9012\frac{\theta}{\theta_s}\right)$

SA: Geometric su rface area $[\mathrm{L}^{-1}] = \frac{6(1-\varphi)}{d_{50}}$

(Costanza-Robinson et al., 2008)

θ_w: *water content*, θ_s: *saturated water content*, φ: *porosity*, s_α: *saturation of* $\alpha -$ *phase*

Effect of PFAS Accumulation at Air-Water Interface on Unsaturated Zone Transport

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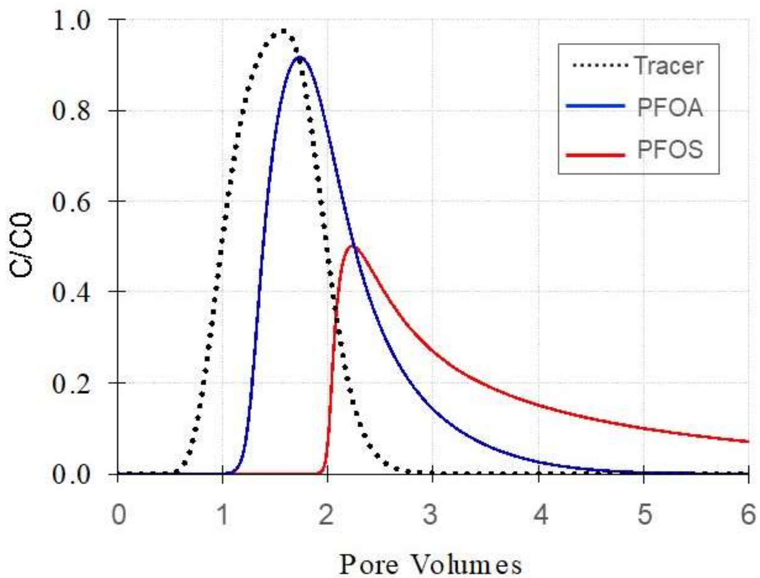
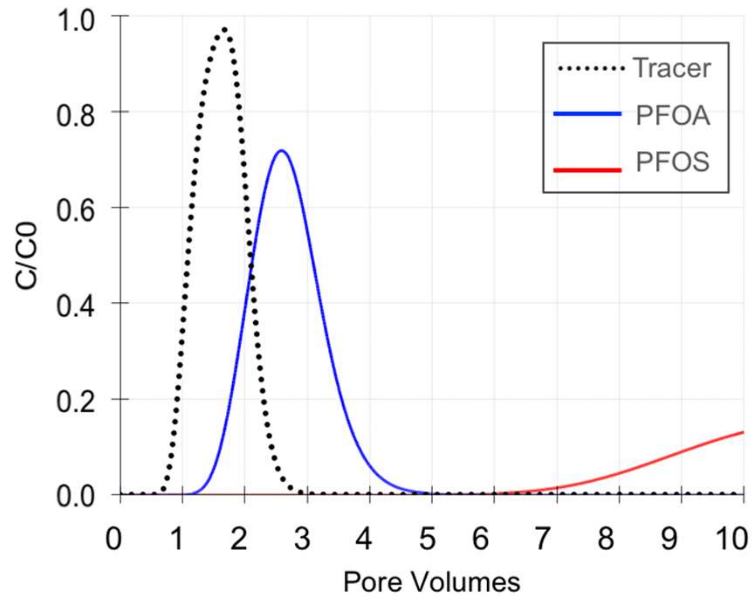
Langmuir/Szyszkowski Equation



Linear Partition Coefficient

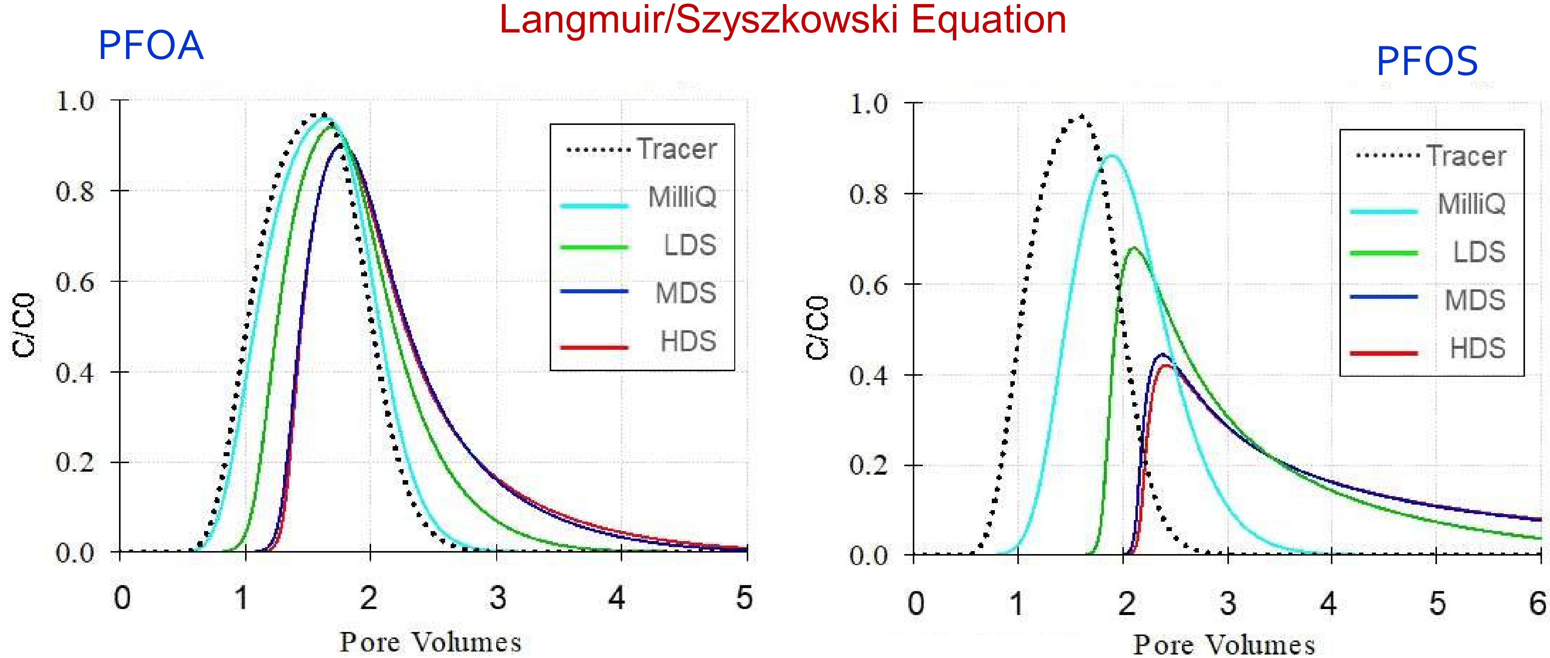


More retention at air-water interface with linear isotherm assumption

- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- Medium level of total dissolved solids (400 mg/L TDS)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

Effect of Salt Concentration on Unsaturated Zone Transport of PFAS

Langmuir/Szyszkowski Equation



- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

Effect of Soil Water Content and TDS on PFOS Transport

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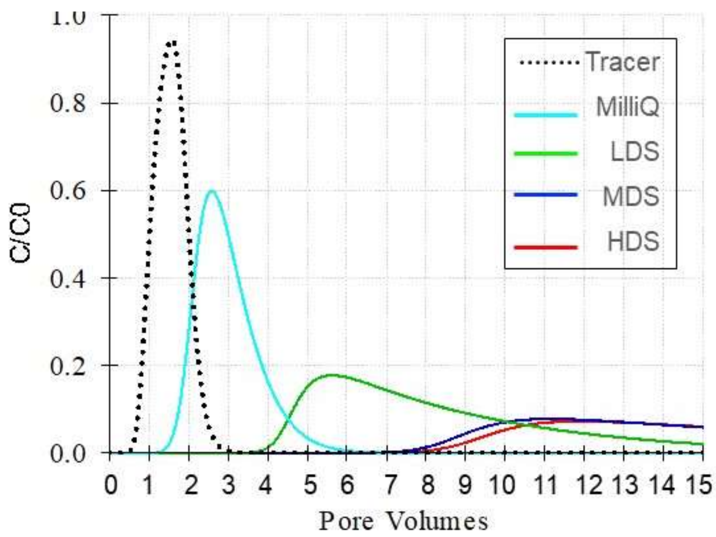
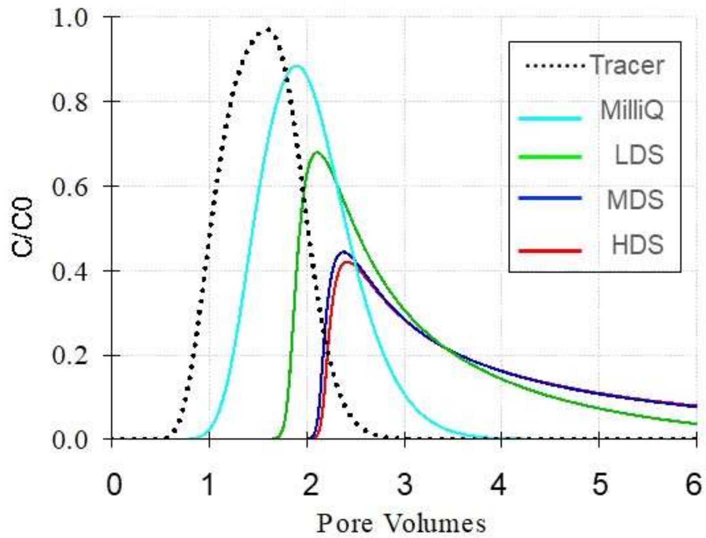
Langmuir/Szyszkowski Isotherm

θ_w= 0.20



θ_w= 0.27



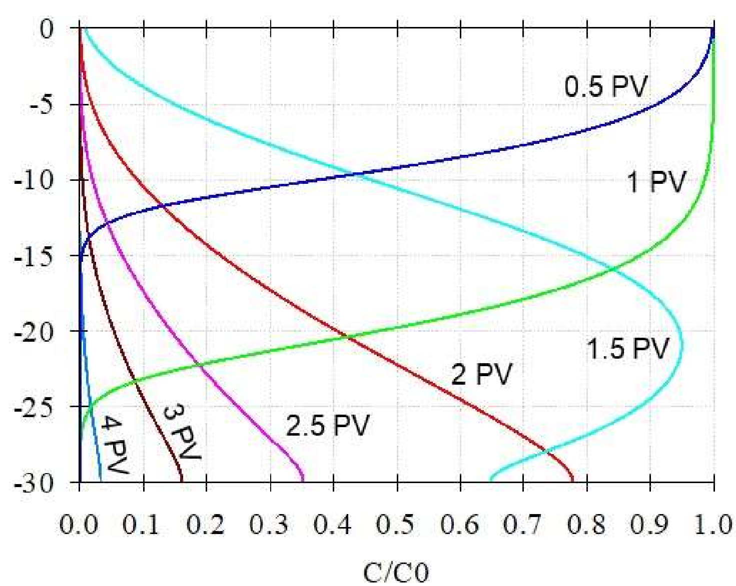
Relatively small changes in soil water content greatly impact accumulation at the air-water interface

- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, θ_w = 0.20 or 0.27

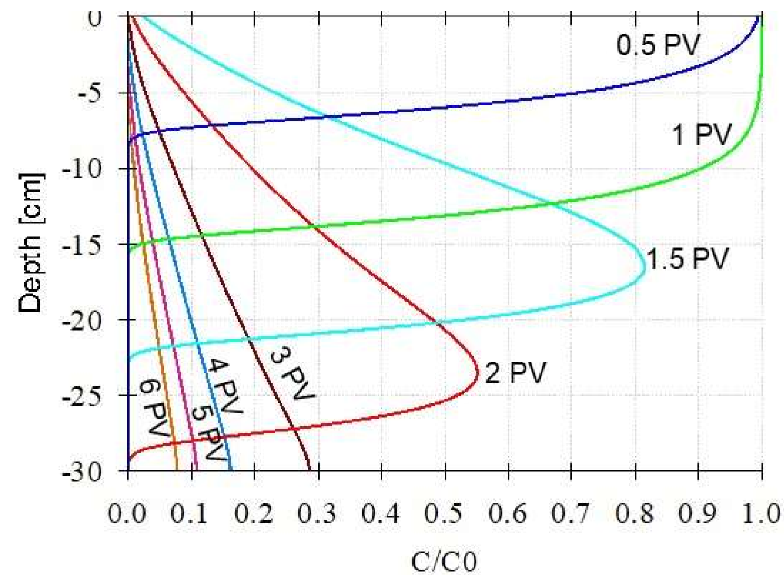
PFAS Concentration Profiles

Langmuir/Szyszkowski Isotherm

PFOA

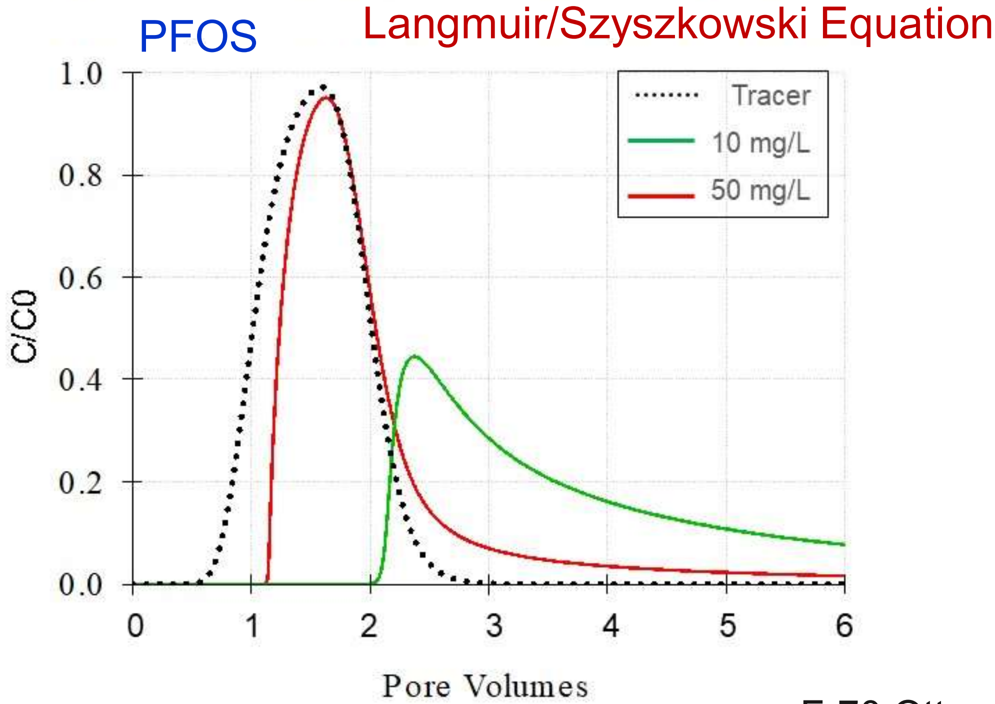


PFOS



- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- Medium level of total dissolved solids (400 mg/L TDS)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

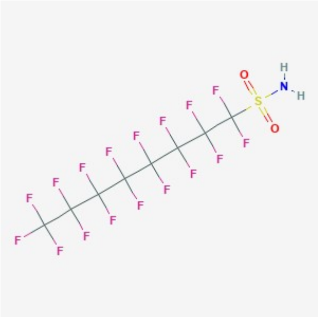
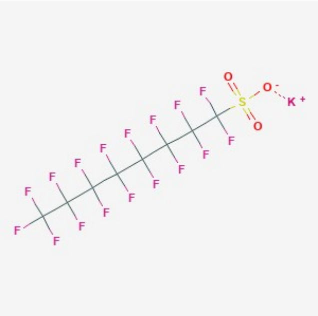
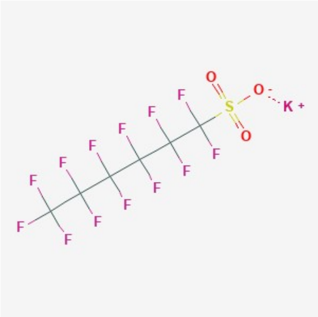
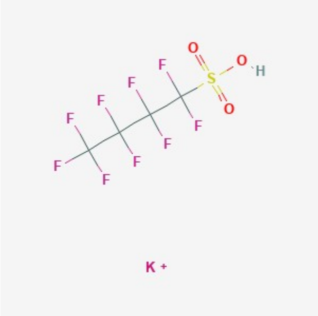
Effect of Input Concentration (PFOS)



Greater proportion PFOS mass retained at lower concentrations (effect of non-linearity)

- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- Medium level of total dissolved solids (400 mg/L TDS)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

Surface Tension of a “PFOS” Mixture

Nonionic	Anionic	Anionic	Anionic
			
Perfluorooctane sulfonamide (FOSA) $C_8F_{17}SO_2NH_2$	KPFOS $C_8F_{17}SO_3K$	KPFHxS $C_6F_{13}SO_3K$	KPFBS $C_4F_9SO_3K$

Effect of PFAS Mixtures on Surface Tension Measurements

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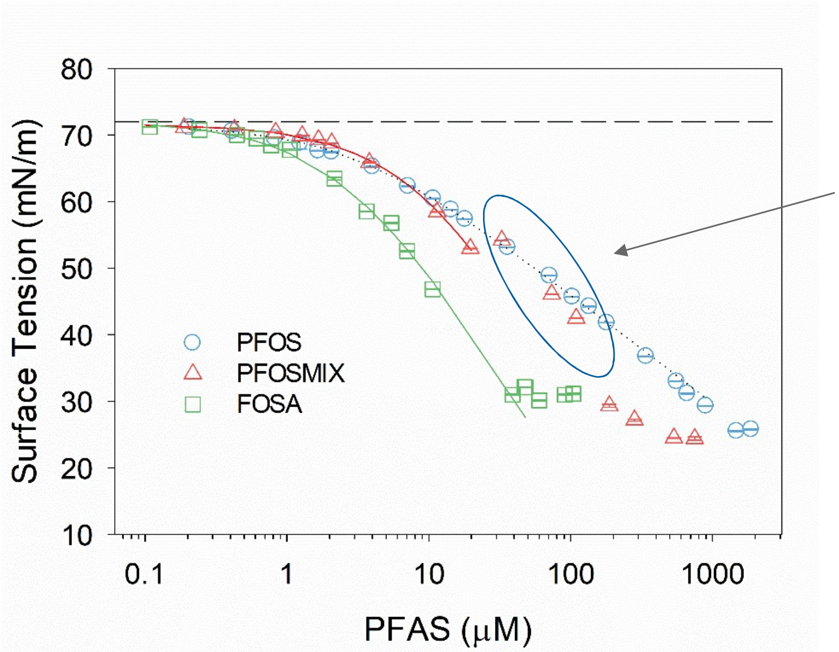

Non-ideal behavior of mixture

- PFBS and PFHxS surface tension of 70 mN/m at 100 mg/L (not surface active)
- FOSA surface tension lowest at equivalent concentration
- PFOS mixture exhibited non-ideal at increasing concentrations

AFFF Phase Behavior with NAPL

JP4 Jet Fuel

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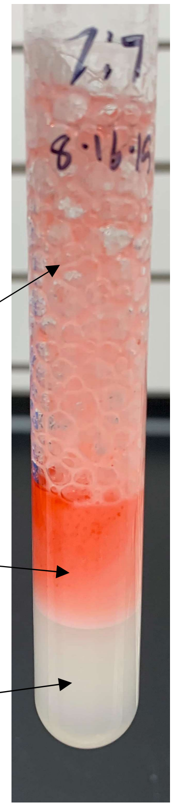
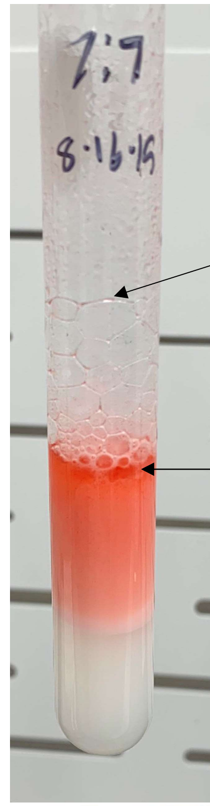


Foam

JP4 Macroemulsion

Aqueous Phase



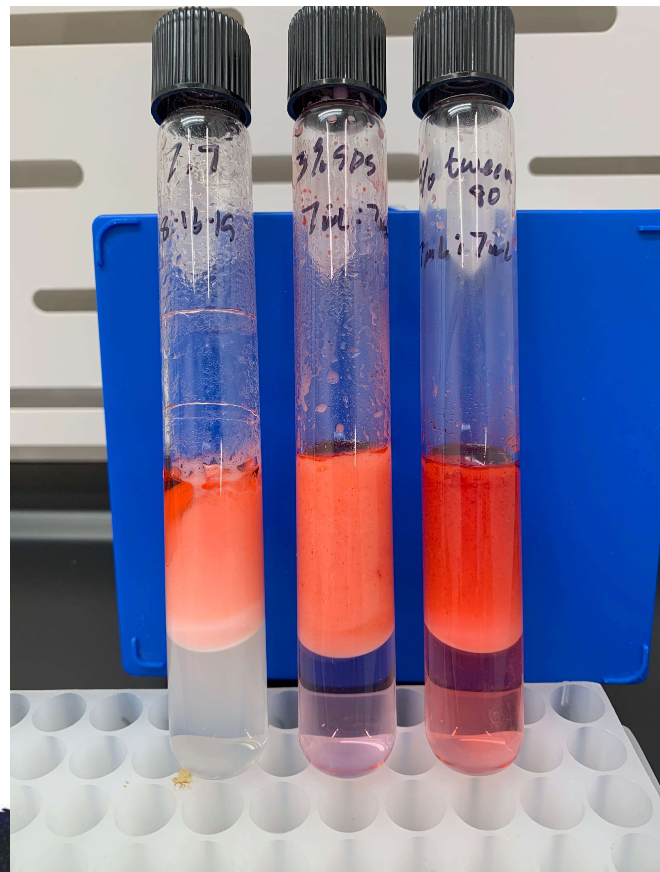
Collapsed Foam

JP4 NAPL Droplets

Comparison AFFF Phase Behavior

JP4 Jet Fuel

3M SDS Tween 80



- 3% active ingredient
- 7 mL JP-4 : 7 mL surfactant solution
- After 24 hr settling

NAPL-Water Interfacial Tension Measurements (PFAS)

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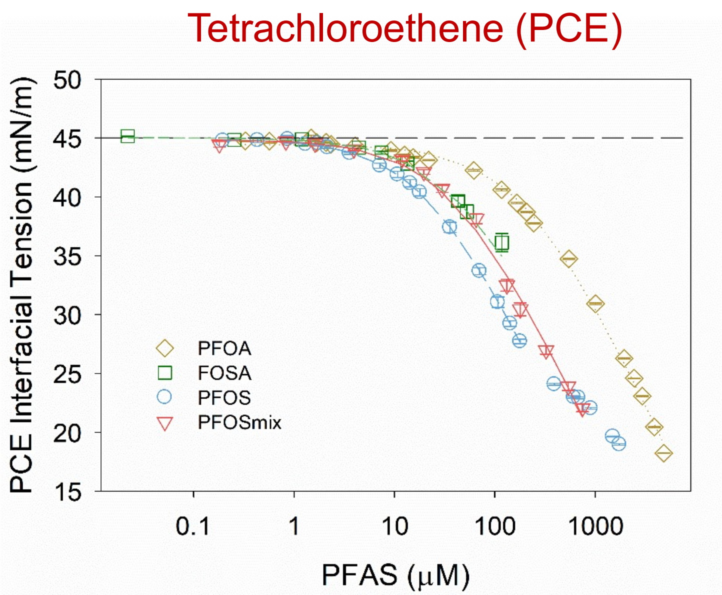
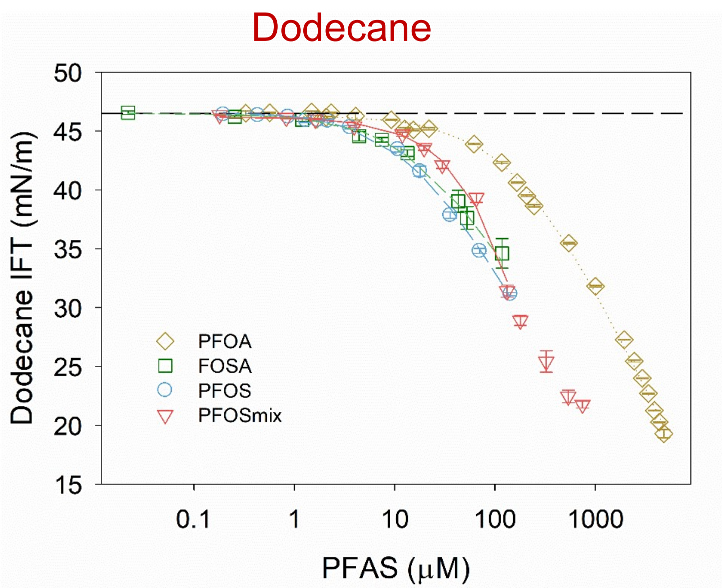
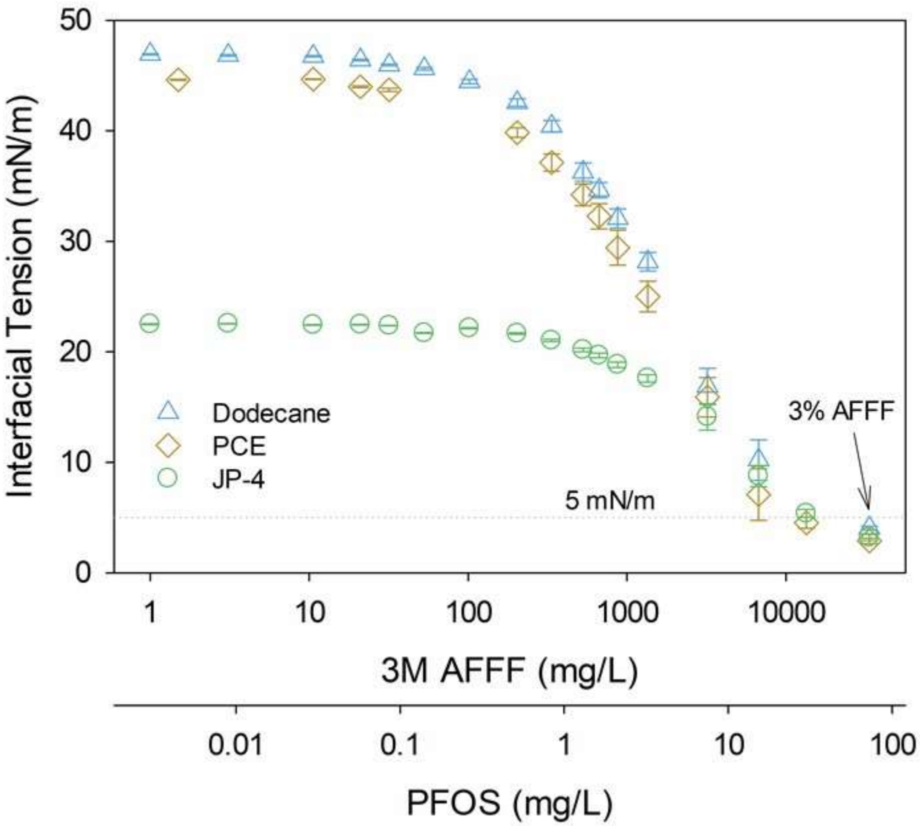




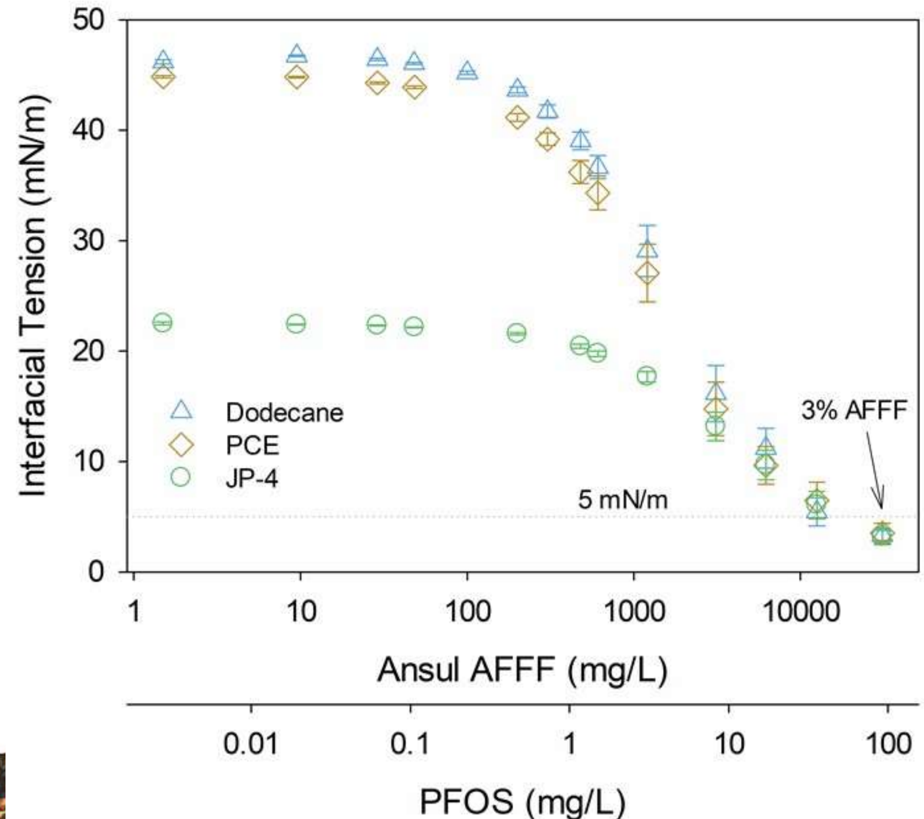
- Drop of NAPL suspended in solutions containing PFAS with ca. 1700 mg/L TDS
- Confirmed oleophobic nature of the perfluorocarbon chain (Moody and Field, 2000)
- Significant reduction in interfacial tension only observed for concentrated solutions (>100 mg/L)

NAPL-Water Interfacial Tension Measurements (AFFF)

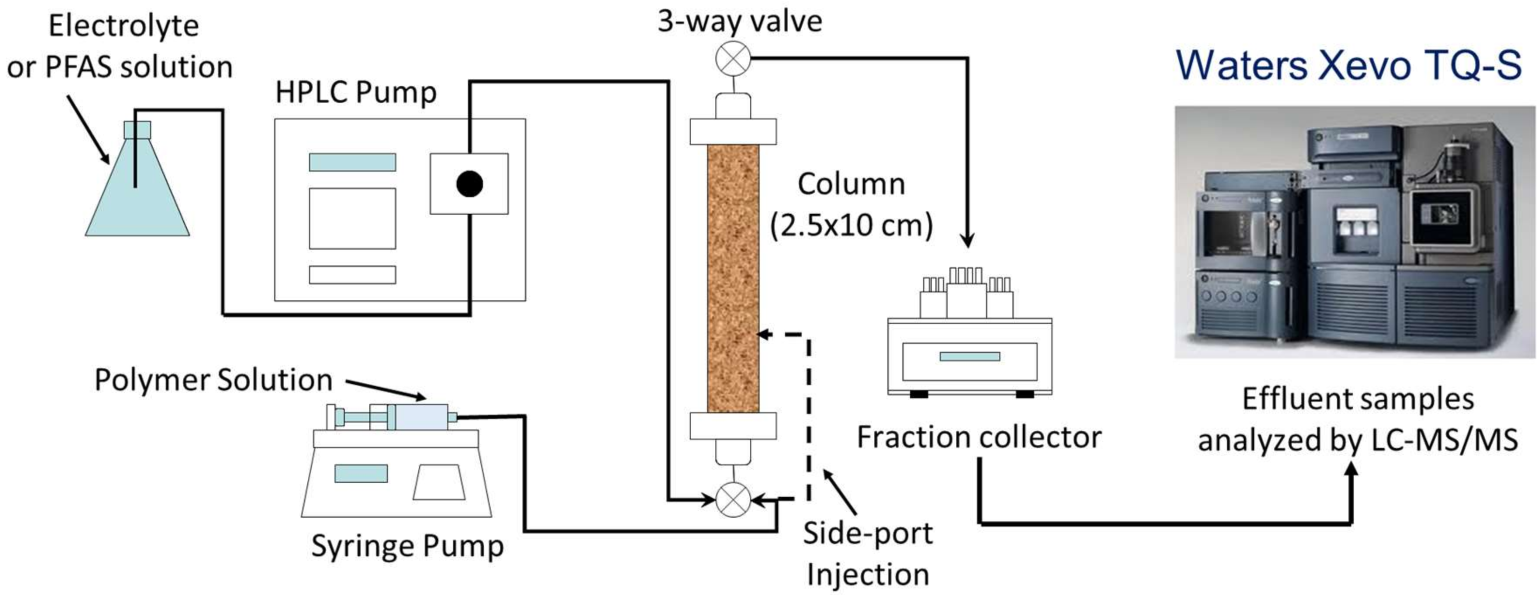
3M AFFF



Ansul AFFF



Development of In Situ Sequestration



- Powdered Activated Carbon (PAC)
- Ion Exchange Resin (IR)

(1) Non-reactive tracer test (pulse injection), (2) Polymer-stabilized sorbent (pulse injection), (3) Flush with background electrolyte solution, (4) Inject PFAS solution (e.g., 100 ug/L PFOS)

Injection of Polymer Stabilized-PAC (S-PAC) Suspension

Flow Direction

0 PV

after 3.5 PV
S-PAC

after 3.5 PV
background

- 40-50 mesh Ottawa Sand
- pore-water velocity ~1.0 m/day
- 26.8 mg of PAC retained in column

PFOS Sequestration in S-PAC treated 40-50 mesh Ottawa Sand

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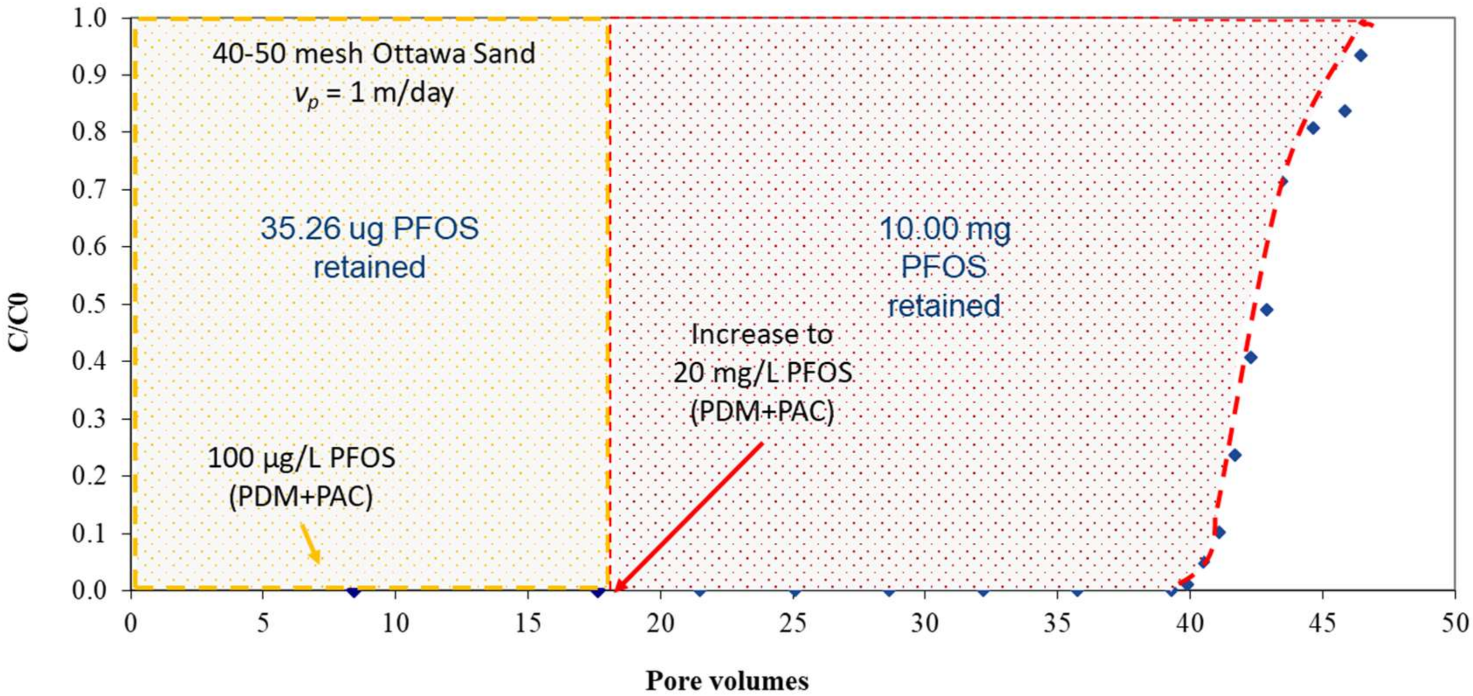

- 10.04 mg of PFOS retained, consistent with PAC $C_{s,max}$ = 316 mg/g
- For a 100 µg/L injection; PAC capacity would be reached after ~5,020 PV

Research Directions

- Unsaturated column studies: PFAS accumulation, water drainage, validate mathematical model
- Multiphase (NAPL) column studies: Potential for NAPL mobilization and emulsion formation
- Sorption and transport studies: Test assumptions of linear, equilibrium, ideal sorption; competitive adsorption
- In situ delivery of polymer-stabilized ion exchange resins for improved retention performance.


Questions??
St. Anton

Effect of Salt Concentration on Unsaturated Zone Transport of PFAS

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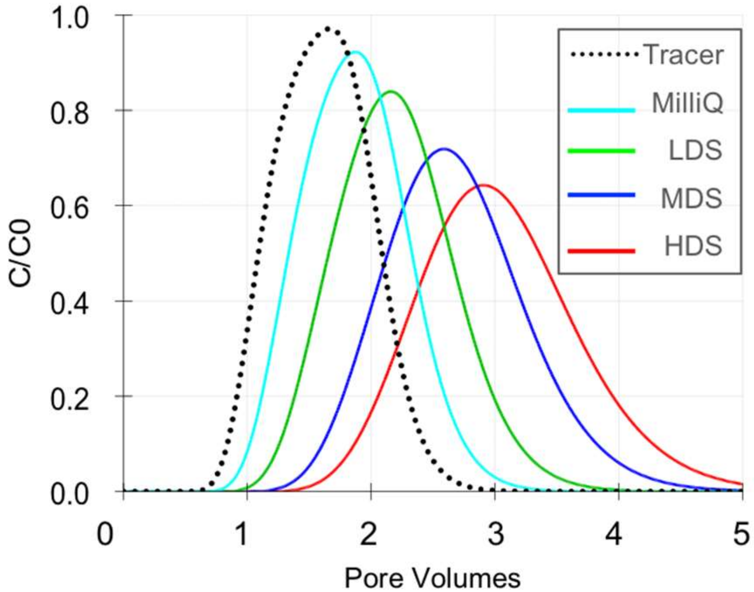
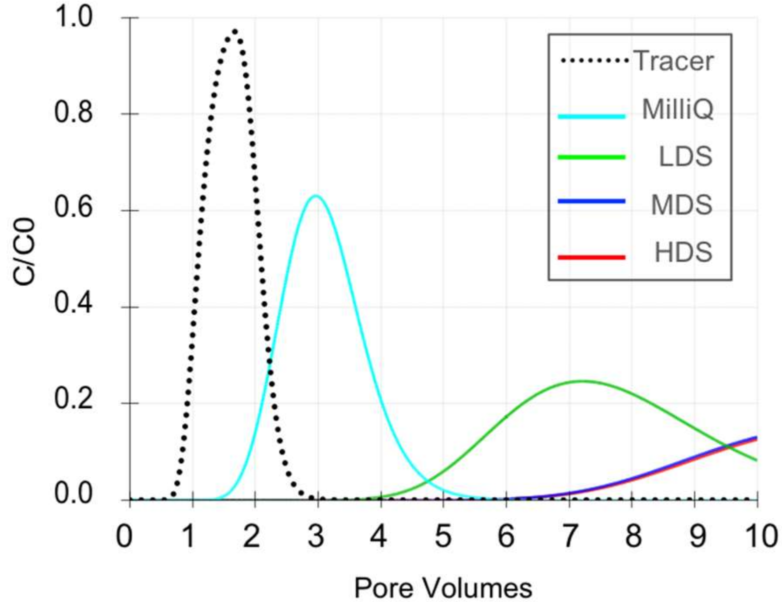
Linear Partitioning: $\Gamma^i = K_i C^i$

PFOA



PFOS



- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, θ_w = 0.27