Processes Influencing PFAS Transport

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Managing Per- and Polyfluoroalkyl Substances (PFAS) at Your Site: Key Technical and Regulatory Issues

1:30-2:15 pm

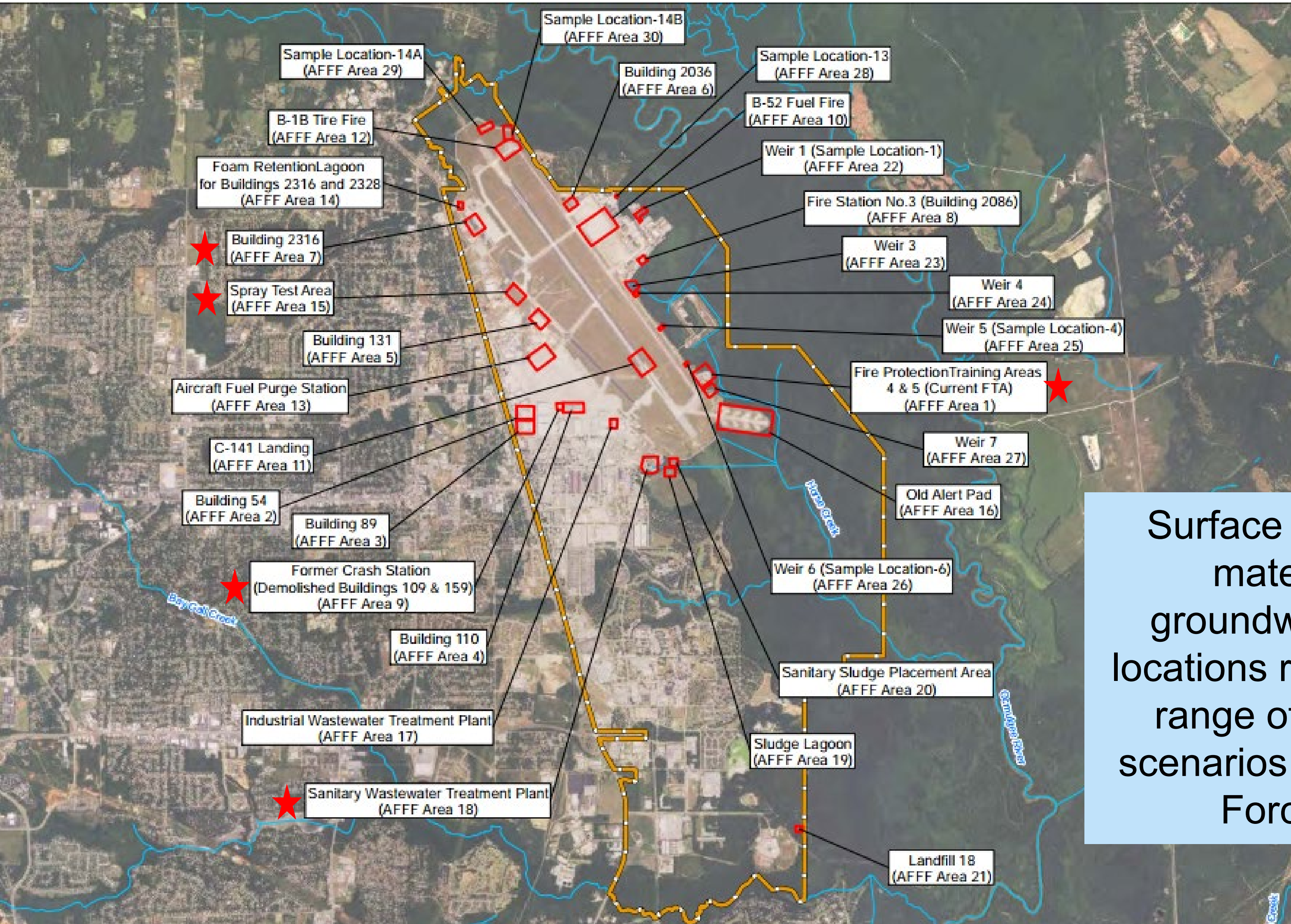
Thursday, September 12, 2019

Presentation Overview

- AFFF Release Scenarios
- (Fluoro)Surfactant Properties and Behavior
- Interfacial Processes Impacting PFAS Transport
- In Situ PFAS Sequestration

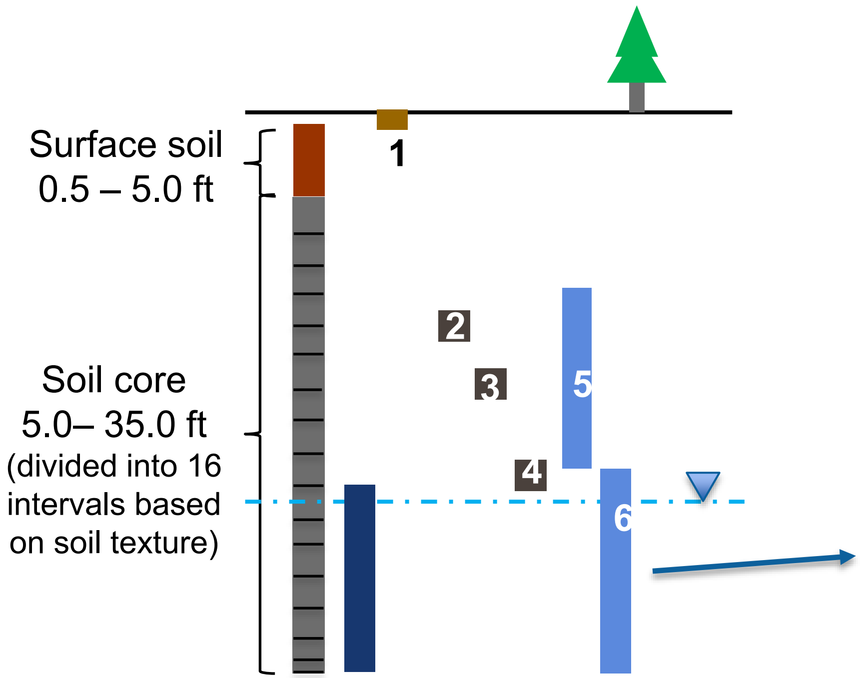
PFAS Release Scenario-AFFF Use and Training

AFFF-impacted Sites at Robins AFB (Georgia)



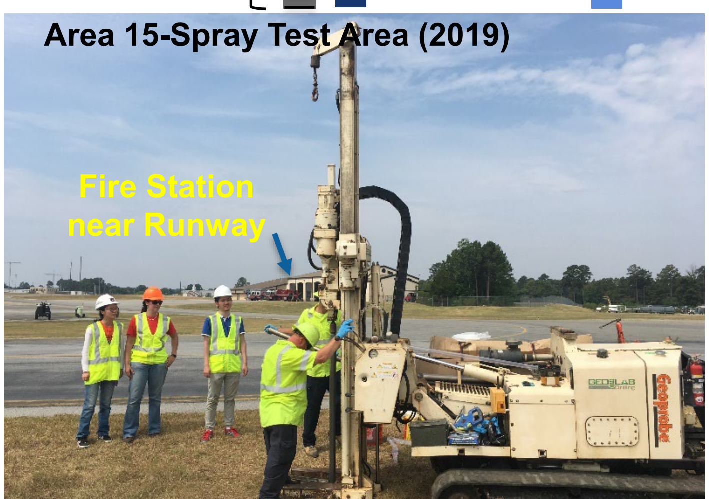
Surface soil, aquifer material and groundwater from 5 locations representing a range of AFFF spill scenarios at Robins Air Force Base

Assess PFAS Concentration and Microbial Community Profiles



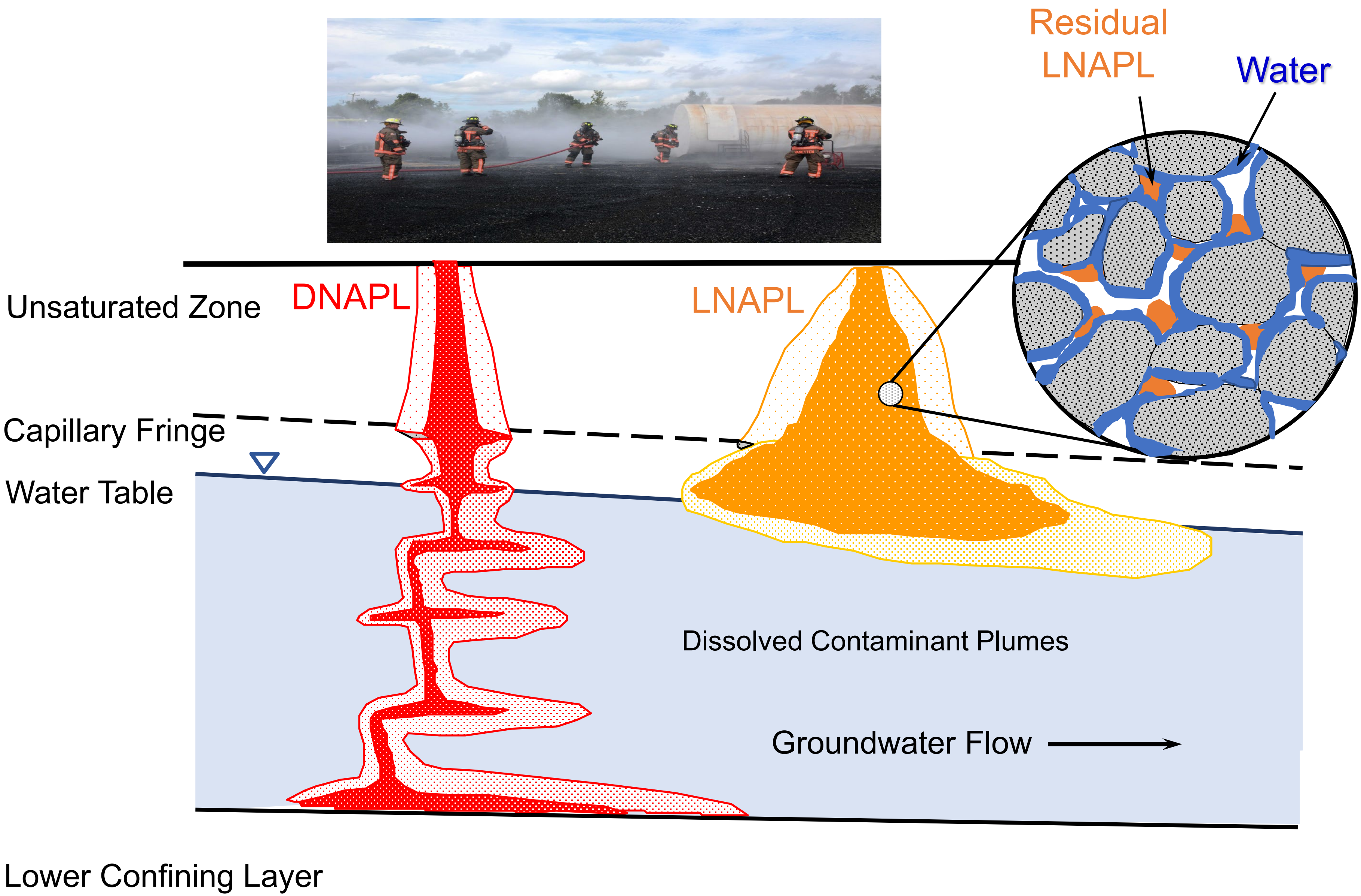
	Depth (ft)	PFBS	PFOA	PFOS
1	0 - 0.5	265.8 ± 490.2	34.5 ± 39.7	2705 ± 2149
2	17 - 18	5.2	0.66	4.4
3	19 - 20	0.66	0.66	2.4
4	26 - 27	37	17	44
5	15 - 25	3.4 ± 1.4	1.6 ± 0.2	22.7 ± 5.5
6	25 - 35	2.4	1.8	8.6

2017 samples (μg/kg for soil, μg/L for water)



- Evaluate PFAS concentration and microbial communities as a function of soil properties
- Prepare microcosms to investigate precursor transformation rates and byproduct formation

PFAS Release Scenario-Mixed Contaminants



(Fluoro)Surfactant Properties and Behavior

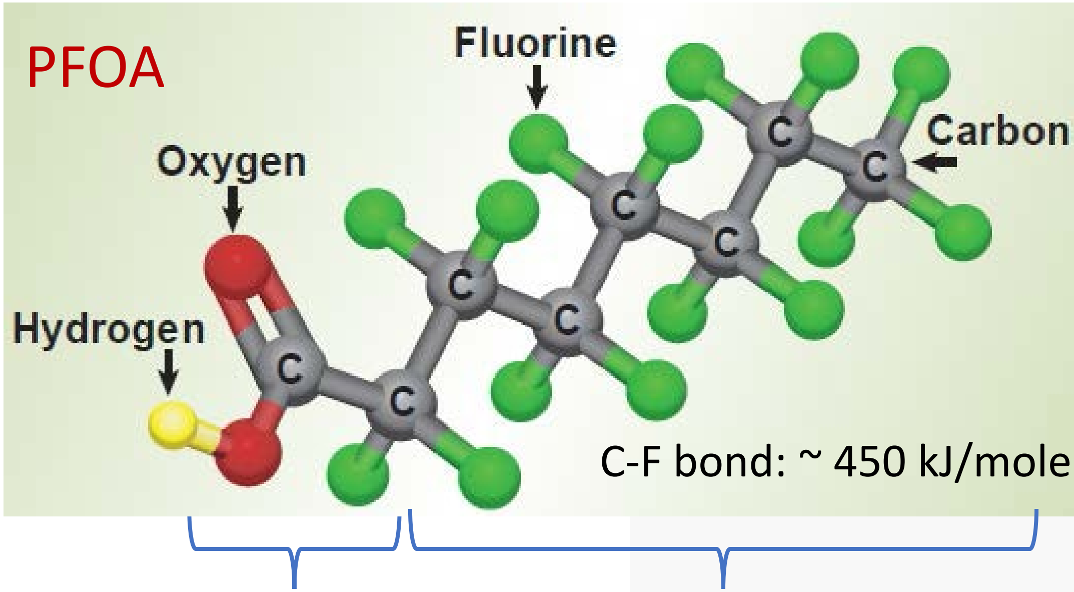
Surface Active Agents (Surfactants)

General 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 is increased
- Classification is based on the polar head group:

  Anionic, Cationic, Nonionic, Amphoteric, Zwitterionic

PFAS Classified as “Fluorosurfactants”



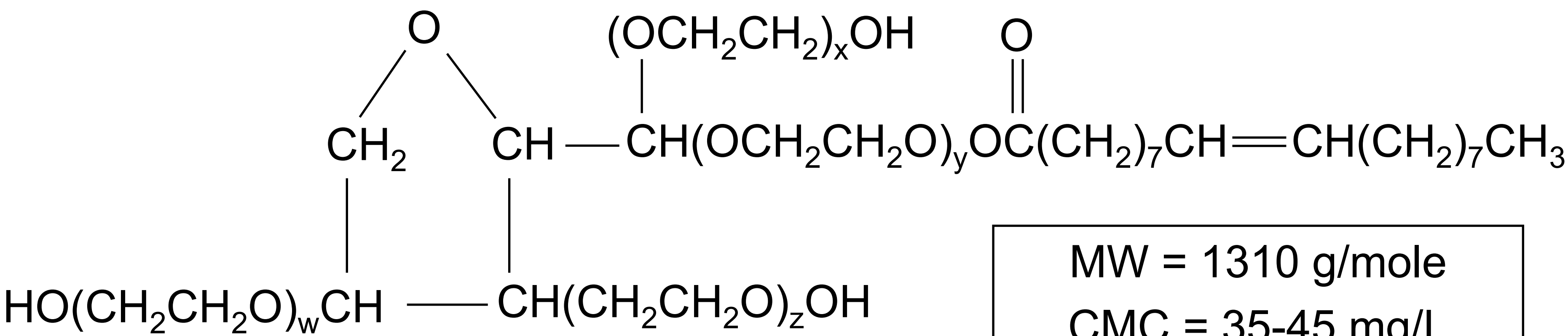
Hydrophilic “head” group

Hydrophobic/lipophilic “tail”

- Low Volatility
- Recalcitrant
- Foam/Emulsion Formation

Examples of Nonionic Surfactants

Polyoxyethylene (20) Sorbitan Monooleate:
(Tween 80, Polysorbate 20, Witconol 2722)



MW = 1310 g/mole
CMC = 35-45 mg/L

Dodecyl Alcohol Ethoxylate:
(Witconol SN-120, Brij 35)

$$C_{12}H_{25}(CH_2CH_2O)OH$$

MW = 583 g/mole
CMC = 50-65 mg/L

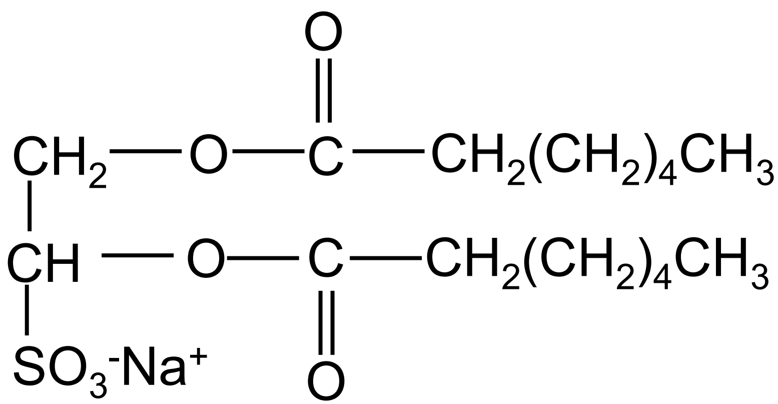
Examples of Anionic Surfactants

Sodium dodecyl sulfate (SDS):

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

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

Sodium dihexylsuflosuccinate (SDHSS, Aersol MA-100):



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

Perfluorooctanesulfonic acid (PFOS)

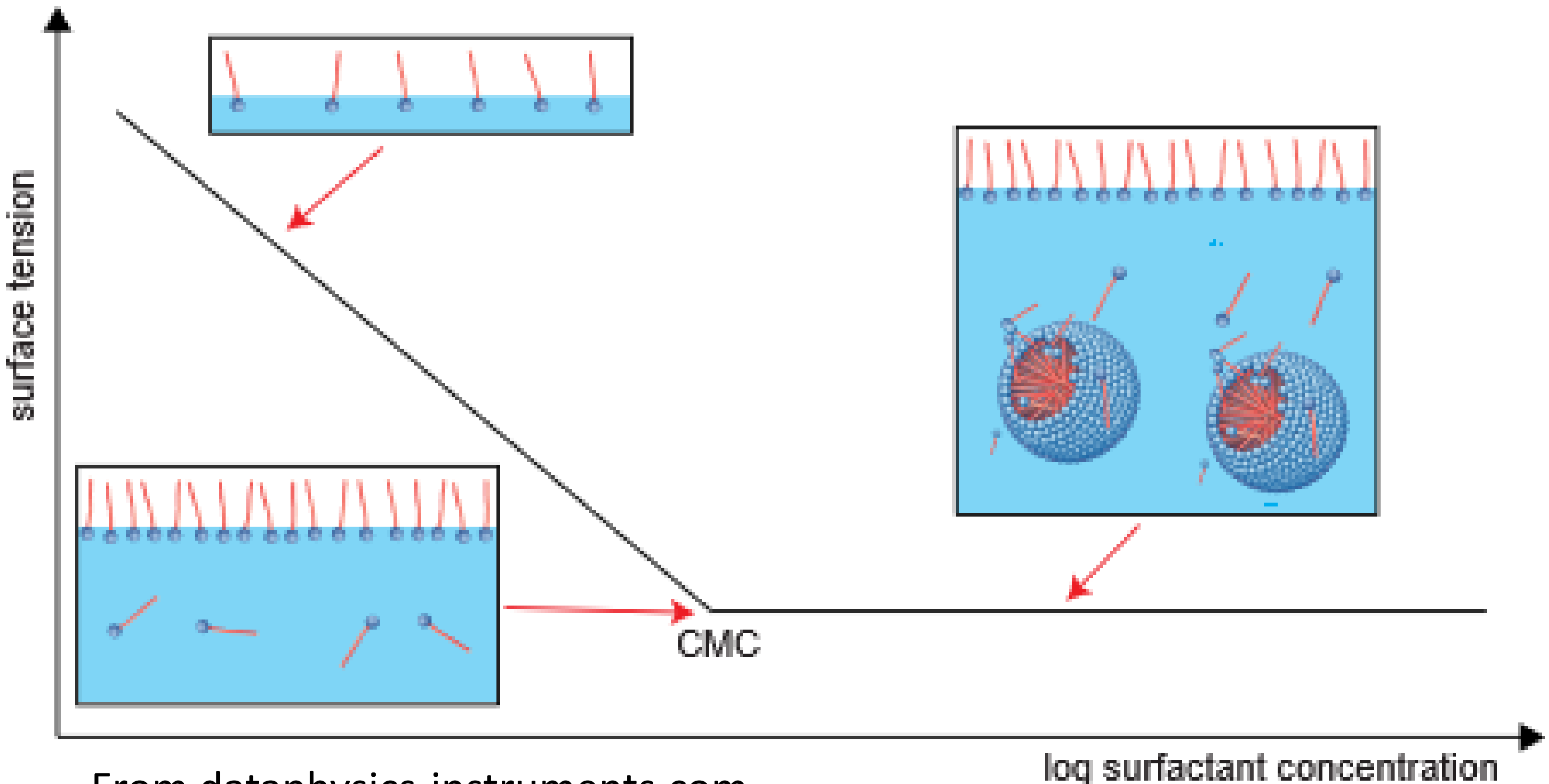
$C_8HF_{17}SO_3$ — MW = 500 g/mole

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

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

…but the solubility is
< 1000 mg/L???

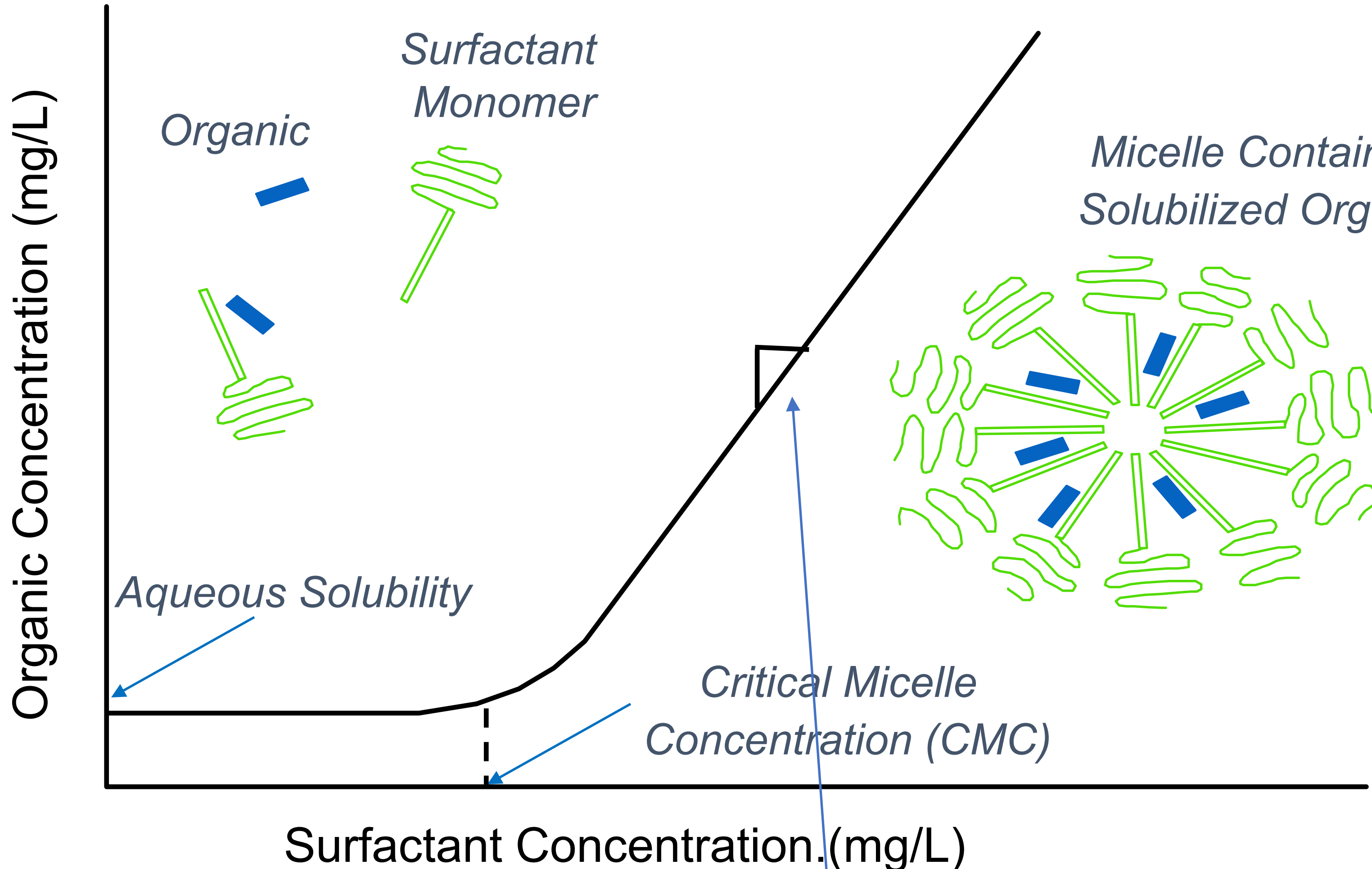
Critical Micelle Concentration (CMC)



From dataphysics-instruments.com

- At concentrations above the CMC, the number of monomers remains constant, while the number of micelles continues to increase
- The surface tension remains constant above CMC because the air-water interface is saturated

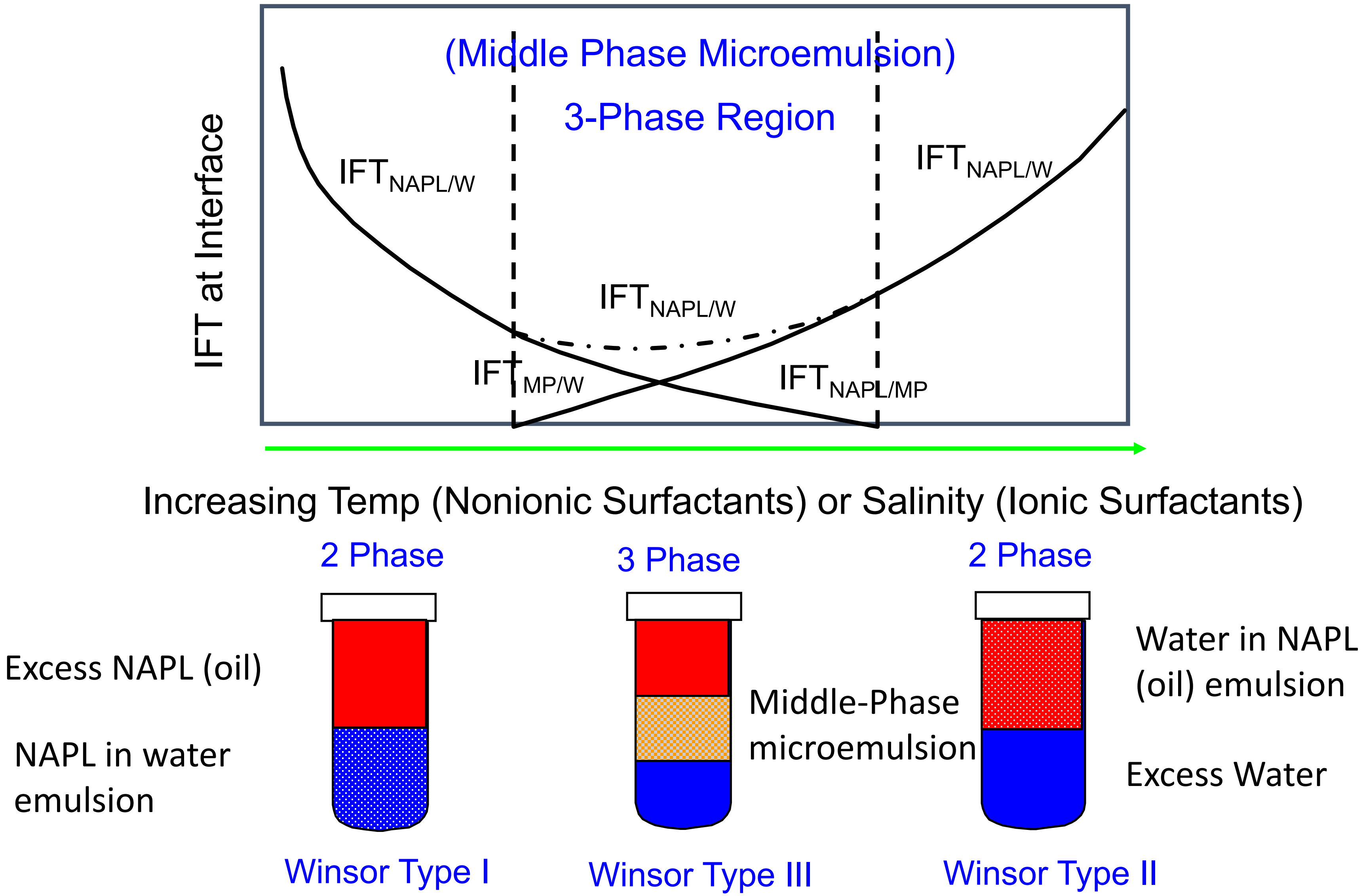
Micellar Solubilization of Organic Compounds



Weight Solubilization Ratio (WSR)

$$WSR = \frac{Co - Co, cmc}{Csurf - Csurf, cmc}$$

Surfactant Phase Behavior: NAPL-Water Interfacial Tension (IFT) and Emulsions

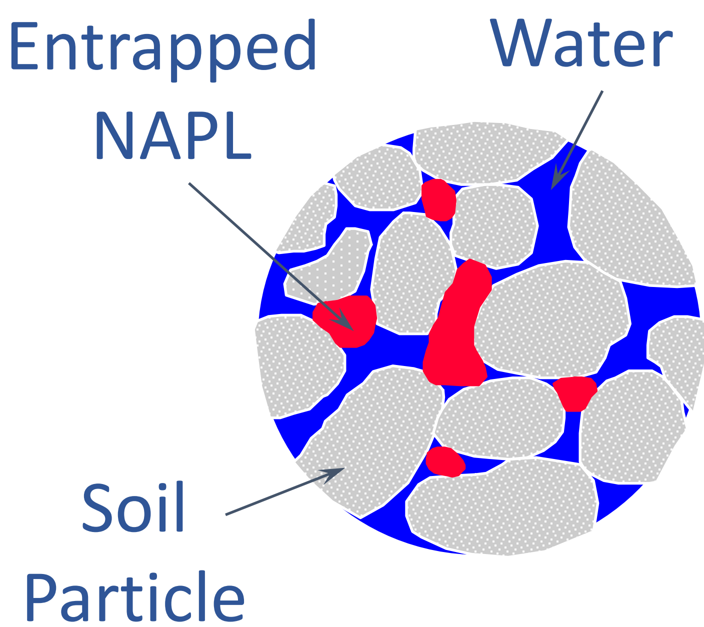


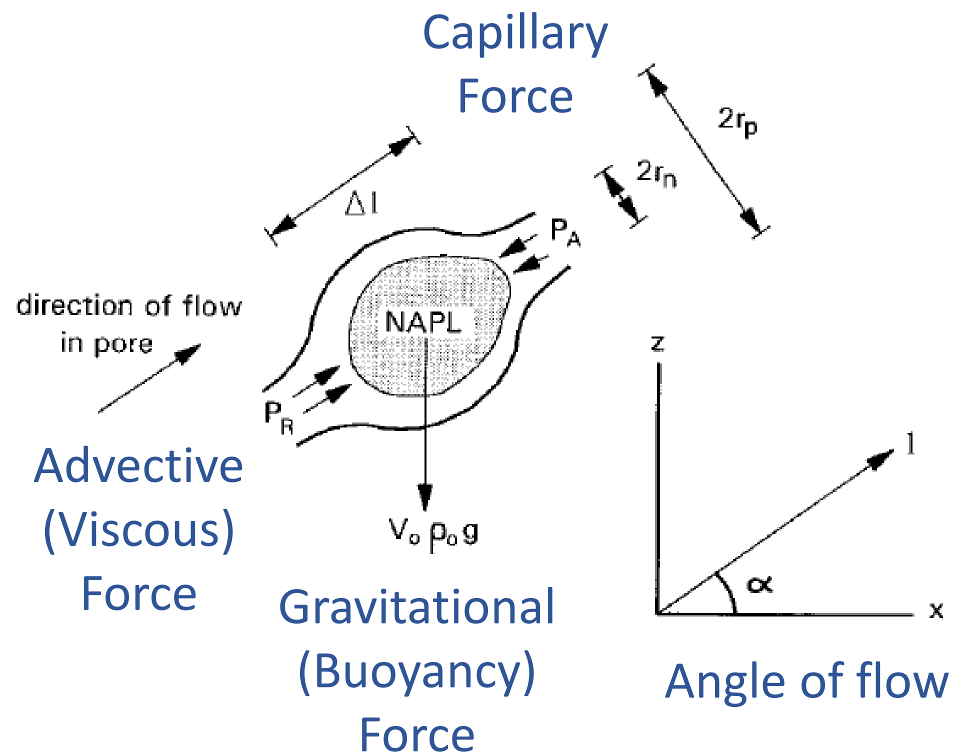
Vertical Displacement (Mobilization) of PCE

Flushed with 4% Aerosol AY/OT (IFT = 0.09 dyne/cm)

Determining Risk of NAPL Mobilization

Total Trapping Number (N_T)





Total Trapping Number (N_T)

Capillary Number:
(viscous forces)

$$N_{Ca} = \frac{q\mu}{\sigma_{ow}\cos\theta}$$

Bond Number:
(gravity forces)

$$N_B = \frac{\Delta\rho g k k_{rw}}{\sigma_{ow}\cos\theta}$$

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B\sin\alpha + N_B^2}$$

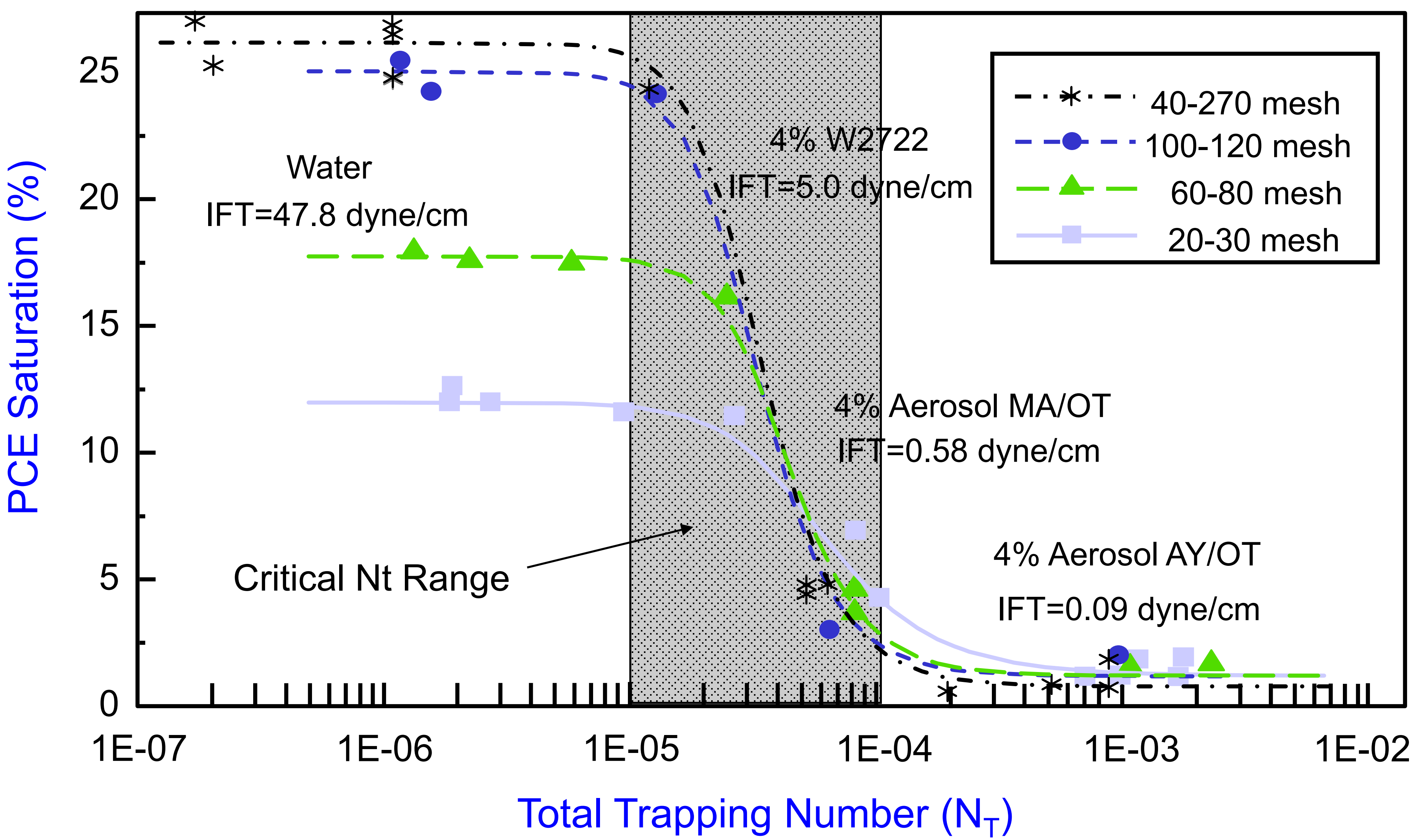
Vertical: $N_T = |N_{Ca} + N_B|$

Horizontal: $N_T = \sqrt{N_{Ca} + N_B}$

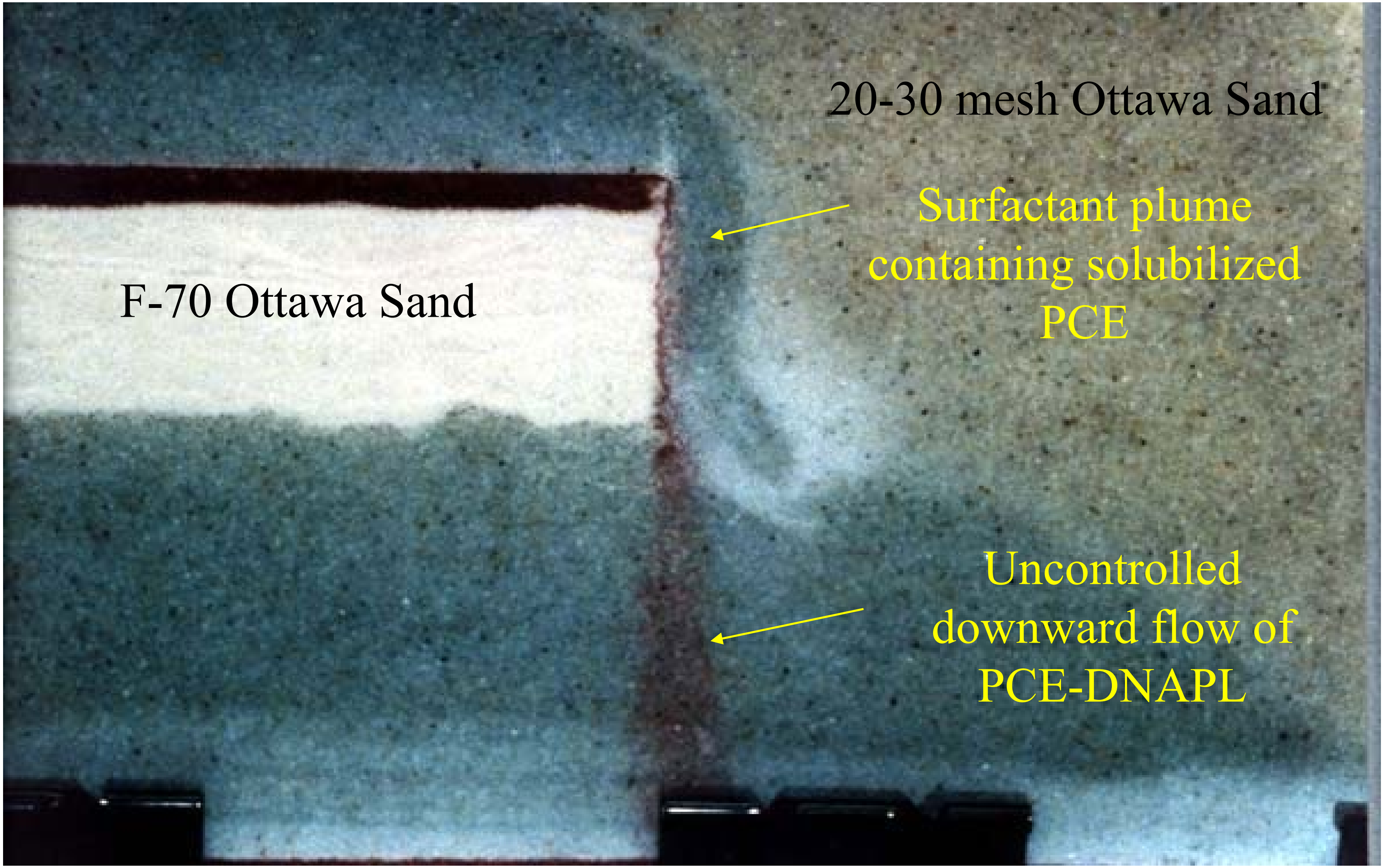
μ = dynamic viscosity
Θ = contact angle
k = intrinsic permeability
k_{rw} = relative permeability to water

ρ = density of fluid
g = gravity constant
q = Darcy velocity
σ_{ow} = interfacial tension (oil-water)

PCE Desaturation Curves for Ottawa Sands



Risk of Uncontrolled DNAPL Mobilization



Questions related to PFAS Transport

- How much PFAS accumulates at the air-water interface in unsaturated soils?
- How does PFAS impact soil water retention characteristics and water drainage during infiltration events?
- How does PFAS interact with NAPLs, and do these interactions result in enhanced N APL solubility or mobilization?
- Can we modify existing mathematical models to describe PFAS fate and transport in complex systems?
- How do we account for mixtures of many surfactants, including PFAS?

Interfacial Processes Impacting PFAS Transport

Interfacial Tension Measurements

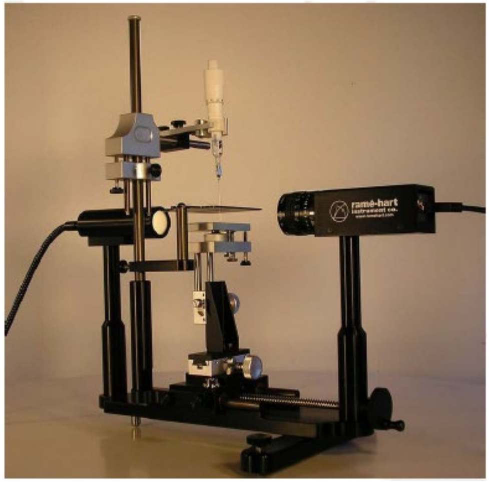
SERDP Projects ER18-1149 and ER-2714

DOD ▪ EPA ▪ DOE

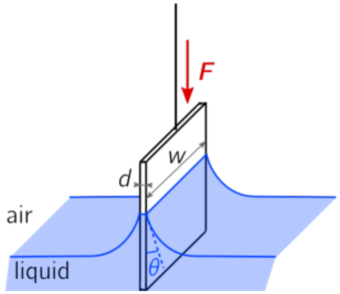
Sigma T700 Tensiometer

Resolution of 0.01 mN/m

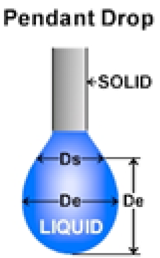
Ramé-Hart Goniometer



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



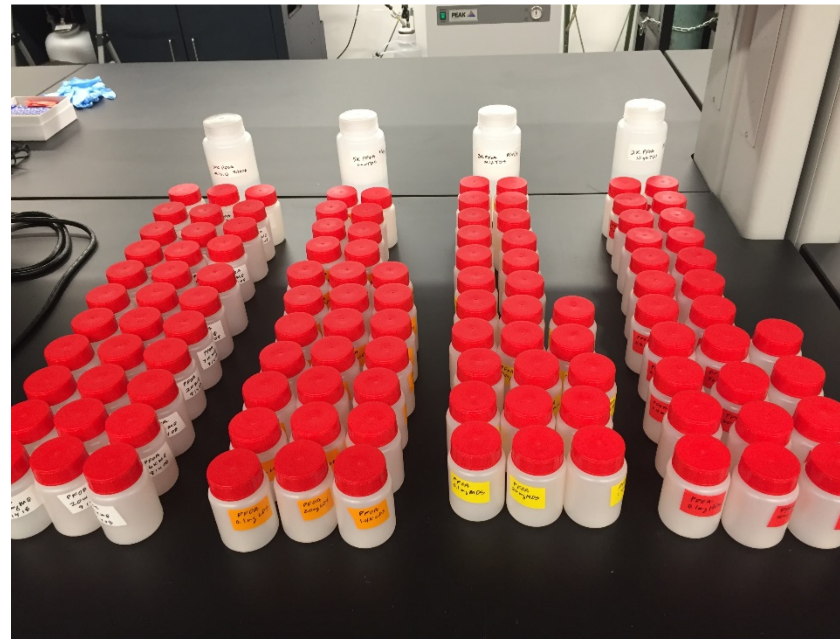
Surface Tension by Wilhelmy Plate



Interfacial Tension by Pendant Drop

Preparation of Solutions for IFT Measurements

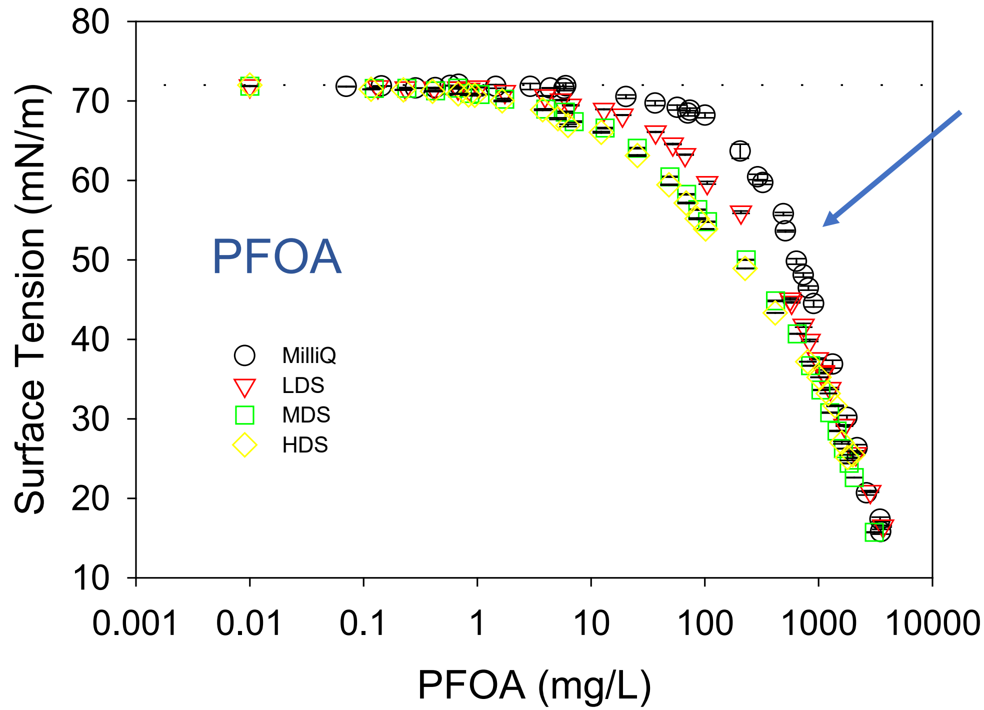
- Stock solutions ranged from 50 to 10,000 mg/L
  - PFOA or KPFOS solids using analytical balance
  - Sonicating for 30 min and heating overnight at 40 °C
- Concentrations from 0.1 to 50 mg/L prepared by serial dilution
- Concentrations verified by LC-MS/MS
- To simulate principal aquifers in US, aqueous 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

Air-Water Interfacial Tension (Surface Tension)

PFOA (Effect of Salts)



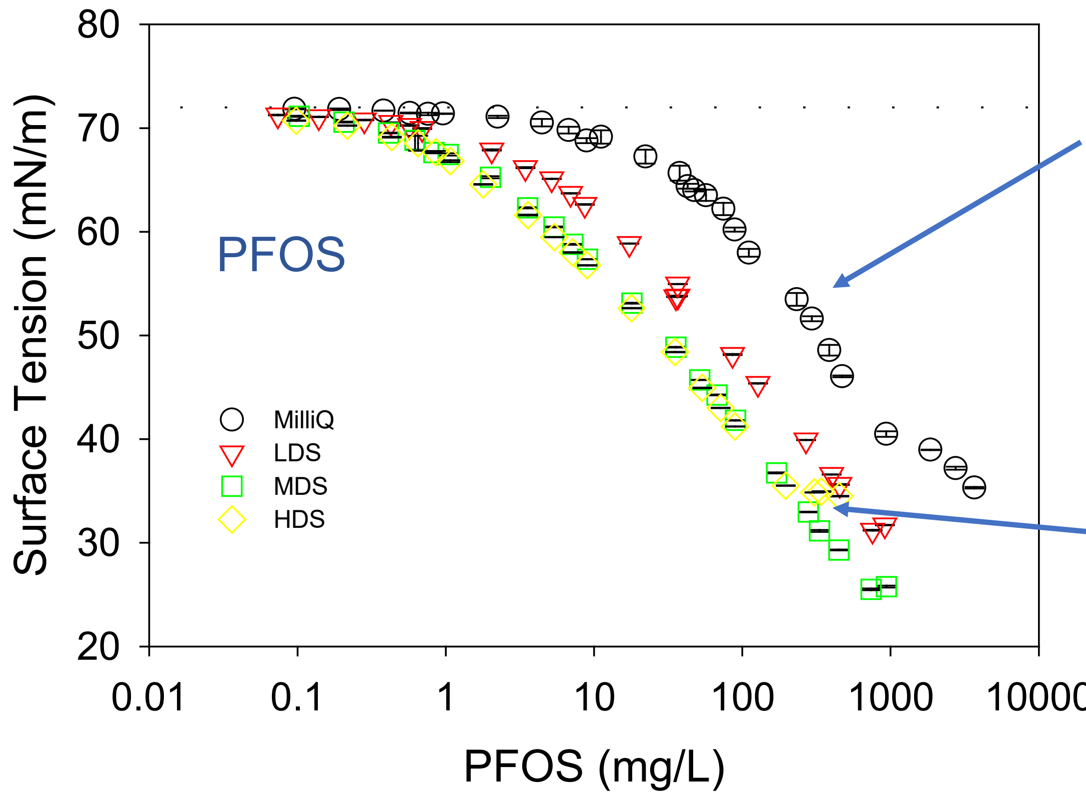
surface tension decreases with increasing salt

- To simulate principal aquifers in US Background solution contains $MgSO_4$, $NaHCO_3$, KCl, and $CaCl_2$
- Dissolved salts resulted in lower surface tension for PFOA
  - **Low Dissolved Solids (LDS)** ca. 40 mg/L (high purity drinking water)
  - **Mid Dissolved Solids (MDS)** ca. 400 mg/L (secondary drinking water standard)
  - **High Dissolved Solids (HDS)** ca. 1,700 mg/L (unpleasant drinking water)

Costanza et al., 2019, ES&T Letters

Air-Water Interfacial Tension (Surface Tension)

PFOS (Effect of Salts)



Similar effect, but more pronounced with PFOS

Minimal effect above 400 mg/L TDS

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

Gibb's Equation → Surface Excess

Interfacial tension is a measure of surface concentration or surface "excess" (Γ) [Langmuir, 1917]

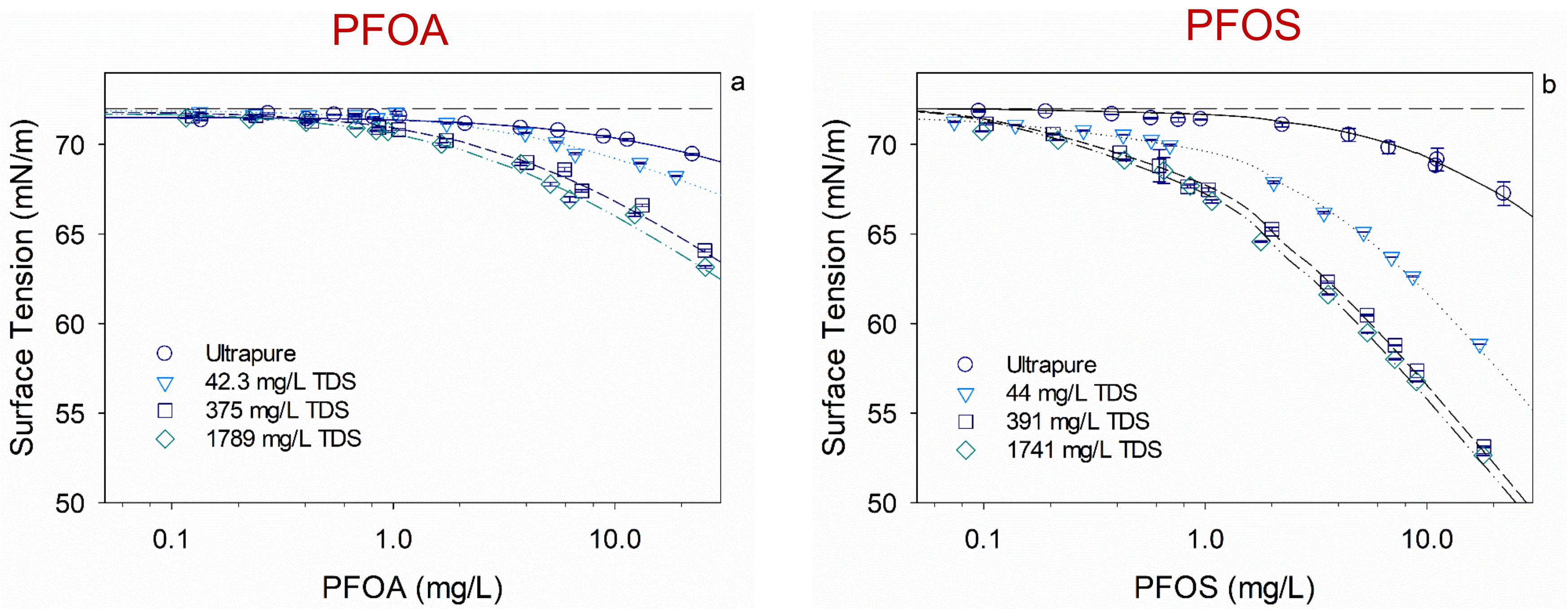
$$\Gamma = -\frac{C}{RT}\left(\frac{\partial \gamma}{\partial C}\right)_T \longrightarrow \gamma = \gamma_0\left[1 - a * ln\left(\frac{C}{b} + 1\right)\right] \longrightarrow \Gamma = \frac{a\gamma_0}{RT}\frac{C}{C+b}$$

Gibb's Equation　　Szyszkowski Equation　　Langmuir/Szyszkowski Eq.

Γ = surface excess
γ = surface tension
C = aqueous conc.
R = gas constant
T = temperature (^{o}K)

- "a" and "b" are nonlinear fitting parameters
- This equation allows you to fit the entire surface tension vs. PFAS concentration curve

Langmuir/Szyszkowski Equation



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

Gibb's Eq.

Szyszkowski Eq. Fit

Langmuir/Szyszkowski Eq.

Surface Excess Calculations

Equation Development

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

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

Linear

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

Natural Log

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

requires an arbitrary reference conc.

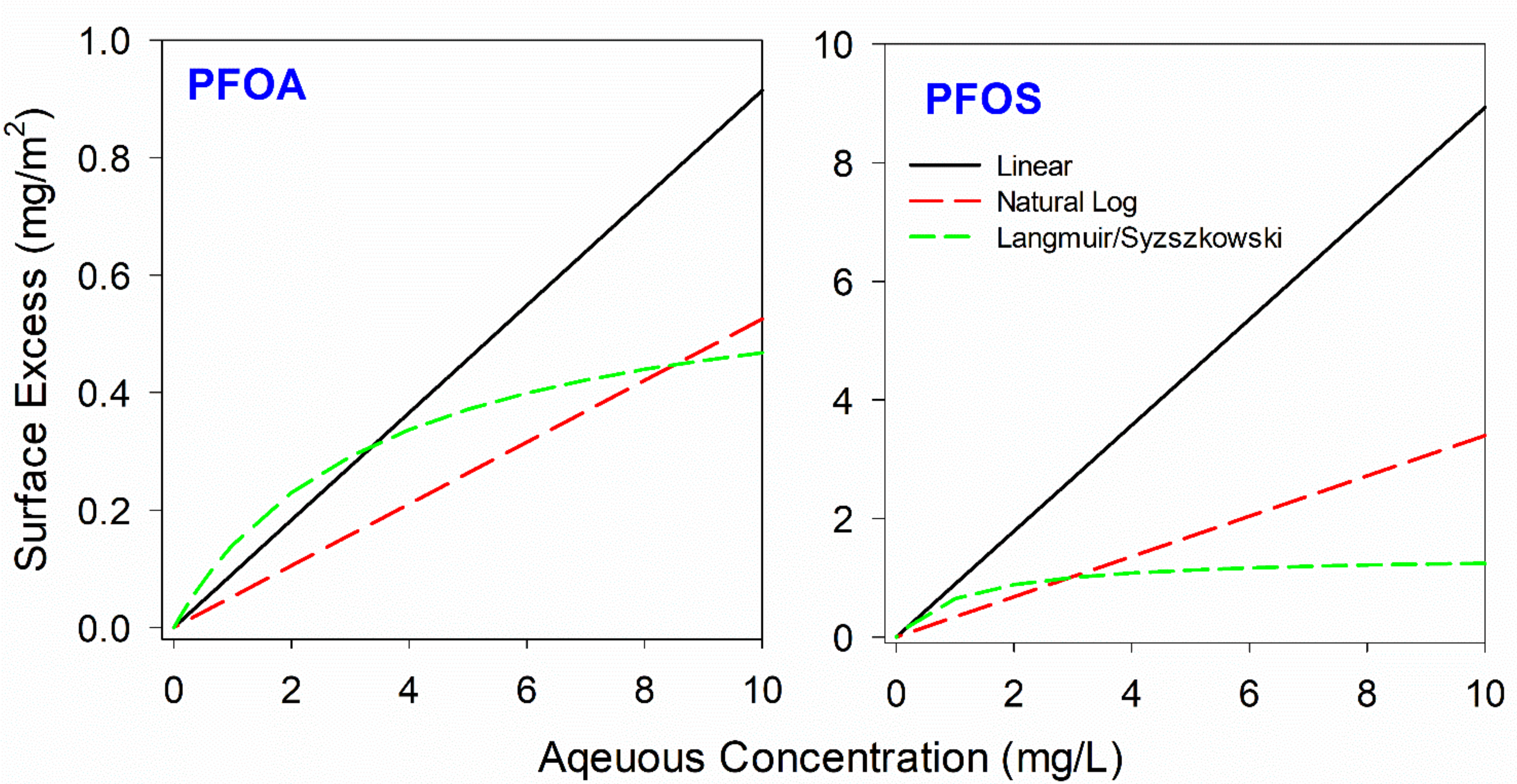
(e.g., Lyu et al., 2018, C_{ref}= 1 mg/L)

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

Nonlinear (Langmuir/Szyszkowski)

Surface Excess Calculations

Comparison of Different Approaches



$$\Gamma = K_i C_w$$

Linear

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

Natural Log

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

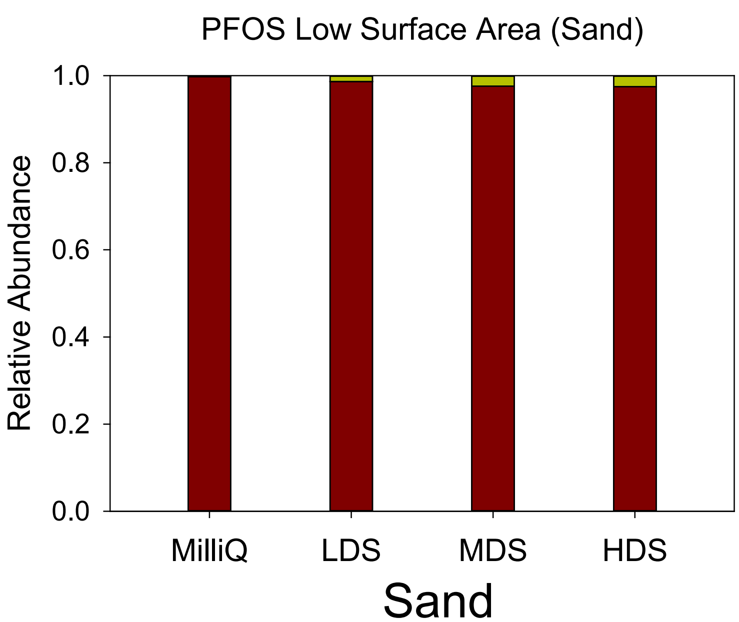
Langmuir/Szyszkowski

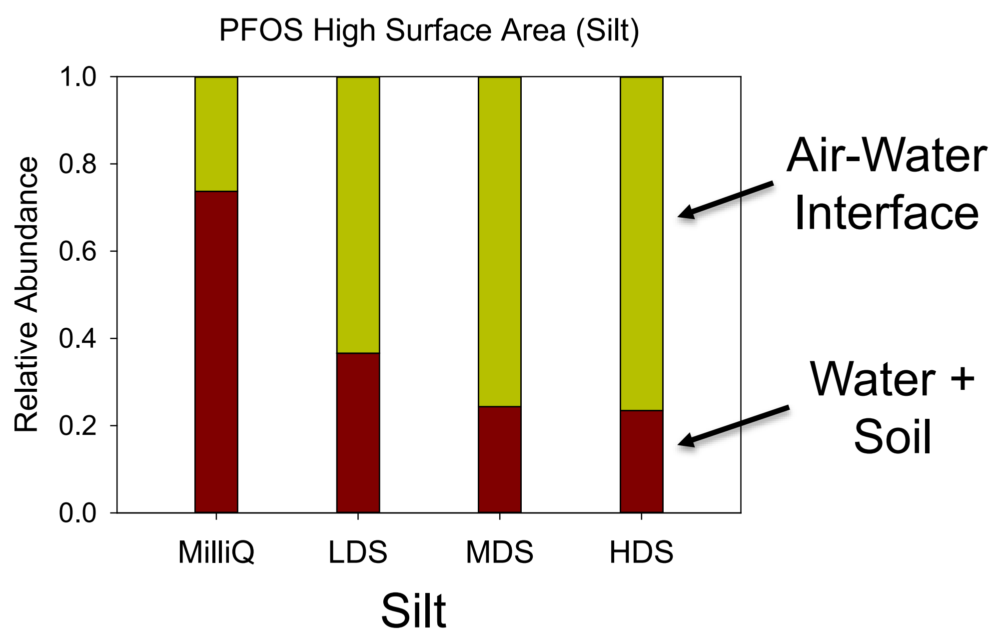
PFOS Phase Distribution in Unsaturated Soils

Nonlinear: Langmuir/Szyszkowski Equation)

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

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

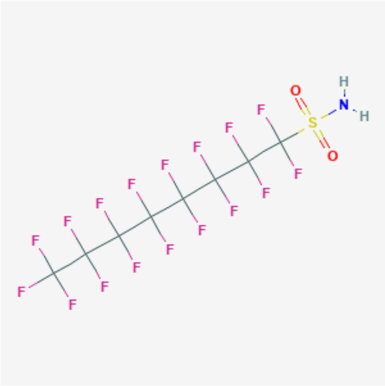




- C_w = 1 mg/L, S_w = 0.26, K_D = 1.14 mg/kg, ρ_b = 1.5 kg/L, S_a = 80 cm^{-1} sand, S_a = 1000 cm^{-1} silt (Brusseau, 2018)

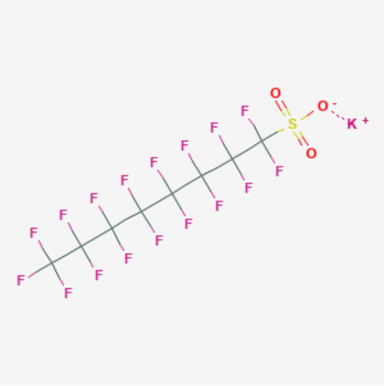
Surface Tension of “PFOS” Mixture

Nonionic



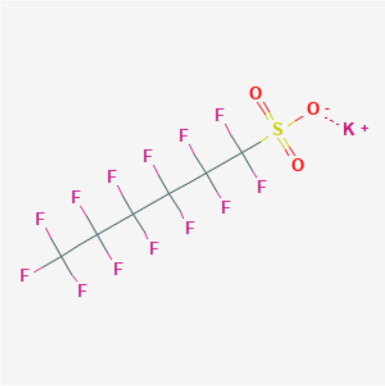
Perfluorooctane sulfonamide (FOSA)
$C_8F_{17}SO_2NH_2$

Ionic



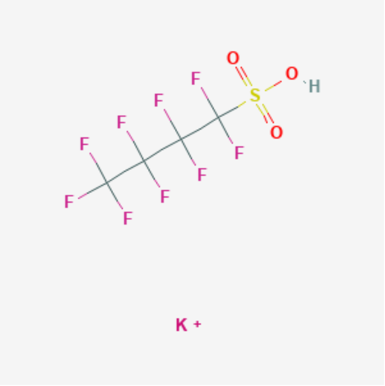
KPFOS
$C_8F_{17}SO_3K$

Ionic



KPFHxS
$C_6F_{13}SO_3K$

Ionic

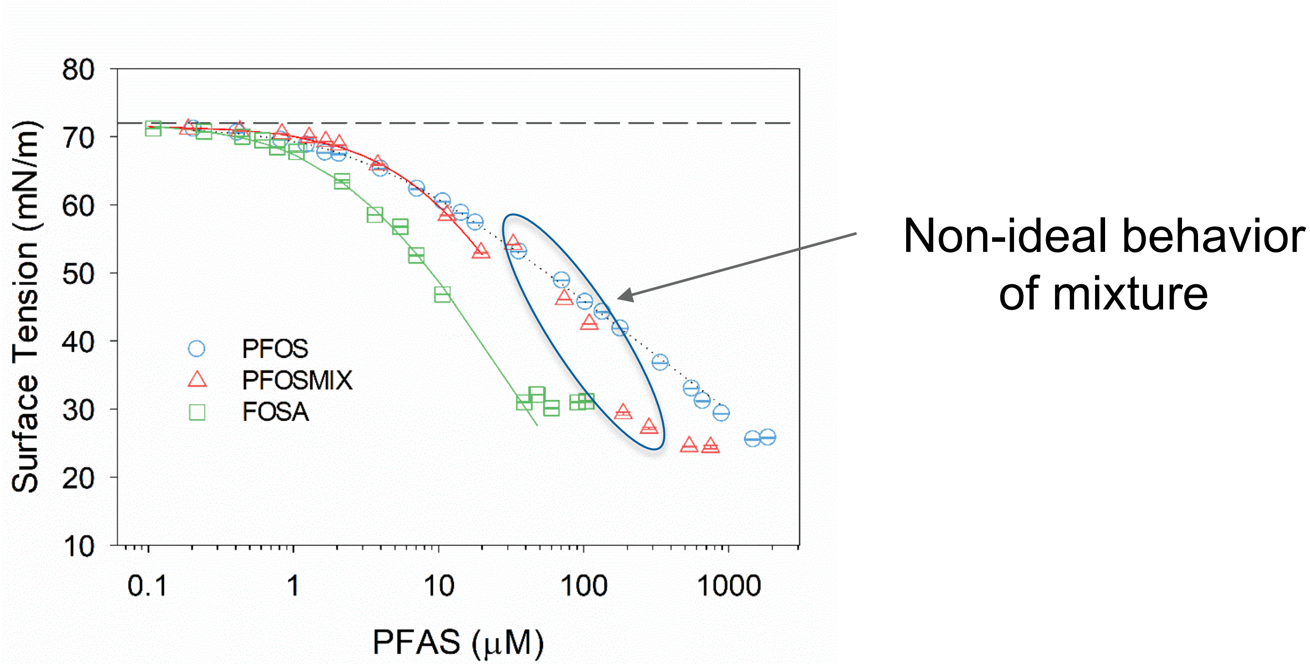


KPFBS
$C_4F_9SO_3K$

“PFOS mixture” consists of a sulfonamide and three sulfonates

- Prepared equimolar stock mixtures from solids with total concentrations of 100, 200, 400, and 600 mg/L
- Dilutions of stock mixtures in range from 0.1 to 80 mg/L
- Solutions in ultrapure water, and water with low, mid, and high dissolved solids

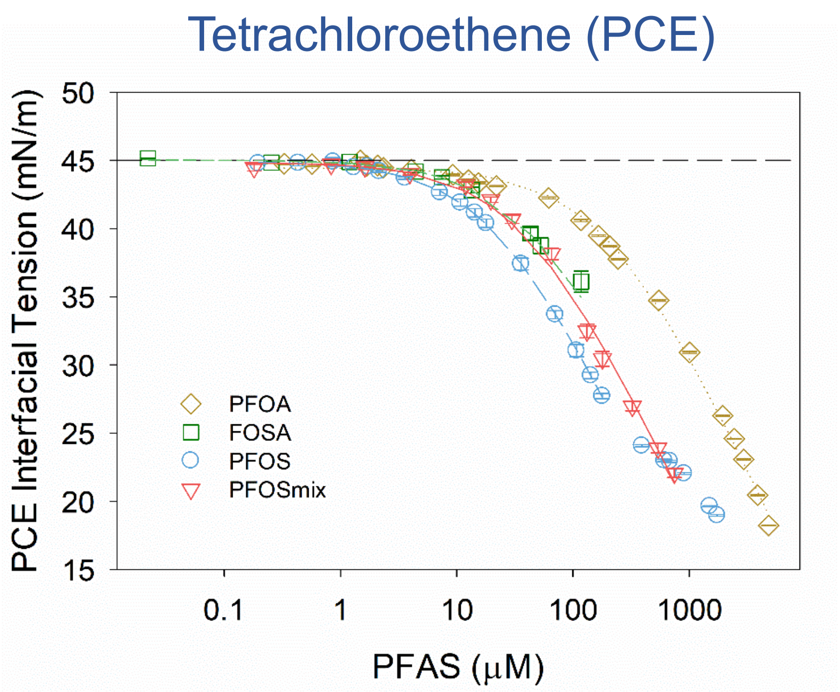
Effect of PFAS Mixtures on Surface Tension Measurements

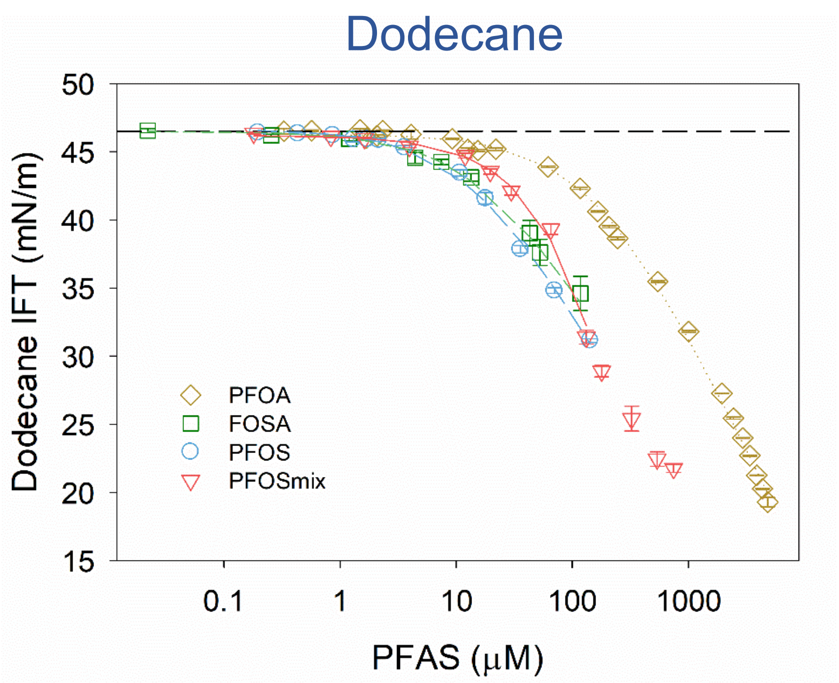


"PFOS mixture" contained a sulfonamide and three sulfonates in ca. 400 mg/L TDS

- PFBS, PFHxS, PFOS and FOSA (0.3:0.3:0.2:0.2 mole fractions)
- 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 "ideal" surface tension behavior from 0.2 to 20 μmol/L, non-ideal at increasing concentrations

NAPL-Water Interfacial Tension





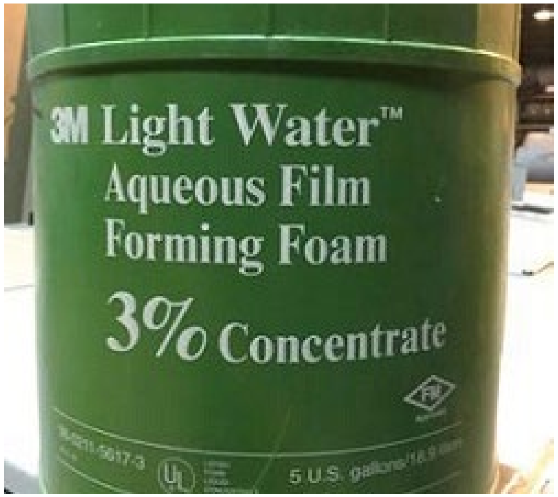
Drop of NAPL suspended in solutions containing PFAS with ca. 1700 mg/L TDS

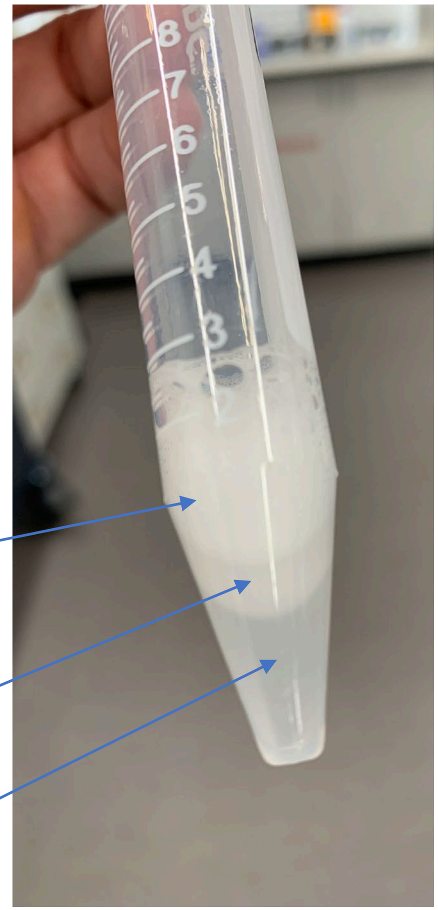
Confirmed oleophobic nature of the perfluorocarbon chain (Moody and Field, 2000)

- Significant reduction in interfacial tension only observed for concentrated solutions (>100 mg/L)
- IFTs less than 5 mN/m (dyne/cm) typically needed for NAPL mobilization

AFFF Phase Behavior

JP4 Jet Fuel





Foam

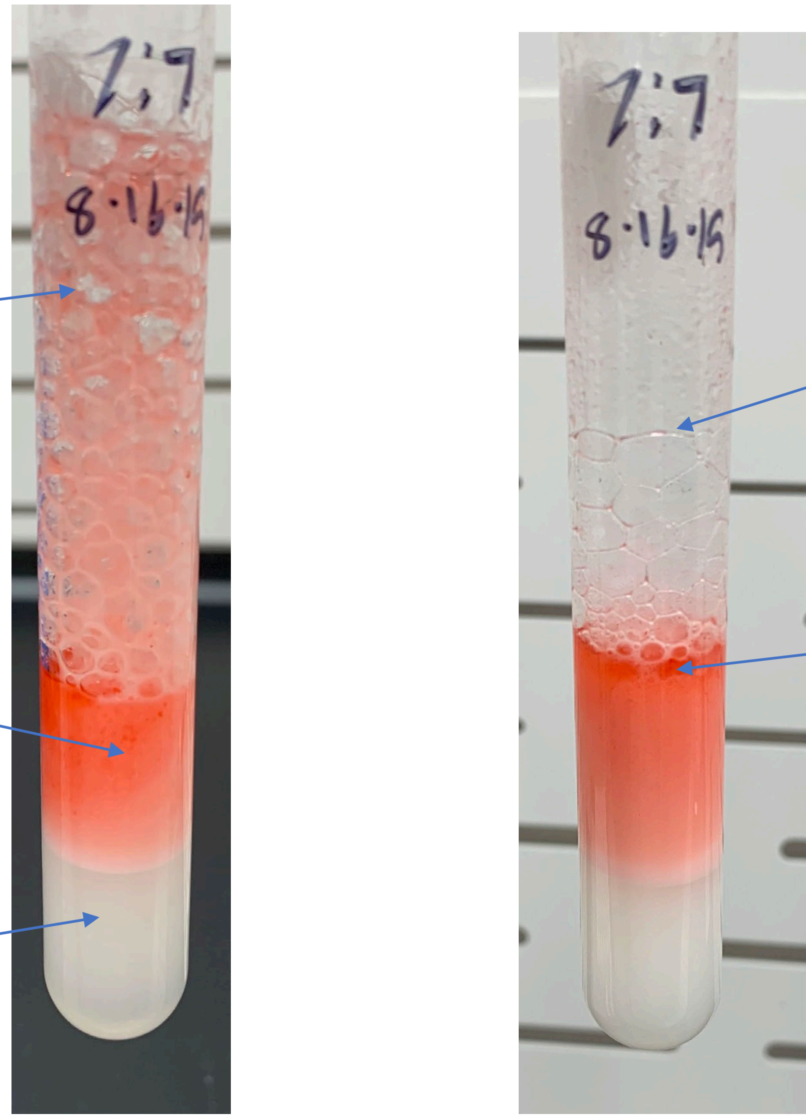
Macroemulsion

Aqueous Phase

4 mL : 4 mL

AFFF Phase Behavior

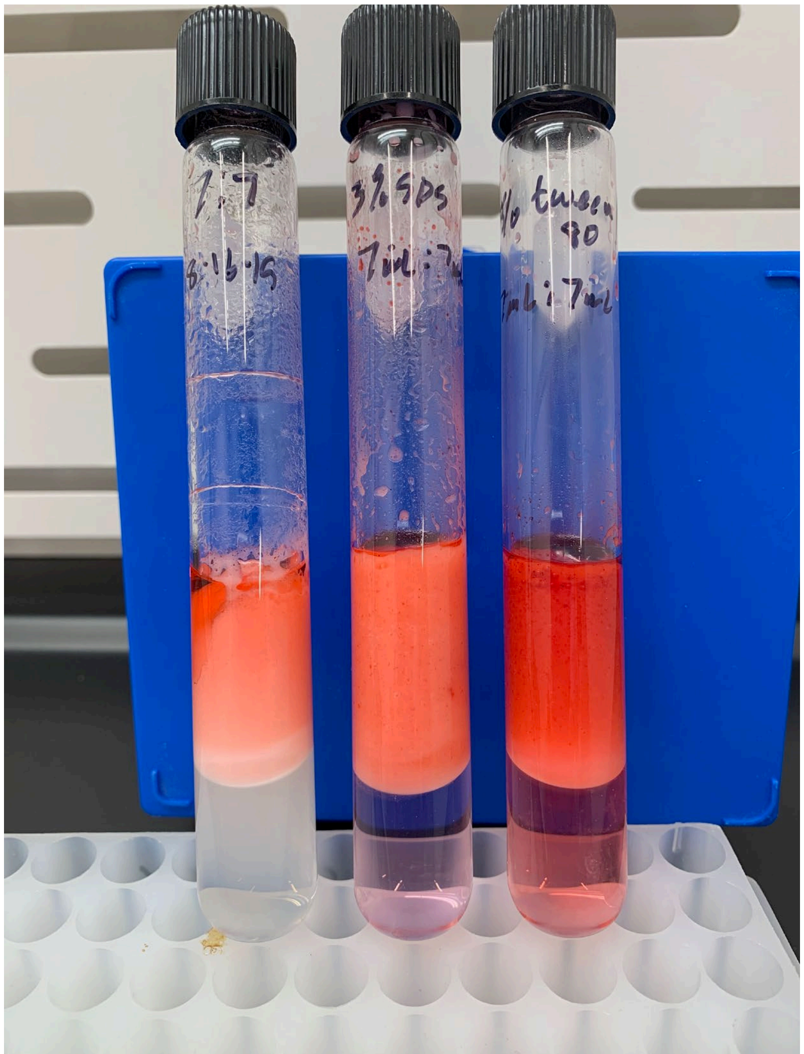
JP4 Jet Fuel (Oil Red O)



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

Mathematical Modeling of PFAS Transport in the Unsaturated Zone

Modeling PFAS Adsorption at Air-Water Interface

Objective: Incorporate nonlinear PFAS adsorption at air-water interface using a modified version of Hydrus 1D

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*

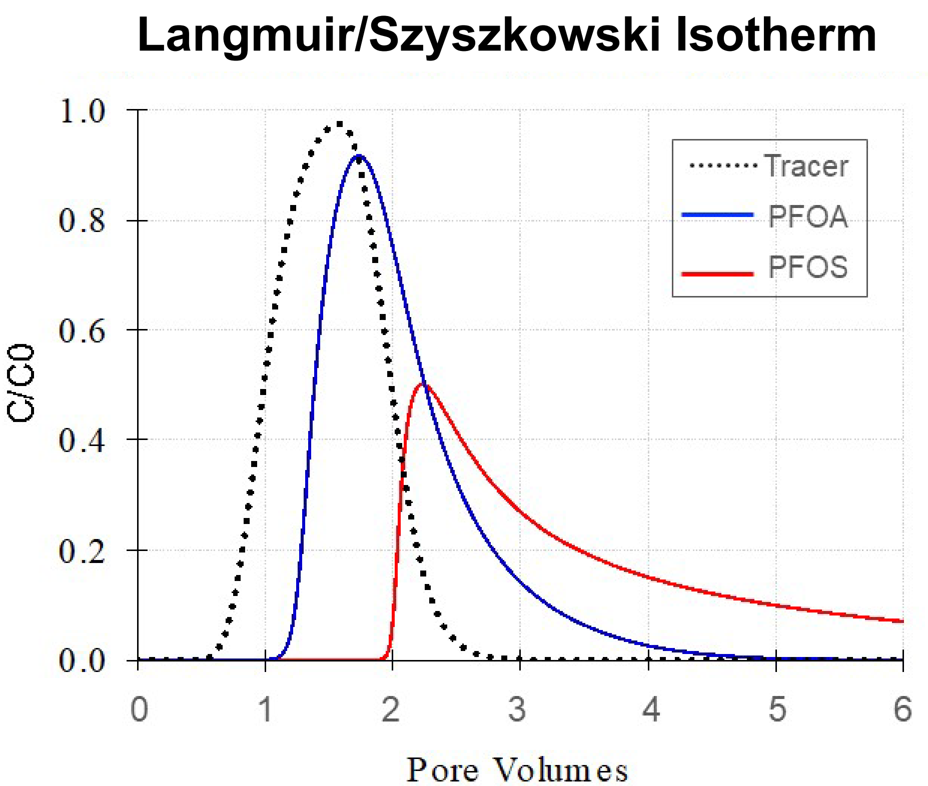
Specific Interfacial Area $\left[L^{-1}\right]$, $A_{ai} = SA\left(0.9031 - 0.9012\frac{\theta}{\theta_s}\right)$

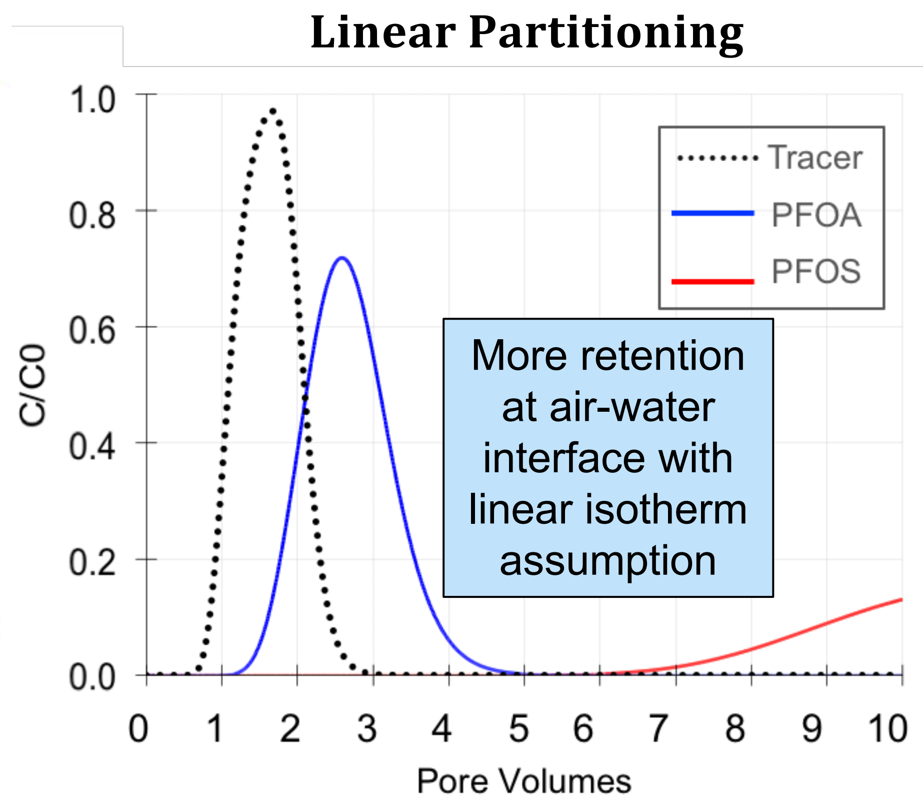
SA: Geometric su rface area $\left[L^{-1}\right] = \frac{6(1-\varphi)}{d_{50}}$

(Costanza-Robinson et al., 2008)

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

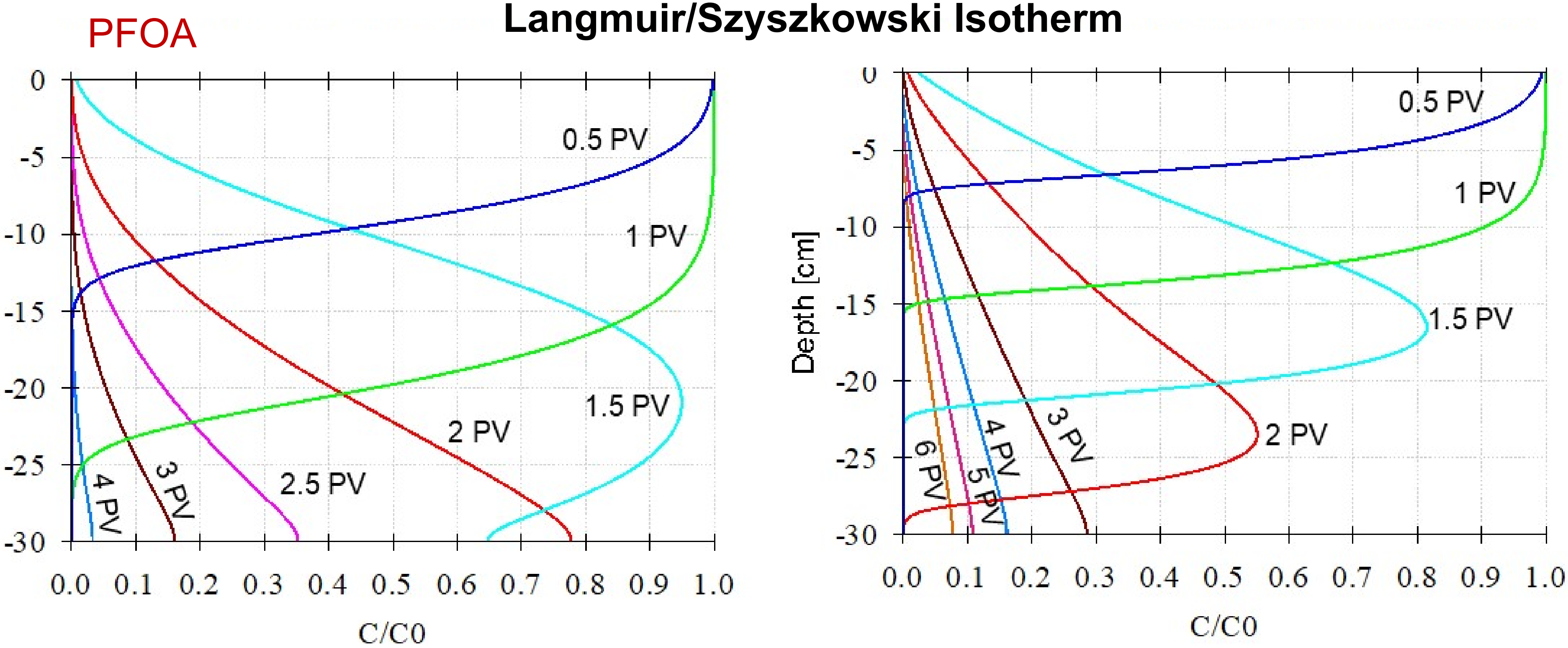
Effect of PFAS Accumulation at Air-Water Interface on Unsaturated Zone Transport





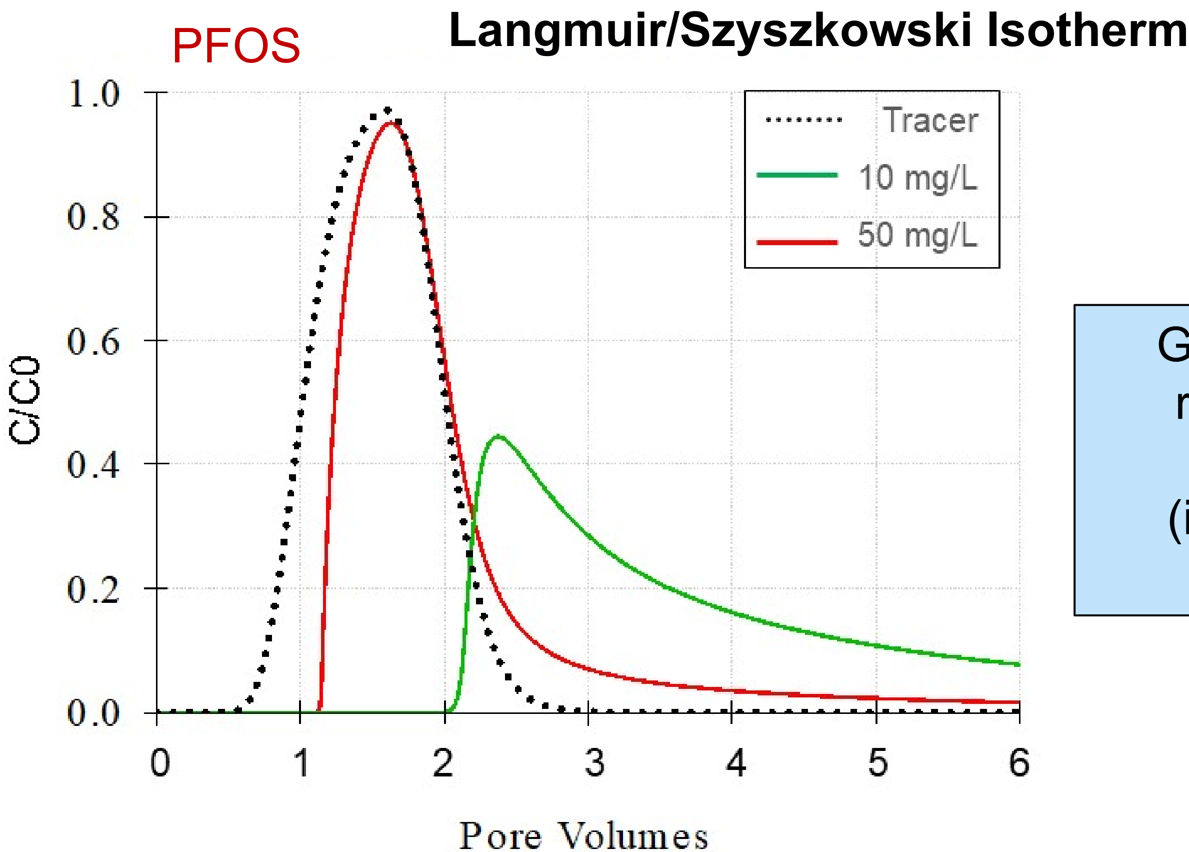
- Pulse injection (1 PV) of PFOA or PFOS (10 mg/L)
- Medium level of total dissolved solids (400 mg/L TDS)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

PFAS Vertical Concentration Profiles in Unsaturated Soil



- 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 on Unsaturated Zone Transport of PFOS



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

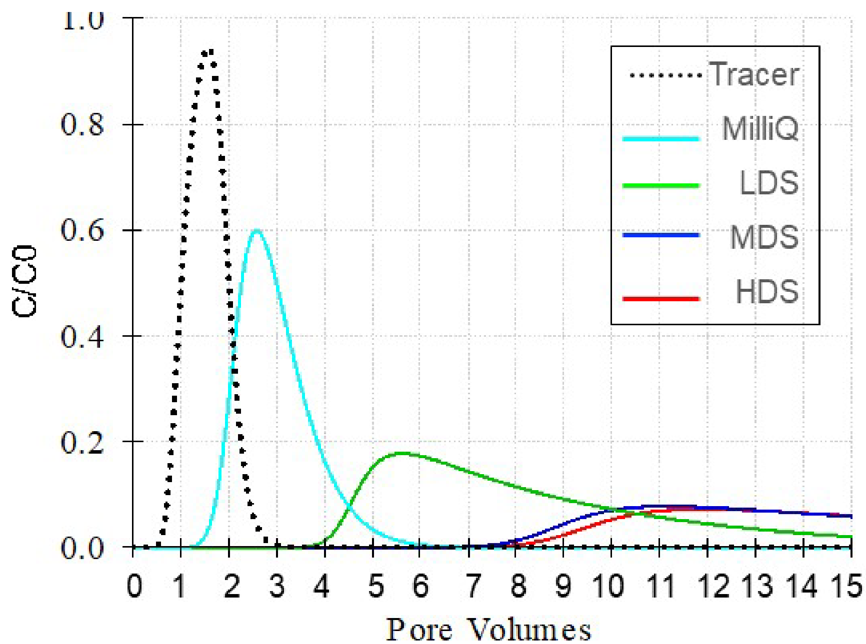
- Pulse injection (1 PV) of PFOS (10 mg/L or 50 mg/L)
- Medium level of total dissolved solids (400 mg/L TDS)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, $\theta_w = 0.27$

Effect of Soil Water Content and TDS on PFOS Transport

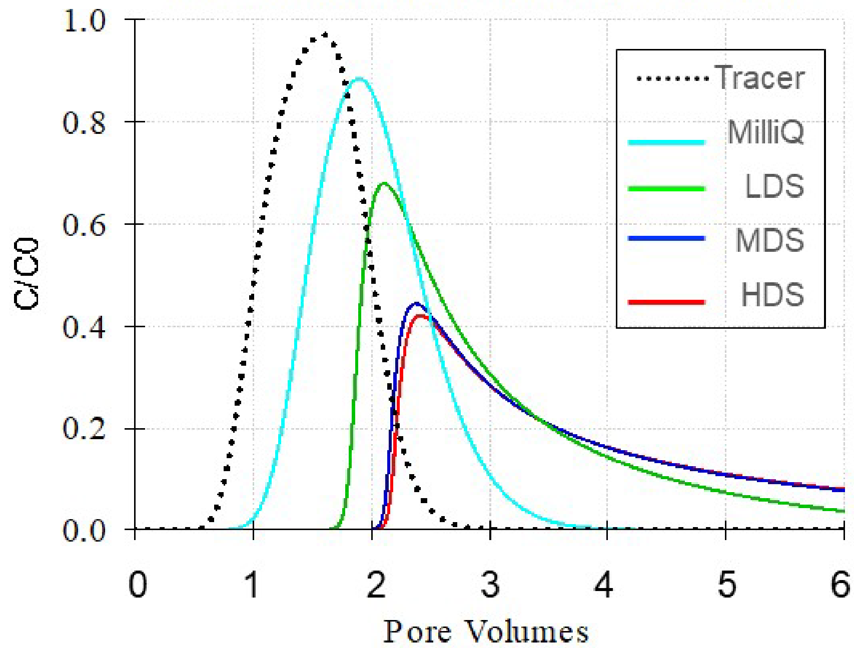
$$\text{Interfacial Area } [L^{-1}], A_{ai} = SA\left(0.9031 - 0.9012\frac{\theta_w}{\theta_s}\right)$$

Langmuir/Szyszkowski Isotherm

θ_w= 0.20



θ_w= 0.27



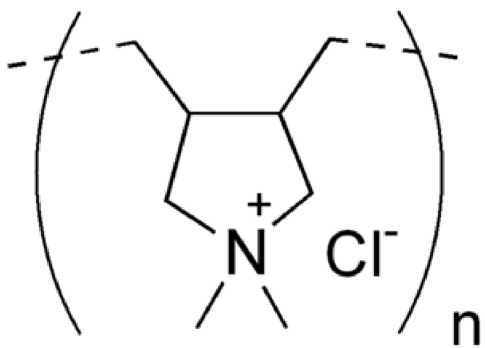
- Pulse injection (1 PV) of PFOS (10 mg/L)
- F-70 Ottawa sand (40-270 mesh)
- Uniform water content, θ_w = 0.20 or 27

In Situ Sequestration of PFAS

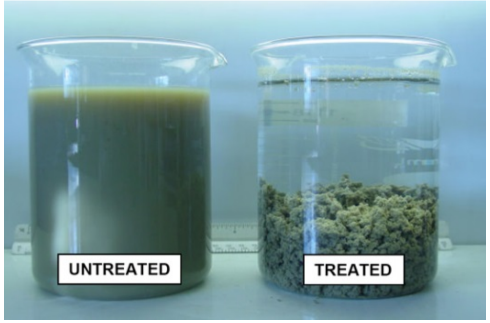
Coagulant polymers (cationic surfactants)

SERDP Project ER-2425

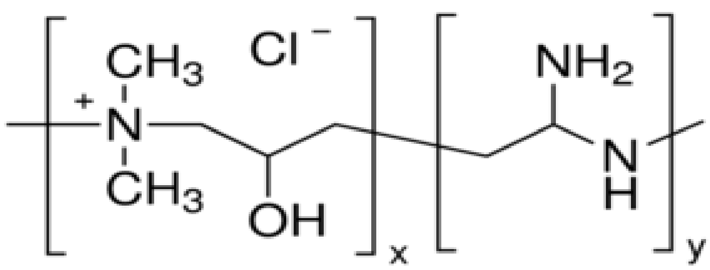
Poly-DADMAC (PDM)



- Accepta 4351
- ~ 28% OC
- Quaternary Amine
- diallyl dimethylamine
- MW ~ 350,000



Polyamine (PA)



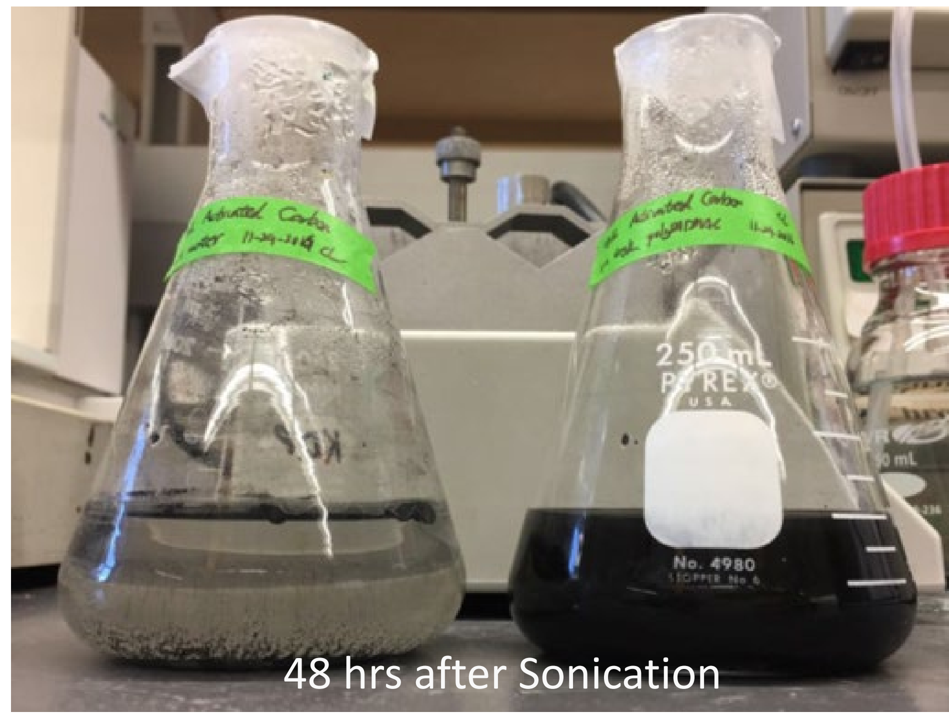
- Accepta 4350
- ~ 26% OC
- Quaternary Amine
- epichlorohydrine and dimethylamine
- MW ~ 240,000

To improve performance….combine Powdered Activated Carbon (PAC) with polyDADMAC (PDM)

- PDM acts to stabilize PAC in suspension, facilitates delivery
- Both PDM and PAC can serve as sorbents (wide range of effectiveness)

1 g/L PAC   1 g/L PAC + 5 g/L PDM

1 g/L PAC   1 g/L PAC + 5 g/L PDM



DARCO® 100 mesh (150 µm)
Powdered Activated Carbon (Sigma Aldrich)

Provisional Patent Application: Reg. No. 41,942, Docket No. 70011-067P01v (September, 2017)

Commercially Available (Proprietary) PFAS Sorbents

RemBind™-Tersus

Activated carbon, aluminum hydroxide, organic matter and other additives, intended for near surface soil mixing

PlumeStop® Liquid Activated Carbon™–Regenesis

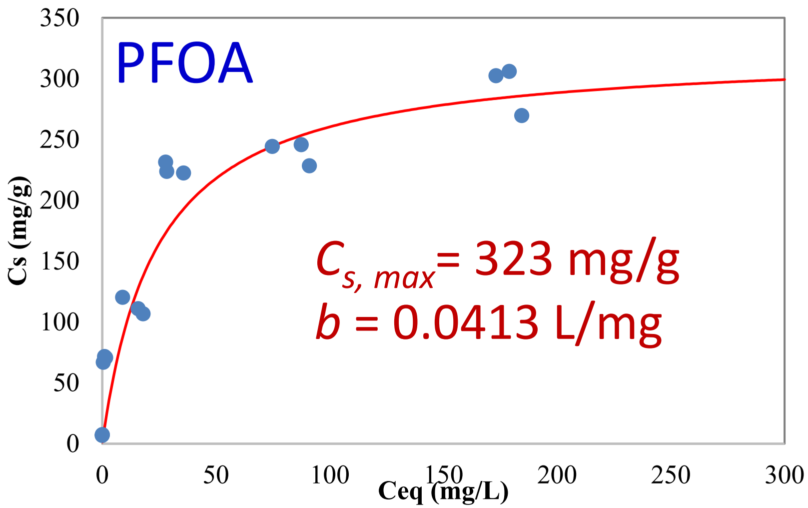
Activated carbon (1-2µm) suspended in water dispersed with organic polymer

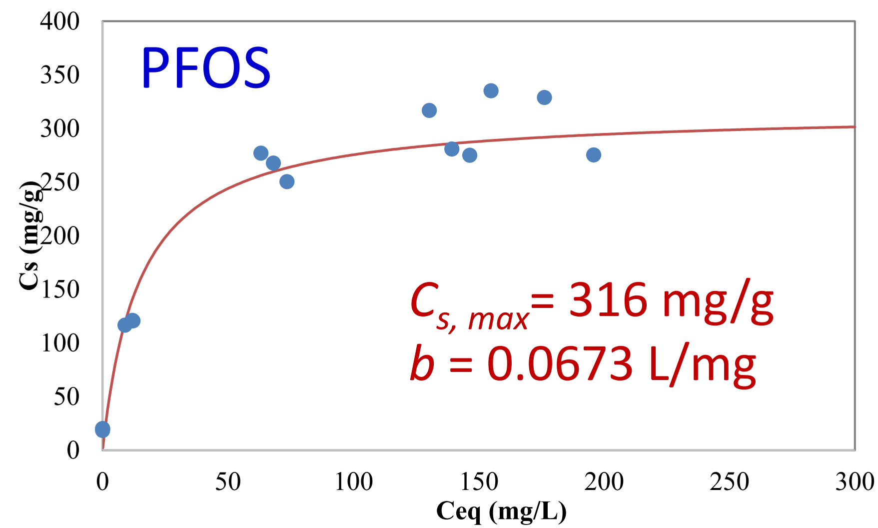
InTreat WATER BY InSite

InTreat SOIL BY InSite

- Limited independent verification
- Limited data (e.g., mass balance)
- In situ delivery issues rarely addressed

PFOA and PFOS Batch Adsorption Studies With Darco® PAC (100-mesh)

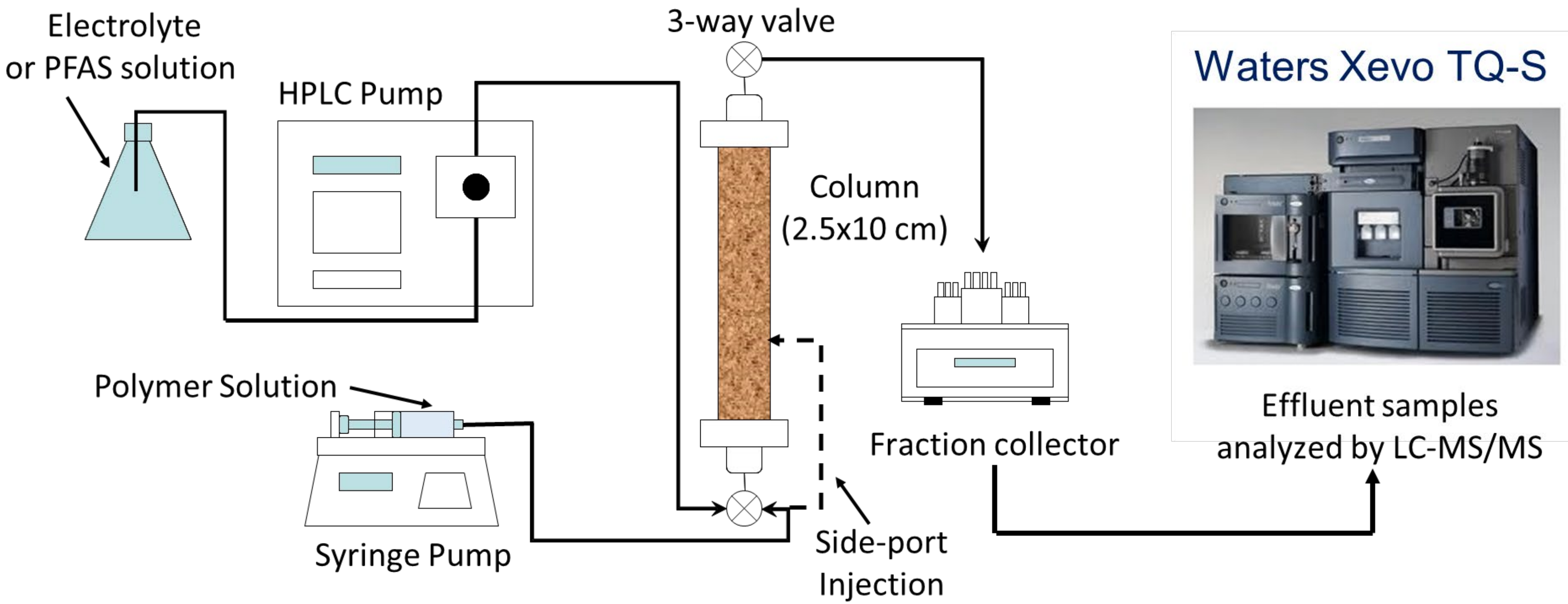




Langmuir Isotherm

$$C_s = \frac{C_{s,\,max} * b * Cw_{,\,eq}}{1 + b * C_{w,\,eq}}$$

Schematic Diagram of 1-D Column System

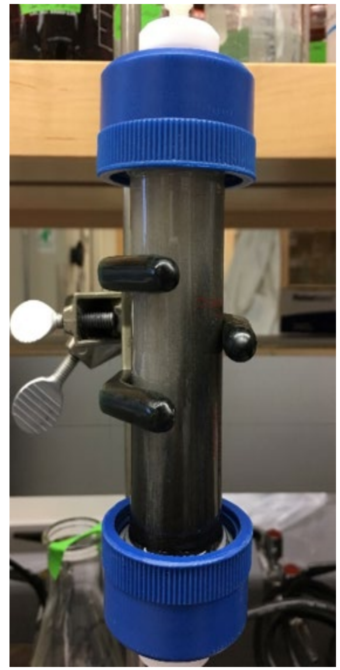


(1) Non-reactive tracer test (pulse injection), (2) Inject PDM+PAC suspension, (3) Inject background electrolyte, (4) Inject PFAS solution (e.g., 100 ug/L PFOS)

Injection of PDM+PAC Suspension

t = 0
PV

after 3.5 PV
PAC+PDM



after 3.5 PV
background

Flow Direction

26.8 mg of PAC retained in column

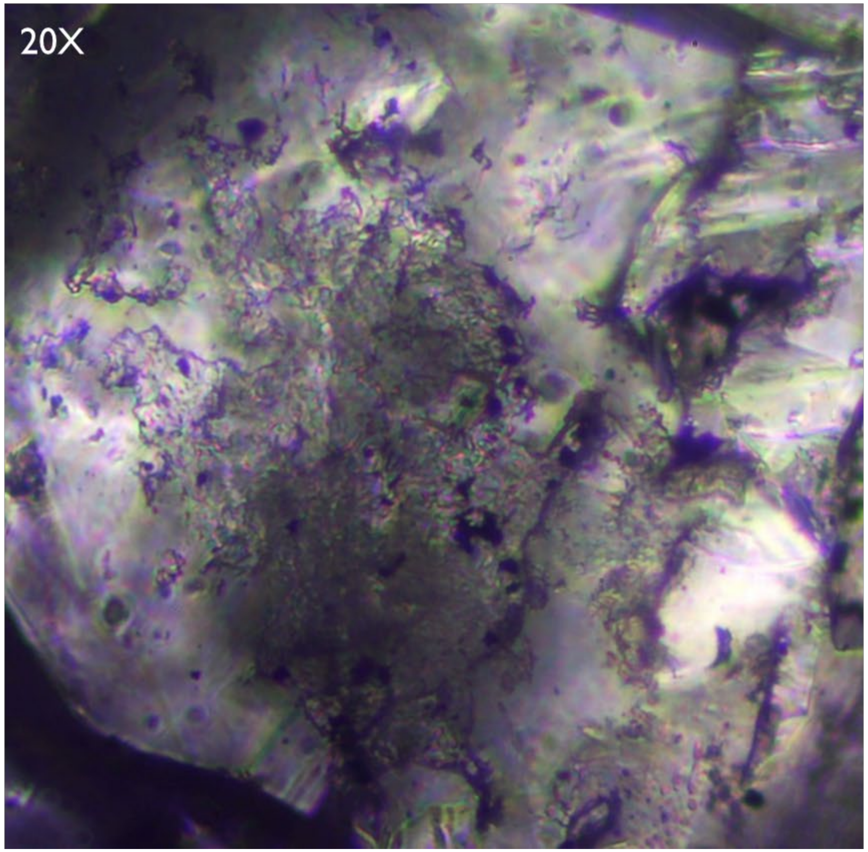
40-50 mesh Ottawa Sand (d_{50} = 358 um), k_i = 7.37x10^{-11} m^2, n = 0.37, SSA = 0.0125 m^2/g, PV = 22 mL

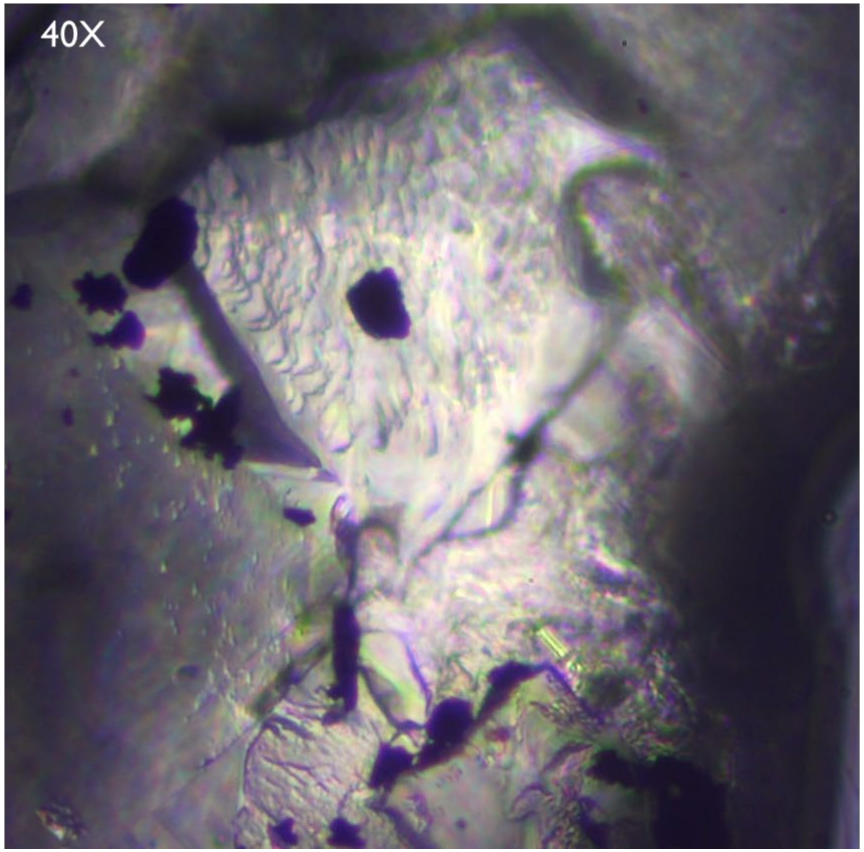
PDM+PAC Suspension: 1,000 mg/L PAC + 5,000 mg/L PDM, viscosity = 1.18 cP

Flow rate: 0.12 mL/min; pore-water velocity ~1.0 m/day

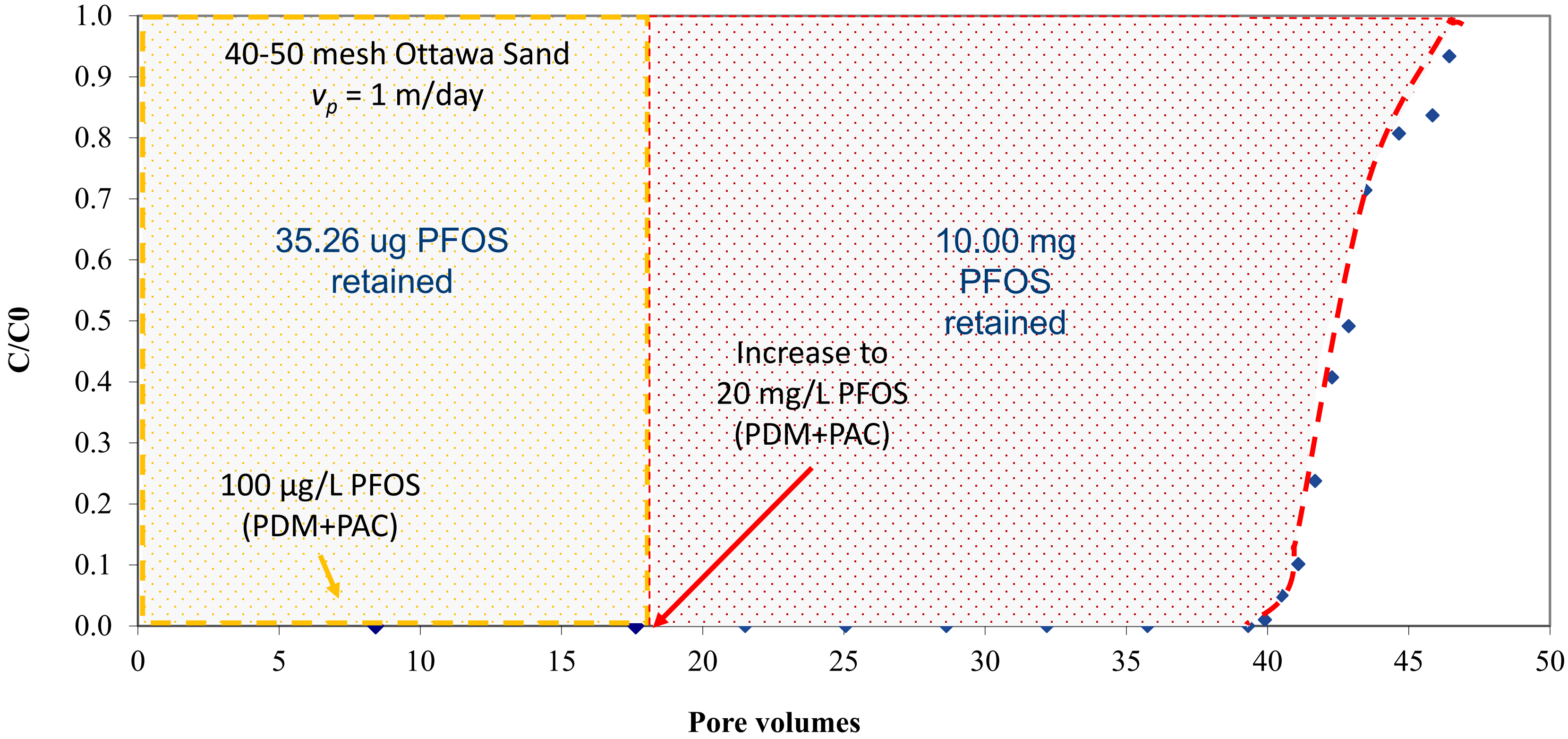
Images of PDM+PAC Treated Ottawa Sand

Leica DM IL LED





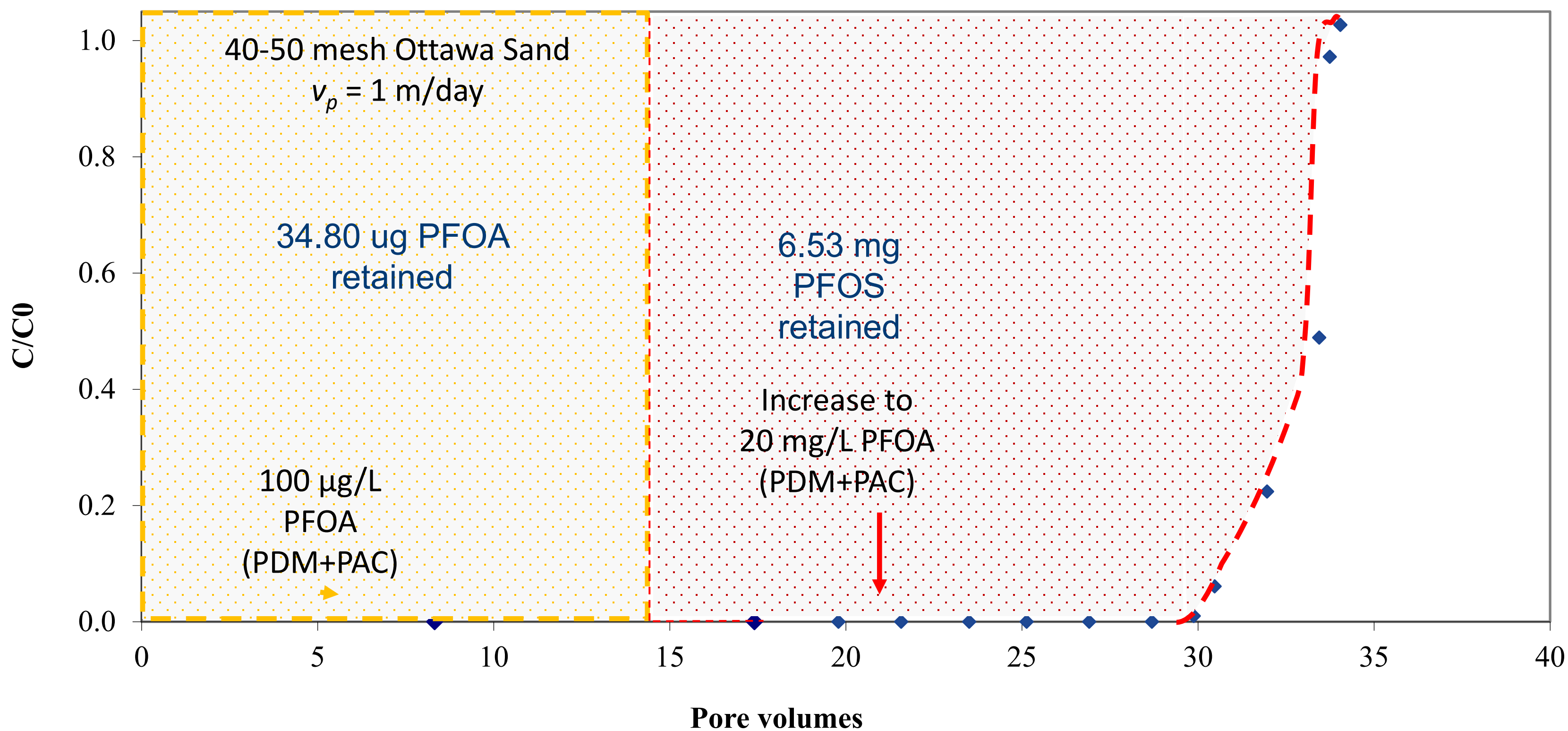
PFOS Column: S-PAC treated 40-50 mesh Ottawa Sand



Based on the measured $C_{s,max}$ = 316 mg/g and mass of retained PAC (~27 mg), the capacity of the column should be ~ 8.65 mg PFOS, consistent with the observed retention of ~10.04 mg PFOS

For a 100 µg/L injection; ~2 ug PFOS retained/PV, capacity would be reached after ~5,020 PV

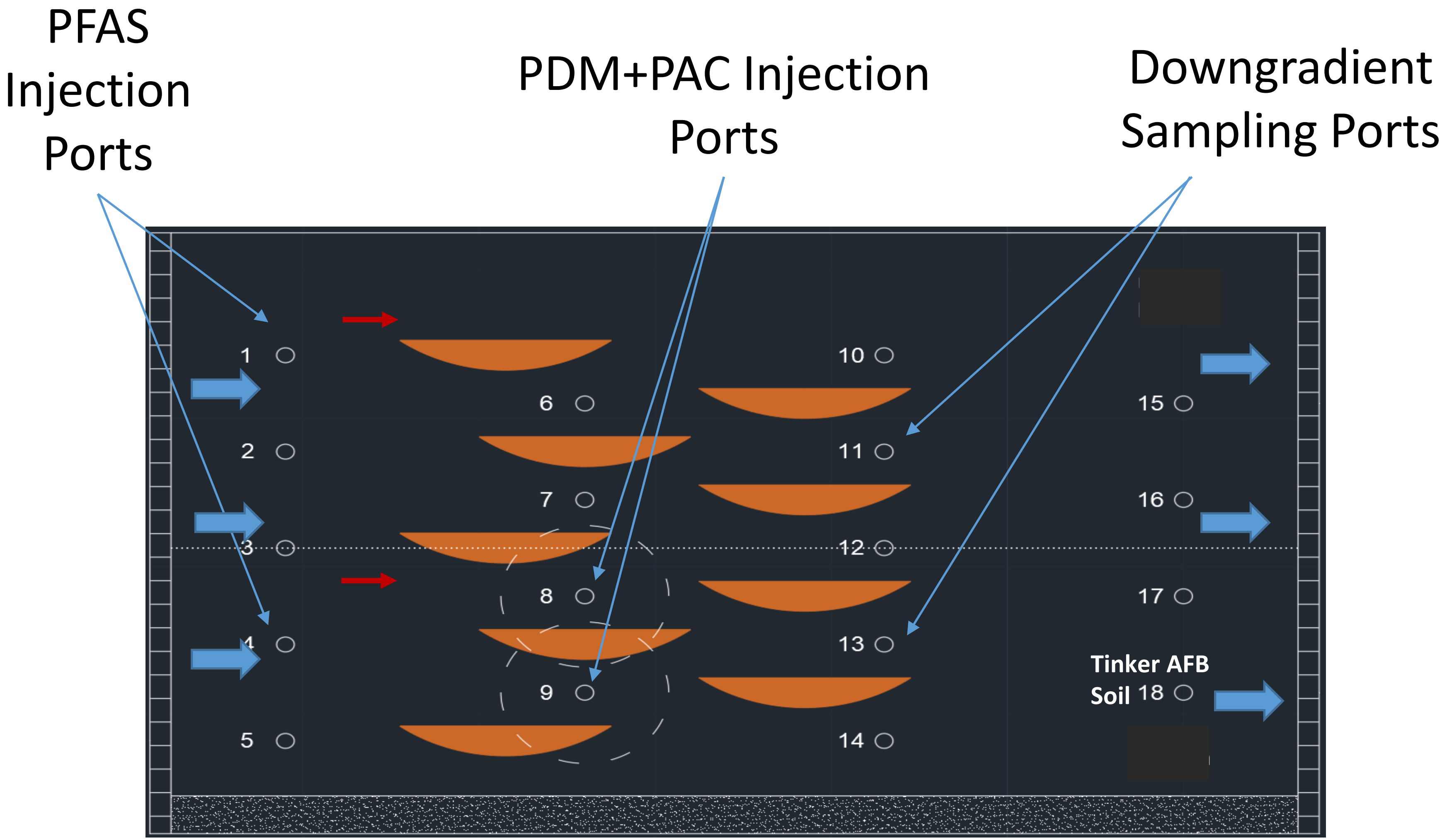
PFOA Column: S-PAC treated 40-50 mesh Ottawa Sand



Based on the measured $C_{s,max}$ = 323 mg/g and mass of retained PAC (~14.8 mg), the capacity of the column should be ~ 4.78 mg PFOS, consistent with the observed retention of ~6.57 mg PFOA

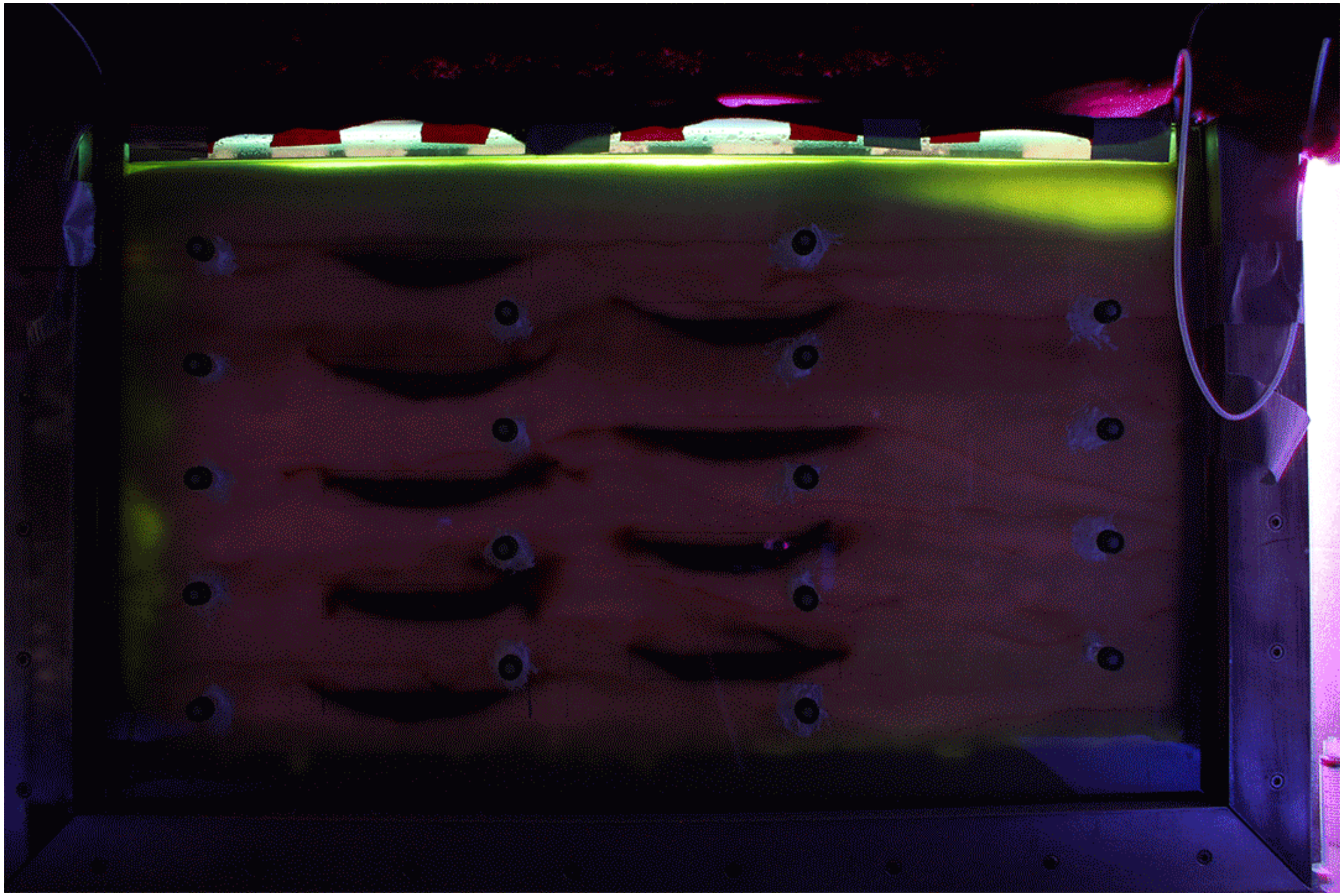
For a 100 µg/L injection; ~2 ug PFOA retained/PV, capacity would be reached after ~3,600 PV

Configuration of Aquifer Flow Cell



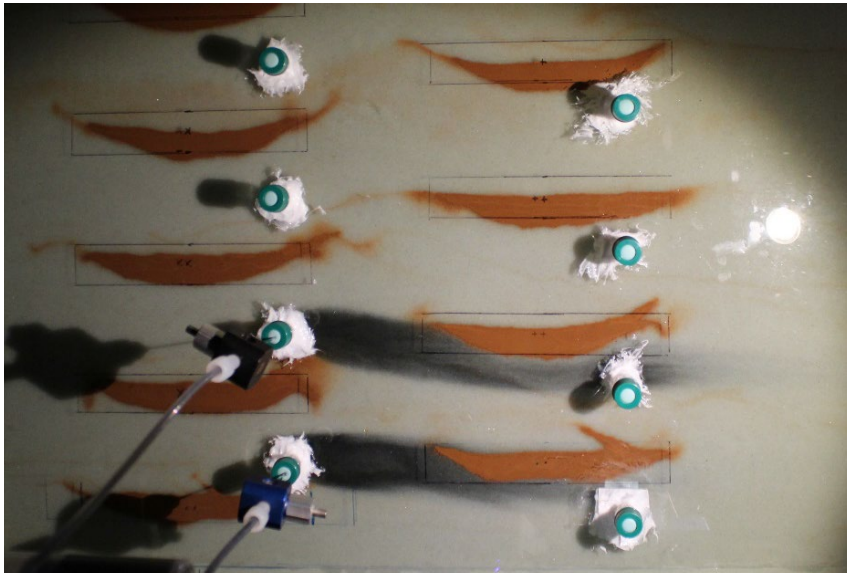
PV=1.45L

Tracer Test Before PDM+PAC Injection

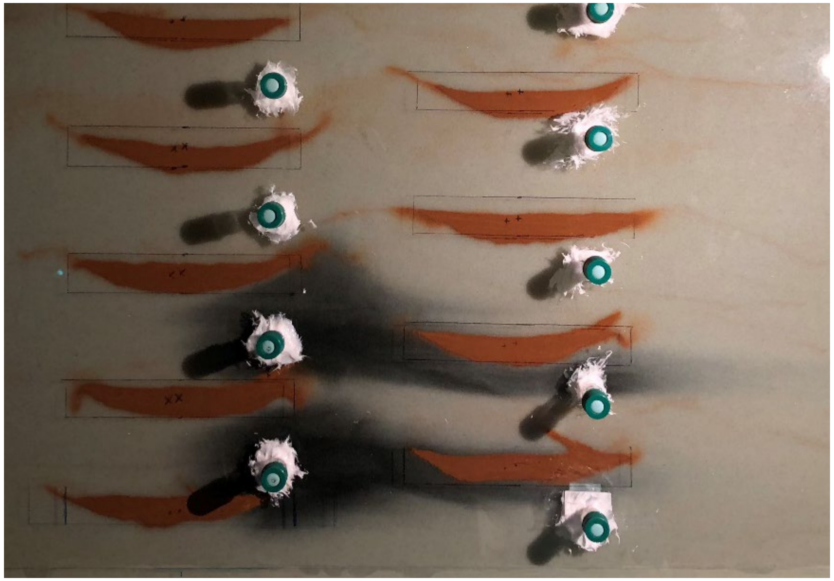


Side-port Injection of 1 g/L PAC + 5 g/L PDM

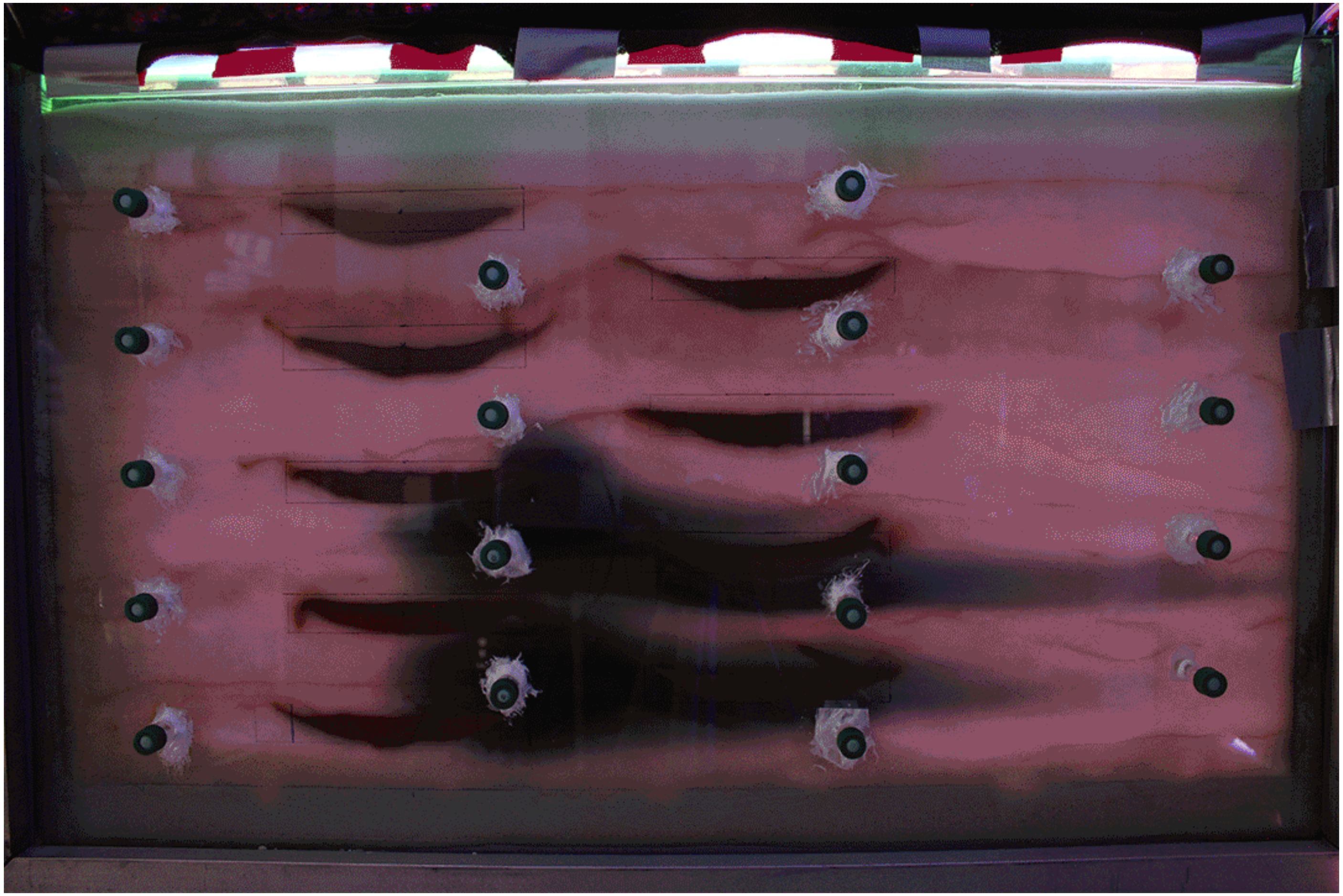
40 mL (0.08 mL/min) with background flow (2.4 mL/min)



80 mL (0.08 mL/min) with no background flow



Tracer Test After PDM+PAC Injection



Acknowledgements

SERDP
DOD ▪ EPA ▪ DOE

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JACOBS