Development and Laboratory Validation of Mathematical Modeling Tools for Prediction of PFAS Transformation, Transport, and Retention in AFFF Source Areas (ER18-1149)

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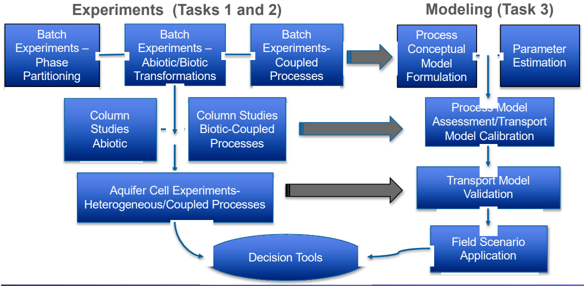
Objectives

The proposed research is an integrated experimental and modeling study designed to:

1. Improve our understanding of sequestration mechanisms and abiotic/biotic transformations that control the transport and persistence of selected PFASs in natural aquifer materials.
2. Develop and validate mathematical models and decision tools that describe the key processes governing transformation, transport, and retention of these selected PFASs in complex AFFF source areas.

Technical Approach



Schedule

Overall Project Plan	2018				2019				2020				2021			
Task 1: Transport and Phase Partitioning Studies																
A. Phase Partitioning Studies			X	X	X	X	X	X								
B. Transport Studies					X	X	X	X	X	X						
Task 2: Coupled Abiotic and Biotic Transformation Studies																
A. Batch Reactor Experiments					X	X	X	★[1]	X	X						
B. Column Studies						X	X	X	X	X	X					
C. Aquifer Cell Studies									X	X	X	X	X	X		
Task 3: Mathematical Modeling and Decision Tool Development																
A. Batch Experiment Modeling			X	X	X	X	X	X	X	X						
B. Model Development and Validation			X	X	X	X	X	X	X	X	X	X				
C. Model Application							X	X	X	★[2]	X	X	X	X		
D. Decision Tool Development							X	X	X	X	X	X	X	X		
Task 4: Research Translation and Project Reporting																
A. Quarterly Progress and Interim Reports									X		X			X		

★ **GO/NO-GO Decisions:** [1] demonstration of reactivity; [2] collection of representative site data for scenario development

Results to Date

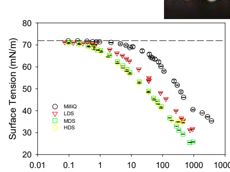
Task 1A: Phase Partitioning Experiments

Dissolved Counterion Effect

- Background is a solution of $MgSO_4$, $NaHCO_3$, KCl, and $CaCl_2$ to simulate principal aquifers in US
  - **Low Dissolved Solids (LDS)** ca. 40 mg/L
  - **Mid Dissolved Solids (MDS)** ca. 400 mg/L
  - **High Dissolved Solids (HDS)** ca. 1,700 mg/L

PFOA and PFOS Stock Preparation

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

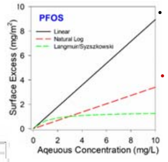


- Dissolved salts lower surface tension for PFOA and KPFOS

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

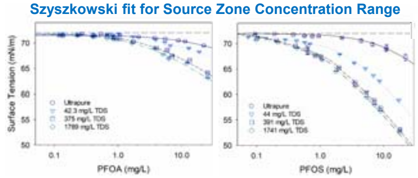
$$\gamma=\gamma_0\left[1-aLn\left(\frac{C}{b}+1\right)\right]\rightarrow\ \Gamma=-\frac{C}{RT}\left(\frac{\partial\gamma}{\partial C}\right)_T\rightarrow\ \Gamma=\frac{a\gamma_0}{RT}\frac{C}{C+b}$$

Szyszkowski Eq. Fit of Surface Tension — Gibb's Eq. — Langmuir-Szyszkowski Eq.



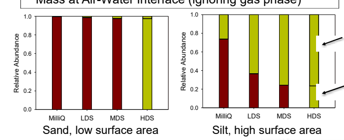
- Linear: $\Gamma=K_iC_w$, $K_i=\frac{1}{RT}\frac{\partial\gamma}{\partial C}$
- Natural Log: $\Gamma=K_i\frac{C_w}{C_{ref}}$, $K_i=\frac{1}{RT}\frac{\partial\gamma}{\partial \ln C}$

Szyszkowski fit for Source Zone Concentration Range



PFOS Phase Distribution in Unsaturated Soils

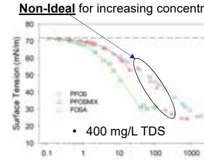
- Total PFOS Mass = Mass in Water + Mass on Solids + Mass at Air-Water Interface (ignoring gas phase)



Sand, low surface area — Silt, high surface area

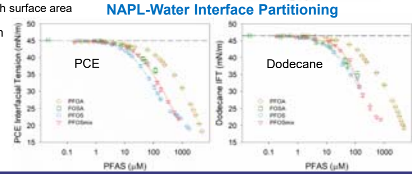
PFAS mixture

- Mix of PFBS, PFHxS, PFOS and FOSA (0.3 : 0.3 : 0.2 : 0.2 mole fractions)
- PFBS and PFHxS not surface active
- FOSA surface tension lowest at equivalent concentration
- PFOS mixture had "ideal" surface tension from 0.2 to 20 µmol/L, was **Non-Ideal** for increasing concentrations



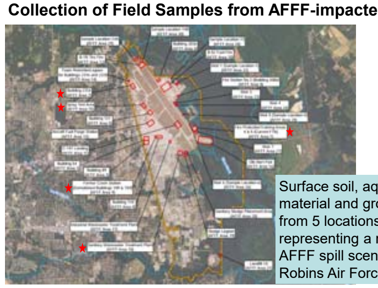
NAPL-Water Interface Partitioning

- Drop of NAPL suspended in PFAS solution
- 1700 mg/L TDS
- Confirmed oleophobic nature of the perfluorocarbon chain
- Significant reduction in interfacial tension only observed for >100 mg/L
- Lowest IFT greater than 5 mN/m needed for mobilization or emulsification

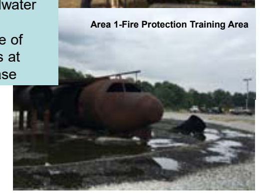


Task 2: Coupled Abiotic and Biotic Transformation Studies

Collection of Field Samples from AFFF-impacted Sites at Robins AFB (Georgia)

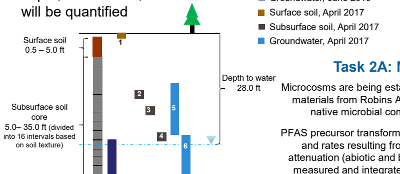


Surface soil, aquifer material and groundwater from 5 locations representing a range of AFFF spill scenarios at Robins Air Force Base



Assessment of PFAS concentration and microbial community structure

- Relationships as a function of soil depth, OC content, and CEC will be quantified



Area 15

	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 collected and analyzed by Aerostar SES LLC
Units: µg/kg for soil, µg/L for water sample.

Task 2A: Microcosm Experiments

Microcosms are being established using materials from Robins AFB with the native microbial community

PFAS precursor transformation products and rates resulting from natural attenuation (abiotic and biotic) will be measured and integrated in Task 3 modeling

Contaminants: Single-component PFAS precursors, 8:2 FTOH or EtFOSE (~100µg/L); additional PFAS single-component or mixtures are under consideration

Microcosm conditions to be investigated:

1. Under either aerobic, nitrate- reducing, sulfate-reducing, or methanogenic redox conditions

2. In the presence of a reactive iron species (e.g., goethite FeO(OH) and magnetite (Fe_3O_4))

3. With dissolved phase (< 10 mg/L) PCE, dodecane, or JP-4 jet fuel to examine the impact of likely co-contaminants

Task 3B: Modeling of PFAS Adsorption to Air-Water Interface

Objective: Implement nonlinear equilibrium adsorption to air-water interface in a modified version of Hydrus 1D using the results from batch experiments in Task 1A.

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/Szyszkowski 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: $\Gamma^i=K_iC^i$ — *K_i : linear partitioning coefficient*

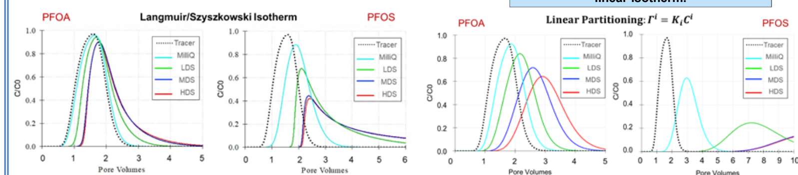
Specific Interfacial Area $[L^{-1}]$, $A_{ai}=SA\left(0.9031-0.9012\frac{\theta}{\theta_s}\right)$ — SA: Geometric surface area $[L^{-1}]=\frac{6(1-\varphi)}{d_{50}}$ (Costanza-Robinson et al., 2008)

$$\theta_w: water\ content, \theta_S: saturated\ water\ content, \varphi: porosity,\ s_\alpha: saturation\ of\ \alpha-phase$$

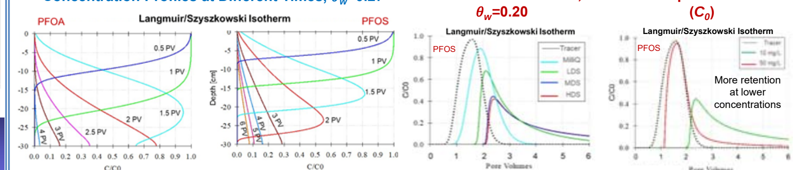
Effect of Salt Concentration and Adsorption Isotherm

- F-70 Ottawa sand, L=30 cm, Pulsed injection of PFAS for 1 PV. C_0=10 mg/L, θ_w=0.27

More retention at air-water interface with **linear isotherm.**

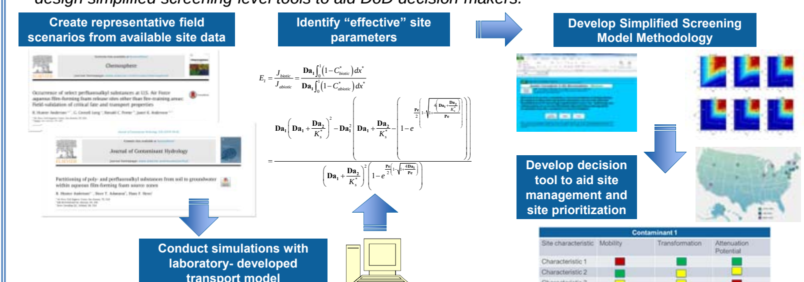


Concentration Profiles at Different Times, θ_w=0.27 — **Effect of water content, θ_w=0.20** — **Effect of Input Concentration (C_0)**



Task 3D: Decision Tool Development

- *Leverage the mathematical models developed in Subtasks 3B-C to evaluate field-scale scenarios and design simplified screening-level tools to aid DoD decision-makers.*



Lesson Learned

- The influence of PFOA and PFOS on interfacial tension was accurately captured by the Szyszkowski equation, yielding Langmuir interfacial partitioning parameters.
- The presence of Total Dissolved Solids (TDS) substantially increases interfacial adsorption of PFOA and PFOS at air-and NAPL-water interfaces.
- An user friendly simulator (HYDRUS) was refined to incorporate PFAS interfacial partitioning processes based on laboratory-measured data.
- Simulations demonstrate the potential significance of interfacial adsorption on PFAS transport in unsaturated soils.
- Use of linear partitioning relations to represent interface accumulation can lead to significant errors in predicted mass retention.

Acknowledgements

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