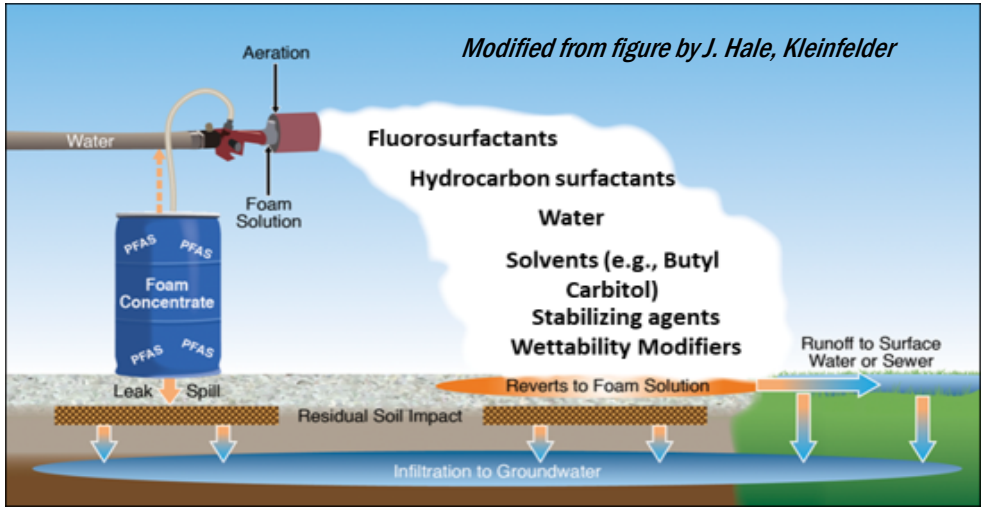
The Influence of Tension-Driven Flow on the Transport of AFFF in Unsaturated Zone

Faran Vahedian[a], Jeff Silva[b], Jiri Simunek[c], John McCray[a]

a Civil & Environmental Engineering Department, Colorado School of Mines
b Arclight Research & Consulting, LLC
c Department of Environmental Sciences, University of California, Riverside

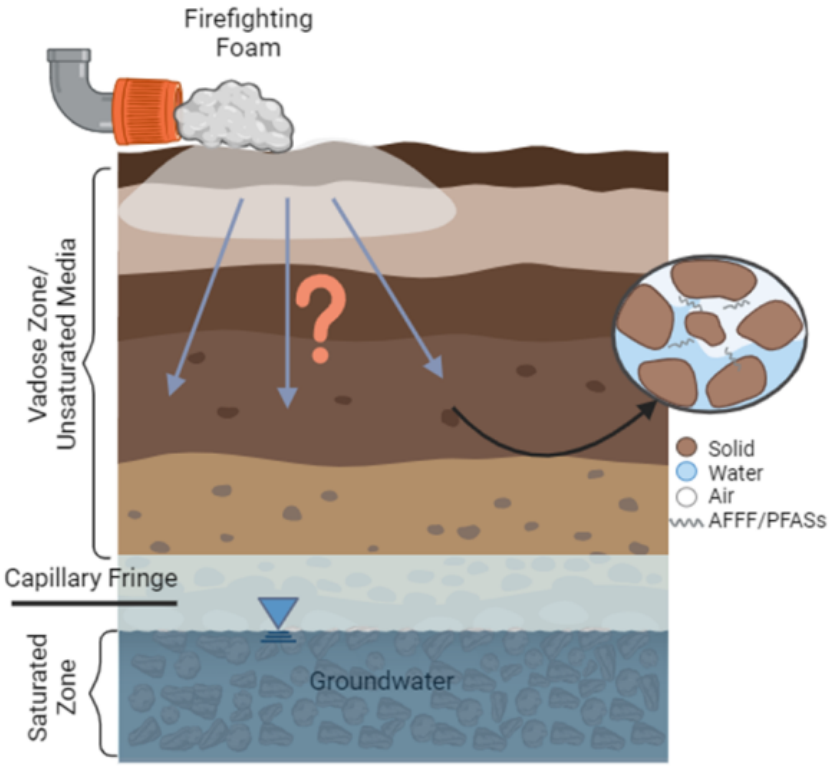
Understanding Source Zones: Key to Conceptual Site Models

- Aqueous film forming foam (AFFF) is a major source of PFAS in the subsurface media
- Complex, exclusive composition.
- PFAS levels in AFFF reach grams per liter.
- Understanding source zones is crucial for conceptual site model development (USAF (1995), USEPA (2011), ITRC (2011), USACE (2012)).



PFAS Transport in the Vadose Zone

- Vadose zone is a significant PFAS retention zone.
- PFAS accumulate at solid surfaces and air-water interfaces.
- AFFF and highest PFAS concentrations found in the top tens of centimeters.
- PFAS modify surface tension in pore water.

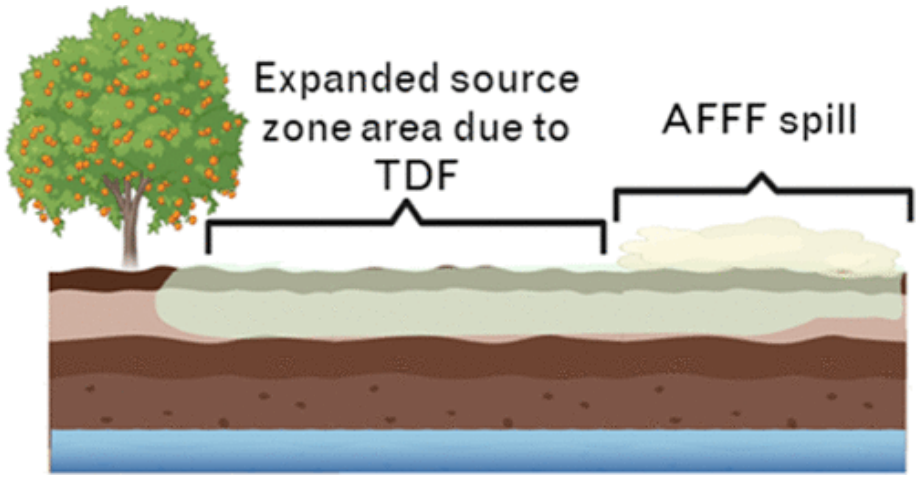


Tension-driven Flow (TDF)

Changes in interfacial tension induced by PFAS or AFFF lead to alterations in capillary pressure gradients, enhancing water movement both laterally and vertically

Motivation

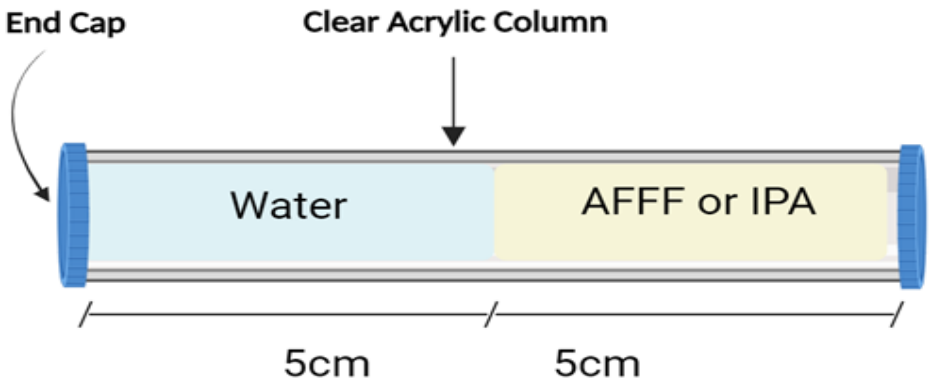
To what extent does the tension-driven flow influence lateral spread of AFFF in unsaturated media?



AFFF typically remains within the application area; however, tension-driven flow can extend its spread beyond the initial boundaries. This suggests that the spill footprint may be larger than commonly assumed.

Methodology- Experiment

- Silica sand
- Isopropyl alcohol (IPA) - surface tension-reducing fluid that does not sorb to soil
- Equal initial moisture content on both sides



- AFFF
  - 0.1% (1,000 mg/L)
  - 1% (10,000 mg/L)

Methodology - Model Formulation

Impact of AWI Solute Adsorption on Flow and interfacial tension (IFT)

Capillary pressure (negative value)

$$h_o = 2\sigma_0 / \rho g r$$

Surface Tension

Soil moisture

$$h_0(\theta, \sigma_0) = \frac{1}{\alpha}\left[S(\theta)^{-\frac{1}{m}} - 1\right]^{\frac{1}{n}}$$

$$S(\theta, \sigma_0) = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1+(\alpha h_0)^n)^m}$$

Unsaturated hydraulic conductivity

$$K(\theta) = K_s S^{0.5}\left[1 - \left(1 - S^{\frac{1}{m}}\right)^m\right]^2$$

Langmuir-Szyszkowski (LS) Eq

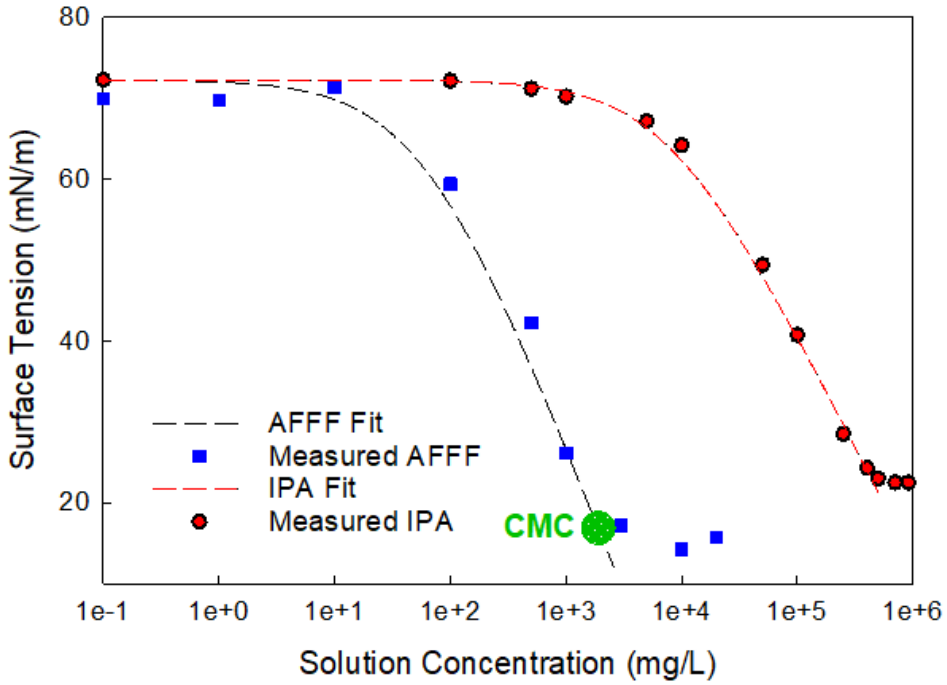
$$\frac{\sigma}{\sigma_0} = 1 - b\ln\left(1 + \frac{C_w}{a}\right)$$

a (ML−3) and b (-) are fitting parameters- Hydrus model input
Cw: Concentration in aqueous phase

$$h(\theta, \sigma) = \left(\frac{\sigma}{\sigma_0}\right) h_0(\theta, \sigma_0) = \alpha_h h_0(\theta, \sigma_0)$$

α_h is the pressure-head scaling factor

Measured surface tension isotherms

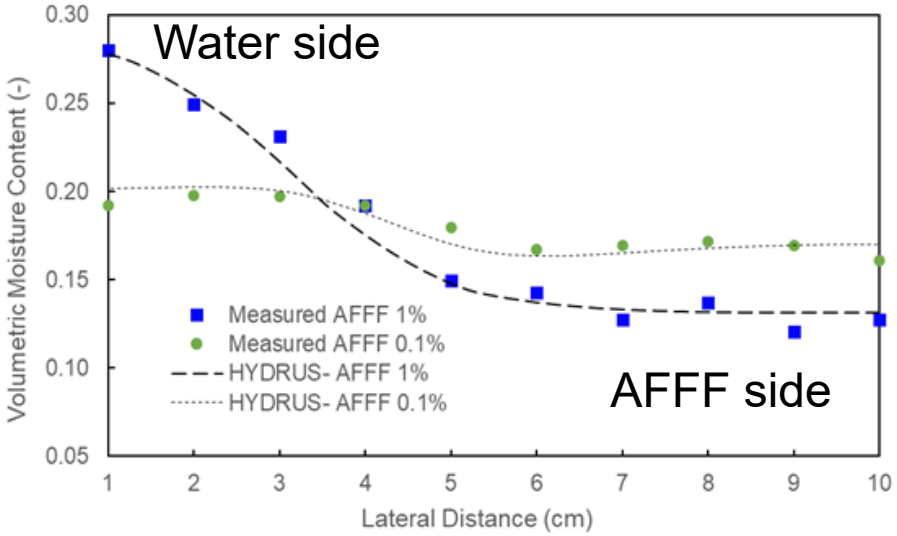


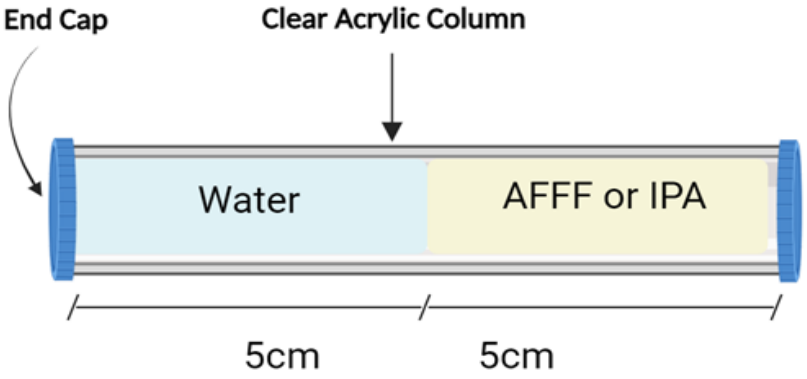
$$\frac{\sigma}{\sigma_0} = 1 - b \ln\left(1 + \frac{C_w}{a}\right)$$ **LS Eq**

For concentrations < CMC, LS EQ is **valid**

For concentrations > CMC, **a consistent IFT** value is integrated into the HYDRUS model

Variations in Moisture Content- AFFF

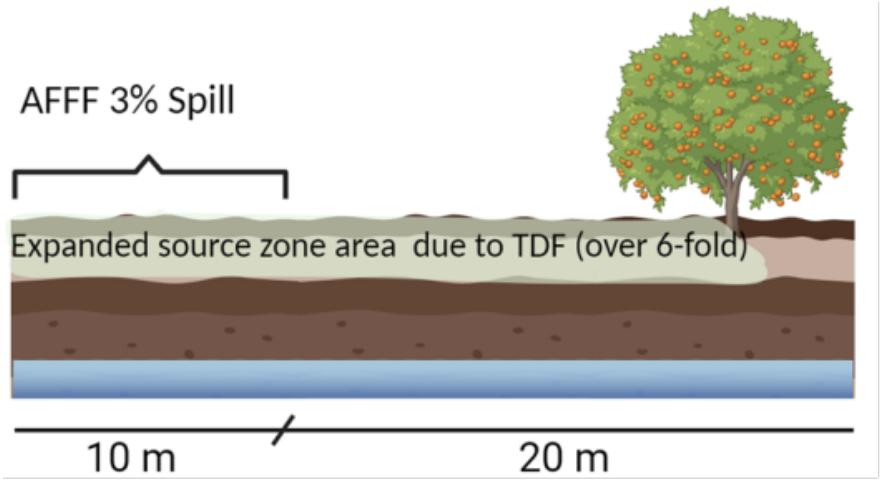


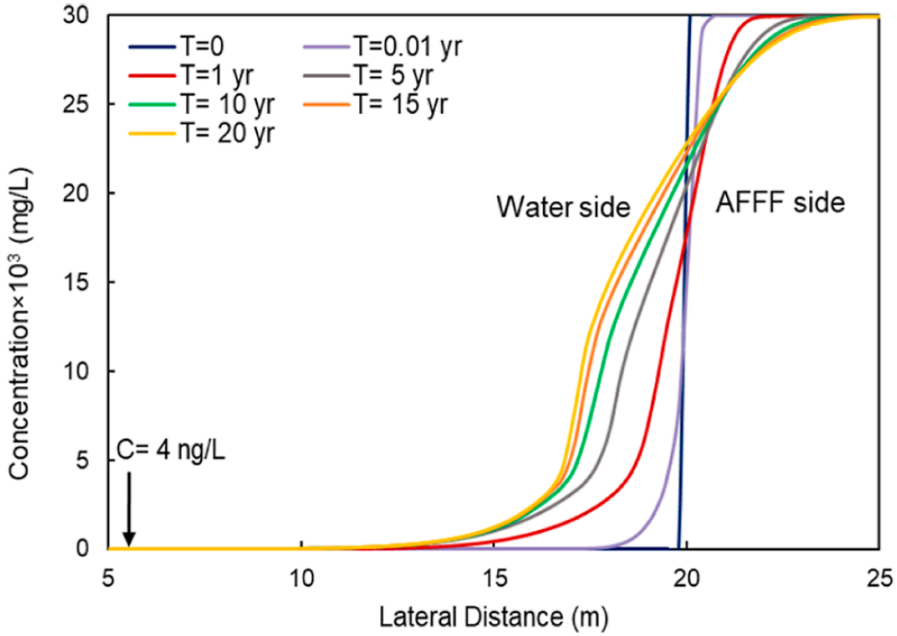


- Alters capillary pressure by up to 60%.
- Modifies unsaturated K(θ), impacting movement rates by up to two orders of magnitude.
- Crucial for predicting multidimensional AFFF transport and travel times.

Numerical Experiments for AFFF 3%

- AFFF 3% contains ~ 200 mg/L of PFOS.
- EPA's 2023 proposed limits for PFOS in drinking water are set at 4 ppt.
- To meet this threshold, AFFF must be diluted to 600 ng/L.
- Initial Moisture Content: 0.28 %





Key Findings

Vahedian et al. "Influence of Tension-Driven Flow on the Transport of AFFF in Unsaturated Media." ACS ES&T Water (2024).

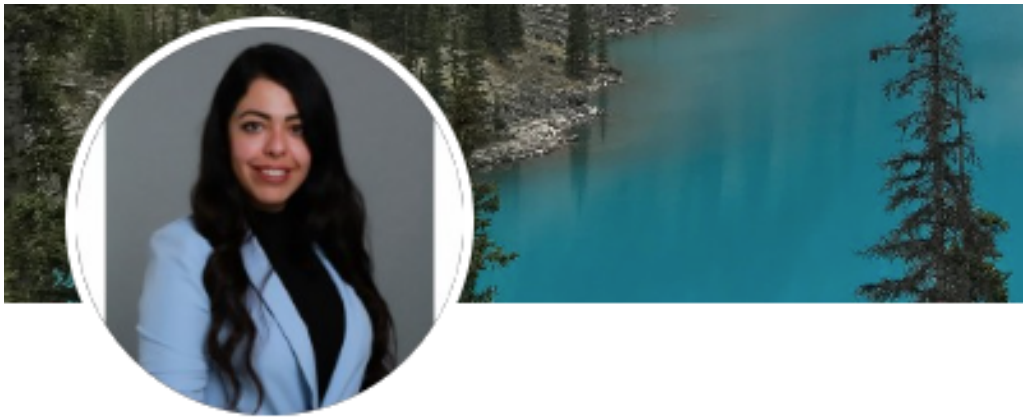
- AFFF introduction enhances tension-driven flow due to altered capillary pressure gradients.
- Modified HYDRUS-1D (HYDRUS 5) effectively simulates TDF with accurate IFT modeling, requiring minimal parameter adjustments.
- AFFF sorption to soil not crucial in clean, sandy media but potentially significant in other soils, and could require longer time for AFFF source zone to achieve final dimensions.
- TDF can significantly expand AFFF source zones during the application period, contradicting traditional assumptions of constant spill footprints.
- Understanding the impact of AFFF application on the footprint of the PFAS source zones is important for establishing accurate site conceptual models to support remediation strategies and groundwater pollution risks.

Follow up Study

- **Project Title:** Evaluate PFAS Transport Processes in AFFF-Impacted Media
- **Methods:**
  - Conducted batch experiments and miscible displacement tests.
  - Utilized analytical LCMS and numerical modeling.
  - Examined both pristine and contaminated media.
- **Results:**
  - Observed enhanced retention of specific PFAS.
  - Noted a transition in PFOS behavior from equilibrium to non-equilibrium.
- **Current Status:** Submitted for review.

Additional Research

- **Project Title:** PFAS transport in unsaturated media under transient flow conditions; impacts of changes in moisture content and air-water interfacial area
- **Methods:**
  - Performed miscible displacement tests.
  - Analyzed the formation and destruction of air-water interfaces.
  - Employed analytical LC-MS and a modified version of the HYDRUS model.
- **Results:**
  - HYDRUS successfully predicted PFAS transport under equilibrium conditions.
  - Observed and simulated kinetic desorption to transport in longer-chain PFAS.
- **Current Status:** currently being drafted; results have been finalized.



LinkedIn:

Faran Vahedian

PhD Candidate

Colorado School of Mines

Email: Fvahedian@mines.edu

Thank you!

Extra slides