

FINAL REPORT

Baseline Data Acquisition and Numerical Modeling to Evaluate
the Fate and Transport of PFAS within the Vadose Zone

SERDP Project ER18-1389

JULY 2019

Jeff Silva
GSI North America Inc.

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Acronyms, Keywords, and Abbreviations

$\geq$	Greater than or equal to
$\leq$	Less than or equal to
$>$	Greater than
$<$	Less than
%	Percent
A_{ia}	Area of the AWI within a given volume of water-unsaturated soil
A_{ni}	Area of the NWI
C_g	Gaseous phase concentration
C_N	Carbon number
C_w	Bulk aqueous concentration
g	Gravitational acceleration
h	Pressure head
I	Ionic strength
k_{ia}	AWI adsorption coefficient
k_{ni}	NWI adsorption coefficient
K_L	Langmuir coefficient
$\log$	logarithm
$\ln$	Natural logarithm
M	Contaminant mass
P_{aw}	Capillary pressure
r	radius
R	Universal gas constant
R_f	Retardation factor
S_w	Water Saturation
T	Temperature of measurement
V	Volume under consideration
ΔG_o^{ads}	Free energy of AWI adsorption
Γ	Surface concentration
Γ_{max}	Maximum surface concentration
Θ_a	Volumetric air content
Θ_r	Residual moisture content
Θ_s	Saturated moisture content
Θ_w	Volumetric moisture content
σ_{aw}	Air-water surface tension
ρ	Solution density
ρ_w	Water density
ω	Contact angle
γ	Surface tension
γ_o	Reference surface tension or that of pure water
1D	One-dimensional
2D	Two-dimensional
$^{\circ}\text{C}$	Degrees Celsius
$\mu\text{g/L}$	micrograms per liter

cm	centimeter
cm/sec	centimeters per second
AFFF	Aqueous film forming foam
APFO	Ammonium salt of perfluorooctanoic acid
ASTM	American Society for Testing and Materials
AWI	Air-water interface
CaSO ₄ •2H ₂ O	Calcium sulfate dihydrate
C _c	Coefficient of Gradation
Cu	Uniformity coefficient
DI	Deionized (water)
DoD	Department of Defense
FLUTe	FLUTe Technologies
g/cm	grams per centimeter
g/L	grams per liter
HYDRUS	Modeling Software
ID	Inside diameter
IPA	Isopropyl alcohol
KCl	Potassium chloride
LHS	Left-hand side
LS	Langmuir-Szyszkowski
MgSO ₄	Magnesium sulfate
MIL-SPEC	U.S. Military Specification
M	Moles
mg/cm	milligrams per centimeter
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
mN/m	milli-Newton per meter
mol/m ²	Moles per square meter
NaCl	Sodium chloride
NaHCO ₃	Sodium bicarbonate
NAPL	Non-aqueous phase liquid
ng/L	nanograms per liter
NH ₄ -PFOA	Ammonium salt of PFOA
NWI	NAPL-water interface
PFAS	Per- and Polyfluoroalkyl substances
PFBS	Perfluorobutanesulfonic acid
PFCA	Perfluorocarboxylic acid
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid

PFPeA	Perfluoropentanoic acid
PFSA	Perfluorosulfonic acid
RHS	Right-hand side
SDoS	Sodium dodecyl sulfonate
SEDRP	Strategic Environmental Research and Development Program
SGW	Synthetic Groundwater
SON	Statement of Need
TCE	Trichloroethylene
U.S.	United States
U.S. EPA	U.S. Environmental Protection Service
VG	van Genuchten
% v/v	Percent by volume
WCC	Water characteristic curve

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Abstract

Introduction and Objectives

Per- and polyfluoroalkyl substances (PFAS) source areas resulting from the use of aqueous film forming foam (AFFF) products exist fully or partially within the vadose zone. However, transport processes for AFFF solutions and PFAS within the vadose zone are not currently well understood. This limited-scope project was conceived to begin to address this knowledge gap.

The specific objectives of this limited-scope project were to:

1. Generate physicochemical properties data that can be used evaluate the significance of AWI adsorption as a source of retention and environmental sink for PFAS within and beneath vadose zone source areas,
2. Investigate the potential for interfacial tension-induced flow and lateral spreading of AFFF solutions infiltrating into the vadose zone to determine the significance of these processes to increase the scale of associated PFAS contamination within source areas, and
3. Incorporate the above mechanisms into an unsaturated flow and contaminant transport model to serve as a numerical tool with which to evaluate (a) concentration-dependent PFAS fate and transport within the vadose zone under variable, dynamic moisture conditions and (b) the transport and spatial disposition of AFFF-fluids within the vadose zone following surface application.

The overriding goal of this project is to develop a numerical tool with which to support DoD efforts to characterize the PFAS source term in the vadose zone environment. Such a model would also improve hydrogeological risk assessments and evaluation of remedial alternatives and/or monitoring strategies.

Technical Approach

The technical approach was divided into three tasks aimed at achieving the stated objectives. In Task 1, aqueous surface tension measurements were made to prepare surface tension isotherms (i.e. concentration-dependence on surface tension) for individual PFAS of environmental significance and PFAS mixtures. These isotherms were used to calculate AWI adsorption constants that were used to assess the significance of AWI adsorption in the vadose zone environment. Linear perfluorocarboxylic acids (PFCA) and perfluorosulfonic acids (PFSA) were employed in this work. In Task 2, bench-scale column experiments were performed to assess the potential for AFFF fluids to spread under concentration-dependent capillary pressure gradients imposed by the surface tension of the AFFF solution. This experimental data was used to assist numerical model validation after model modifications were made to include mechanisms specific to AFFF solution transport. In Task 3, the focus was incorporating AWI adsorption as an additional source of retention for PFAS within the HYDRUS unsaturated flow and transport model.

Results

Over 900 individual surface tension measurements were made to complete this work. From these, 68 aqueous surface tension isotherms for PFCAs and PFSA as single components were prepared for DI water and 4 simulated groundwaters of varied ionic strength). An additional 23 surface tension isotherms were developed for PFCA binary mixtures and one ternary mixture. Adsorption constants derived from these isotherms were used to characterize the dependence of AWI adsorption on PFAS concentration, the length of the PFCA/PFSA hydrophobic chain length, and on groundwater ionic strength. The HYDRUS unsaturated flow and transport model was modified to include the dependence of AWI adsorption on bulk pore-water concentration, the area of the AWI (A_{ia}) as it changes in response to changes in soil moisture content (θ_w) during drainage and imbibition cycles, and on changes in pore-water ionic strength. A framework analytical approach was presented to address AWI adsorption of PFAS mixtures.

Bench-scale column experiments were completed to evaluate AFFF solution transport in the vadose zone and provide data with which to validate modifications made to the numerical model to simulate AFFF transport. Strong solid-phase sorption of one or more components of the AFFF solution dominated other mechanisms of transport. However, facilitated transport related to a combination of concentration-dependent capillary pressure gradients (i.e. tension-driven flow) and changes in the wettability of porous media surfaces was observed. The HYDRUS model was modified to include the effects of tension-driven flow. A good match of simulated and experimental results was achieved when both Langmuir adsorption and tension-driven flow were included. However, additional research is needed to include the effects of solid-phase wettability changes and multi-component nature of these AFFF solutions.

Benefits

This limited-scope research project provided:

1. An improved understanding of AWI adsorption of PFASs as single components and mixtures of components.
2. Measured AWI adsorption constants for a range of PFAS of current environmental significance for simulated groundwaters of varied ionic strength, and a summary analysis relating to prediction of these adsorption constants based on physical properties of the PFAS.
3. Preliminary data relating to the drainage and infiltration of AFFF solutions within unsaturated porous media that will be useful in developing a more comprehensive proposal for additional research.
4. A modified and data-conditioned HYDRUS model for simulating AFFF flow in porous media based on the results of this preliminary research.
5. A modified and data-conditioned HYDRUS model for simulating AWI adsorption based on the results of this preliminary research.

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Executive Summary

Introduction

PFAS source zones on Department of Defense (DoD) facilities resulting from the use of aqueous film-forming foams (AFFF) during fire-suppression, fire-fighter training, or leaking storage containers generally exist within the vadose zone environment underlying the site of surface application. Therefore, AFFF-related per- and polyfluorinated substance (PFAS) contaminants contributing to groundwater plumes must first transport through the vadose zone. Likewise, PFAS contaminants originating from DoD solid waste landfills must also migrate within and through a water-unsaturated porous media environment prior to being components of collected leachate or, in the case of unlined landfills, directly contributing to groundwater plumes. However, transport processes for AFFF solutions and PFAS within the vadose zone are not currently well understood.

Many PFAS of current environmental concern exhibit surface-active properties that favor their accumulation at fluid-fluid interfaces, including air-water interfaces (AWI), surface-water interfaces, and the interfaces between pore water and co-contaminant non-aqueous phase liquids (NAPL) within the vadose zone. The adsorption of PFAS at these environmental interfaces has the effect of slowing, or retarding, the rate of transport during unsaturated flow events. Additionally, interfacial adsorption could serve as an environmental sink for PFAS, providing an additional potential long-term source of groundwater contamination following transformation of precursor components within the source area. Evaluating the significance of PFAS AWI adsorption and its effect on the transport of these contaminants within the vadose zone was a key focus area of this research.

Evaluating PFAS retention due to adsorption at NAPL-water interfaces (NWI) in porous media was not a stated project objective in our original proposal. However, because PFAS solution standards were already being prepared for the AWI assessment, the project team concluded that a limited NWI investigation would be worthwhile, because residual NAPL contamination can also be present within PFAS source zones beneath AFFF fire-fighter training facilities. This evaluation was limited to two NAPL phases (i.e., trichloroethene and kerosene and a surrogate for jet fuel) and the linear PFCAs identified previously.

AFFF solutions applied to the ground surface also infiltrate into the vadose zone and have been identified as a source of PFAS contamination. The Department of Defense (DoD) has recently performed a significant number of site investigations at AFFF application sites to begin to understand the scale of PFAS contamination at DoD facilities. Generally, this has involved the collection of soil and groundwater samples that are analyzed for PFAS content and the data used to gauge the nature and extent of contamination at a suspected source area. Much attention has been focused on PFAS as a contaminant product of AFFF degradation, but comparatively little attention has been paid to the transport of AFFF itself as the source of PFAS contamination. These AFFF solutions are formulated to encourage the rapid spreading of the solution across AWIs and fuel-water interfaces to promote fuel fire suppression. AFFF solution formulations also include many individual components (e.g., surface-active solvents and wettability modifiers

and surfactants, including PFAS), each of which could interact with environmental interfaces differently to affect the unsaturated transport of the overall solution and its components. For example, the surface-active properties of these AFFF solutions will promote concentration-dependent capillary pressure gradients that could enhance the rate of vertical transport of these solutions and contribute to the lateral spreading of these fluids during infiltration within the vadose zone. Likewise, the sorption of one component to soil surfaces could facilitate the sorption of other components in the mixture. Evaluating the complexities of AFFF solution transport in the vadose zone and characterizing the significance of these processes to increase the scale of AFFF-related PFAS source areas is an additional focus of this research.

The overarching goal of this research is to appropriately incorporate AWI adsorption and the specific mechanisms governing AFFF solution transport into an unsaturated flow and contaminant transport model that can ultimately be used as a numerical tool to assist DoD efforts to characterize and remedy sites impacted by PFAS. As a result of this limited-scope research project, the project team have met the first requirements toward achieving this goal. We have modified the HYDRUS model to simulate the dependence of AWI adsorption on bulk pore-water concentration, the area of the AWI (A_{ia}) as it changes in response to changes in soil moisture content (θ_w) during drainage and imbibition cycles, and on changes in pore-water ionic strength. HYDRUS was additionally modified to scale the water content-pressure head relationship to changes in surface tension and solution viscosity to simulate the release of AFFF solutions into the vadose zone environment. Model modifications were validated against experimental data and example one- and two-dimensional simulations are presented to demonstrate the current capability of the model.

Additional model modifications, based on the knowledge gained from the results of the current limited-scope research project, were proposed as a part of a future research. Much of this proposed work centers on improving the capability and accuracy of the simulations. Once model development has been completed, the project team will deliver a full three-dimensional version of the modified HYDRUS simulator. HYDRUS is being used in this work. However, the modifications made in this work would also be applicable to alternative unsaturated flow and transport models.

Objectives

The project's specific objectives were to:

1. Generate fundamental physicochemical properties data that can be used evaluate the significance of AWI adsorption as a source of retention and environmental sink for PFAS within and beneath vadose zone source areas, which can then contribute to groundwater contamination and sustained groundwater plumes,
2. Investigate the potential for interfacial tension-induced flow and lateral spreading of AFFF solutions infiltrating into the vadose zone to determine the significance of these processes to increase the scale of associated PFAS contamination within source areas, and

3. Incorporate the above mechanisms into an unsaturated flow and transport model to serve as a numerical tool with which to evaluate (1) concentration-dependent PFAS fate and transport within the vadose zone under variable, dynamic moisture conditions and (2) the transport and spatial disposition of AFFF-fluids within the vadose zone following surface application.

Technical Approach

The technical approach was divided into three tasks aimed at achieving the stated objectives. In Task 1, aqueous surface tension measurements were made to prepare surface tension isotherms (i.e. concentration-dependence on surface tension) for 8 perfluorocarboxylic acids (PFCA) and 5 perfluorosulfonic acids (PFSA) as representative PFAS contaminants. Surface tension isotherms were prepared for 5 simulated groundwater (SGW) solutions of increasing ionic strength. Finally, surface tension isotherms were prepared for 6 binary mixtures and 1 ternary mixture. Over 900 individual surface tension measurements were made to complete this work. The Langmuir-Szyszkowski (LS) equation was used to fit the measured data. The fit to the data was then used to calculate AWI adsorption coefficients (k_{ia}) and Langmuir constants (K_L) for each test PFAS and SGW solution. k_{ia} values were used to evaluate the significance of AWI adsorption for PFAS by calculating and comparing retardation factors (R_f) for PFAS transport in unsaturated porous media and by evaluating the potential mass of PFAS contaminants that could be retained in the vadose zone when AWI adsorption is isolated as the only source of retention. NWI adsorption of PFAS was similarly evaluated.

In Task 2, bench-scale column experiments were performed to assess the potential for AFFF fluids to spread under concentration-dependent capillary pressure gradients imposed by the surface tension of the AFFF solution. A modern AFFF solution was used (National Foam product: AER-O-Water® 3EMC6) that meets U.S. Military Specification MILPRF-24385F(SH). Moisture redistribution data resulting from these experiments were evaluated and used to condition the numerical model, which was performed as a part of Task 2. The specific modification made to the simulator to include the effects of AFFF surface tension on transport are presented in Section 3 of this report. Model modifications were incorporated into the one-dimensional (1D) and two-dimensional (2D) versions of HYDRUS, and simulations were performed to complete a preliminary evaluation of AFFF solution transport and to identify additional data needs.

Task 3 focused on implementing AWI adsorption into the numerical simulator and validating the simulated results against experimental data. The specific modification made to the simulator are presented in Section 3 of this report. However, the dependence of AWI adsorption on PFAS concentration, A_{ia} as it relates to changes in Θ_w , and on changes in pore-water ionic strength were incorporated into the model as a part of this preliminary work. Bench-scale experiments were not included in this limited-scope project. Therefore, model validation centered on comparing the results of the simulator to available PFAS transport data from literature sources. These sources were limited, however, and the project team has proposed to conduct additional PFAS transport experiments as a part of future work to for additional validation purposes.

Experiments are also proposed to meet specific data needs to improve the simulator's ability to capture additional PFAS transport mechanisms and improve simulation accuracy. Example 1D and 2D simulations were performed to demonstrate the capabilities of the current modified simulator.

Results and Discussion

Evaluating the Significance of AWI Adsorption (Task 1)

The following summarizes the key finding of this limited-scope project and the implications for PFAS fate and transport:

- Recent site characterization efforts have demonstrated that PFAS concentrations in groundwater, including those for the PFCAs and PFSAAs used in this research, are largely present at concentrations in the sub-mg/L range. Our research has shown that for pore-water concentrations less than 1 mg/L, k_{ia} values stabilize around a common value that is specific for each PFAS, and therefore k_{ia} could be treated as a constant for most sites. These values have been reported herein.
- Groundwater concentrations reported in the literature were for samples collected from below the water table and therefore may not accurately represent PFAS concentrations within tension-held pore waters within and underlying PFAS source zones. Direct sampling and analysis of PFAS concentration within tension-held pore waters within and beneath PFAS source areas should be performed to assess the true range of vadose zone pore water and groundwater concentrations present at these sites. Where sub-mg/L concentrations cannot be confirmed, we propose the use of the K_L offers a concentration-independent alternative to k_{ia} values.
- AWI adsorption of PFAS contamination in the vadose zone is dependent on the molecular structure of the particular PFAS component under consideration, solution concentration, groundwater ionic strength, and the area of the AWI that is in turn dependent on the soil moisture condition.
- AWI adsorption and retention within the vadose zone can be significant and is, in part, dependent on the length dimension of the PFAS molecule (or carbon number). As shown in Figure ES-1, R_f values, which characterize the rate of contaminant transport relative to that of water, range from a value of 1.2 for PFPeA ($k_{ia} = 5.35 \times 10^{-5}$ cm), 10.9 for PFOA ($k_{ia} = 3.68 \times 10^{-3}$ cm), and 165 ($k_{ia} = 8.81 \times 10^{-2}$ cm) for PFDA for SGW and at a pore-water saturation = 0.33 (i.e., at field capacity for the representative sand). Therefore, PFAS with k_{ia} values similar to those of PFPeA will transport to the water table roughly 9 times faster than PFOA and 139 times faster than PFDA. Given that retardation factors for the most common regulated organic pollutants (TCE, PCE, TCA, BTEX, etc) are often in the range from 1-3, these PFAS R_f values are highly significant from a practical perspective.

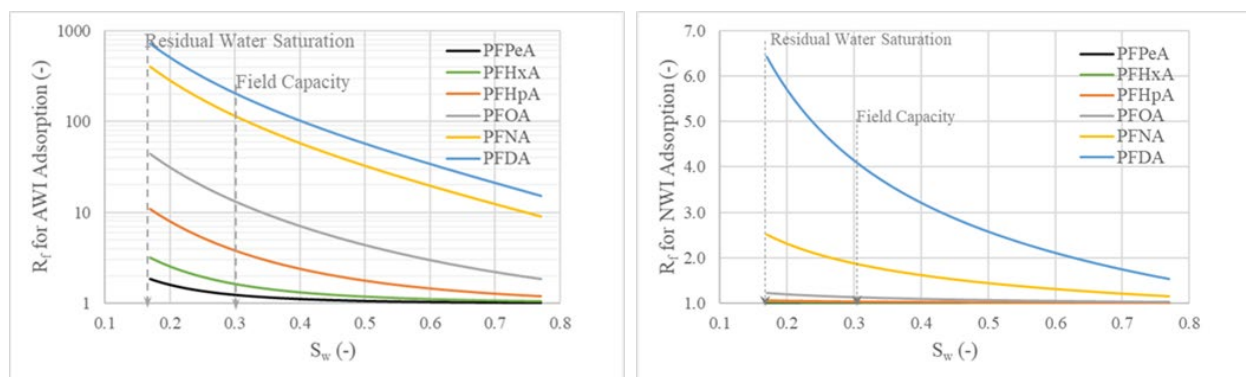


Figure ES-1. PFCA $R_f(S_w)$ functions calculated for AWI and NWI adsorption as the only source of retention.

- AWI adsorption in the vadose zone can also be a significant environmental sink for PFAS contributing to the continued release of PFAS contaminants to sustain groundwater plumes. Therefore, the assessing the strength of this source of contamination should be included as a part of initial site investigations. Methods to monitor pore-water content and concentrations exist and when modified for PFAS should be implemented to characterize AWI adsorption as a component of the PFAS source term
- Predictive methods for AWI adsorption constants based on molecular structure descriptors alone (i.e., those based on the size and/or structure of the hydrophobe) appear to be of limited utility for natural groundwaters. Our research demonstrates that for natural waters where the ionic strength is greater than 0.01M and containing a combination of monovalent and divalent ions, k_{ia} values can deviate considerably from log-linear trends that are based in the hydrophobic effect alone. Rather, a method that includes the contribution of the hydrophobic effect, electrostatic contributions related to groundwater geochemical considerations, and Debye length considerations of the interface and effective Debye diameter of the surfactant is thought to be the better approach.
- Given the dynamic and transient nature of pore-water flow within the vadose zone, and its effect on the creation and destruction of air-water interfaces, we conclude that a properly conditioned numerical simulator would be a better tool to support PFAS fate and transport calculations compared to methods that rely on retardation factors and representative and uniform k_{ia} values. This approach does not account changes pore-water PFAS concentrations and changes in A_{ia} , both of which can greatly impact PFAS retardation.

Regarding PFAS mixtures:

- PFAS contamination typically exists as a complex multi-component mixture of individual PFAS and other surface-active components.

- At low solution concentrations (e.g., < 0.1 mg/L) our data suggests that AWI interfacial adsorption of individual PFAS present in a mixture can be estimated using k_{ia} values measured for single-component solutions.
- However, as solution concentrations increase and AWI adsorption approaches the monolayer regime, competitive adsorption between individual PFAS in solution can occur and the adsorption of a fraction of PFAS components can be significantly reduced relative to that predicted by single-component k_{ia} values. This is demonstrated in Figure ES-2, which shows the dominance of PFDA AWI adsorption over the other solution components.

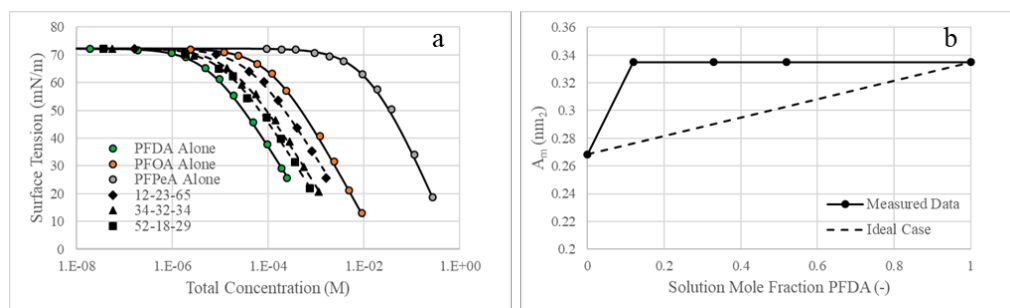


Figure ES-2. Measured data for a PFCA ternary mixture: a) surface tension isotherms for each PFCA as a single component as mixtures, b) calculated area of the minimum adsorbed surface areas per molecule (A_m) with changes in the solution mole fraction of the most surface-active component of the mixture.

- Models were proposed to characterize the adsorbed composition of PFAS at the AWI. Knowledge of the adsorbed composition allows rescaling of adsorption models to accommodate both linear adsorption at low concentration and competitive adsorption as solution concentrations increase. A rescaling of the Langmuir equation resulted in the $k_{ia}(C_w)$ functions presented in Figure ES-3, for one of the PFCA ternary mixtures presented in Figure ES-2. Note that the dominance of PFDA AWI adsorption, as the total solution concentration increases, results in a reduction in k_{ia} for PFOA compared to the single-component function.

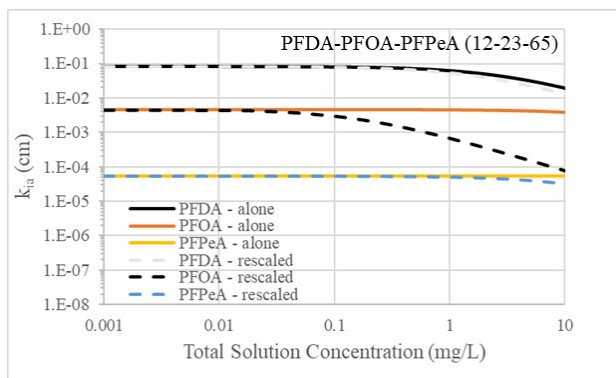


Figure ES-3. $k_{ia}(C_w)$ function for a PFCA ternary mixture.

- Additional research was proposed to develop and evaluate alternative surface compositional models to characterize the AWI adsorption of more complex multi-component PFAS mixtures. Such models would be most useful for predicting the rate of transport or mass retention of target PFAS components of specific regulatory interest in the presence of other PFAS contaminants. These models can also be used to track changes in adsorbed surface/interfacial composition with changes in bulk solution composition, a capability that can also be implemented into numerical simulators.

Task 2: AFFF Evaluation and HYDRUS Model Modifications

The sorption of one or more components of the AFFF solution to the sand was found to be significant. As shown in Figure ES-3, mineral sorption was significant enough to virtually eliminate the effects of AFFF solution tension-driven flow to solution concentrations less than 5000 mg/L, even though the bulk surface tension at these lower concentrations were low enough to initiate flow. A hypothetical re-scaled surface tension isotherm was prepared to simulate the observed results. The use of the hypothetical re-scaling of the surface-tension isotherm to represent AFFF solution transport is neither ideal nor mechanistically accurate but did allow us to perform simulations to test the modifications made to the HYDRUS code and conclude that the strong sorption of one or more components of the AFFF solution was responsible for the observed experimental results.

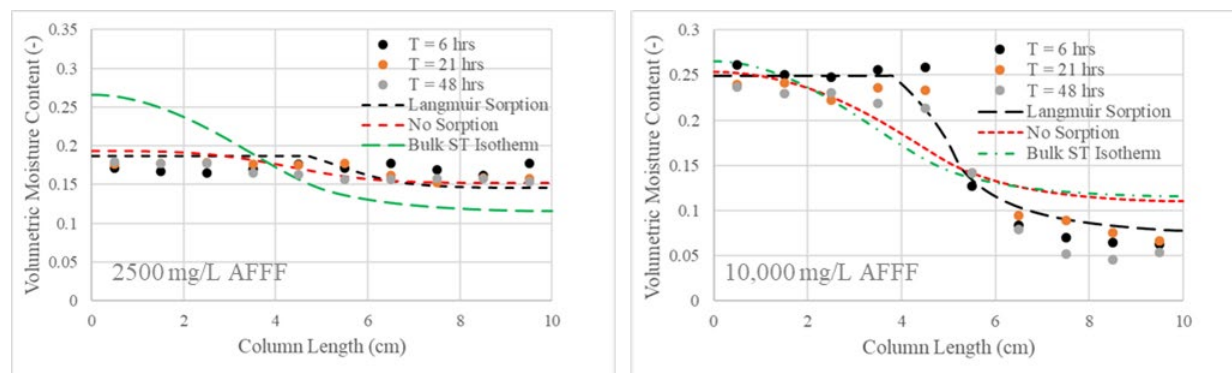


Figure ES-3. Experimental and simulated moisture redistributions for the National Foam AER-O-Water® CEM⁶ AFFF solutions used in this work. The “No Sorption” line is the simulated result utilizing the proposed hypothetical surface tension scaling alone. The “Langmuir Sorption” line combines both sorption and the re-scaling of the surface tension isotherm.

The flow AFFF solutions in unsaturated porous media is affected by the viscosity of the solution (particularly at concentrations used for fire suppression), its surface activity, and its ability to modify the solid-water contact angles at porous media surfaces. As a part of this limited-scope project, the effects of concentration-dependent surface tension were the primary focus and this mechanism was incorporated into the HYDRUS flow and transport model. The effect of solution viscosity was also incorporated into the model but physical measurement of the concentration-dependence of solution viscosity was not a part of this initial work. However, the effects of changes in solution viscosity and changes in the wettability of the solid phase in the

presence of AFFF solutions is proposed be included as a component of future research, which will allow the model to more accurately simulate AFFF solution transport in the vadose zone.

Task 3: Implementing AWI Adsorption within HYDRUS

As a result of this limited-scope project, we have modified the 1D and 2D versions of HYDRUS to simulate the dependence of AWI adsorption on bulk pore-water concentration, A_{ia} as it changes in response to changes in Θ_w during drainage and imbibition cycles, and on changes in pore-water ionic strength. The concentration-dependence on AWI adsorption was implemented by including Langmuir adsorption constants (K_L) and maximum adsorbed surface concentration values (Γ_{max}) as user-defined input. K_L and Γ_{max} values were determined directly from the fit of the LS-equation fit to the measured PFAS surface tension isotherms.

Rather than relying on literature-derived relationships to describe the dependence A_{ia} on changes in Θ_w , a more practical approach was implemented in which A_{ia} is calculated directly from the pressure head-saturation relationship. Maximum A_{ia} values correspond to the geometric surface area of the media as Θ_w approaches zero. This approach allows the model to accommodate different $A_{ia}(\Theta_w)$ functions for different soil types. In this way, the model captures the dynamic and transient nature of the $A_{ia}(\Theta_w)$ function and its effect on PFAS AWI adsorption in the presence of soil textural heterogeneity. Example simulations used for validating HYDRUS model modifications are presented in Figure ES-4.

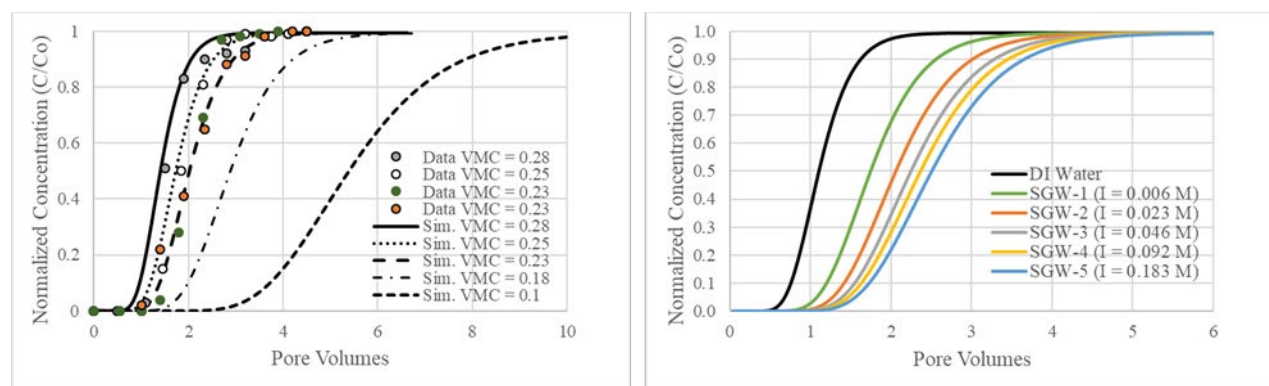


Figure ES-4. Example results of 1D HYDRUS simulations: a) model validation of soil moisture content dependence of PFOA AWI adsorption and b) demonstration of ionic strength (I) dependence on PFOA AWI adsorption. VMC refers to volumetric moisture content. Experimental data was derived from the work of Lyu et al. (2018), *Environ. Sci. Technol.*, 52, 7745.

Example 2D simulations of AWI adsorption within water-unsaturated porous media were performed to demonstrate the capability of the HYDRUS model modifications. The initial and boundary conditions used in these simulations are provided in Figure ES-5. The arrangement of porous media categories is obviously contrived but was selected to demonstrate differences in PFAS transport resulting from differences in the $A_{ia}(\Theta_w)$ for each media category. PFAS and a non-reactive tracer was emplaced at the upper boundary of the model domain as a 1 mg/L solution at $\Theta_w = 0.35$. Periodic simulated water applications applied to the upper boundary at a rate of 0.5 cm/hour, each lasting for 5 hours. A total of 7 water application events were simulated

starting at 100 hours into the simulation and reoccurring every 300 hours thereafter. The total simulation time was 2880 hours or 120 days. The results of this simulation are presented in ES-6. To our knowledge, this is the first 2D representation of PFAS transport within water-unsaturated porous media that includes the effects of solid-phase sorption and AWI adsorption.

AWI adsorption is shown to delay the transport of the PFCAs relative to the non-reactive tracer. Retention increases with increasing PFCA carbon number, in keeping with trends in the AWI adsorption constants. Generally, the rate of PFCA transport is observed to be lower in the finest of the finer-grained media categories due to a combination of generally higher A_{ia} values and low unsaturated hydraulic conductivity. The rate of PFCA transport is also lower in the coarsest porous media categories due to hydraulic limitations, in that water application rates are much lower than the hydraulic conductivities of these media. The Loam media appears to have the right combination of unsaturated hydraulic conductivity and range of A_{ia} values that combine to enhance the rate of infiltration of water and surface-active contaminant relative to the other porous media categories used in this example.

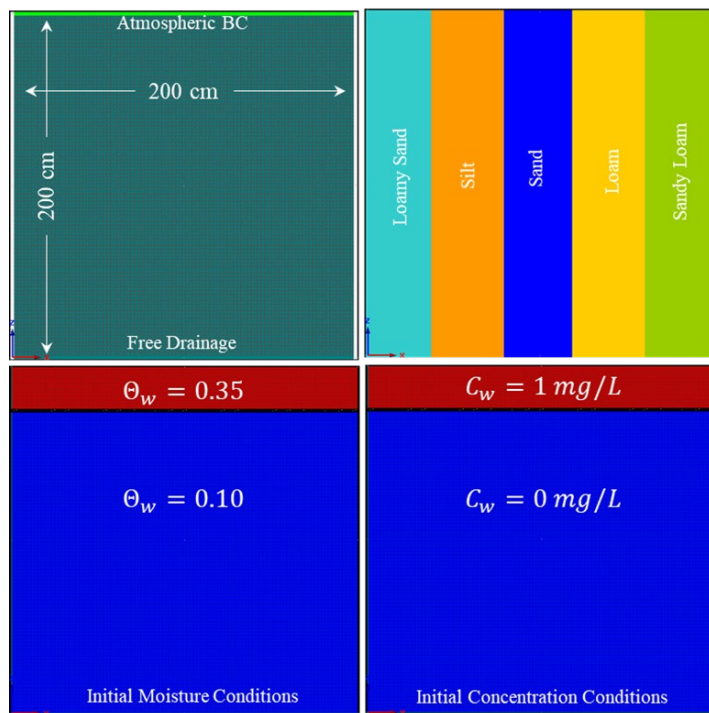


Figure ES-5. Initial and boundary conditions used in the example 2D simulations.

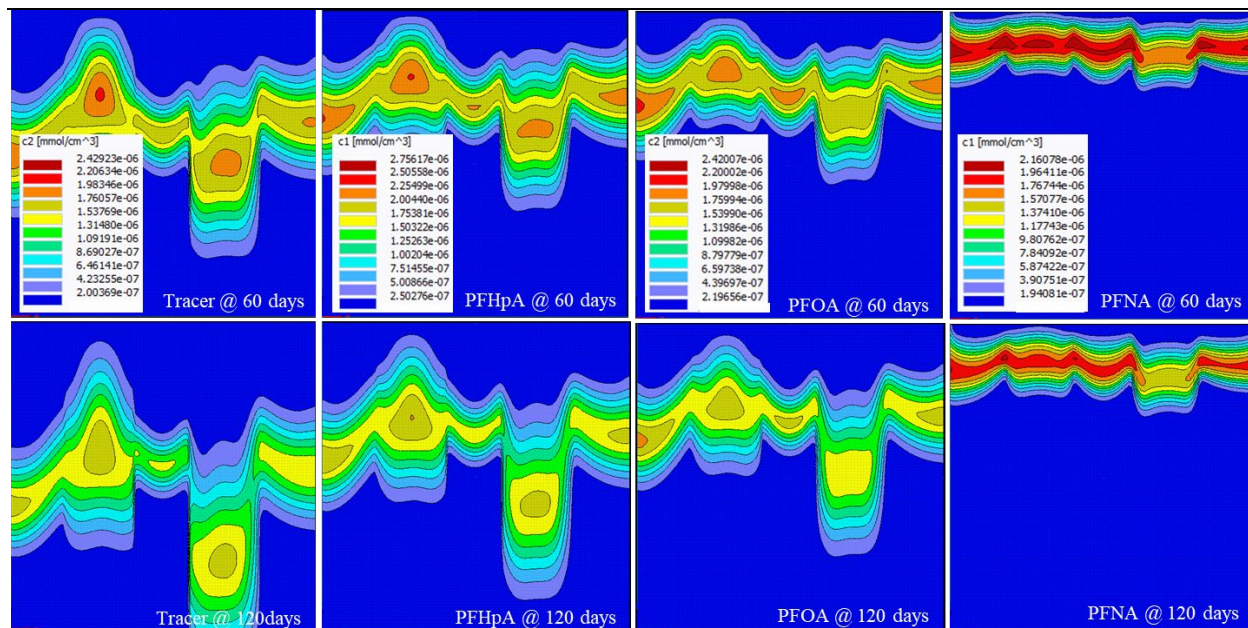


Figure ES-6. 2D HYDRUS simulation of PFCA AWI adsorption during transport in unsaturated porous media.

Implications for Future Research and Benefits

At the completion of this limited-scope project, we have demonstrated the significance of AWI adsorption of PFAS as a source of retention within the vadose zone. We have also demonstrated that mineral sorption of AFFF fluids is considerable and that multiple retention mechanisms are at play during AFFF transport within the vadose zone environment that warrant further investigation such that these mechanisms can be properly incorporated within unsaturated flow and transport models. We have also successfully modified the HYDRUS unsaturated flow and contaminant transport model to include AWI adsorption of PFAS and its dependence on solution concentration. The dependence of PFAS AWI adsorption on A_{ia} was modeled using an approach in which A_{ia} is calculated directly from the pressure head-saturation relationship. This approach allows the model to accommodate different $A_{ia}(\theta_w)$ functions for different soil types. In this way, the model captures the dynamic and transient nature of the $A_{ia}(\theta_w)$ function and its effect on PFAS AWI adsorption in the presence of soil textural heterogeneity. The model was also modified to account for changes in solution ionic strength, utilizing additional data generated as a result of this limited-scope project.

Additional research has been proposed to improve the utility and capability of the model to accurately represent AWI adsorption and other retention processes in the vadose zone. Such a model would provide a useful numerical tool with which to support DoD efforts to characterize the PFAS source term and would improve hydrogeological risk assessments and evaluation of remedial alternatives and/or monitoring strategies.

With regard to AFFF applications, such a numerical model would find use where it is necessary or advantageous to simulate AFFF application history (i.e. rates and frequencies of application) in support of site characterization efforts aimed at determining the vertical and

lateral extent of PFAS source areas. This model would be additionally useful in assessing the longevity of PFAS source areas to assist management decisions.

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1.0 Objectives

The objectives of Limited-Scope Project ER18-1389 were to:

4. Generate fundamental physicochemical properties data that can be used evaluate the significance of AWI adsorption as a source of retention and environmental sink for PFAS within and beneath vadose zone source areas, which can then contribute to groundwater contamination and sustained groundwater plumes,
5. Investigate the potential for interfacial tension-induced flow and lateral spreading of PFASs in the vadose zone to determine whether these processes could increase the scale of PFAS contamination, and
6. Incorporate the above mechanisms into an unsaturated flow and transport model to serve as a numerical tool with which to evaluate (1) concentration-dependent PFAS fate and transport within the vadose zone under variable, dynamic moisture conditions and (2) the transport and spatial disposition of AFFF-fluids (i.e., as imbibing aqueous solutions) within the vadose zone following surface application.

Each of these initial project objectives were developed to specifically address the following SERDP statements of need (SON):

1. **SON Objective #1:** *Increase understanding of the key characteristics of AFFF source zone areas (vadose zones and/or saturated zone source areas) that affect the risk that PFASs pose to groundwater quality.*
2. **SON Objective #3:** *Investigate the nature and permanence of PFAS retardation mechanisms, and the potential use of these mechanisms in natural or enhanced attenuation.*
3. **SON Objective #5:** *Develop analytical or mathematical tools to predict the fate and impacts of PFASs in source zones and the potential for continuing releases to groundwater plumes.*

1.1 Air-Water Interfacial Adsorption Evaluation (Task 1)

When the project pre-proposal and final proposal were submitted (January 2017 and March 2017, respectively), little to no data pertaining to AWI adsorption as it relates to PFAS fate and transport existed in the published literature. This fact was identified in our proposal as a critical data gap with respect to evaluating PFAS fate and transport within and beneath vadose zone source areas. As a limited-scope project, the research proposed for Task 1 centered on developing surface-tension isotherms under relevant solution conditions and for limited number of PFAS constituents to develop a data set from which to: (1) improve our general understanding of PFAS AWI adsorption and its dependence on solution composition, and (2) to determine whether PFAS AWI adsorption and its contribution to overall PFAS fate and transport within the vadose zone environment was significant enough to warrant further study. Success criteria for Task 1, then, consist of answering the following technical questions related to PFAS fate and transport:

1. Within the vadose zone, beneath and adjacent to AFFF source zones, is AWI partitioning a significant source of retention for PFASs, precursor chemicals, and co-contaminant hydrocarbon surfactants?
2. For the relevant processes above, to what degree could AWI adsorption contribute to source longevity?
3. Can the degree and/or net contribution of AWI adsorption be predicted, based on molecular structure (or similar molecular metric), for PFAS mixtures and additional individual PFAS components that are not included in this Limited Scope Proposal?
4. Can mathematical relationships developed to describe the concentration dependence of AWI adsorption be incorporated within existing numerical unsaturated flow and transport models to assist site source investigation and support evaluations of future remediation efforts?

1.2 Tension-Driven Flow Evaluation (Task 2)

The test PFASs selected in this work, by their molecular composition, possess surface-active properties. Therefore, it is natural to question whether aqueous surface tension reductions associated with the adsorption of these chemicals at the AWI would contribute to spontaneous spreading and/or tension-driven flow of pore water within the vadose zone. PFAS-specific contributions to tension-driven flow was the initial focus of this work. However, shortly after project award it became clear, from data presented in recently published site characterization efforts, that typical PFAS aqueous concentrations observed in environmental samples were low enough that surface tension reduction resulting from this residual contamination would not be significant enough to support tension-driven flow. With approval from the SERDP Environmental Restoration Program Manager, our tension-driven flow work-scope was modified to focus on tension-driven flows associated with AFFF releases, as explained in more detail below.

Revised project objectives associated with the use of AFFF include: (1) evaluating the significance of interfacial tension-induced flow, in general, for surface-active solutes, (2) evaluating the significance of tension-driven flow and lateral spreading of AFFF solutions within the vadose zone environment, and (3) determine whether the bulk characteristics of these multicomponent solutions can be used to represent AFFF solution transport in the vadose zone. As a scoping-level project task, success criteria for Task 2 center on addressing these stated objectives and, from the results, assessing whether additional research is warranted to further develop a numerical simulator for use as a site management tool to characterize longevity of AFFF-related PFAS source areas.

1.3 Unsaturated Flow Model Modification and Simulations (Task 3)

PFAS source zones on Department of Defense (DoD) facilities resulting from AFFF use during fire-suppression, fire-fighter training, or leaking storage containers generally exist within the vadose zone environment underlying the site of surface application. Therefore, PFAS contributing to groundwater plumes must first transport through the vadose zone. Likewise, PFAS contaminants originating from DoD solid waste landfills must also migrate within and

through a water-unsaturated porous media environment prior to being components of collected leachate or, in the case of unlined landfills, directly contributing to groundwater plumes. Many PFAS of current environmental concern exhibit surface-active properties that favor their accumulation at fluid-fluid interfaces, including the AWI within the vadose zone. The adsorption of PFAS at AWI's has the effect of slowing, or retarding, the rate of transport under unsaturated flow. Additionally, AWI adsorption could serve as an environmental sink for PFAS, providing an additional potential long-term source of groundwater contamination following transformation of precursor components within the source area.

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Task 3 was proposed and budgeted as a separate numerical modeling work scope, but all three tasks are ultimately inter-related. Because evaluating the significance of tension-driven flow for AFFF solutions required the results of numerical simulation in addition to experimental data, discussion of the result of AFFF simulation work is described as a part of Task 2. In this report, Task 3 will focus on implementing AWI interfacial adsorption as a retention component within the HYDRUS unsaturated flow and contaminant transport model. The specific objectives of Task 3 were to: (1) develop mathematical relationships needed to implement AWI adsorption within the HYDRUS model, and (2) utilize recently published transport data to validate the model with respect to AWI adsorption and demonstrate the capability of the model. Success criteria for Task 3 centers on completion of the stated objectives.

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2.0 Background

2.1 Air-Water Interfacial Adsorption of PFAS

PFAS source zones on Department of Defense (DoD) facilities resulting from AFFF use during fire-suppression, fire-fighter training, or leaking storage containers generally exist within the vadose zone environment underlying the site of surface application. Therefore, PFAS contributing to groundwater plumes must first transport through the vadose zone. Likewise, PFAS contaminants originating from DoD solid waste landfills must also migrate within and through a water-unsaturated porous media environment prior to being components of collected leachate or, in the case of unlined landfills, directly contributing to groundwater plumes. Many PFAS of current environmental concern exhibit surface-active properties that favor their accumulation at fluid-fluid interfaces, including the AWI within the vadose zone. The adsorption of PFAS at AWI's has the effect of slowing, or retarding, the rate of transport under unsaturated flow. Additionally, AWI adsorption could serve as an environmental sink for PFAS, providing an additional potential long-term source of groundwater contamination following transformation of precursor components within the source area.

At the time of submittal of our project proposal, previous research into PFAS adsorption to AWIs were limited phenomenological studies utilizing aqueous solutions prepared with deionized water (e.g., Shinoda et al., 1972; Mukerjee and Handa, 1981; Lunkenheimer et al., 2015). While very useful as general reference and in selecting initial aqueous concentrations in the present work, these studies were considered only indirectly useful for evaluating AWI adsorption in groundwater systems because AWI adsorption is dependent on solution ionic strength and ionic composition of the aqueous phase being evaluated. For example, Downes et al. (1995) and Psillakis et al. (2009) observed enhanced adsorption at the AWI for perfluoroalkyl sulfonic and carboxylic acids in the presence of dissolved 1:1 salts, specifically sodium and ammonium chloride salts. Additional evidence for enhanced PFAS adsorption at AWIs were provided from studies investigating PFAS accumulation at gas bubble interfaces in support of cavitation-based remediation technologies (Vectis et al., 2008) and as a source of excess adsorption when carbonaceous adsorbents are used for PFAS removal from solution (Meng et al., 2014). At this point in time, AWI adsorption and non-aqueous phase liquid (NAPL)-water interfacial (NWI) adsorption, as sources of retention for PFAS was postulated (e.g., Weber et al., 2017; McKenzie et al., 2016) but not yet rigorously evaluated.

Just prior to project award, Brusseau (2018) presented a compartment-based model for evaluating PFAS retention in the vadose zone that included an evaluation of the contributions of AWI adsorption, sorption to soils, and NWI adsorption. The model is based on much earlier work related to evaluation of hydrocarbon, chlorinated solvent, and hydrocarbon surfactant transport in water-unsaturated porous media (e.g., Brusseau et al., 1992; Brusseau et al., 1997; Kim et al., 1997, Silva, 1997, Kim et al., 1998; Costanza and Brusseau, 2000, Kim et al., 2001; Silva et al., 2002) and was parameterized for PFAS using data from the literature. Both AWI and NWI adsorption were identified as significant contributors to PFAS retention. Shortly thereafter, Lyu et al. (2018) presented the results of one-dimensional unsaturated column experiments that

supported the conclusions of Brusseau (2018) that PFAS retention due to AWI adsorption is significant, representing as much as 50-75% of the total retention for PFOA and PFOS in their experimental systems. Adsorbed concentrations associated with this level of PFAS retention is still very low (i.e. on the order of 10^{-6} mol/m²) and would not contribute to tension-driven flow, as discussed in Section 2.2. The greatest benefit to our current project was that Lyu et al. (2018) provided experimental data that demonstrated adsorption parameters derived from surface tension measurements can be used to evaluate PFAS AWI adsorption.

More recently, Brusseau et al. (2019) again demonstrated the capability of their compartment-based modeling approach utilizing both experimentally derived and estimated parameters to compare model results of unsaturated flow experiments utilizing PFOA and PFOS. AWI and NWI adsorption parameters presented in our own recent publication (Silva et al., 2019, selected results to be presented in this report) are in general agreement with those presented in these concurrently published works with the exception that our study evaluated AWI adsorption utilizing simulated groundwaters of varied ionic strength and NWI adsorption utilizing TCE and kerosene (as a surrogate for jet fuels), which are common co-contaminants at DoD fire-fighting training sites. Based on this rapid pace of recent publication, it is clear that interfacial adsorption of PFAS is an active area of ongoing research.

2.2 Tension-Driven Flow

To date, most work performed on assessing the characteristics of AFFF solutions has centered on evaluating their utility for fire suppression and characterizing their composition to support analytical chemistry related to assessing PFAS contamination. The project team was unable to locate a single published investigation relating to the imbibition of AFFF solutions into water-unsaturated soils. This was surprising given that PFAS source areas associated with fire-training areas and/or leaks AFFF storage locations were established because of AFFF releases and subsequent infiltration into the underlying vadose zone. Therefore, understanding the physicochemical characteristics of flow of AFFF solutions within the vadose zone environment is an overlooked and potentially important research need.

Prior research on tension-driven flow has centered on assessing the effectiveness of single-component surface-active agents (i.e. surfactants) as water-moving agents under surface tension induced capillary pressure gradients within unsaturated porous media (e.g., Tschapek et al., 1981, 1984; Kakare et al., 1993; Kakare and Fort, 1996; Henry et al., 1999). In each of these cases, tension-driven flow was evaluated in initially static one-dimensional sand column experiments in which tension-held pore water was observed to transport from the surfactant-containing side of the column to the initially surfactant-free side of the column due to surface tension induced capillary pressure gradients established in the presence of surfactants.

Further work under unsaturated flow conditions (Smith and Gillham, 1994, 1999) have demonstrated enhanced drainage within unsaturated porous media when surface-active agents are present. Henry and Smith (2006) developed a 2-D mathematical model that utilized a modified form of the van Genuchten equation in which the pressure head term was scaled by the ratio of the surface tension of the surfactant (i.e. concentration dependence) to that of pure water (after

Leverett, 1941). Numerical results showed significant differences between the infiltration of pure water and alcohol (70 g/L 1-butanol)-containing water into a fine sand.

In each of these cases, the surface-active solutes used did not interact with the solid phase (only with the air-water interface). For surface-active adsorbing solutes, like many commercial hydrocarbon surfactants, there is some question as to whether modifications to the van Genuchten equation by surface-tension scaling alone would accurately describe unsaturated flow in these cases. Complicating the situation further, AFFF solutions that are the subject of this proposed investigation are composed of multiple surface-active solvents and surfactants (including, but not limited to, perfluorinated surfactants), each of which can affect the surface tension of the solution and are susceptible to mineral or soil adsorption to varied degrees. In the present limited-scope project, we start our evaluation of the effects of AFFF solution on the flux of water and AFFF components in unsaturated porous media.

2.3 Technical and Scientific Benefits

The benefits of this limited-scope research project include:

1. An improved understanding of AWI adsorption of PFASs as single components and mixtures of components.
2. Experimentally derived AWI adsorption coefficients for a range of PFAS of current environmental significance using simulated groundwaters of varied ionic strength, including relevant mathematical relationships to allow for the inclusion of AWI adsorption as a retention process in numerical unsaturated flow and transport simulators.
3. Preliminary data relating to the drainage and infiltration of AFFF solutions within unsaturated porous media that will be useful in developing a more comprehensive proposal for additional research.
4. A modified and data-conditioned HYDRUS model for simulating AFFF flow in porous media based on the results of this preliminary research.
5. A modified and data-conditioned HYDRUS model for simulating AWI adsorption based on the results of this preliminary research.

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3.0 Materials and Methods

3.1 Air-Water Interfacial Adsorption and Retention Evaluation

3.1.1 Chemicals and Materials

Except for kerosene all chemicals were purchased from Sigma-Aldrich Co. and used without further purification. Perfluoropentanoic acid (PFPeA, 97% purity), perfluorohexanoic acid (PFHxA, 98%), perfluoroheptanoic acid (PFHpA, 99% purity), PFOA (96%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 95%), and were selected as representative perfluorocarboxylic acids (PFCAs). The free acid form of these PFCAs were selected to mirror that produced in situ by the degradation and/or oxidation of precursor compounds. The ammonium salt of PFOA (NH₄-PFOA, $\geq 98\%$) was selected for comparison. The potassium salts of perfluorobutane sulfonate (K-PFBS, 98%), perfluorohexane sulfonate (K-PFHxS, $\geq 99\%$), and perfluorooctane sulfonic acid (K-PFOS, $\geq 98\%$) were selected as representative perfluorosulfonic acids (PFSAs); the free acid forms of PFOS (H-PFOS, 40% solution in water – purity not specified) and PFBS (H-PFBS, 97%) were included for comparative evaluation. Finally, sodium dodecyl sulfate (SDoS) was selected as a representative hydrocarbon surfactant.

It was our intention to also include a selection of PFCA and/or PFSA precursor chemicals as a part of this limited-scope evaluation project. However, during the initial stages of the project it became clear that these chemicals were available in small quantities, which would complicate solution standards preparation and measurement using the proposed du Nuoy ring methodology. If selected for additional funding in a forthcoming proposal, we would contract preparation of solution standards and modify our measurement method by adopting a pendant-drop methodology that would be amenable to lower volumes of test solutions.

Deionized (DI) water used in this work conformed to the American Society for Testing and Materials (ASTM) Type II specification. Sodium bicarbonate (NaHCO₃), calcium sulfate (CaSO₄·2H₂O), magnesium sulfate (MgSO₄), and potassium chloride (KCl) salts were used to prepare solutions of synthetic groundwater (SGW). Non-aqueous phase liquids (NAPL) used in this work included trichloroethene (TCE, reagent grade, Sigma-Aldrich Co.) and kerosene (1-K Grade, purchased from a local hardware store), with kerosene serving as a surrogate for aviation fuels.

3.1.2 Solutions Preparation

SGW solutions were prepared from DI water in batches representing five different ionic strengths, as shown in Table 1. These SGWs were selected to represent a range of values typical of natural groundwaters (U.S. EPA, 2002). From these solutions, individual PFAS test solutions were prepared within 100 mL high-density polyethylene bottles and the preparations slowly agitated for 48 hours prior to use. PFAS standards were also similarly prepared using DI water. PFCA solution standards were prepared to characterize the complete surface tension isotherms, up to and including the monomer solubility limit, as indicated by the stabilization of measured tension values.

Table 3-1. Characteristics of Synthetic Groundwaters.

	Reagent Salt Added (mg/L)				Water Quality Parameters		
	NaHCO ₃	CaSO ₄ ·2H ₂ O	MgSO ₄	KCl	TDS (mg/L)	pH	Ionic Strength (M)
SGW-1	12	7.5	7.5	0.5	27.5	6.8	0.006
SGW-2	48	30	30	2	110	7.3	0.023
SGW-3	96	60	60	4	220	7.8	0.046
SGW-4	192	120	120	8	440	8	0.092
SGW-5	384	240	240	16	880	8.4	0.183

NWI standards were prepared by adding 15 mL of NAPL and 15 mL of aqueous PFAS solution into 60 mL clear glass jars. Only the PFCAs were used in this initial work. TCE-PFCA solution standards were prepared by first adding TCE to the jar followed by PFCA solution to the TCE surface. Conversely, the kerosene-PFCA standards were prepared by adding the aqueous PFAS solutions to the test jars first, followed by kerosene as the less dense phase. The dual-phase preparations were allowed to stabilize for a period of 48-72 hours prior to use.

3.1.3 Surface Tension and AWI Adsorption Coefficients

Surface tension measurements were made using a du Nouy ring tensiometer (Fisher Surface Tensiomat, Model 21, Fisher Scientific) using standard ring methods (ASTM, 1989). Measurements were repeated until the measured tension remained constant across three consecutive measurements (usually over the course of one hour). The results of these measurements were used to construct isotherms of surface tension (γ) versus bulk aqueous concentration (C_w).

The following form of the Langmuir-Szyszkowski (LS) equation was selected to fit the tension isotherm data (Adamson and Gast, 1997):

$$\gamma = \gamma_0 - b \ln \left(1 + \frac{C_w}{a} \right) \quad [3-1]$$

where γ_0 is the surface tension of water (for pure water or water at the ionic strength of interest), and a and b are fitting parameters. Equation 1 was fit to the data by minimizing the sum of the squared error between measured and predicted values. The LS-equation fit was then used in all further analyses as it provided a data set of higher resolution for calculating interfacial parameters.

AWI adsorption coefficients (k_{ia} , units of cm³/cm² or cm) were calculated from the surface tension isotherms using the following form of the Gibbs equation (Kim et al., 1997; Szymczyk and Janczuk, 2007):

$$k_{ia} = \frac{\Gamma}{C_w} = -\frac{1}{RT} \left(\frac{\delta \gamma}{\delta C_w} \right)_T \quad [3-2]$$

where Γ is the surface concentration (mole or mass per unit area), R is the universal gas constant and T is the temperature of measurement. This involved calculating the incremental change in

the slope of the fitted tension isotherm data (i.e. dy/dC_w) across the range of solution concentrations of interest and applying Equation 3-2. Lyu et al. (2018) demonstrated, by comparison with the results of transport experiments, that measured surface tension isotherms can be used to predict AWI adsorption coefficients and estimate retardation factors resulting from AWI adsorption in porous media.

Because k_{ia} values are concentration dependent, one must select a specific solution concentration when comparing retention characteristics for different PFAS. To simplify comparisons between individual PFASs, the concentration-independent Langmuir coefficient (K_L) is additionally used in this report. K_L is determined from fitting Equation 3-1 to the measured surface tension data. The LS-equation can also be written as:

$$\gamma = \gamma_0 - RT\Gamma_{max} \ln(1 + K_L C_w) \quad [3-3]$$

where Γ_{max} is the maximum surface concentration observed as dissolved concentrations approach the solubility limit and R and T are the universal gas constant and temperature of measurement, respectively. The a parameter in Equation 3-1 is $1/K_L$ and $b = \gamma_0 RT\Gamma_{max}$. Equation 3-3 is useful because K_L and Γ_{max} can be directly calculated from the surface-tension isotherm data and, as demonstrated in Section 3.3.5, can be used to model the concentration dependence of k_{ia} .

3.1.4 AWI Retention of PFAS in Porous Media

Individual PFAS k_{ia} values were used to assess the significance of PFAS retention in porous media. The retardation factor (R_f) describing the contribution of AWI partitioning under water-unsaturated flow in the vadose zone is as follows (Kim et al., 1998):

$$R_f = 1 + \frac{k_{ia}A_{ia}}{\Theta_w} = 1 + \frac{k_{ia}A_{ia}}{S_w n} \quad [3-4]$$

where A_{ia} is the area of the AWI within a given volume of water-unsaturated soil (cm^2/cm^3 or cm^{-1}), Θ_w is the volumetric moisture content (-), S_w is the water saturation (fraction of the pore space filled with water) and n is the media porosity (-). Equation 3-4 assumes chemical equilibrium between the aqueous phase and the AWI. $R_f = 1$ indicates AWI retention is negligible, while $R > 1$ indicated retardation, or slowed velocity, due to AWI partitioning. Retention resulting from AWI adsorption can be evaluated independently under the condition that at system equilibrium the dissolved contaminant remains in excess in solution with respect to the AWI and additional sources of retention (e.g., sorption to solid phase).

For water-unsaturated porous media, previous research has shown that A_{ia} increases with decreasing S_w until achieving a maximum value near the surface area of the solid at extremely low S_w (e.g. Kakare and Fort, 1996; Kim et al., 1997; Silva, 1997; Brusseau et al., 1997; Kim et al., 1999; Silva et al., 2002; Costanza-Robinson and Brusseau, 2002; Peng and Brusseau, 2005). The following $A_{ia}(S_w)$ relationship was used in this evaluation (Peng and Brusseau, 2005):

$$A_{ia} = s[1 + (\alpha S_w)^a]^{-b} - c \quad [3-5]$$

where s is the specific solid surface area and α , b , and c are fitting parameters (which in this case $s = 5200 \text{ cm}^{-1}$, $\alpha = 19.78$, $b = 1.1$, $c = 104$, and $a = 1/(2-b)$). Parameters used by Lyu et al.

(2018) were also directly used to calculate retardation factors (i.e., $A_{ia} = 73 \text{ cm}^{-1}$ and $S_w = 0.77$ or $\Theta_w = 0.23$) in this work for comparative purposes. A graphical representation of this $A_{ia}(S_w)$ relationship calculated using Equation 3-5 and the aforementioned parameters for a model sand is provided as Figure 1a.

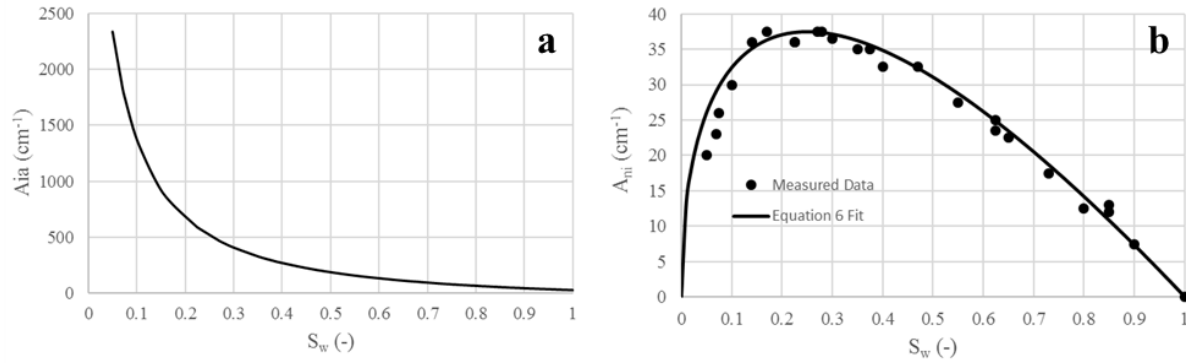


Figure 3-1. $A_{ia}(S_w)$ and $A_{ni}(S_w)$ functions used in this work: (a) $A_{ia}(S_w)$ relationship determined from Equation 3-5 applied to a model sand, (b) Equation 3-9 fit to the data presented by Porter et al. (2010).

PFAS retention, as it relates to retardation during transport, is not the only factor warranting consideration. Mass storage of surface-active contaminants in the vadose zone is possible, particularly within contaminant source areas where the phase equilibrium conditions supporting AWI-accumulation can be sustained. Generally, assessing the potential for retention as mass storage involves performing mass budget calculations to include all possible storage compartments, e.g.

$$M_{Total} = M_w + M_{soil} + M_{vap} + M_{ia} \quad [3-6]$$

where M_{Total} is the total contaminant mass, M_w is the mass in the aqueous phase, M_{soil} is the mass associated with the solid phase, M_{vap} is the mass of contaminant partitioned into the air-filled porosity (as appropriate), and M_{ia} is the mass adsorbed to the AWI. Here we will limit the analysis to evaluating specific mass (S_M) of PFAS that could be stored at the AWI, as determined by:

$$S_M = M_{ia}/V_{soil} = C_w k_{ia} A_{ia} \quad [3-7]$$

where V_{soil} is the volume of vadose zone under consideration. Further, this evaluation assumes the PFAS of interest exist within a vadose zone beneath a hypothetical source area (e.g. former AFFF fire-training area) wherein phase equilibrium conditions exist to maintain a uniform aqueous phase concentration. A steady-state condition is also assumed to allow a uniform S_w of 0.33 (field capacity for the system) which provides an A_{ia} of 357.7 cm^{-1} by Equation 3-5.

3.2 NAPL-Water Interfacial Adsorption and Retention Evaluation

Evaluating PFAS retention due to adsorption at NAPL-water interfaces (NWI) in porous media was not a stated project objective in the proposal. However, because PFAS solution standards were already being prepared for the AWI assessment, the project team concluded that a limited NWI investigation would be worthwhile, because residual NAPL contamination can also

be present within PFAS source zones beneath AFFF fire-fighter training facilities. This evaluation was limited to two NAPL phases (i.e., TCE and kerosene) and the linear PFCAs identified previously.

3.2.1 NAPL-Water Interfacial Tension

NWI tension measurements were also performed using standard ring methods (ASTM, 1989) and the same du Nouy ring tensiometer referenced previously. The measurement method consisted of positioning the du Nouy ring within the PFCA solution phase and, in the case of kerosene, slowly lifting the ring into the NWI and recording the measured tension required to rupture the interface. Similarly, the TCE-PFCA solution systems recorded the tension required to rupture the interface when a downward force is applied on the interface (i.e. du Nouy ring “pushed” into TCE phase). The LS-equation (Equation 3-1) was again used to fit the measured data, with γ_0 in the present case being the interfacial tension of the NAPL-water system in the absence of PFCA. Concentration-dependent NWI adsorption coefficients (k_{ni}) were again determined from the Equation 3-1 fit to the measured data.

3.2.2 NWI Retention PFAS in Porous Media

The retardation factor (R_f) describing the contribution of NWI adsorption under water-unsaturated flow in the vadose zone is described by (Saripalli et al., 1998):

$$R_f = 1 + \frac{k_{ni}A_{ni}}{\theta_w} \quad [3-8]$$

where k_{ni} is the NWI adsorption coefficient (cm) and A_{ni} is the area of the NWI. In this evaluation, NAPL contamination is assumed to occur as entrapped NAPL ganglia within the porous media. As the non-wetting fluid in a typical vadose zone environment, only a small fraction of the total NAPL area (and thus NWI) will be exposed to the advecting aqueous phase relative to the AWI at the same soil moisture condition. Therefore, the dependence of interfacial area on S_w for the NWI will differ from that for the AWI. To facilitate this evaluation, the following $A_{ni}(S_w)$ relationship was derived from the main imbibition curve of the computed microtomography measurements made by Porter et al. (2010) for NAPL at residual saturation using the following equation to fit the data:

$$A_{ni} = d + eS_w + f\sqrt{S_w} \quad [3-9]$$

where d , e , and f are fitting parameters (which in this case $d = 10^{-4}$, $e = -1.5$, and $f = 1.5$). NAPL saturation was at residual, or $< 10\%$ as estimated based on reported properties of the sand. A graphical representation of this dataset and the Equation 3-6 fit to the data used in subsequent calculations is provided as Figure 3-1b.

3.3 Tension-Driven Flow Evaluation

The objective of this work was to perform one-dimensional sand column tests to evaluate the significance of tension-driven transport of AFFF solutions within water-unsaturated porous media. Subsequently, this data was used to assist validation of modifications made to the HYDRUS unsaturated flow and transport model to include tension-driven flow effects. The practical end product of this work is a data-conditioned numerical tool capable of appropriately

simulating the release of AFFF fluids into the vadose zone. Such a tool will find use where it is necessary or advantageous to simulate AFFF application histories (i.e. rates and frequencies of application) in support of site characterization efforts aimed at determining the vertical and lateral extent of PFAS source areas.

3.3.1 Materials

The AFFF product purchased for use in these experiments was a modern C6-based National Foam product (AER-O-Water® CEM^{C6}) that meets U.S. Military Specification (MIL-SPEC) MILPRF-24385F(SH) and was used as purchased. Isopropyl alcohol (IPA) was also used as an inert surface tension reducing solute. The porous media used in this work was a 30-mesh silica sand. The sand was washed with DI water to remove dust and dried at 100°C prior to use. The test columns were prepared from stock acrylic pipe with an inner diameter of 4.5 cm and length of 10 cm.

3.3.2 Solutions Characterization

Surface tension isotherms for the AFFF solution and IPA were prepared using the methods described previously. AFFF was diluted to a 3% solution (operating solution for the product) per the manufacturer's instructions using SGW-2; lower concentration standard solutions were prepared by step dilution. Dilutions were similarly made for the IPA solution standards. Surface tension isotherms were developed to select initial test solution concentrations and for use in numerical simulations.

3.3.3 Porous Media Characterization

In addition to a sieve analysis, the sand was further characterized to provide unsaturated flow parameters needed to apply the van Genuchten (VG) equation during numerical simulations. The VG equation is as follows (van Genuchten, 1980):

$$\Theta(h) = \begin{cases} \Theta_r + \frac{\Theta_s - \Theta_r}{(1 + |\alpha h|^n)^m}, & h \leq 0 \\ \Theta_s, & h > 0 \end{cases} \quad [3-10]$$

where Θ_r is the residual moisture content, Θ_s is the saturated moisture content, h is the pressure head, and α , n , and m ($m=1-1/n$) are soil-specific fitting parameters. Relevant properties for the test sand are provided in Table 3-2 and Figure 3-2. The saturated hydraulic conductivity of the sand was determined to be 6×10^{-2} cm/sec.

Table 3-2. Test Sand Sieve Analysis Results.

Sieve No.	Sieve Opening (mm)	% Retained	Cummulative % Retained	Cummulative % Passing
20	0.841	0	0	100
30	0.595	1	1	99
40	0.42	37.9	38.9	61.1
50	0.297	33.2	72.1	27.9
70	0.21	24.9	97	3
100	0.149	2.7	99.7	0.3
140	0.105	0.2	99.9	0.1
200	0.074	0.1	100	0
270	0.053	0	100	0
PAN	-	0	100	0

Effective Size = 0.105 mm

Uniformity Coeff (Cu) = 4

Coeff of Gradation (Cc) = 0.503

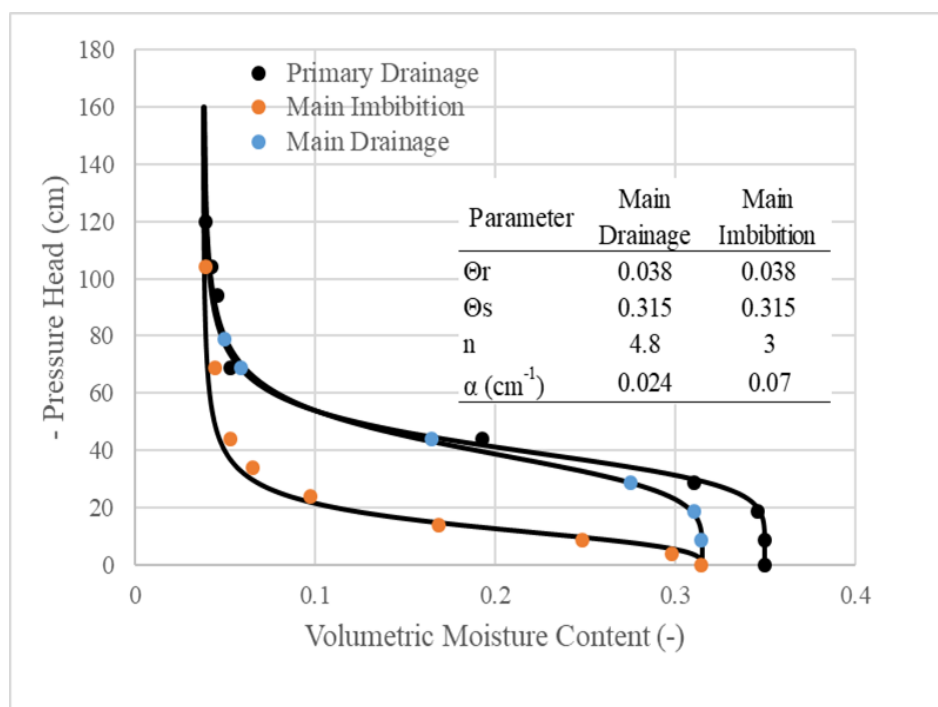


Figure 3-2. Water Characteristic Curves for the Test Sand.

3.3.4 Column Experiments

Tension-driven pore-water redistribution resulting from the presence of AFFF solution within water-unsaturated porous media was evaluated using the horizontal column methods previously presented by Kakare et al. (1993) for insoluble surface-active alcohols, and later by Smith and Gillham (1999) and Henry et al. (2001) for water-soluble surface-active alcohols. The method consisted of preparing two samples of unsaturated sand (one containing SGW and the other containing the surface-active solution). Experiments were performed using either AFFF or IPA. Solutions were added to dry sands to achieve a common moisture content. The sands were mixed thoroughly for two minutes, stored in an air-tight container for 24 hours to allow for possible redistribution of fluids, and mixed again prior to packing the test columns.

As demonstrated in Figure 3-3 the left-hand side (LHS) of the column was packed, using a tamp-and-fill procedure, with the sand containing SGW at a given moisture content. The right-hand side (RHS) of the column was then similarly packed with sand containing the AFFF solution of interest at the same θ_w . Vented high-density polyethylene end pieces were added to each end of the column to maintain the positioning of the pack. The columns were wrapped in plastic wrap to minimize evaporation and held horizontal during a given moisture redistribution period.

The moisture content profile within the columns as a function of horizontal distance was determined gravimetrically by carefully extruding the soil core while sectioning it into samples of approximately 1 cm in length. The samples were then oven dried at 100°C for 24 hours. Each experiment was run in duplicate for a given redistribution time period.

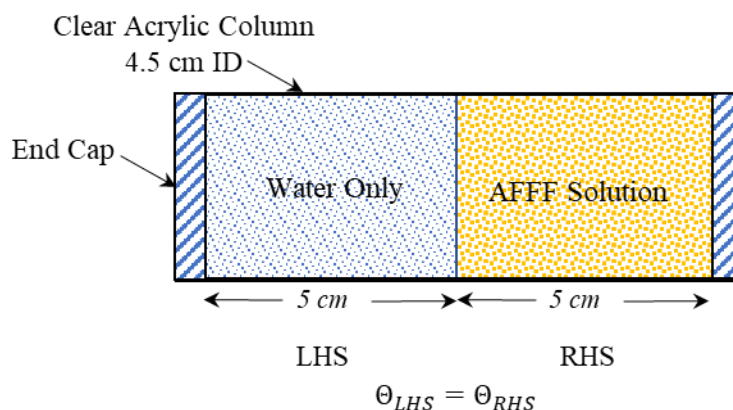


Figure 3-3. Apparatus used in tension-driven flow experiments.

3.3.5 Numerical Model Modifications

The following discussions describe the approach used to implement AWI adsorption and tension-driven flow into the HYDRUS unsaturated flow and contaminant transport model.

AWI Adsorption (Implementing concentration, moisture content, and ionic strength dependence)

The Henry's law component in HYDRUS describing the distribution of solute between the aqueous and gaseous phase was replaced with solute adsorption at the air-water interface as follows:

$$\frac{\delta \Theta_a C_g}{\delta t} = \frac{\delta \Gamma A_{ia}}{\delta t} \quad [3-11]$$

where Θ_a is the volumetric air content (-), C_g is the concentration in the gaseous phase (ML^{-3}), and Γ is the interfacial adsorbed concentration (ML^{-2}). A_{ia} is calculated directly from the pressure head-saturation relationship using the approach described by Bradford and Leij (1997) and Bradford et al (2015):

$$A_{ia}(\Theta) = \frac{1}{\gamma_o} \int_{\Theta}^{\Theta_s} P_{aw}(\Theta) d\Theta = \frac{\rho_w g}{\gamma_o} \int_{\Theta}^{\Theta_s} h(\Theta) d\Theta$$

$$\frac{dA_{ia}(\Theta)}{d\Theta} = \frac{P_{aw}}{\gamma_o} = \frac{\rho_w g h}{\gamma_o} \quad [3-12]$$

where P_{aw} is the capillary pressure ($\text{ML}^{-1}\text{T}^{-2}$), Θ_s is the saturated water content (-), ρ_w is the density of water (ML^{-3}), and g is the gravitational acceleration (LT^{-2}).

The dependence of Γ on C_w was modeled using the Langmuir adsorption isotherm equation:

$$\Gamma = \frac{\Gamma_{max} K_L C_w}{1 + K_L C_w}$$

$$\frac{\delta \Gamma}{\delta t} = \frac{\Gamma_{max} K_L}{(1 + K_L C_w)} \frac{\delta C}{\delta t} + \frac{K_L C_w}{(1 + K_L C_w)} \frac{\delta (\Gamma_{max})}{\delta t} \quad [3-13]$$

where K_L can be dependent on the ionic strength (I) of the solution via:

$$K_L(I) = K_{L,0} + \frac{K_{L,max} b I^n}{1 + b I^n} \quad [3-14]$$

where $K_{L,0}$ is the Langmuir coefficient for $I = 0$ (DI water in this case), $K_{L,max}$ is the maximum value for the dataset, and b and n are input parameters describing the curvature of the $K_L(I)$ relationship.

Tension-Driven Flow Modifications (Implementing concentration-dependent surface tension)

The primary impact of surface-active organic solutes on unsaturated water flow is through the dependence of soil water pressure, h , on surface tension (Bear, 1972; Henry et al., 2001):

$$h = \frac{2\gamma \cos \omega}{\rho_w g r} \quad [3-15]$$

where ω is the contact angle, and r is the radius of an equivalent circular tube. AWI adsorption of surface-active contaminants then contributes to the flow of contaminants. The dependence of surface tension on solute concentration can be described as:

$$\frac{\gamma(C)}{\gamma_0} = 1 - b \ln \left(\frac{c}{a} + 1 \right) \quad [3-16]$$

where a and b are constants for the compound of interest, $\gamma(C)$ the surface tension at concentration C . Note that Equation 3-16 is the same form of the LS equation described previously. This allows LS equation parameters to be used directly in scaling hydraulic properties with changes in tension. With respect to initiating tension-driven flow, it is also important to note that the concentration of the surface-active solute needs to be great enough to cause a sufficient reduction in surface tension to cause a capillary pressure gradient.

The VG equation in terms of capillary pressure is:

$$S = \frac{1}{(1 + (\alpha h)^n)^m}$$

$$h = \frac{1}{\alpha} \left[S^{-\frac{1}{m}} - 1 \right]^{\frac{1}{n}} \quad [3-17]$$

The capillary pressure of the target liquid can be scaled by γ as

$$h = h_0 \left(\frac{\gamma}{\gamma_0} \right) = h_0 \alpha_h \quad [3-18]$$

where α_h is the pressure head scaling factor. Note that solute can also affect the surface tension, and then

$$h = h_0 \left(\frac{\gamma}{\gamma_0} \frac{\cos \omega}{\cos \omega_0} \right) \quad [3-19]$$

which is currently not implemented as a part of our current HYDRUS modifications.

AFFF solutions, when applied during fire training activities or during fire suppression, can also exhibit viscosities greater than water, which can reduce unsaturated hydraulic conductivity during subsurface infiltration. To account for this, we adopted the method of Smith (1995) to implement concentration-dependent viscosity into HYDRUS. This approach used a similar expression to the surface-tension function above to model viscosity changes as a function of solute concentration:

$$\frac{\nu(C)}{\nu_0} = \left[1 - e \ln \left(\frac{c}{a} + 1 \right) \right]^{-1} \quad [3-20]$$

where d and e are constants for the compound of interest, $\nu(c)$ the kinematic viscosity at concentration c , and ν_0 is kinematic viscosity at the reference concentration ($\nu_0 = 0.9017$ cSt at $c_0 = 0$).

The resulting concentration-dependent hydraulic conductivity, $K(\theta, c)$, is (Henry et al., 2001):

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

$$K(\theta, c) = \left(\frac{\nu_0}{\nu} \right) K(\theta, c_0) = \alpha_K K(\theta, c_0) = \alpha_K K^*(h^*) \quad [3-21]$$

where α_K is the hydraulic conductivity scaling factor. This approach assumes that viscosity is Newtonian (does not change with shear-rate).

4.0 Results and Discussion

4.1 Surface Tension Isotherms and AWI Adsorption

When the project pre-proposal and final proposal were initially submitted (January 2017 and March 2017, respectively), little to no data pertaining to AWI adsorption as it relates to characterizing PFAS fate and transport in the vadose zone existed in the published literature. This fact was identified in our proposal as a critical data gap that limited our understanding of PFAS fate and transport within and beneath vadose zone source areas. Therefore, our stated objective was to generate a fundamental physicochemical properties dataset with which to evaluate the potential significance of AWI adsorption as a source of retention and as an environmental sink within PFAS source zones and the underlying vadose zone that could contribute to groundwater contamination and sustained groundwater plumes. To begin to meet this objective over 900 surface tension measurements were made to prepare surface tension isotherms for 14 individual PFASs of environmental significance and as solution mixtures.

4.1.1 PFCA Measurements

Examples of the surface-tension isotherms developed for the PFCAs are presented in Figure 4-1 for the DI water solutions and two SGW solutions (i.e., SGW-1 and SGW-5, Table 3-1) representing the lowest and highest SGW ionic strengths used in this work. The solid lines in Figure 4-1 are the LS equation (Equation 3-1) fit to the measured data. Again, complete surface-tension isotherms were prepared to provide sufficient data to effectively anchor the interpolation of the LS equation between the limits of the measured data and the pure water surface-tension (γ_0). In all cases, the LS equation was found to well represent the measured surface-tension isotherms across the range of PFCA solution concentrations utilized. LS equation fitting parameters, Langmuir parameters describing the surface adsorbed concentration, and goodness-of-fit statistics for each PFCA at each SGW ionic strength condition used in this work are presented in Table 4-1.

The results presented in Figure 4-1 exhibit some anticipated trends. Measured aqueous surface tensions were observed to decrease with increasing PFCA solution concentration and with increasing number of $-\text{CF}_2-$ groups comprising the monomer chain (i.e. increasing PFCA chain length or carbon number (C_N) for these homologous chemicals). AWI adsorption was also observed to increase with increasing SGW ionic strength. This result is demonstrated by the change in the positioning of the surface-tension isotherms (i.e. leftward shift in the complete isotherm plots in Figure 4-1) and is generally attributed to a hydrophobic effect that combines a reduction in bulk aqueous solubility of the amphiphile and decreased electrostatic repulsion of the ionic portion of the amphiphile when positioned at the AWI (Gurkov et al., 2005). Another interesting observation presented in Figure 4-1 is that while the tension isotherms shift in response to increasing SGW ionic strength, the magnitude of the shift for PFDA appears to decrease relative to the other PFCAs, indicating a reduction in AWI adsorption that will be discussed further in Section 4.1.6. Additional observations related to solution ionic strength and PFCA interfacial adsorption will be addressed in greater detail in subsequent sections.

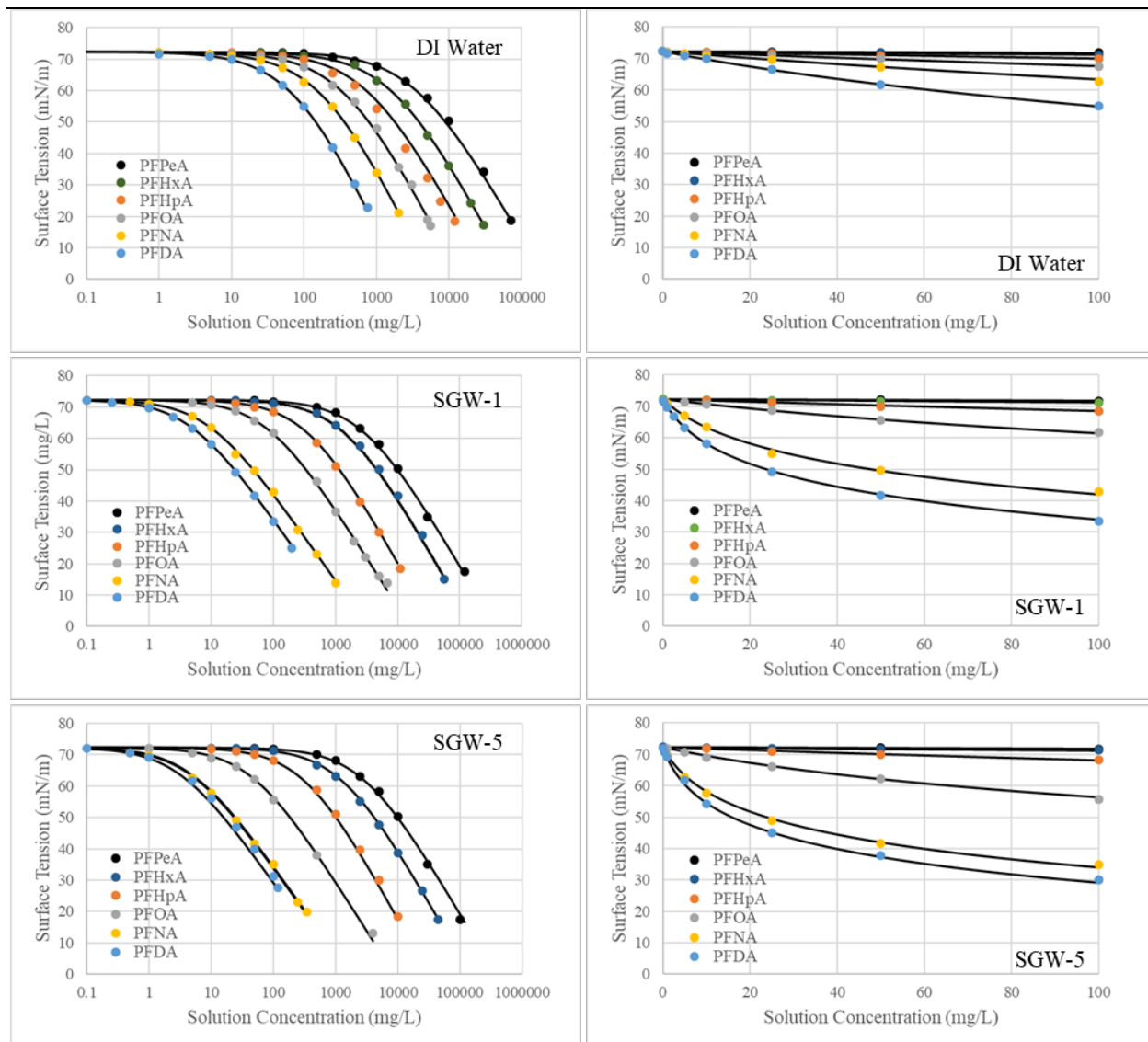


Figure 4-1. Example PFCA surface-tension isotherms for DI water and two SGWs.

Table 4-1. Parameters associated with PFCA surface-tension isotherms and fits to data.

Water	PFCA	Szyszkowski Eq. Parameters			Langmuir Parameters		Goodness of Fit Parameters		
		a (mol/L)	b (-)	$\gamma_{\min}$ (mN/m)	K_L (L/mol)	$\Gamma_{\max}$ (mol/m ²)	n	R^2	χ^2
DI	PFPeA	1.29E-02	0.22	18.7	77.5	6.42E-06	11	0.997	0.022
	PFHxA	5.40E-03	0.26	17.2	185	7.58E-06	10	0.999	0.002
	PFHpA	2.10E-03	0.27	18.4	476	7.88E-06	10	0.998	0.011
	PFOA	8.97E-04	0.27	16.5	1115	7.92E-06	9	0.999	0.031
	PFNA	4.00E-04	0.29	21.2	2500	8.33E-06	8	0.998	0.011
	PFDA	1.57E-04	0.30	22.9	6372	8.75E-06	9	0.998	0.007
	PFDoA	2.00E-05	0.30	28.5	50000	8.75E-06	8	0.994	0.060
SGW-1	PFPeA	1.20E-02	0.22	18.7	83.3	6.42E-06	9	0.997	0.026
	PFHxA	4.40E-03	0.21	17.2	227	6.13E-06	10	0.998	0.014
	PFHpA	1.00E-03	0.22	18.4	1000	6.42E-06	7	0.997	0.019
	PFOA	2.00E-04	0.19	14	5000	5.54E-06	7	0.998	0.022
	PFNA	1.50E-05	0.16	13.9	66667	4.67E-06	7	0.998	0.034
	PFDA	9.50E-06	0.17	26.2	105263	4.96E-06	6	0.996	0.019
	PFDoA								
SGW-2	PFPeA	1.20E-02	0.22	18.7	83	6.42E-06	10	0.997	0.041
	PFHxA	4.30E-03	0.21	17.2	233	6.13E-06	10	0.998	0.021
	PFHpA	9.50E-04	0.22	18.4	1053	6.42E-06	8	0.999	0.012
	PFOA	1.50E-04	0.19	13.9	6667	5.54E-06	7	0.998	0.023
	PFNA	1.10E-05	0.16	13.9	90909	4.67E-06	7	0.997	0.014
	PFDA	7.20E-06	0.17	25.7	138889	4.96E-06	6	0.996	0.039
	PFDoA	4.00E-06	0.17	43	250000	4.96E-06	7	0.997	0.113
SGW-3	PFPeA	1.20E-02	0.22	18.7	83	6.42E-06	11	0.999	0.002
	PFHxA	4.20E-03	0.21	17.2	238	6.13E-06	10	0.999	0.001
	PFHpA	9.20E-04	0.22	18	1087	6.42E-06	7	0.999	0.027
	PFOA	1.30E-04	0.19	13.5	7692	5.54E-06	7	0.997	0.037
	PFNA	9.50E-06	0.16	13.9	105263	4.67E-06	7	0.999	0.003
	PFDA	6.00E-06	0.17	24.2	166667	4.96E-06	7	0.998	0.012
	PFDoA								
SGW-4	PFPeA	1.20E-02	0.22	18.7	83	6.42E-06	9	0.998	0.012
	PFHxA	4.00E-03	0.21	17.2	250	6.13E-06	11	0.997	0.042
	PFHpA	9.10E-04	0.22	18	1099	6.42E-06	6	0.999	0.055
	PFOA	1.20E-04	0.19	13	8333	5.54E-06	7	0.999	0.016
	PFNA	8.90E-06	0.16	13.9	112360	4.67E-06	7	0.999	0.004
	PFDA	5.00E-06	0.17	22.2	200000	4.96E-06	7	0.998	0.021
	PFDoA								
SGW-5	PFPeA	1.20E-02	0.22	18.7	83	6.42E-06	9	0.998	0.015
	PFHxA	4.00E-03	0.21	17.2	250	6.13E-06	10	0.998	0.11
	PFHpA	9.08E-04	0.22	18	1101	6.42E-06	7	0.999	0.009
	PFOA	1.10E-04	0.19	13	9091	5.54E-06	7	0.999	0.011
	PFNA	8.50E-06	0.16	19.8	117647	4.67E-06	7	0.999	0.040
	PFDA	4.70E-06	0.17	22.2	212766	4.96E-06	9	0.999	0.085
	PFDoA	3.00E-06	0.17	48.9	333333	4.96E-06	5	0.975	0.315

Note: a and b are the fitting parameters for the Szyszkowski Equation fit to the measured data, $\gamma_{\min}$ is the minimum surface tension for these measurements, K_L is the Langmuir coefficient, $\Gamma_{\max}$ is the maximum surface concentration, n is the number of measurements, R^2 is the regression coefficient, χ^2 is the chi-square statistic, probability statistic $P = 1$ in all cases.

4.1.2 PFSA Measurements

Surface-tension isotherms generated for the three PFSA (potassium salts) homologues are presented in Figure 4-2. The same general trends were observed as for PFCAs (i.e., surface tensions increasing with increased PFSA C_N and with increasing SGW ionic strength, and surface tensions decrease with increasing PFSA concentration). The PFSAs were also found to be more surface active (i.e. greater adsorption per unit concentration) compared to PFCAs of equivalent C_N but with lower minimum surface tension achieved. LS equation fitting parameters, Langmuir parameters describing the surface adsorbed concentration, and goodness-of-fit statistics for each PFSA at each SGW ionic strength condition used in this work are presented in Table 4-2. As was observed for the PFCAs, the LS equation fit the measured data well.

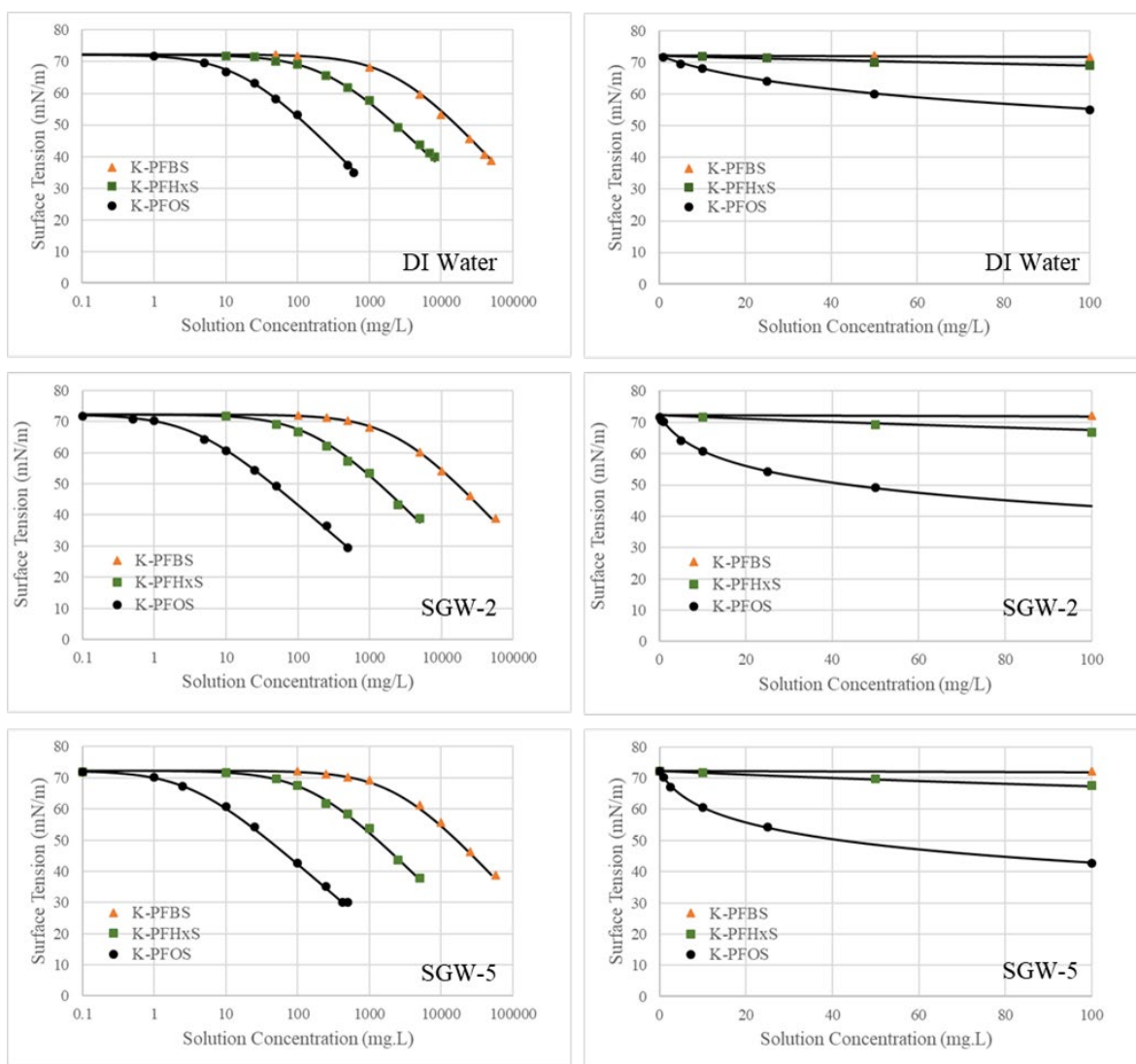


Figure 4-2. Example PFSA surface-tension isotherms for DI water and two SGWs.

Table 4-2. Parameters associated with PFSA surface-tension isotherms and fits to data.

Water	PFSA	Szyszkowski Eq. Parameters			Langmuir Parameters		Goodness of Fit Parameters		
		a (mol/L)	b (-)	$\gamma_{\min}$ (mN/m)	K_L (L/mol)	$\Gamma_{\max}$ (mol/m ²)	n	R^2	χ^2
DI	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	9	0.999	0.045
	K-PFHxS	6.71E-04	0.14	39.8	1490	3.93E-06	12	0.999	0.073
	K-PFOS	3.35E-05	0.12	35	29872	3.50E-06	10	0.999	0.04
SGW-1	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	10	0.998	0.062
	K-PFHxS	4.76E-04	0.14	38.8	2100	4.08E-06	10	0.997	0.023
	K-PFOS	9.07E-06	0.12	30.2	110200	3.50E-06	9	0.999	0.051
SGW-2	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	8	0.998	0.048
	K-PFHxS	4.20E-04	0.14	38.8	2381	4.08E-06	9	0.998	0.064
	K-PFOS	7.30E-06	0.12	29.4	136986	3.50E-06	10	0.999	0.041
SGW-3	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	9	0.999	0.044
	K-PFHxS	4.03E-04	0.14	38.8	2481	4.08E-06	9	0.999	0.062
	K-PFOS	7.16E-06	0.12	29.4	139623	3.50E-06	10	0.996	0.074
SGW-4	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	9	0.998	0.042
	K-PFHxS	3.99E-04	0.14	37.8	2509	4.08E-06	9	0.999	0.027
	K-PFOS	7.09E-06	0.12	28.5	140968	3.50E-06	9	0.998	0.063
SGW-5	K-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	8	0.998	0.098
	K-PFHxS	3.90E-04	0.14	37.8	2564	4.03E-06	9	0.997	0.064
	K-PFOS	6.50E-06	0.12	28.5	153846	3.50E-06	10	0.999	0.079

Note: a and b are the fitting parameters for the Szyszkowski Equation fit to the measured data, $\gamma_{\min}$ is the minimum surface tension for these measurements, K_L is the Langmuir coefficient, $\Gamma_{\max}$ is the maximum surface concentration, n is the number of measurements, R^2 is the regression coefficient, χ^2 is the chi-square statistic, probability statistic $P = 1$ in all cases.

4.1.3 Comparisons to Additional PFAA Salts, Acids, and SDoS

It is well known that PFAS salts and acid forms can exhibit different surface adsorption and micellization behavior (Kissa, 2001). For the PFCA and PFSA salts, these differences in solution physicochemical properties have been shown to be dependent on the specific counterion selected (Shinoda et al., 1972; Kissa, 2001). Many of these examples, however, are for solutions prepared in deionized water or salt solutions containing cations that match the PFAS counterion. In the interest of comparison, additional surface-tension isotherms were prepared to examine the dependence of AWI adsorption on the PFAS counterion when solutions are prepared in SGWs. H-PFOS and H-PFBS were purchased for comparison with the results of K-PFOS and K-PFBS, and NH₄-PFOA was likewise purchased for comparing the results of the acid form of PFOA (referred to in this section as H-PFOA for clarity of presentation). The isotherms prepared for these measurements are presented in Figure 4-3.

For PFOS and PFHxS, solutions were prepared up to and including the solubility limit, as evidenced by the stabilization of surface-tension measurements with increasing concentration. PFBS solutions were not prepared to include the solubility limit given that it greatly exceeds the limit of interest with respect to environmentally relevant concentrations. Surface-tension isotherms for both H-PFBS and K-PFBS were found to be entirely coincident; i.e. individual measured surface tensions were the same across the entire range of PFBS solution concentrations

and the similarity of measured surface tension was consistent for the DI water case as well as for each SGW used. For PFBS solutions, the coincidence of surface-tension isotherms was anticipated based on a comparable degree of solution composition insensitivity observed for the low C_N PFCAs.

Similarly, the isotherms for H-PFOS and K-PFOS were coincident regardless of the ionic strength of the solution. The coincidence of the isotherms for the free-acid and potassium salt forms of PFOS across the range of SGW ionic strength conditions evaluated (see Figure 4-3) was unexpected. Solubility limits and associated minimum tension values vary with increasing ionic strength, but the rate of increase with decreasing concentration trends similarly regardless of the character of the ionic head group. For K-PFOS in DI water, the solubility limit and minimum surface tension determined here was 1,570 mg/L and 33 mN/m, which is remarkably consistent with that presented by Shinoda et al. (1972) and suggests the measurements made were accurate. The free-acid form of PFHxS due to cost and availability constraints. However, a similar tension response can be anticipated for H-PFHxS and K-PFHxS.

Surface-tension isotherms developed for H-PFOA and NH₄-PFOA also exhibit some interesting characteristics. NH₄-PFOA (or APFO as it is commonly known) was selected because it is a common form of PFOA used at contaminated manufacturing sites, and to evaluate the effects of a larger counterion in solution. As shown in Figure 4-3, NH₄-PFOA exhibited decreased surface activity, relative to H-PFOA, for DI water and SGW-2 conditions, with the relative surface activity apparently decreasing with increasing ionic strength. However, the effect was observed to diminish considerably for the SGW-5 condition. It appears that the effect of the NH₄ cation as a component of the is diminished as the concentration of additional ions in solution increase.

Finally, as stated in our proposal, the hydrocarbon surfactant SDoS was selected for inclusion in this work. SDoS was selected as a representative sodium alkyl hydrocarbon surfactant that could be used in AFFF formulations. Therefore, SDoS was additionally used as a component in a binary mixture, as an example case, to evaluate effects of hydrocarbon and fluorocarbon surfactant mixtures on AWI adsorption and retention. The SDoS isotherms (Figure 4-4) followed anticipated trends (i.e., increased surface activity with increased solution ionic strength). LS equation fitting parameters, calculated Langmuir parameters, and associated goodness-of-fit parameters are presented in Table 4-3.

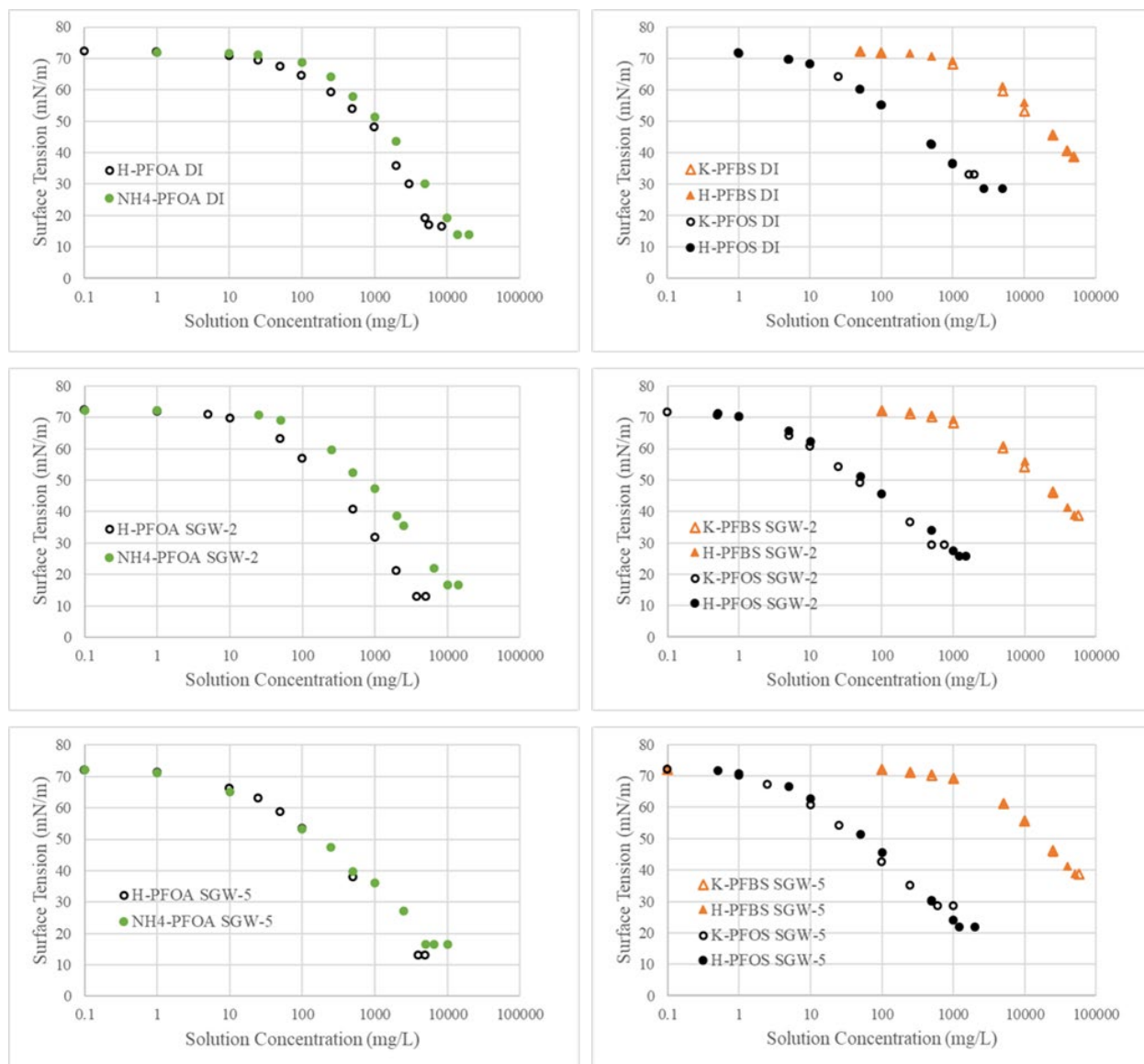


Figure 4-3. Comparison of surface-tension isotherms for free-acid and salt forms of PFOA, PFBS, and PFOS at three SGW ionic strengths.

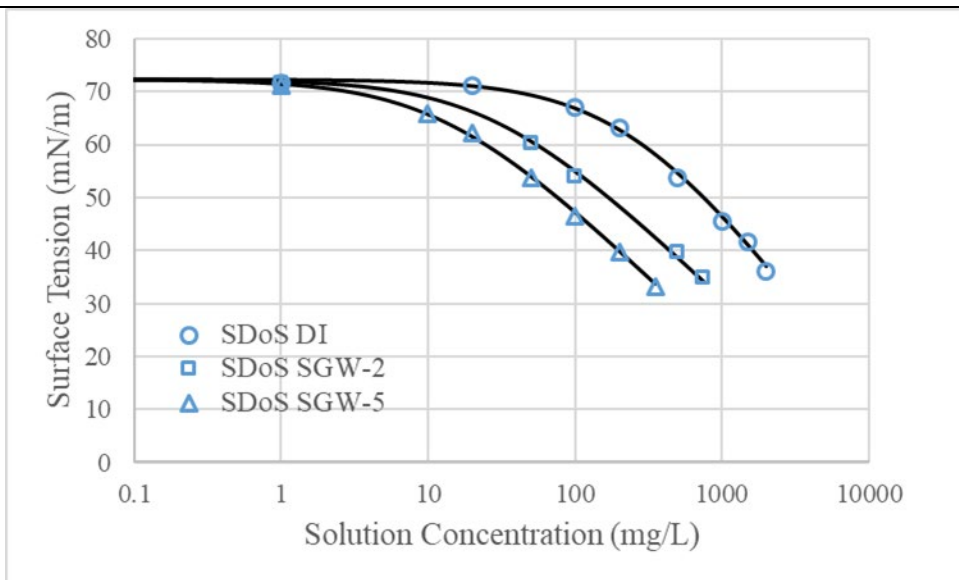


Figure 4-4. Surface-tension isotherms for SDoS in DI water and two SGWs.

Table 4-3. Parameters associated with PFSA surface-tension isotherms and fits to data.

Water	PFSA	Szyszkowski Eq. Parameters			Langmuir Parameters		Goodness of Fit Parameters		
		a (mol/L)	b (-)	γ_{min} (mN/m)	K_L (L/mol)	Γ_{max} (mol/m ²)	n	R^2	χ^2
DI	SDoS	8.50E-04	0.22	35	1176	6.42E-06	11	0.999	0.069
	NH ₄ -PFOA	1.02E-03	0.23	14	981	6.71E-06	11	0.999	0.067
	H-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	11	0.998	0.079
	H-PFOS	3.26E-05	0.12	28.5	30641	3.50E-06	9	0.999	0.019
SGW-2	SDoS	1.30E-04	0.16	35	7692	4.67E-06	10	0.998	0.075
	NH ₄ -PFOA	4.20E-04	0.19	16.6	2381	5.54E-06	10	0.998	0.091
	H-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	10	0.998	0.075
	H-PFOS	7.50E-06	0.11	25.7	133333	3.21E-06	9	0.999	0.044
SGW-5	SDoS	4.50E-05	0.16	33.1	22222	4.67E-06	9	0.999	0.024
	NH ₄ -PFOA	1.70E-04	0.18	16.6	5882	5.25E-06	10	0.997	0.092
	H-PFBS	8.00E-03	0.15	38.8	125	4.38E-06	9	0.997	0.071
	H-PFOS	1.20E-05	0.13	22	83333	3.79E-06	9	0.999	0.021

Note: a and b are the fitting parameters for the Szyszkowski Equation fit to the measured data, γ_{min} is the minimum surface tension for these measurements, K_L is the Langmuir coefficient, Γ_{max} is the maximum surface concentration, n is the number of measurements, R^2 is the regression coefficient, χ^2 is the chi-square statistic, probability statistic $P = 1$ in all cases.

Each of the surface-tension isotherms developed in this work can be reproduced using the a and b parameters presented in Tables 4-1, 4-2, and 4-3, and applying Equation 3-1. The high concentration limit is where C_w provides the minimum tension (γ_{min}) and the low concentration limit being $C_w = 0$ at $\gamma = \gamma_0$. k_{ia} values can be determined using the LS equation parameters provided in the same tables to first plot the surface-tension isotherms and thereafter calculating the incremental slope at the solution concentration of interest. Alternatively, the Langmuir parameters can be used to calculate k_{ia} directly for a given solution concentration using the Langmuir equation:

$$\Gamma = \frac{\Gamma_{max} K_L C_w}{1 + K_L C_w} \quad [4-1]$$

and applying $k_{ia} = \Gamma / C_w$ (as in Equation 3-2). An example of the results of these calculations are presented in Figure 4-5. These surface-tension isotherms have value not only for the objectives of the current work, but are also useful for alternative environmental calculations involving estimating PFCA mass associated with aqueous aerosols or for calculating removal efficiencies for remediation technologies that rely on AWI adsorption to air bubbles to remove PFCA mass from the aqueous phase, as examples.

4.1.4 Environmentally Significant AWI Adsorption

Calculated k_{ia} values are presented graphically in Figure 4-5. k_{ia} values were observed to decrease with increasing PFCA concentration and continued to decrease across the range of values used, up to and including the apparent solubility limit. This trend may initially seem counter-intuitive when considering Γ increases with increasing concentration. However, because k_{ia} represents the equilibrium condition between the PFCA adsorbed at the AWI and that dissolved within the bulk aqueous phase, at lower concentration small increases in C_w result in larger increases in Γ which, by Equation 3-2, provides a larger k_{ia} .

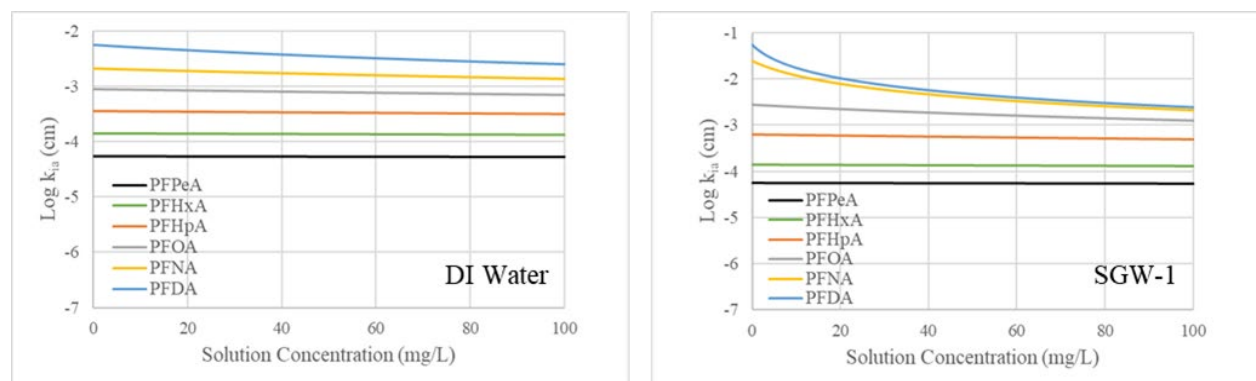


Figure 4-5. Example calculate k_{ia} values for individual PFCAs.

However, as shown in Figure 4-6, when the LS equation fit is extended to include very low aqueous concentrations (sub-mg/L), the magnitude of k_{ia} values stabilize (i.e. k_{ia} concentration-dependence diminishes as slope of the tension isotherm becomes linear). k_{ia} values in Figure 4-6 were calculated from the parameters presented in Tables 4-1 and 4-2 for a 6-order of magnitude range of solution concentrations. The lines in Figure 4-6 are the LS equation fit to the surface-tension data and interpolated between the surface tension of pure water and the lowest measured data point allowed by the measurement method. When this data is presented in a log-log format, a key finding of this research is revealed. As the concentrations of these representative PFAS compounds decrease, the k_{ia} value that governs the degree of AWI adsorption achievable begins to stabilize about a common value. This occurs because the slope of the isotherms within this low concentration region (i.e., the first-order or linear region) approach and achieve a constant

value as the solution concentration decreases, consistent with the Langmuir isotherm equation. Therefore, within this lower concentration range, which includes the range of environmentally significant concentrations, a single k_{ia} value can be used to characterize individual PFCA and PFSA adsorption and retention due to AWI adsorption. Similar plots for NH₄-PFOA and SDOs are presented in Figure 4-7. Note that the magnitude of the k_{ia} values in these figures vary depending on the ionic strength of the aqueous solution, in keeping with the shifts in the positioning of the surface-tension isotherms. Therefore, just because the surface-tension isotherms all approach a common value as solution properties approach that of pure water (DI water in this case), this does not necessarily mean that k_{ia} values do the same.

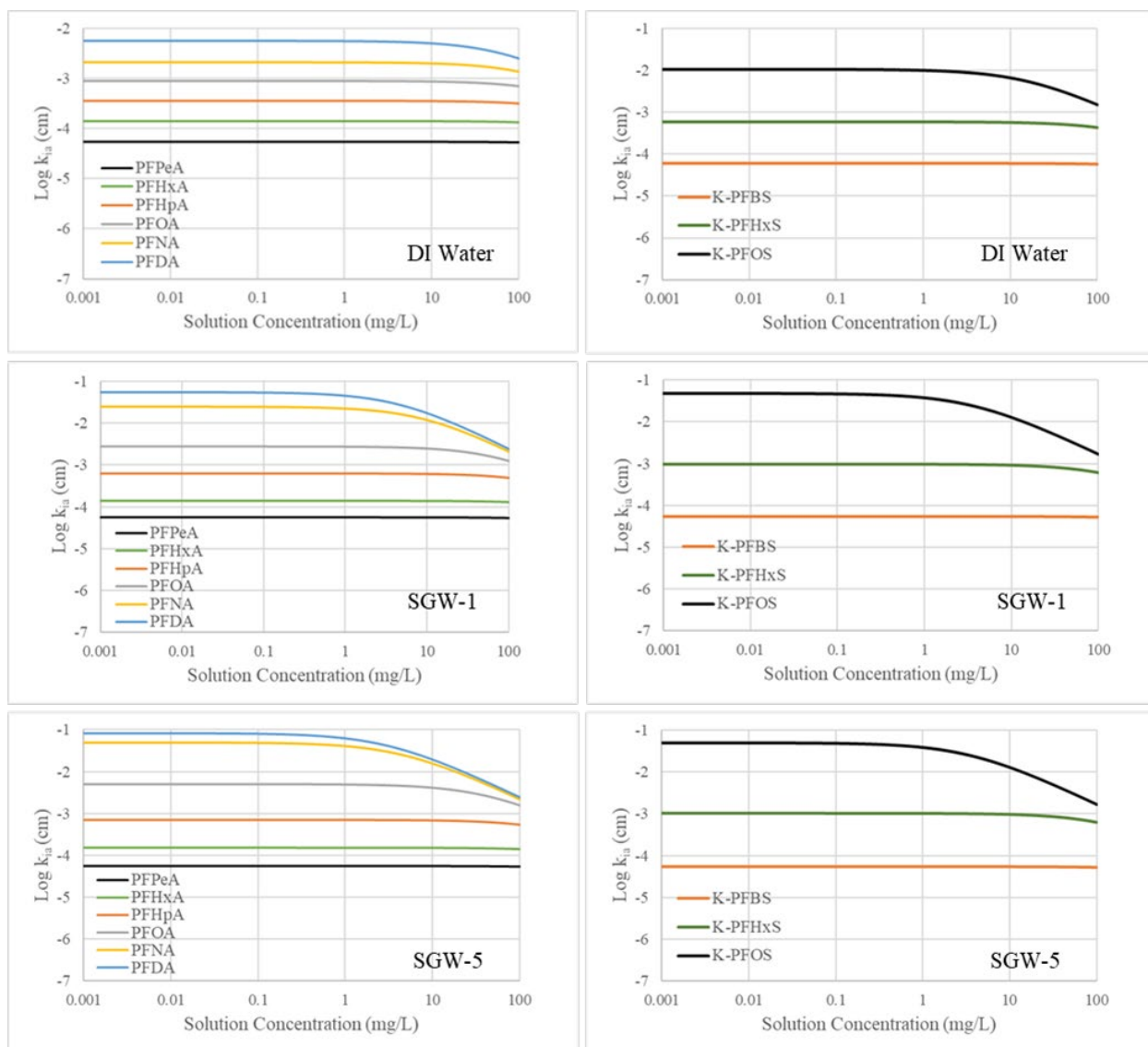


Figure 4-6. Calculated Concentration-Dependent PFCA and PFSA k_{ia} values.

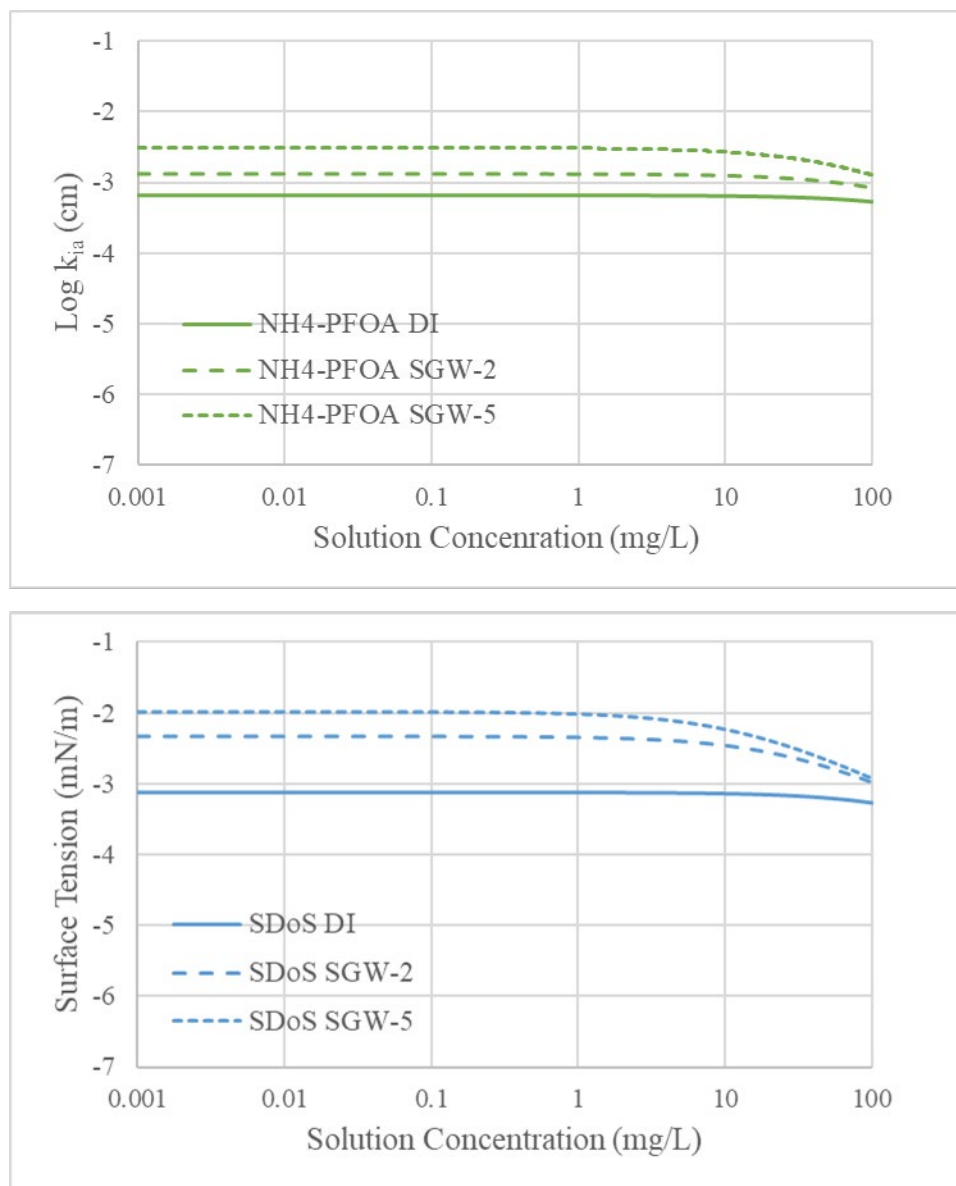


Figure 4-7. Calculated Concentration-Dependent k_{ia} values for NH₄-PFOA and SDoS.

Published PFAS site characterization efforts have demonstrated that PFAS groundwater contamination in the vicinity PFAS source areas generally occurs at concentrations between one and into the hundreds of $\mu\text{g/L}$ (e.g., Moody and Field, 1999; McGuire et al., 2014; Anderson et al., 2016; Weber et al., 2017), with the exception of PFOA in a few samples collected from a monitoring well adjacent to a former fire-fighter training area at Naval Air Station Fallon, NV (Moody and Field, 1999) which averaged 6.57 mg/L. These results would suggest that the single representative k_{ia} value approach would be applicable to characterize AWI adsorption within the vadose zone beneath PFAS source areas. However, these groundwater samples were collected from wells screened below or across the water table. Typical low-flow sampling techniques collect groundwater samples that are representative of the mean concentration of contaminants

across the length of the screened interval, which could vary between 5 and 10 feet in length and could bias the concentrations low for typical plumes which are non-uniform vertically (i.e., some depth zones may have high contamination and other depth zones may be clean). Additionally, these sample concentrations are not necessarily representative of PFAS concentrations within tension-held pore water within the source area and above the water table (or capillary fringe), which could be elevated relative to samples collected from beneath the water table. To our knowledge, direct sampling and analysis of PFAS concentrations in tension-held pore waters within and beneath PFAS source areas has not been performed to provide an informed comparison.

Given the uncertainty in PFAS concentrations possible within the vadose zone, we generally propose that the concentration-independent Langmuir coefficient (K_L) and Equation 4-1 are more appropriate to describe the overall concentration-dependent adsorption mechanism, particularly for numerical computations. However, because k_{ia} values are needed to evaluate the significance of AWI adsorption as a part of this report, values calculated from the surface-tension isotherm data developed in this work are provided as Tables 4-4 and 4-5 for a 1 mg/L PFCA and PFSA solution concentrations. Values for SDoS solutions are provided for comparison. The 1 mg/L concentration was selected for comparison with previous work and generally represents the upper range of values observed at field sites for PFCAs (e.g., fire training areas at Naval Air Station Fallon, NV - Moody and Field, 1999). However, as shown in Figure 4-6, calculations for lower PFCA and PFSA concentrations would provide similar results as k_{ia} values do not change considerably it at all within this concentration region.

Table 4-4. Example k_{ia} values for 1 mg/L PFCA solutions.

Water	PFPeA (C5)	PFHxA (C6)	PFHpA (C7)	PFOA (C8)	PFNA (C9)	PFDA (C10)	PFDoA (C12)
DI	4.97E-05	1.30E-04	3.75E-04	8.83E-04	2.07E-03	5.51E-03	4.00E-02
SGW-1	5.35E-05	1.39E-04	6.25E-04	2.74E-03	2.55E-02	4.53E-02	7.40E-02
SGW-2	5.35E-05	1.42E-04	6.67E-04	3.68E-03	3.55E-02	5.93E-02	8.81E-02
SGW-3	5.35E-05	1.46E-04	6.95E-04	4.30E-03	4.00E-02	6.73E-02	1.00E-01
SGW-4	5.35E-05	1.53E-04	7.03E-04	4.60E-03	4.22E-02	6.73E-02	1.05E-01
SGW-5	5.35E-05	1.53E-04	7.05E-04	4.93E-03	4.11E-02	6.66E-02	1.07E-01

Table 4-5. Example k_{ia} values for 1 mg/L PFSA solutions.

Water	K-PFBS (C4)	K-PFHxS (C6)	K-PFOS (C8)	SDoS (C12)
DI	5.47E-05	5.84E-04	9.87E-03	7.52E-04
SGW-1	5.47E-05	8.53E-04	3.16E-02	1.76E-03
SGW-2	5.47E-05	9.66E-04	3.76E-02	4.51E-03
SGW-3	5.47E-05	1.01E-03	3.82E-02	6.70E-03
SGW-4	5.47E-05	1.02E-03	3.85E-02	8.82E-03
SGW-5	5.47E-05	1.03E-03	3.89E-02	9.63E-03

While the general published environmental dataset for PFCAs and PFSA continues to grow and improve, the current dataset is still problematic. For example, aqueous solubilities (useful in validating isotherm solubility limits) presented in many published reports on PFAS fate and transport vary widely among publications, and many reference the same data sources (e.g., the

U.S Environmental Protection Agency’s EPI Suite) that ultimately report solubility data based on estimates made from other physical properties measurement. The surface-tension data for these chemicals are considerable but conditions under which these measurements were made vary greatly with respect to the PFAS salt/counterion salt form and solution composition, temperature, type of counterion (gegenion), PFAS purity). With respect to AWI adsorption, Lyu et al. (2018) presented k_{ia} values for PFOA, prepared in 0.01M NaCl solution and DI water (2.0×10^{-3} cm and 9.55×10^{-3} cm, respectively, per the reported regression equation provided by these authors), that are very similar to those presented in Table 4-4, where SGW-1 ionic strength was 0.006 M.

4.1.5 Effect of SGW Ionic Strength on AWI Adsorption

While it is well known that dissolved electrolytes cause increased interfacial adsorption of surfactants, the data and descriptions presented in this section (also presented in Silva et al., 2019) represent, to our knowledge, the first time solutions simulating groundwater compositions have been used to evaluate the effect of AWI adsorption on the retention of PFAS-specific compounds in the vadose zone. Also, we demonstrate that the rate of increase of adsorption drops off considerably with increasing SGW ionic strength and that the effect can be simply modeled using Langmuir-like equation.

Note that the magnitude of the k_{ia} values in Figures 4-6 and 4-7 vary depending on the ionic strength of the aqueous solution, in keeping with the observed shifts in the positioning of the surface tension isotherms. Therefore, just because the surface tension isotherms all approach a common value as solution properties approach that of pure water (DI water in this case), this does not necessarily mean that k_{ia} values do the same. This statement is best defended in Figure 4-8, where the logarithm of k_{ia} values for individual PFCAs and PFSA are plotted as a function of SGW ionic strength.

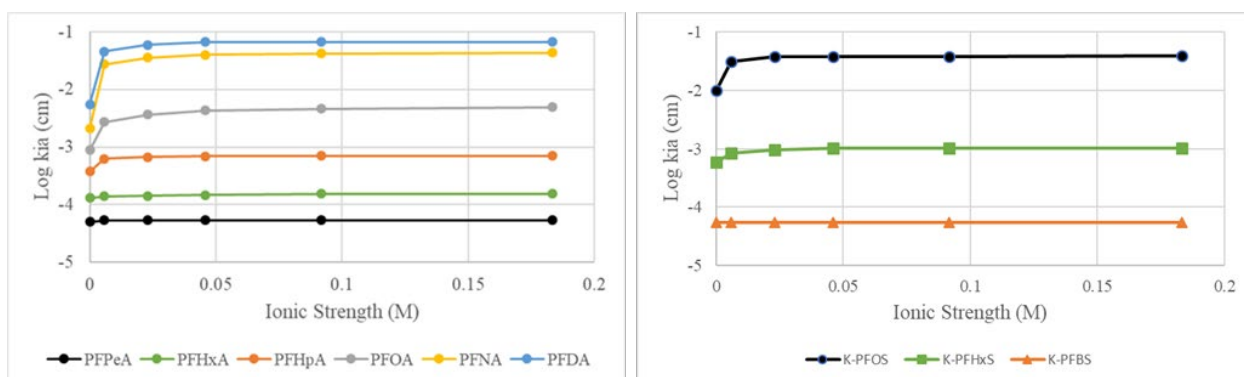


Figure 4-8. Ionic strength dependence on calculated k_{ia} values for 1 mg/L PFCA and PFSA solutions.

AWI adsorption was observed to increase with increasing ionic strength and is consistent with the hydrophobic effect described previously. However, the effects of amphiphile hydrophobicity appears to have a limit for the SGW solutions used in this work, in that the rate of change of adsorption decreases markedly once a threshold ionic strength condition was achieved.

For PFCAs and PFSA of lower C_N (e.g. PFPeA and PFBS), k_{ia} values were found to be largely insensitive to changes in ionic strength, within the range of values investigated. However, for PFCAs of higher C_N a clear threshold ionic strength condition exists above which the rate of further increases in k_{ia} is marginal. Gurkov et al (2005) observed a similar threshold AWI adsorption stabilization for SDoS in NaCl solutions when the concentration of NaCl exceeded 0.01M, which is a similar threshold condition observed for the cases and condition presented in Figure 4-8. The fact that this phenomenon occurs for PFAS and hydrocarbon surfactants of varied hydrophobe structure suggests that once the threshold solution ionic strength is achieved, the degree of AWI adsorption, and thus k_{ia} , becomes less dependent on the ionic composition of the bulk solution and more dependent on the arrangement of ions at the surface and the spatial dimension of the hydrophobe.

This result is an additionally significant in that it potentially simplifies modeling of the effect of ionic strength (I) on k_{ia} . For example, given the results presented in Figure 4-8, $k_{ia}(I)$ could be modeled directly using a Langmuir-like expression. Further, Gurkov et al (2005) described an additional simplification that suggests normalization of the effect of I on interfacial adsorption parameters can be achieved by re-evaluating the surface tension isotherms in terms of the mean ionic activity the solutions. Evaluating this simplifying approach to describe PFAS AWI adsorption for the current and alternative SGW compositions is considered by the project team to be a fruitful avenue for future research.

4.1.6 AWI Adsorption Observations and Comments on Predictive Relationships

When evaluating surfactant adsorption processes it is often useful to represent characteristic parameters related to adsorption with molecular descriptors based on the size and/or structure of the amphiphile to support interpretation of trends or facilitate prediction of adsorption parameters. Common molecular descriptions used for this purpose include molar volume, C_N , and the molecular connectivity index.

As this work investigates PFCA and PFSA homologues, we have opted to evaluate AWI adsorption processes in relation to C_N . The k_{ia} values provided in Tables 4-4 and 4-5 for the DI water case and two SGWs are presented as a function of C_N in Figure 4-9. The regression equation presented by Lyu et al (2018) (i.e., $\log k_{ia} = 0.56C_N - 7.5$) describing $k_{ia}(C_N)$ for a homologous series of PFCA sodium salts (solutions prepared in DI water) is also presented in this same figure for comparison. This regression equation was derived from data originally presented by Lunkenheimer et al. (2015). A reworking of the same Lunkenheimer et al. (2015) Na-PFCA dataset, recently presented by Brusseau (2019), is also presented in Figure 4-9 along with a K-PFSA dataset also reported by Brusseau (2019).

For the DI water cases, calculated k_{ia} values present log-linearly with increasing C_N . As shown, the slope of the $\log k_{ia}(C_N)$ relationship for the DI water solutions prepared in the current work differs from those prepared by Lyu et al. (2018) and Brusseau (2019). We attribute this difference to counterion effects and the use of PFCA sodium salts by Lunkenheimer et al. (2015). PFSAs in DI water also present log-linearly with increasing C_N for the current dataset, within the range: $4 \geq C_N \geq 8$, which suggests this relationship can be used to interpolate k_{ia}

values for PFCAs within this range of C_N . k_{ia} values in the Brusseau (2019) datasets are generally lower than those in the current datasets in both the PFCA and PFSA cases (and by approximately the same amount) and exhibit a slight upward curvature that is absent in the current datasets. We are at a loss to explain this discrepancy, particularly when both datasets use the same base surface tension isotherms. Clearly a correction was made. Lunkenheimer et al. (2015) synthesized the PFCAs used in their work and document a significant effort to achieve a high level of purity for both the PFCAs prepared and the solutions prepared. It is possible that the differences in the k_{ia} values presented by Brusseau (2019) and the current datasets reflect differences in PFAS purity. However, PFCAs and PFSA found in the environment are likely not present in their highest level of purity, and therefore predictive relationships based on measurements using high purity chemicals will tend to underestimate AWI adsorption in environmental systems. Nonetheless, the current dataset is valid for use in environmental calculations as monomer solubility limits and minimum tension values provided by the measured surface tension isotherms are reasonably similar to those reported in the existing literature for these chemicals.

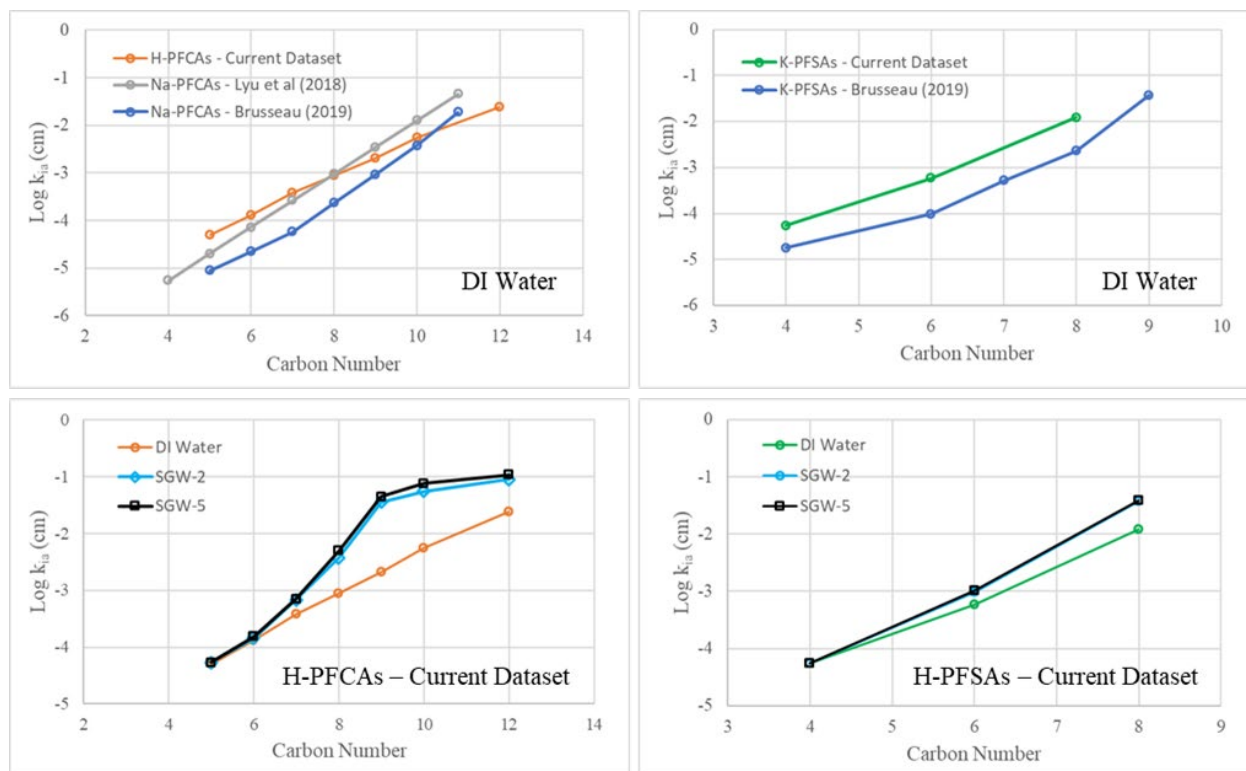


Figure 4-9. $\log k_{ia}(C_N)$ relationships for 1 mg/L solutions of the PFCAs and PFSA.

While a log-linear $k_{ia}(C_N)$ relationship holds for PFCA solutions prepared in DI water, this was not the case for the SGW solutions. As shown in Figure 4-9, the $\log k_{ia}(C_N)$ relationship for the SGW solutions exhibit a positive deviation from a log-linear trend that increases slightly with increasing C_N between $C_N = 5$ and 9. Beyond $C_N = 9$, the rate of increase in the $\log k_{ia}(C_N)$ relationship was observed to diminish. Replicate solutions and subsequent surface tension measurements provided the same result, indicating the reduced AWI adsorption for PFDA and

PFD_oA is real for these SGW solutions. Plots of the $k_{ia}(C_N)$ relationship for 0.01 mg/L PFCA solution show the same behavior, again reflecting an apparent decrease in AWI adsorption for PFDA and PFD_oA for the SGW solutions. It is possible that impurities in the PFCA reagents selected could have contributed to these results. However, given the linearity observed in the log $k_{ia}(C_N)$ relationship for the DI water, the deviation from log-linearity observed for the SGW solutions is more likely related to the presence of dissolved ions in solution and concomitant electrostatic effects at the AWI. PFSA_s used in this work exhibit a log-linear $k_{ia}(C_N)$ relationship. However, as the current PFSA dataset does not extend beyond $C_N = 8$, continued log-linearity beyond this range is not certain.

While the exact mechanism responsible for this observed behavior is not entirely clear, some explanation can be gleaned from a few relevant literature sources. For example, Lunkenheimer et al. (2015), using highly purified sodium-PFCA homologues, observed a non-linear increasing trend in the free energy of AWI adsorption (ΔG_0^{ads}) with increasing C_N that may help to explain some of the non-linearity in the $5 \geq C_N \geq 9$ range of the SGW log $k_{ia}(C_N)$ functions. These authors argued that the non-linearity in the $\Delta G_0^{ads}(C_N)$ relationship was due to variability in the Debye screening length of the electrostatic double layer established at the AWI that allows an incrementally increasing adsorption with increasing PFCA C_N that is in excess of that due to amphiphilic nature of these molecules alone. As shown in Figure 4-10, this incrementally increasing adsorption phenomenon may be occurring for the SGW cases. For comparison with the present work, ΔG_0^{ads} was calculated as (Lunkenheimer et al., 2015):

$$\Delta G_0^{ads} = -RT \ln a_L \quad [4-2]$$

where a_L is the surface activity determined as fitting parameter a in the Equation 3-1 fits to the surface tension isotherms. In the absence of additional electrolytes, the $\Delta G_0^{ads}(C_N)$ relationship for the free acid PFCAs presents as a linear function across the range of C_N investigated. However, in the presence of available counterions, a similar degree of upward curvature is observed in both datasets. In Figure 4-10, ΔG_0^{ads} is enhanced for the SGW solutions in response to the elevated ionic strength of the SGW solutions.

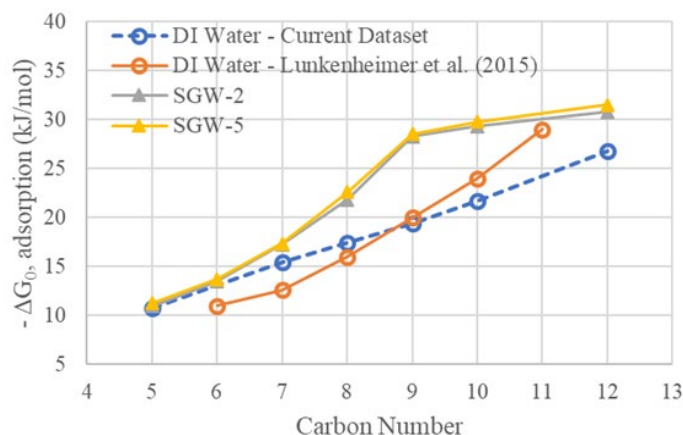


Figure 4-10. PFCA standard free energies of adsorption as a function of C_N .

Additionally, the Lunkenheimer et al. (2015) dataset presented in Figure 4-10 combines the results for even and odd numbered PFCA amphiphile carbon numbers, which were presented separately in their original manuscript. These authors further demonstrated variability in the magnitude of PFCA AWI adsorption that is dependent on whether the PFCA contains an even or odd number of carbons in the chain. Psillakis et al. (2009) also observed differing degrees of AWI adsorption for both the PFCAs and perfluoro-n-alkyl sulfonates when C_N was odd or even. These results suggest that an additional cause of the non-linearity observed in the $5 \geq C_N \geq 9$ range SGW $\log k_{ia}(C_N)$ dataset may be related to inherent differences in surface activity between odd and even homologues that manifest more intensely when an excess of dissolved ions is present in solution.

The exact mechanism for the observed decrease in PFCA adsorption from SGW solutions for $C_N > 9$ is also not entirely clear. For ionic surfactants, the addition of electrolytes in aqueous solution decreases the solubility of the surfactant in the bulk aqueous phase, which enhances the hydrophobic effect driving the surfactants from the bulk liquid and toward surfaces. The addition of salt also reduces the electrostatic repulsion between the surfactant's ionized headgroups, allowing surfactant molecules to pack closer together at surface saturation and should provide a surface favorable to enhanced adsorption at lower concentrations of environmental significance. Both mechanisms generally combine to enhance surface adsorption. However, the decreased adsorption for $C_N > 9$ in Figure 4-10 and the threshold adsorption limitation in the $k_{ia}(I)$ function described in Section 4.1.5, suggests an electrostatic condition at the AWI where SGW-associated ions are competing with adsorption of PFCAs at the same interface. As each PFCA shares a common carboxylate anion, this process should occur for all PFCAs. However, the effect is clearly not occurring proportionately across the range of PFCA homologues employed herein. For example, for PFCA $C_N \leq 6$, AWI adsorption is largely not affected by the magnitude of SGW ionic strength. For $C_N > 9$, SGW-associated ions appear to out-compete interfacial adsorption of PFCAs.

It is also important to consider that for many of the PFCA and PFSA test solutions prepared in this work, the total concentration of ions associated with the SGWs used (cf. Table 3-1) is often greater than the concentration of perfluorocarboxylate and perfluorosulfonate anions in solution. The SGW solutions used also contain divalent anions and cations that can significantly affect the ordering and charge potential at the AWI. These two conditions could combine to negatively impact PFCA adsorption, particularly where the size of the surfactant approaches the Debye length established at the surface (Psillakis et al., 2009; Lunkenheimer et al., 2015).

Irrespective of the actual mechanism(s) at work here, the current results provide evidence that log-linear $k_{ia}(C_N)$ relationships may not be appropriate to predict AWI adsorption in natural groundwaters where $I > 0.01\text{M}$ and the water contains a mixture of divalent and monovalent ions in solution. Although not demonstrated, this will likely also be the case for molar volumes and connectivity indices as structural descriptors, as these descriptors only characterize the hydrophobic component of adsorption from solution. We hypothesize that a successful predictive relationship for AWI adsorption of PFAS in natural waters will be one that includes both the hydrophobic effect (e.g., structural descriptors) and electrostatic effects that relate charge densities and Debye lengths associated with excess ions at the interface to the effective Debye length of the PFAS molecules.

4.1.7 Significance of AWI Adsorption within the Vadose Zone

As described in Section 3.1.4, the significance of AWI adsorption to PFAS fate and transport in the vadose zone was evaluated with regard to its impact on slowing infiltration velocities (i.e., retardation). Our approach utilizes data-informed calculations of contaminant specific R_f values, assuming AWI adsorption is the only mechanism for retention. This approach is viable under the condition that at system equilibrium, the dissolved contaminant remains in excess in solution with respect to the AWI and additional sources of retention (e.g., sorption to solid phases). Although this evaluation was limited to the linear PFCAs and PFSA's, this same approach can be applied to alternative PFAS as k_{ia} values for these compounds become available either by measurement or prediction.

Calculated R_f values are presented in Figure 4-11 (a) for DI water and SGW-2 and SGW-5 solutions as a function of C_N . The analysis utilized the same soil moisture condition and corresponding A_{ia} used by Lyu et al. (2018). The $R_f(C_N)$ relationship developed from the regression equation presented by Lyu et al. (2018) is also provided for comparison.

For these PFCAs, and for all datasets presented in Figure 4-11 (a), AWI retention is observed to be minimal for $C_N < 6$, as R_f values are not significantly different from unity for both DI water and SGW cases. AWI retardation is considerably increased for the SGWs, relative to the DI water cases, due to the increased interfacial adsorption observed for these SGWs. This result is significant and highlights the importance of accounting for groundwater ionic strength when attempting to predict AWI retention. For the SGW cases, R_f values for the higher carbon number homologues (i.e. $C_N > 8$) are shown to range between 5 and 20. Given that retardation factors for the most common regulated organic pollutants (e.g., TCE, PCE, TCA, BTEX) are often in the range from 1-3, these PFAS values are highly significant from a practical perspective. As was observed for the $\log k_{ia}(C_N)$ relationship, the predicted SGW $R_f(C_N)$ relationship deviates from its smoothly increasing function at $C_N = 9$ in response to the stabilization of surface tension observed for the PFDA isotherms for all SGWs. Similar surface tension stabilization effects were observed for measurements utilizing PFDoA.

R_f values presented in Figure 4-11 (a), were calculated for a single soil moisture condition and a PFCA concentration of 1 mg/L. The moisture content condition in this analysis is quite high (i.e. $\Theta_w = 0.23$ or 77% of the total pore volume, assuming a porosity of 0.3 for a well sorted sand). Therefore, the results presented in Figure 5a provides a limited assessment of the degree of AWI retention possible.

To provide a more comprehensive evaluation, k_{ia} values determined for SGW-2 (Table 4-4) were used to estimate AWI adsorption-specific R_f values for soil moisture conditions ranging from $S_w = 0.77$ to 0.17 (the assigned residual moisture condition for this hypothetical sand). The results presented in Figure 4-11 (b) demonstrate the range of R_f values possible for these PFCAs as A_{ia} changes with changes in S_w for a 1 mg/L PFCA solution concentration. For example, at $S_w = 0.77$, a condition potentially met when and while water infiltrates into a volume of vadose zone, the R_f for PFOA is 1.9, whereas R_f increases by at most a factor of 24 at the residual

moisture condition. R_f values estimated for the higher carbon number PFCA homologues at residual moisture were determined to range between 407 and 723.

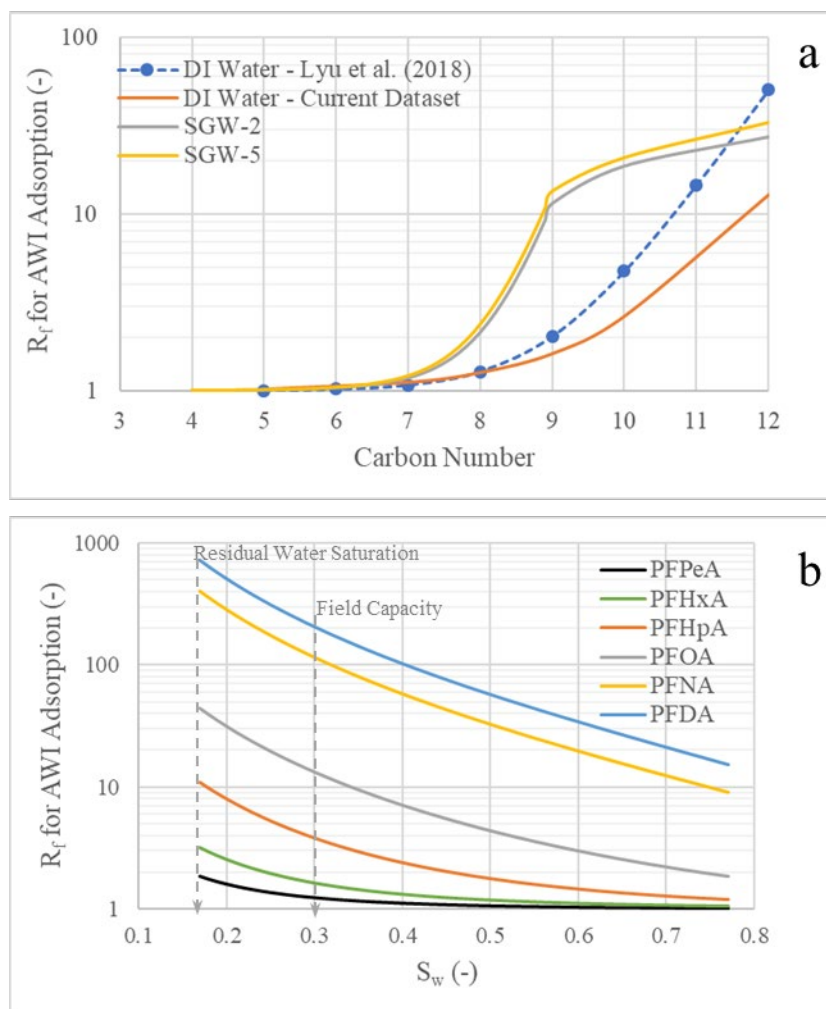


Figure 4-11. PFCA retardation factors for AWI adsorption as the sole source of retention: (a) R_f values are for $[PFCA] = 1 \text{ mg/L}$ ($A_{ia} = 73 \text{ cm}^{-1}$, $S_w = 0.77$ per Lyu et al. (2018)), (b) R_f values possible across a range of soil moisture conditions and for $[PFCA] = 1 \text{ mg/L}$ and SGW-2.

Given the results presented in Figure 4-11 (b), it is clear that these PFCAs should experience a wide range of R_f values within the vadose zone during a given infiltration event, where imbibition and subsequent drainage processes would cause the A_{ia} to vary considerably during the event. Furthermore, during an infiltration event it is likely that the concentration of perfluorosurfactants in the mobile phase (i.e., convecting aqueous phase) will vary, resulting in variability in k_{ia} values temporally and spatially. The interplay between these variables complicates the typical use of R_f values via Equation 3-4 (e.g., to directly predict the time of arrival of contaminant at a particular depth in soil) for water-unsaturated flow. Generally, the application of a R_f to characterize the transport of a surface-active chemical under water-unsaturated flow at field-scale is an ill-considered chromatography problem, in which (1) the

area of the reactive stationary phase in question (i.e., the AWI) is not constant spatially or temporally under typical field conditions, (2) phase transfer is concentration-dependent and non-linear, and (3) flow of mobile phase is not constant, but rather dynamic and intermittent. This may explain why methods successfully utilizing surface-active tracers to characterize A_{ia} under water-unsaturated flow conditions are typically performed at high and constant water saturation where variability in A_{ia} is minimized and uniform flow can be maintained within the porous medium, and where the surface-active tracer is introduced at a step-input to maintain constant tracer concentration. Numerical methods are likely better suited to resolve the complexity of variables that govern the transport of surface-active contaminants under water-unsaturated flow conditions.

Finally, transport retardation is not the only consideration when evaluating PFAS retention. PFAS mass retained in the vadose zone can act as a long-term source of contamination sustaining groundwater contaminant plumes. To evaluate the potential PFAS mass that could be retained in the vadose zone due to AWI adsorption, the k_{ia} values presented in Table 4-4 for the PFCAs are used in combination with Equation 3-7 to provide specific mass estimates (i.e. mass per unit volume of vadose zone) for AWI adsorption. A uniform and constant S_w and A_{ia} was assumed in these calculations and calculations were made for a representative range of PFCA concentrations. The results of these calculations, provided in Table 4-6, illustrates the potential significance of the AWI as a source of PFCA retention in the vadose zone. Brusseau (2019) recently presented first-order estimates of k_{ia} values for a wide range of PFAS (including linear and branched perfluoroalkyls, polyfluoroalkyls, nonionics, and fluorotelomer alcohols) estimated from literature data sources that ranged between 10^{-1} cm and 10^{-5} cm. This is the same range of values reported in Table 4-4. Therefore, the results in Table 4-6 can be considered generally representative for PFAS contamination.

Admittedly, the assumption of a uniform A_{ia} is highly idealized, as moisture contents and associated AWI area can vary considerably as tension-held pore waters drain and imbibe during infiltration events, which will affect the magnitude of PFAS retained. Fluid flow dynamics within the vadose zone will therefore also affect the magnitude and distribution of PFAS aqueous-phase concentrations. However, even if PFAS concentrations were assumed to vary across the range provided in Table 4-6, the averaged retained mass is still considerable, particularly when considering the potential for this adsorbed mass to contribute to the continued release of PFAS contaminants to groundwater plumes when the current federal health advisory limits for PFOA and PFOS that are triggering remedial action for municipal well waters is 70 parts per trillion.

Table 4-6. Estimates of the specific mass of PFCAs potentially retained in the vadose zone.

C_w (mg/L)	Specific Mass (mg/m ³)					
	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA
1	19.1	50.9	239	1317	12690	21202
0.1	1.91	5.09	23.9	132	1269	2120
0.01	0.19	0.51	2.39	13.2	127	212
0.001	0.02	0.05	0.24	1.32	12.7	21
Average	5.32	14.1	66.3	366	3525	5889

Note: k_{ia} values for SGW-2 used. $A_{ia} = 357.7$ @ $S_w = 0.33$.

4.1.8 Implications and Relevance (AWI Adsorption in the Vadose Zone)

The following summarizes the key findings of this work and the implications for PFAS fate and transport:

The following summarizes the key findings of this work and the implications for PFAS fate and transport:

- Recent site characterization efforts have demonstrated that PFAS concentrations in groundwater, including those for the PFCAs and PFSAAs used in this research, are largely present at concentrations in the sub-mg/L range. Our research has shown that for pore-water concentrations less than 1 mg/L, k_{ia} values stabilize around a common value that is specific for each PFAA, and therefore k_{ia} could be treated as a constant for most sites. These values have been reported herein.
- Groundwater concentrations reported in the literature were for samples collected from below the water table and therefore may not accurately represent PFAS concentrations within tension-held pore waters within and underlying PFAS source zones. Direct sampling and analysis of PFAS concentration within tension-held pore waters within and beneath PFAS source areas should be performed to assess the true range of vadose zone pore water and groundwater concentrations present at these sites. Where sub-mg/L concentrations cannot be confirmed, we propose the use of the Langmuir coefficient (examples presented in Tables 4-1, 4-2, and 4-3) as a concentration-independent alternative to k_{ia} values representative of adsorption in the linear region.
- Predictive methods for AWI adsorption constants based on molecular structure descriptors (i.e., those based on the size and/or structure of the hydrophobe) appear to be of limited value for natural groundwaters. Our research demonstrates that for natural waters where the ionic strength is greater than 0.01M and containing a combination of monovalent and divalent ions, k_{ia} values can deviate considerably from log-linear trends that are based in the hydrophobic effect alone. Rather, a method that includes the contribution of the hydrophobic effect, electrostatic contributions related to groundwater geochemical considerations, and Debye length considerations of the interface and effective Debye diameter of the surfactant is thought to be the better approach.

- AWI adsorption and retention within the vadose zone can be significant and is dependent on the length of the surfactant hydrophobe and electrostatic conditions. For example, R_f values, which characterize the rate of contaminant transport relative to that of water, range from a value of 1.2 for PFPeA ($k_{ia} = 5.35 \times 10^{-5}$), 10.9 for PFOA ($k_{ia} = 3.68 \times 10^{-3}$), and 165 for PFDA ($k_{ia} = 8.81 \times 10^{-2}$) for SGW-2 and $S_w = 0.33$ (i.e., at field capacity for this representative sand). Therefore, PFAS with k_{ia} values similar to those of PFPeA will transport to the water table roughly 9 times faster than PFOA and 139 times faster than PFDA. This suggests that groundwater source zones that result from a near-surface source zone will exhibit temporally variable source-zone PFAS composition.
- Adsorption of PFAS at the AWI in the vadose zone can also be significant environmental sink for PFAS contributing to the continued release of PFAS contaminants to sustain groundwater plumes. Therefore, assessing the strength of this source of contamination should be included as a part of initial site investigations. Methods to monitor pore-water content and concentrations exist and when modified for PFAS should be implemented to characterize AWI adsorption as a component of the PFAS source term
- Given the dynamic and transient nature of pore-water flow within the vadose zone, and its effect on the creation and destruction of air-water interfaces, we conclude that a properly conditioned numerical simulator would be a better tool to support PFAS fate and transport calculations compared to methods that rely on retardation factors and representative and uniform k_{ia} values. This approach does not account changes in pore-water PFAS concentrations and changes in AWI area, both of which can greatly impact PFAS retardation.

4.2 Significance of NWI Adsorption and Retention within the Vadose Zone

NAPL-water (NWI) interfacial isotherms for each PFCA prepared for TCE and kerosene as NAPL phases are presented in Figure 4-12. Again, complete NWI adsorption isotherms were prepared and Equation 3-1 was used to fit the data. NWI isotherms were prepared for a single SGW composition (i.e., SGW-2), as a similar relative surface/interfacial tension response to ionic strength was expected for both the AWI and NWI. NWI adsorption isotherms were not prepared for additional PFAS. The results of Equation 3-1 fits to the measured data are provided in Table 4-7. The LS equation was again found to well represent the measured NWI tension isotherms across the entire range of PFCA solution concentrations employed. k_{ni} values for a 1 mg/L PFCA solution are presented in Table 4-8. As was done for the AWI results, PFCA k_{ni} values for both NAPLs are presented as a function of C_N in Figure 4-13.

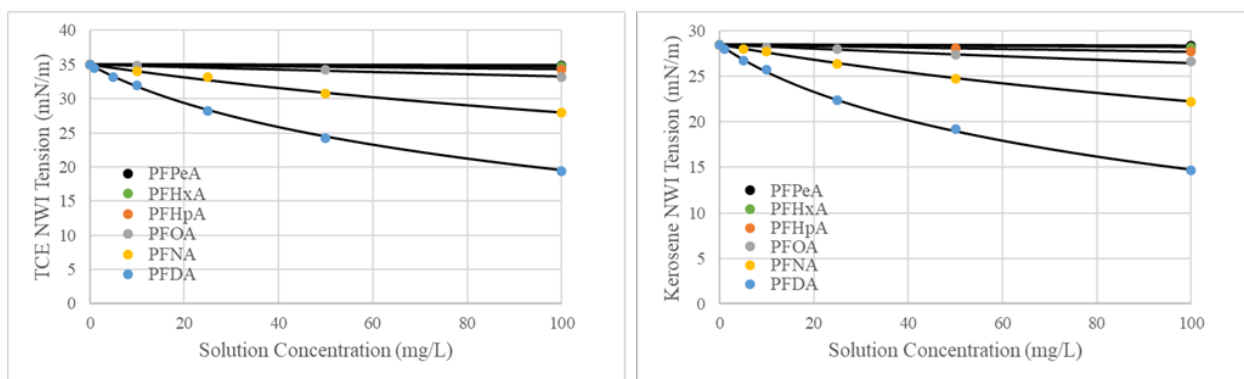


Figure 4-12. PFCA NWI tension isotherms for TCE and kerosene as NAPL phases.

Table 4-7. Parameters associated with PFCA-NWI surface tension isotherms and fits to data.

Water	PFSA	Szyzskowski Eq. Parameters			Langmuir Parameters		Goodness of Fit Parameters		
		a (mol/L)	b (-)	γ_{min} (mN/m)	K_L (L/mol)	Γ_{max} (mol/m ²)	n	R^2	χ^2
TCE	PFPeA	5.50E-02	0.3	15.4	18	4.18E-06	8	0.997	0.055
	PFHxA	1.40E-02	0.29	10	71	4.04E-06	8	0.999	0.034
	PFHpA	4.00E-03	0.29	13	250	4.04E-06	7	0.998	0.014
	PFOA	1.27E-03	0.29	11.2	787	4.04E-06	8	0.996	0.082
	PFNA	1.83E-04	0.28	10.4	5464	3.91E-06	8	0.998	0.093
	PFDA	4.94E-05	0.28	10.4	20243	3.91E-06	9	0.996	0.055
Kerosene	PFPeA	2.98E-02	0.32	6.8	34	3.73E-06	9	0.998	0.064
	PFHxA	9.80E-03	0.31	7.7	102	3.56E-06	7	0.999	0.019
	PFHpA	2.89E-03	0.31	8.1	346	3.56E-06	7	0.998	0.051
	PFOA	9.02E-04	0.3	9.5	1109	3.56E-06	9	0.998	0.053
	PFNA	2.00E-04	0.3	8.6	5000	3.56E-06	8	0.999	0.025
	PFDA	4.23E-05	0.28	6.8	23641	3.22E-06	9	0.999	0.046

Note: a and b are the fitting parameters for the Szyzskowski Equation fit to the measured data, γ_{min} is the minimum surface tension for these measurements, K_L is the Langmuir coefficient, Γ_{max} is the maximum surface concentration, n is the number of measurements, R^2 is the regression coefficient, χ^2 is the chi-square statistic, probability statistic $P = 1$ in all cases.

Table 4-8. NWI adsorption coefficients for 1 mg/L PFCA solutions (SGW-2).

NAPL	PFPeA (C5)	PFHxA (C6)	PFHpA (C7)	PFOA (C8)	PFNA (C9)	PFDA (C10)
TCE	7.60E-06	2.91E-05	1.01E-04	3.16E-04	2.12E-03	7.60E-03
Kerosene	1.25E-05	3.64E-05	1.23E-04	3.86E-04	1.71E-03	7.27E-03

Note: k_{ia} values have units of cm^3/cm^2 or cm .

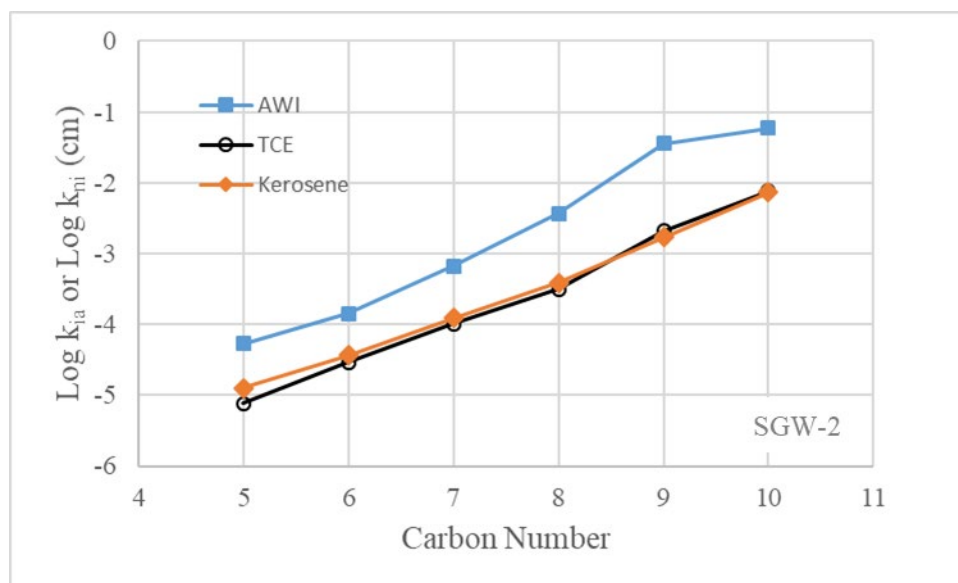


Figure 4-13. Comparison of $k_{ia}(C_N)$ and $k_{ni}(C_N)$ relationships for 1 mg/L PFCA solutions.

As shown in Figure 4-13, PFCA k_{ni} values were observed to be roughly an order of magnitude lower than those calculated for adsorption at the AWI for all PFCA homologues. These results are consistent with those previously reported by Mukerjee and Handa (1981) who similarly observed lower adsorption for the sodium salt of PFOA, from dilute aqueous solution, at the hexane-water interface than was observed at the AWI. This result is not altogether surprising when considering the perfluorocarbon tails of these anionic surfactants are at the same time hydrophobic and oleophobic (Kovalchuk et al., 2014). At the AWI, theory holds that the perfluorocarbon tails of the amphiphile are to be oriented into the air-phase to minimize the overall free energy of the system. On the other hand, theory surrounding the orientation of perfluorinated amphiphiles at the NWI is not as clear. Solvency theory would suggest that the oleophobicity of the perfluorocarbon tails would limit, if not negate, their orientation into the hydrocarbon phase, resulting in lower overall adsorption at the NWI. This theory appears to be supported by the fact that while PFCA k_{ia} values here were found to be the essentially the same for both TCE and kerosene, which possess similar polarity and intermolecular hydrogen bonding potentials (Hansen, 2007; Batista et al., 2015). k_{ia} values calculated from the data of Mukerjee and Handa (1981) were about a factor of 4 larger for sodium PFOA and PFDA at the hexane-

water interface (i.e., 1.5×10^{-2} cm and 2.4×10^{-1} cm, respectively). n-Hexane is essentially non-polar, with its solvency dependent solely on intermolecular dispersion forces. Therefore, there appears to be a relationship between the degree of NWI adsorption and the solvation properties of the NAPL that warrants additional research. Note also that the NWI $k_{ia}(C_N)$ function exhibits greater log-linearity compared to the AWI function. This suggests that proposed electrostatic effects observed for PFCA adsorption at the AWI were not as impactful for NWI adsorption.

R_f values representing NWI adsorption as a sole source of retention were calculated using Equation 3-8 and the $A_{ni}(S_w)$ relationship described in Section 3.2.2. Again, the moisture condition limits for this analysis were $S_w = 0.77$ to 0.17 (the assigned residual moisture condition for this hypothetical sand). The results of this analysis are presented in Figure 4-14.

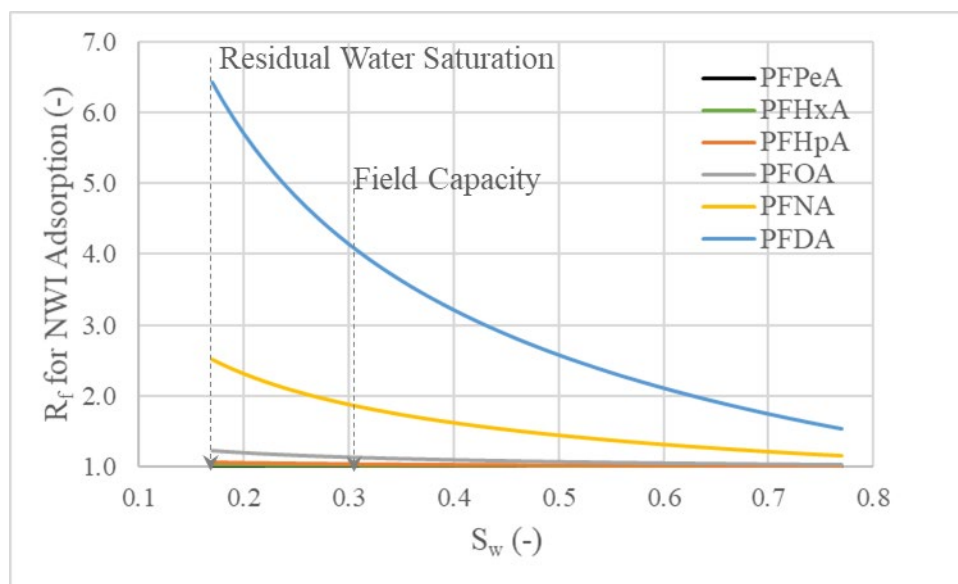


Figure 4-14. PFCA retardation factors for NWI adsorption as the sole source of retention.

The combination of the lower k_{ni} values and the lower A_{ni} exposed to the convecting aqueous phase during water-unsaturated flow results in overall lower R_f values for PFCA transport. Calculated R_f values were only appreciably greater than 1 for $C_N > 8$ and at very low soil moisture conditions (i.e. where the surface area of the NAPL phase has its greatest exposure to the conducting fluid). The NAPL saturation used to develop the $A_{ni}(S_w)$ relationship used in this analysis (Figure 3-1) can be considered moderate for this system. For entrapped NAPL ganglia, an increase or decrease in NAPL saturation would be expected to affect R_f values somewhat, but not significantly in that this would not be expected to change the $A_{ni}(S_w)$ relationship significantly. R_f decreases with increasing S_w in response to the corresponding decrease in A_{ni} across the range of S_w considered.

The results of this preliminary evaluation of PFAS-NWI retention indicate that for $C_N < 8$, NWI adsorption is not a significant contributor to linear PFCA retention. Unfortunately, the experimental database is not extensive enough at present to expand this conclusion to include a wider range of alternative PFAS components, as was done for the AWI. However, Brusseau et al

(2019) did provide a few first-order k_{ni} values (i.e., those calculated from NWI tension data presented in the existing literature for alternative NAPL phases in DI water) that are within the same 10^{-4} cm and 10^{-5} cm range of values calculated and presented in the present work. While NWI adsorption could be important for other PFAS constituents, it does not appear to be a significant source of retention for PFCAs with $C_N > 8$.

4.3 Preliminary Evaluation of AWI Adsorption and Retention for PFAS Mixtures

PFAS contamination exists as a mixture of numerous chemicals including per- and polyfluorinated alkyl acids and perfluoro alkyl sulfonamides of varying chain-length, anionic/cationic/non-ionic/zwitterionic forms, and fluorotelomer precursor chemicals. At fire-training sites associated with AFFF use, co-contaminants can include, alcohol solvents (e.g., glycol ethers and ethylene or propylene glycol), corrosion inhibitors, and hydrocarbon surfactants. Each of these varied chemical species can impact the adsorption and retention of target PFAS components, including retention resulting from AWI adsorption in the vadose zone.

To begin to understand the effects of surface-active co-solutes on the adsorption and retention of PFAS constituents of current regulatory significance, we proposed to evaluate a limited set of binary mixtures to examine whether this data could provide mathematical relationships useful for predictive purposes. As the PFCAs purchased for this work possessed the widest range of C_N values (i.e. surface activity), initial work focused on binary PFCA solutions. However, one ternary PFCA mixture and one PFSA-PFCA binary mixture was also evaluated. Finally, one SDoS-PFCA mixture (with SDoS as a representative sodium alkyl sulfate hydrocarbon surfactant used in AFFF formulations) was evaluated. All solutions were prepared using SGW-2.

4.3.1 PFCA Mixture Evaluations

Surface-tension isotherms for the PFCA binary mixtures developed as a part of this limited-scope project are presented in Figure 4-15. Specific PFCA binary pairs were selected to evaluate a range of surface activity. Also provided in Figure 4-15 are the changes in the minimum adsorbed surface areas per molecule (A_m) with changes in the solution mole fraction (X_w) of the most surface-active component of the mixture. A_m is calculated from the LS-equation fit to the measured data as (Kissa, 2001):

$$A_m(nm^2) = \frac{10^{14}}{\Gamma_{max}N_A} \quad [4-3]$$

where N_A is Avagadro's number. Here A_m is used to demonstrate the adsorbed surface composition at monolayer coverage. Calculated A_m values that fall between those determined for the individual components of a binary mixture is here interpreted as the formation of a mixed-component adsorbed monolayer at the AWI. The results of the LS equation fits to the measured data are provided in Table 4-9. The pC20 results, also presented in Table 4-9, are the solution concentrations where the solution reduces the surface tension of the SGW by 20 mN/m and are commonly used to describe the efficiency of interfacial adsorption or the degree of surface activity. Higher pC20 values indicate lower surface-activity.

For each PFCA mixture, the surface tension isotherms are positioned entirely within the bounds of the single-component isotherms, which suggests a lack of synergistic (or cooperative) adsorption at the AWI (Rosen, 2012). For the PFDA-PFOA, PFNA-PFHpA, and PFDA-PFPeA pairs, the relative positioning of the isotherms indicates non-ideal adsorption. This is best observed in Figure 4-15, for the 50-50 mixture isotherms where the positioning of the isotherm is weighted toward the most surface-active component of the pair. This result suggests competitive adsorption for these PFCAs and that AWI adsorption favors the most surface-active component in the mixture,

which is also demonstrated in the pC_{20} values (Table 4-9) and associated A_m plots in Figure 4-15. Note that as the solution mole fraction of the most surface-active component increases, adsorption of the most surface-active component is dominant, as indicated by A_m equaling that of the single-component values. The degree of non-ideal adsorption appears to generally decrease as the comparative surface-activity of the pair decreases. For the PFOA-PFPeA binary pair, ideal adsorption behavior was observed until the solution mole fraction of PFOA was greater than 0.75, where after PFOA dominates AWI adsorption. This suggests competitive adsorption may not be significant for mixtures of the less surface-active linear PFCAs of lower carbon number (C_N).

To take this preliminary evaluation further, three ternary PFPeA-PFOA-PFDA mixtures were prepared. As shown in Figure 4-16, a similar result was observed for the PFCA ternary mixture, where the three mixture isotherms are altogether more surface-active (i.e., positioned to the left) of the single-component PFOA isotherm and less surface active (i.e., positioned to the right) of the single component isotherm of the most surface-active PFDA component. The significance of competitive adsorption at the AWI for this mixture is best demonstrated in Figure 4-16b, which shows that when the mixture isotherms are plotted using the solution concentration of PFDA, all mixture isotherms practically fall on top of the single-component PFDA isotherm, indicating the dominance of PFDA adsorption and that the concept of a mixed-monolayer for this system may not hold for the ternary mixtures selected. The dominance of PFDA adsorption at the AWI is again reinforced in Figure 4-16c, where the value of A_m calculated for each ternary mixture equaled that of PFDA as a sole adsorbate.

The practical implication of these results is that when competitive adsorption of the most surface-active component dominates, AWI adsorption of the less surface-active components of the mixture can be either negligible or greatly minimized and the transport of these less surface-active components could be accelerated relative to predictions made using their single-component AWI adsorption parameters. However, when adsorbed concentrations fall entirely within the linear adsorption regime for all components, interaction between adsorbed molecules at the AWI would become increasingly less likely and the adsorption of individual components of a mixture would theoretically follow their single-component trend of concentration-dependent values.

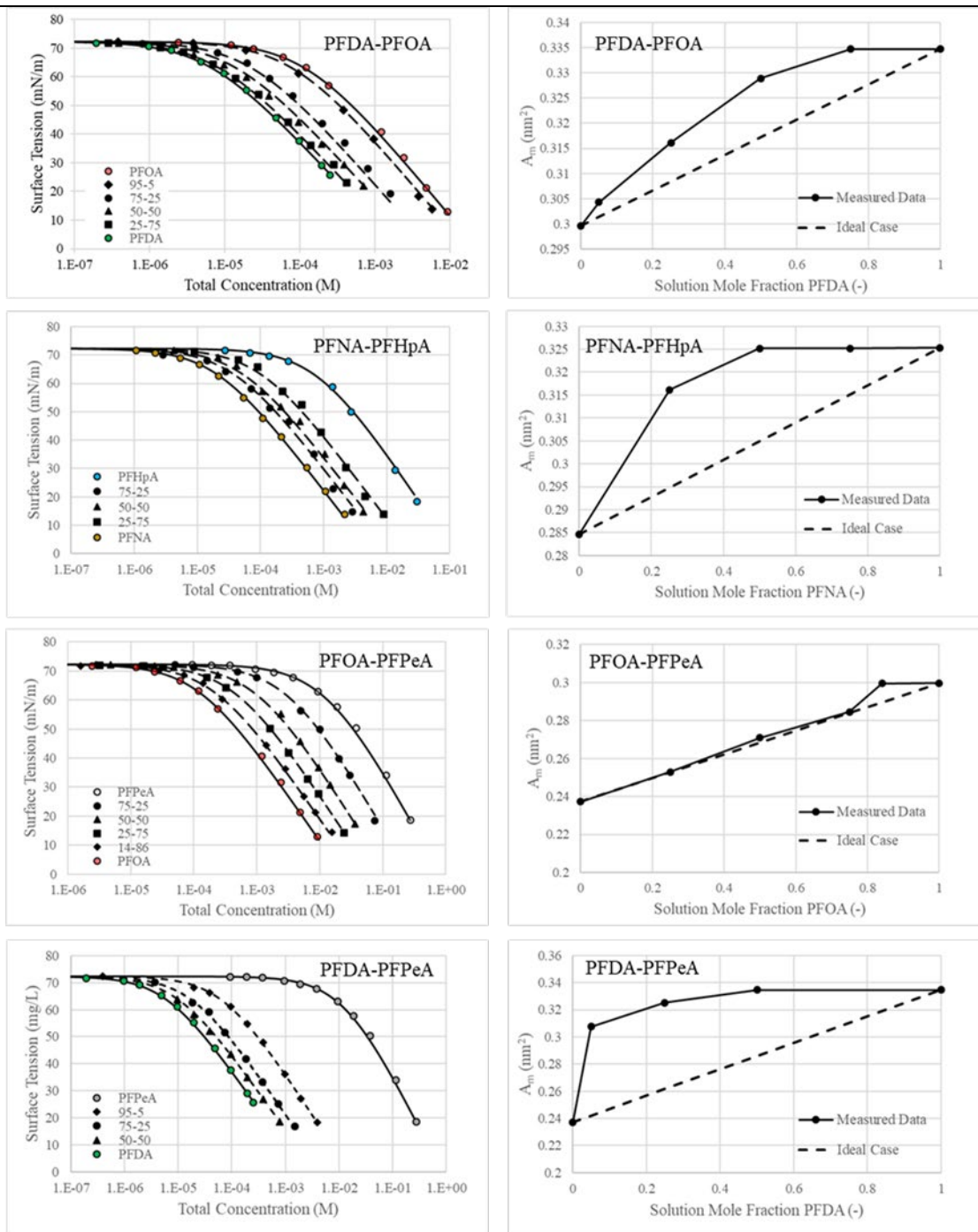


Figure 4-15. Surface-tension isotherms for PFCA binary mixtures. Numbers in legends indicate different mixtures (i.e., 50-50 refers to the relative mole percentages for the mixture).

Table 4-9. Result of fitting LS-equation to PFAS mixture AWI tension isotherms.

Solutes	PFCA or Mixture	pC20 (mg/L)	LS-Equation Parameters			Adsorption Parameters			Goodness of Fit Parameters		
			a (mol/L)	b (-)	$\gamma_{\min}$ (mN/m)	K_L (L/mol)	$\Gamma_{\max}$ (mol/m ²)	$A_{\min}$ (nm ²)	n	R^2	χ^2
PFDA-PFOA Mixtures	5-95	66	8.00E-05	0.187	13.9	12500	5.46E-06	0.304	8	0.999	0.030
	25-75	20	2.20E-05	0.180	19.3	45455	5.25E-06	0.316	10	0.999	0.001
	50-50	14	1.30E-05	0.173	22.0	76923	5.05E-06	0.329	10	0.998	0.003
	75-25	8.4	7.50E-06	0.170	23.0	133333	4.96E-06	0.335	10	0.999	0.012
PFNA-PFHpA Mixtures	25-75	80	1.00E-04	0.18	13.9	10000	5.25E-06	0.316	9	0.998	0.025
	50-50	46	5.00E-05	0.175	14.8	20000	5.11E-06	0.325	10	0.999	0.001
	75-25	35	3.60E-05	0.175	14.8	27778	5.11E-06	0.325	7	0.995	0.015
PFOA-PFPeA Mixtures	25-75	1410	2.10E-04	0.190	18.8	313	6.57E-06	0.253	10	0.999	0.024
	50-50	553	1.00E-03	0.210	17.3	1000	6.13E-06	0.271	9	0.998	0.059
	75-25	299	4.50E-04	0.200	14.2	2222	5.84E-06	0.285	9	0.999	0.014
	86-14	158	2.10E-04	0.190	14.1	4762	5.54E-06	0.299	10	0.999	0.025
PFDA-PFPeA Mixtures	5-95	38.7	7.00E-05	0.185	18.4	14286	5.40E-06	0.308	8	0.999	0.032
	25-75	13	1.80E-05	0.175	17	55556	5.11E-06	0.325	8	0.999	0.033
	50-50	9.2	1.00E-05	0.17	18.6	100000	4.96E-06	0.335	7	0.998	0.028
PFDA-PFOA-PFPeA Mixtures	34-32-34	17	1.80E-05	0.17	20.7	55556	4.96E-06	0.335	8	0.997	0.130
	12-23-65	33	4.30E-05	0.17	25.7	23256	4.96E-06	0.335	7	0.998	0.120
	52-18-29	13	1.30E-05	0.17	22.2	76923	4.96E-06	0.335	8	0.997	0.014

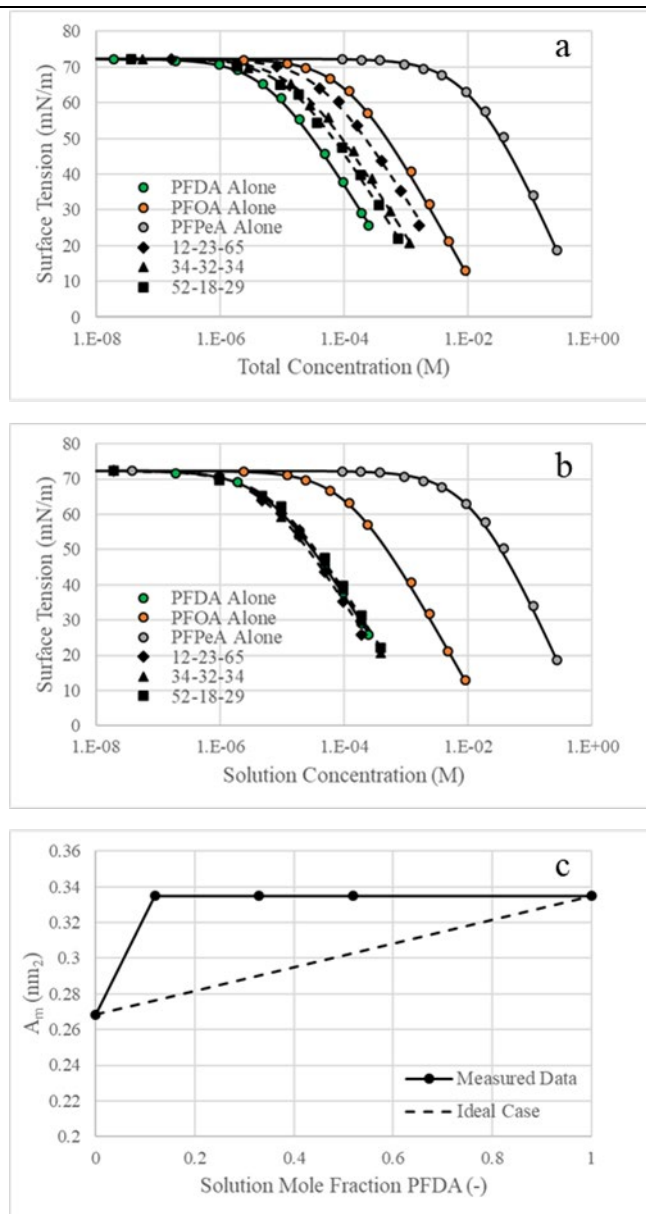


Figure 4-16. Surface-tension isotherms for the PFPeA-PFOA-PFDA ternary mixtures plotted as (a) total concentration, (b) mixture isotherms as PFDA concentration, and (c) presents the $A_m(X_{PFCA})$ function characterizing the adsorbed composition. The lower A_m value is the arithmetic average value for PFPeA and PFOA.

4.3.2 Modeling PFAS AWI Adsorption with Surface Compositional Changes

Our objective here is to examine mathematical models that would represent both the competitive adsorption behavior observed at higher PFAS solution concentrations and linear adsorption as concentrations decrease. This approach would provide a single model with which to calculate changes in adsorbed concentrations at the AWI with changes in solution

concentration across a wider practical range of values. To achieve this objective, the Langmuir adsorption model was rescaled to couple these two surface adsorption regimes.

The rescaling first required estimating the surface-adsorbed mole fractions for the PFAS mixtures at the AWI at monolayer coverage. There are several variations of the mixed-monolayer approach initially presented by [Rosen and Hua \(1982\)](#) that are often used for this purpose ([Huang et al., 1996](#); [Cui and Canselier, 2000](#); [Cui et al., 2005](#); [Rosen, 2012](#)). However, the well-known Rosen's approach is most appropriate for surfactant mixtures where synergistic adsorption is observed, which is not the case here. For simplicity, the approach selected here utilized the calculated A_m data previously reported, where the surface mole fraction (X_s) of the most surface-active component (X_{1s}) was estimated by:

$$X_{1s} = \frac{A_{m,mix} - A_{m,min}}{A_{m,max} - A_{m,min}} \quad [4-4]$$

where $A_{m,mix}$ is the A_m value determined from the mixture isotherm, $A_{m,min}$ is the minimum value associated with the least surface-active component of the binary system and $A_{m,max}$ is the value for the most surface-active component. For the binary mixtures, the surface mole fraction of the least surface-active component (X_{2s}) is determined as: $X_{2s} = (1 - X_{1s})$. The results of these calculations are presented in [Table 4-10](#).

The calculated surface mole fractions were then used to determine Γ_{max} values for the individual mixture components as: $\Gamma_{max,1} = X_{1s}\Gamma_{max,mixture}$. These Γ_{max} values were used as one anchor point with which to rescale the Langmuir equation, with the second anchor point being the minimum Γ value for the single-component isotherms. Using the Langmuir equation ([Equation 4-1](#)), K_L was then adjusted until the low concentration end of the rescaled $\Gamma(C_w)$ isotherm matched the single-component isotherm for a given mixture component. An example of the result of this procedure is presented in [Figure 4-17](#) and scaled Langmuir equation parameters are provided in [Table 4-10](#). k_{ia} values for each component of a given mixture were then calculated as a function of solution concentration (i.e., $k_{ia}(C_w)$) using the rescaled surface excess isotherms and the Gibbs equation ([Equation 3-2](#)). Examples of these scaled $k_{ia}(C_w)$ functions are compared to those calculated for the single-component data in [Figures 4-18 and 4-19](#).

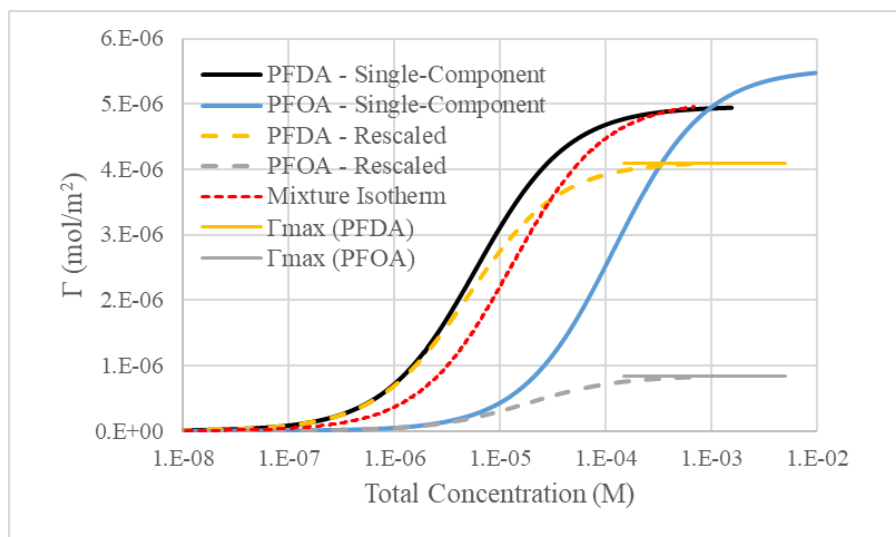


Figure 4-17. Example Langmuir model rescaling to account for competitive adsorption of PFCAs at monolayer coverage. Dashed lines are the rescaled models.

Table 4-10. Calculated surface mole fractions and rescaled Langmuir parameters for binary mixtures.

Solutes	Mole % for Mixtures	X _{1s} (-)	X _{2s} (-)	K _L (1) (L/mol)	K _L (2) (L/mol)	Γ _{max} (1) (mol/m ²)	Γ _{max} (2) (mol/m ²)
PFDA(1)-PFOA(2) Mixtures	5-95	0.130	0.870	1200000	9500	7.3E-07	4.7E-06
	25-75	0.470	0.530	340000	17000	2.5E-06	2.8E-06
	50-50	0.830	0.170	200000	55000	4.2E-06	8.6E-07
	75-25	0.990	0.010	170000	970000	4.9E-06	5.0E-08
PFNA(1)-PFHpA(2) Mixtures	25-75	0.770	0.230	65000	6200	4.04E-06	1.21E-06
	50-50	0.996	0.004	52000	370000	5.09E-06	2.04E-08
	75-25	0.996	0.004	52000	370000	5.09E-06	2.04E-08
PFOA(1)-PFPeA(2) Mixtures	25-75	0.163	0.837	45000	100	1.07E-06	5.50E-06
	50-50	0.460	0.540	14500	200	3.31E-06	2.82E-06
	75-25	0.758	0.242	10800	390	4.42E-06	1.41E-06
	86-14	0.997	0.003	8500	32500	5.53E-06	1.66E-08
PFDA(1)-PFPeA(2) Mixtures	95-5	0.722	0.278	215000	370	3.90E-06	1.50E-06
	75-25	0.902	0.098	181000	1100	4.61E-06	5.00E-07
	50-50	0.995	0.005	175000	22000	4.94E-06	2.48E-08
PFOS(1)-PFOA(2) Mixtures	75-25	0.258	0.742	395000	13200	1.24E-06	3.57E-06
	50-50	0.531	0.469	215000	23800	2.25E-06	1.98E-06
	12-88	0.890	0.110	147000	115000	3.25E-06	4.01E-07
SDoS(1)-PFHpA(2) Mixtures	50-50	0.782	0.218	16500	9000	2.66E-06	9.83E-07
	25-75	0.581	0.419	23000	5100	2.58E-06	9.175E-07
	5-95	0.465	0.535	28500	3900	2.63E-06	8.72E-07

Note: 1 is the most surface-active component

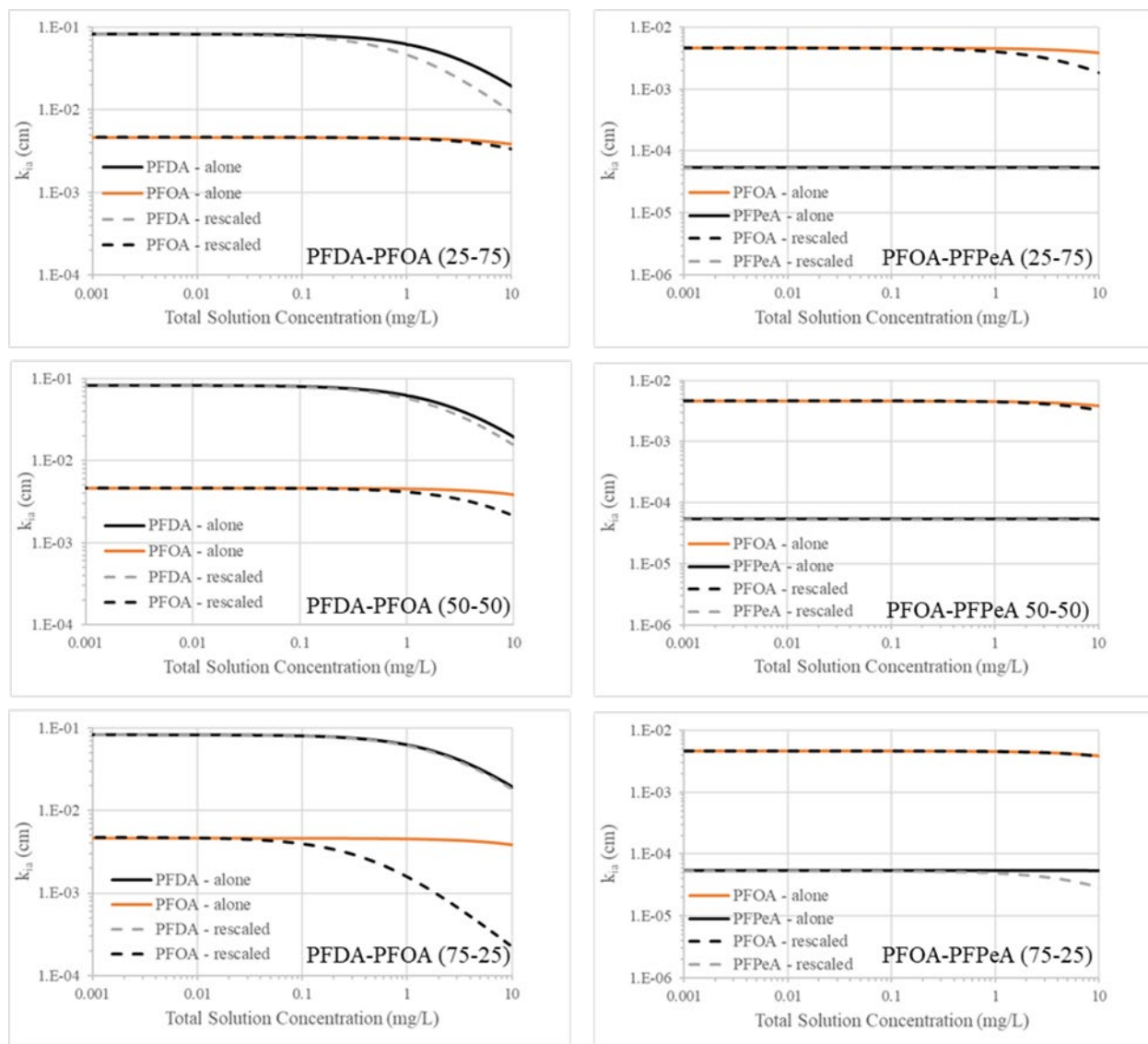


Figure 4-18. Calculated k_{ia} (C_w) functions for the PFDA-PFOA and PFOA-PFPeA binary pairs. Note these are double-logged plots.

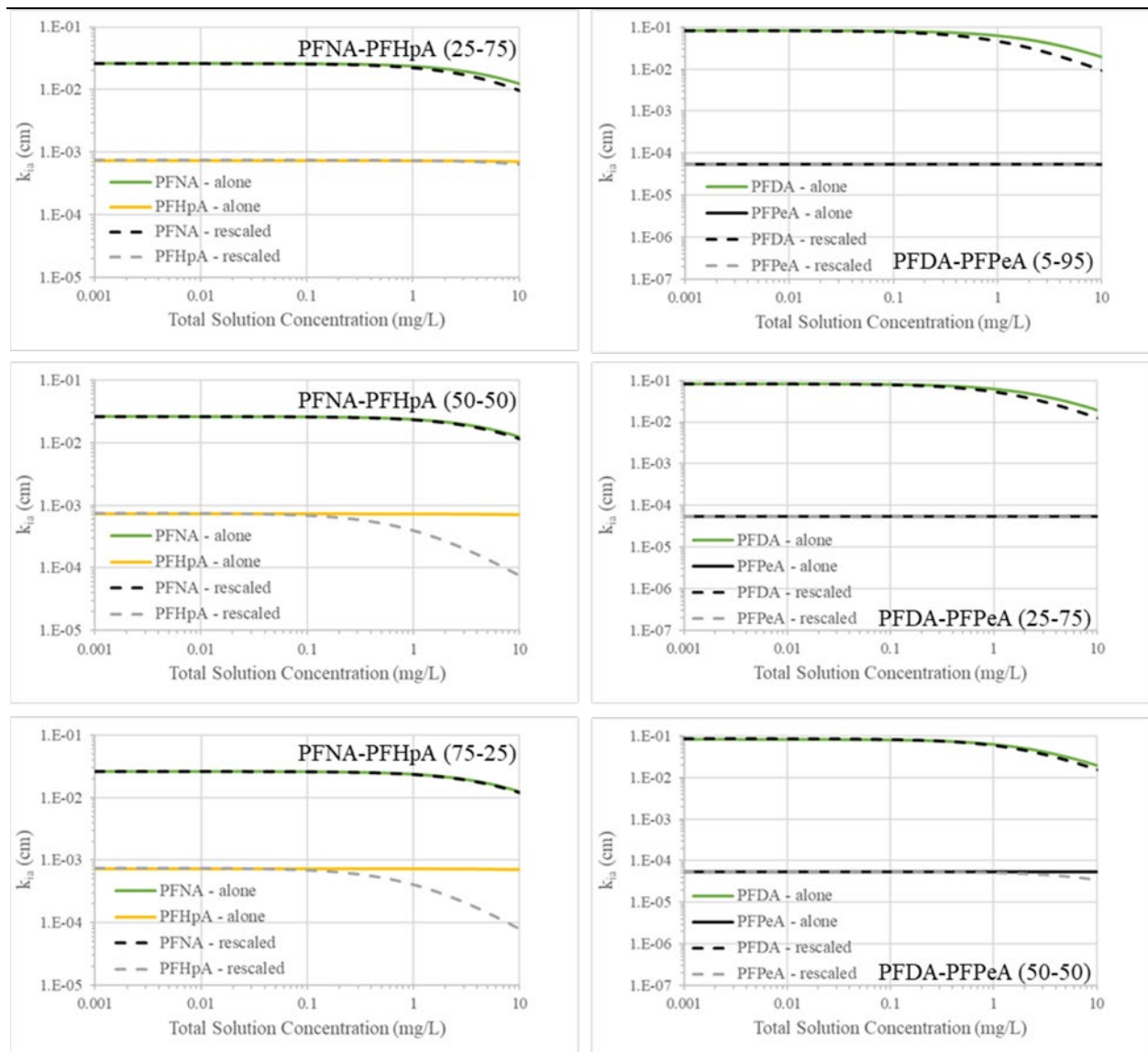


Figure 4-19. Calculated $k_{ia}(C_w)$ functions for the PFNA-PFHpA and PFDA-PFPeA binary pairs. Note these are double-logged plots.

The same treatment was applied to the PFDA-PFOA-PFPeA ternary mixtures and the resulting $k_{ia}(C_w)$ function plots are shown in [Figure 4-20](#). Although the calculated adsorbed surface composition was shown to be dominated by PFDA, a low surface-adsorbed mole fraction value of 0.005 was assigned to PFOA and PFPeA to allow computation. Calculated adsorption parameters for the ternary mixtures are provided in [Table 4-11](#).

For this PFCA ternary mixture, PFOA is the only component for which the $k_{ia}(C_w)$ function deviates from its respective single-component function within the range of solution concentrations evaluated. The degree of departure and the solution concentration in which the departure is initiated is the practically the same, regardless of the relative mole fractions of the components used in these mixtures. As was the case for the binary mixtures, the PFDA was anticipated to dominate AWI adsorption in these systems, and its $k_{ia}(C_w)$ function was

additionally anticipated to largely mirror its single-component function. The surface-activity of PFPeA is so much lower than that of the other PFCAs that its $k_{ia}(C_w)$ function was also anticipated to track along its single-component function within this range of solution concentrations. On the other hand, the combined effect of the presence of PFDA and PFPeA in solution is shown to have reduced the adsorption of PFOA at the AWI beginning at roughly 0.1 mg/L, with the effect increasing as the solution concentration of PFOA increases thereafter. The effect was similar within the range of solution mole fractions selected and suggests that much lower mole fraction of the most surface-active component PFDA would be required to improve the adsorption of PFOA at the AWI in this mixture. As PFAS contamination exists as a complex mixture of many components, the results presented in [Figure 4-20](#) highlight the probability that the transport of PFAS contamination components could be accelerated relative to predictions made using single-component adsorption constants.

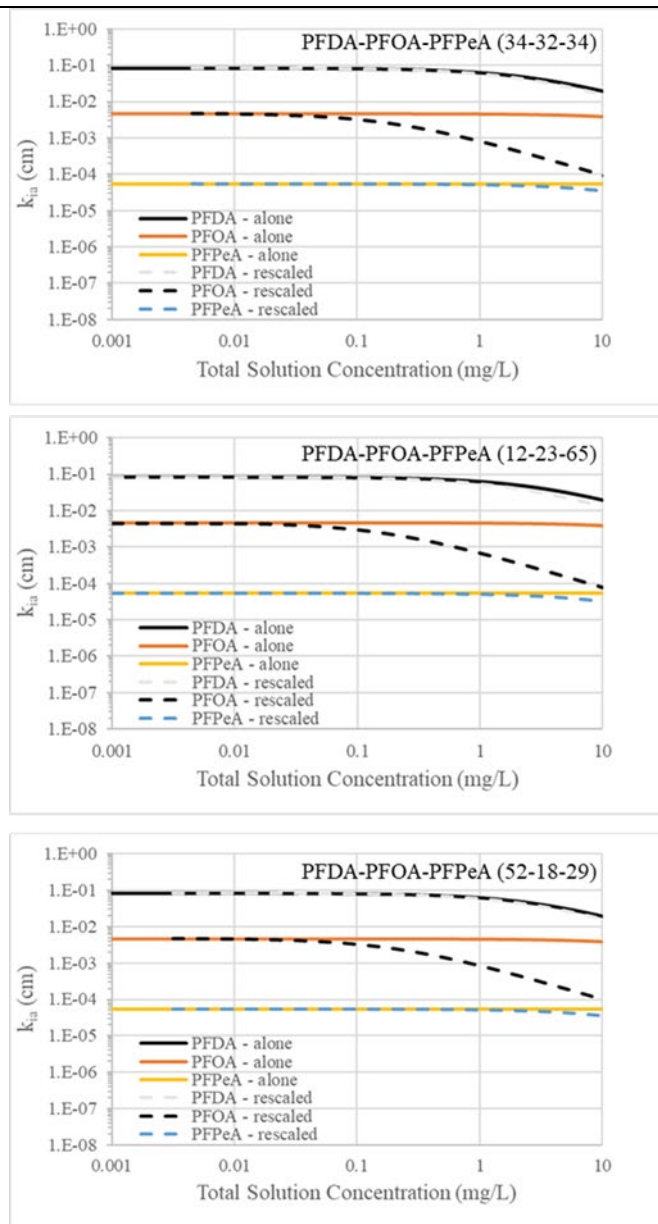


Figure 4-20. Calculated $k_{ia}(C_w)$ functions for the ternary PFDA-PFOA-PFPeA mixture. Note these are double-logged plots.

Table 4-9. Surface mole fractions and rescaled Langmuir parameters for the PFDA-PFOA-PFPeA ternary mixtures.

Mole % for Mixtures	$K_L(1)$ (L/mol)	$K_L(2)$ (L/mol)	$K_L(3)$ (L/mol)	$\Gamma_{max}(1)$ (mol/m ²)	$\Gamma_{max}(2)$ (mol/m ²)	$\Gamma_{max}(3)$ (mol/m ²)
34-32-34	172000	1960000	22200	4.85E-06	2.45E-08	2.45E-08
12-23-65	172000	1960000	22200	4.79E-06	2.42E-08	2.42E-08
52-18-29	172000	1960000	22200	4.84E-06	2.44E-08	2.44E-08

4.3.3 Additional Binary Mixtures

To this point, our preliminary PFAS mixture evaluation has been limited to mixtures of the linear PFCA homologues. Here, two additional binary mixtures were evaluated as a part of this initial work: PFOS-PFOA and SDoS-PFHpA. The PFOS-PFOA pairing was selected because they are two PFAS of considerable regulatory interest and to investigate the effect of the differences in hydrophile structure (i.e., sulfonate vs. carboxylate) on binary adsorption. The SDoS-PFHpA pairing was selected to investigate the effect of a hydrocarbon surfactant (SDoS) on the adsorption of a PFCA. PFHpA was selected over PFOA because PFOA and SDoS exhibited very similar surface activity. SDoS was selected as a representative sodium alkyl sulfate surfactant used in AFFF formulations (3M, 1991).

As was observed for the PFCA mixtures, the surface tension isotherms for each of the PFOS-PFOA mixtures provided in Figure 4-21 are positioned entirely within the bounds of the single-component isotherms. Additionally, as shown in corresponding $A_m(X_w)$ function plot, ideal adsorption behavior was observed across the range of PFOS solution mole fractions. This result is consistent with the nearly ideal mixing behavior observed by Yoda et al. (1989) for the AWI adsorption of lithium perfluorooctane sulfonate and lithium perfluorooctanoate solution mixtures. These results also suggest the presence of mono-valent and divalent counterions provided by the SGW solution effectively swamps the potential electrostatic contributions to adsorption that would otherwise impact adsorption based on the structure of the PFAS hydrophile when adsorbed concentrations are in the range of monolayer coverage (Aveyard, 2019). However, given that both components share a common C_N it is yet unclear whether the ideal adsorption condition would hold as the surface activity or C_N of the PFCA component is increased.

Of all the mixtures explored in this work, the SDoS-PFHpA mixtures were the only ones that demonstrated true synergistic (or cooperative) adsorption at the AWI. Synergism as defined by Rosen (2012) is demonstrated in Figure 4-21 by the positioning of the SDoS-PFHpA mixture surface-tension isotherms below, or to the left of, the most surface-active component, or SDoS in this case. Likewise, the corresponding $A_m(X_w)$ function plot that shows calculated A_m values for the mixtures were, in all cases explored here, greater than the single-component values of both components. These results are consistent with those reported by Li et al. (2016), who also observed a significant increase in the total adsorption at the AWI for mixtures of SDoS and the zwitterionic surfactant dodecyldimethylammonium acetate than was observed for the pure surfactant solutions. These results are also consistent with the role of hydrocarbon-fluorocarbon surfactant mixtures to provide beneficial synergistic interfacial effects for AFFF solutions (Kovalchuk et al., 2014).

Here, the $A_m(X_w)$ function is not useful for estimating adsorbed surface composition. However, as synergism was observed, the well-known regular solution approach presented by Rosen and Hua (1982) can be used, where the relative surface mole fractions of surfactants present in the mixed monolayer is determined by:

$$\frac{X_{1S}^2 \ln(X_{1w}C_{12}/X_{1S}C_1)}{(1-X_{1S})^2 \ln\left(\frac{(1-X_{1w})C_{12}}{(1-X_{1S})C_2}\right)} = 1 \quad [4-5]$$

where X_{1S} and X_{1W} are the mole fraction of surfactant 1 in the mixed monolayer and bulk solution, respectively and C_1 , C_2 , and C_{12} are the solution molar concentrations of surfactants 1, 2, and their mixture, respectively, required to produce a given surfactant concentration. X_{1S} is determined by solving Equation 4-5 numerically, with all other parameters known from the experimental tension isotherm data and $X_{2S} = (1 - X_{1S})$. Calculated interfacial interaction parameters (β^S) for the SDoS-PFHpA mixtures were -6.6, -3.2 and -1 for the 95-5, 75-25 and 50-50 mole percent mixtures, respectively. Calculated surface mole fractions and the rescaled Langmuir isotherm parameters for the mixture components are provided in Table 4-12.

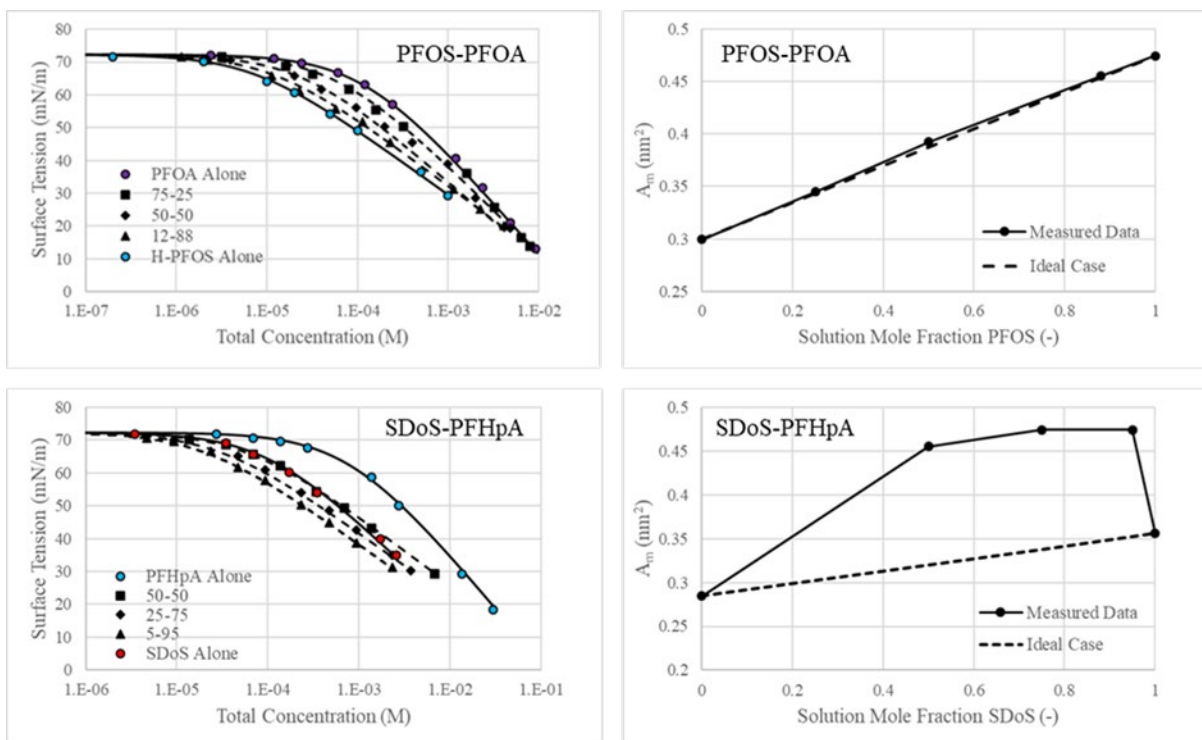


Figure 4-21. Surface-tension isotherms for the PFOS-PFOA and SDoS-PFHpA binary mixtures. Numbers in legends indicate different mixtures (i.e., 50-50 refers to the relative mole percentages for the mixture). Figures in the right-hand column are calculated A_m values with changes in solution mole fraction of the most surface-active component.

Table 4-10. Surface mole fractions and rescaled Langmuir parameters for the PFOS-PFOA and SDoS-PFHpA binary mixtures.

Solutes	Mole % for Mixtures	X _{1S} (-)	X _{2S} (-)	K _L (1) (L/mol)	K _L (2) (L/mol)	Γ _{max} (1) (mol/m ²)	Γ _{max} (2) (mol/m ²)
PFOS(1)-PFOA(2) Mixtures	25-75	0.260	0.740	395000	13000	1.23E-06	3.55E-06
	50-50	0.530	0.470	215000	23300	2.24E-06	1.97E-06
	88-12	0.890	0.110	147000	115000	3.24E-06	4.00E-07
SDoS(1)-PFHpA(2) Mixtures	50-50	0.730	0.270	17600	7500	2.64E-06	9.75E-07
	75-25	0.738	0.262	17700	7900	2.57E-06	9.11E-07
	95-5	0.751	0.249	17900	8400	2.61E-06	8.65E-07

Single-component and rescaled $k_{ia}(C_w)$ functions for the PFOS-PFOA and SDoS-PFHpA pairings are presented in Figure 4-22. As was the case for the PFCA binary mixtures, the PFOS-PFOA results show how the k_{ia} of one component can decrease as the solution mole fraction of the other component is increased. However, below a solution concentration on 0.1 mg/L the $k_{ia}(C_w)$ functions track along their single-component values.

This was not the case for PFHpA when present in a mixture with SDoS. As shown in Figure 4-22, the $k_{ia}(C_w)$ function for PFHpA did not deviate from its single-component function throughout the assumed environmentally-significant range of solution concentration values (i.e. < 1 mg/L) regardless of the increase in the solution mole fraction of SDoS. Clearly this result relates to the cooperative adsorption observed for PFHpA at the AWI when SDoS is present, in that the attractive forces between adsorbed molecules appear to stabilize the adsorption of PFHpA at the interface. SDoS solution mole fractions used in these mixtures were high (i.e., altogether greater than 0.5) and it is possible that a departure of the SDoS $k_{ia}(C_w)$ function from its single-component function would occur at lower SDoS solution mole fractions. However, it is not likely that the PFHpA $k_{ia}(C_w)$ function would deviate from its single-component function as SDoS mole fractions decrease. Although additional research is needed to elucidate these findings, it would appear that low concentrations of hydrocarbon surfactants can help stabilize PFCA adsorption at the AWI, resulting in greater retention during transport than would otherwise occur in the absence of such surfactants.

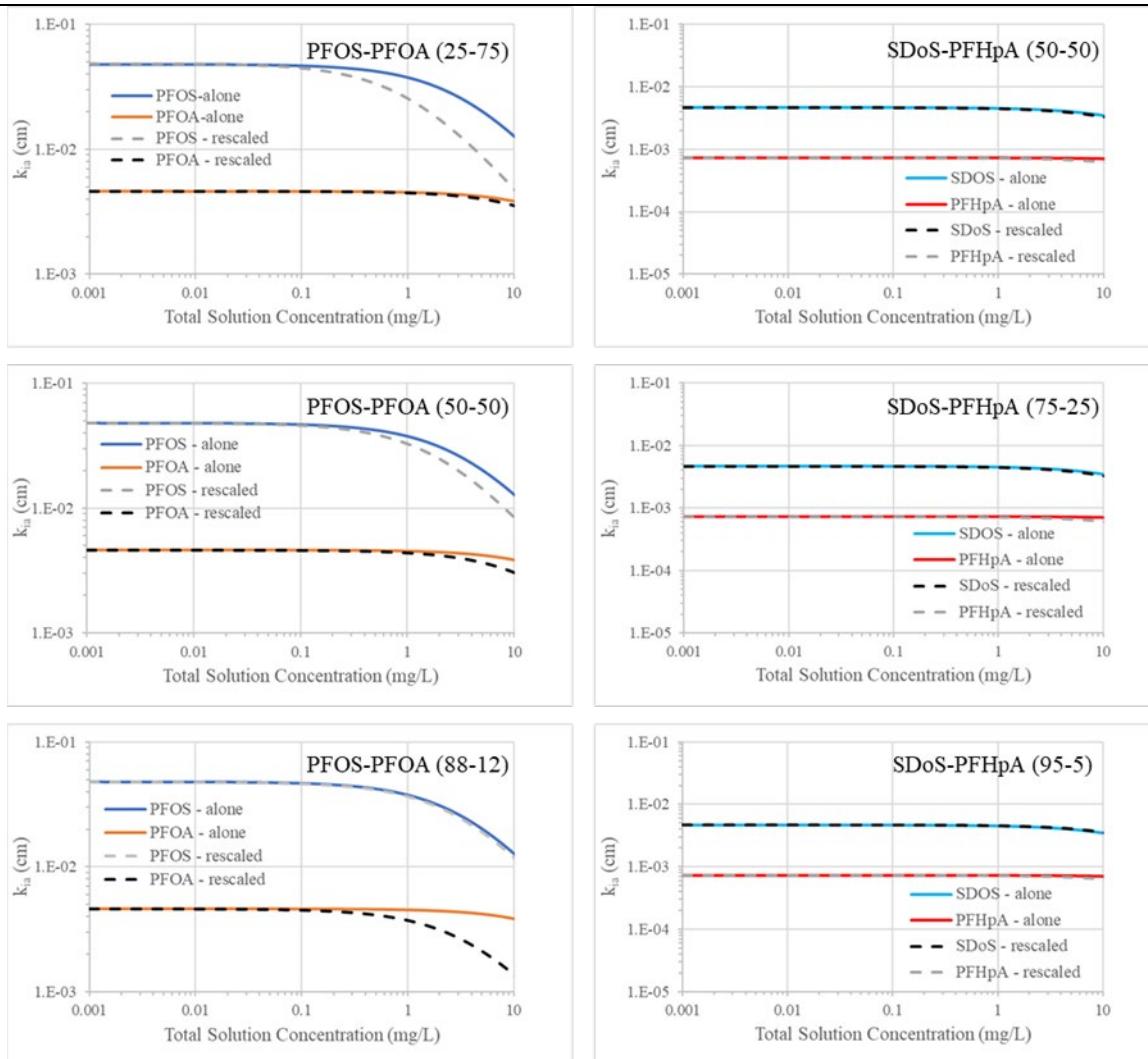


Figure 4-22. Calculated $k_{ia}(C_w)$ functions for the binary PFOS-PFOA and SDoS-PFHpA mixtures. Note these are double-logged plots.

4.3.4 Implications and Relevance (AWI Adsorption of PFAS Mixtures)

The following summarizes the key findings of this work with respect to this preliminary evaluation of AWI adsorption of PFAS mixtures:

- The AWI adsorption of PFASs in mixtures can differ from that predicted for single-component solutions.
- Both non-ideal competitive AWI adsorption and ideal adsorption for linear PFCAs can occur, depending on the relative surface activities of the PFCAs in the mixture.
- Competitive adsorption was observed as adsorbate concentrations approach monolayer coverage for the mixture. When competitive AWI adsorption was observed, the most surface-active surfactant was dominant. Dominance of adsorption of one component limits the adsorption of the other components. Therefore, the less dominant PFAS

components would transport more readily than predicted using adsorption constants derived from single-component solutions.

- Models exist to characterize the composition of adsorbed PFAS mixtures at the AWI. Two such models were presented in this work. As shown, these models can be used to rescale AWI adsorption isotherm equations for individual PFAS components in a solution mixture such that both linear adsorption at low adsorbate concentrations and non-ideal competitive adsorption are represented by a single relationship.
- Additional research is needed to assess the ability to extend these models to more complex PFAS solution mixtures. This will allow incorporation into numerical simulators.

The objectives of this subtask, and those for Task 1 as a whole, have been met as described in Section 1.1 of this report. We have improved our understanding of the adsorption of PFAS at the AWI and have presented a method of predicting the transport of individual PFAS within PFAS mixtures based on a thermodynamic evaluation of the data generated that will improve our ability to model the fate and transport of PFAS within vadose zone source areas. We have also developed a working hypothesis for simplifying AWI adsorption predictions for PFAS mixtures. These simplifying relationships are highly useful because measurement of k_{ia} values for the hundreds of PFAS of potential environmental concern would be impractical. Testing and ultimately finalizing these predictive methods for AWI adsorption is an important research need as it would be useful in supporting regulatory risk calculations.

4.4 AFFF Tension-Driven Flow Evaluation (Task 2)

As mentioned previously, our original objective for this task was to evaluate the potential for PFAS contamination to spread on the AWI and contribute to tension-driven flow. However, shortly after project award it became clear from available site characterization efforts that typical PFAS aqueous concentrations were sufficiently low to exclude these processes from further consideration. With approval from the SERDP Environmental Restoration Program Manager, our tension-driven flow work-scope was modified to focus on tension-driven flows associated with AFFF solution releases.

The mechanics of the original scope of work remained the same. However, the objective shifted to performing one-dimensional sand column tests to evaluate the significance of tension-driven transport of AFFF solutions within water-unsaturated porous media. Specifically, our objectives were as follows:

Objective 1: Examine the significance of tension-driven flow to enhance the transport of surface-active solutes and co-solutes.

Objective 2: Determine the significance of tension-driven flows to enhance the transport of AFFF fluids.

Objective 3: Incorporate tension-driven flow into HYDRUS.

Data provided by physical experiments was used to assist validation of modifications made to the HYDRUS unsaturated flow and transport model to include the effects of concentration-dependent tension-driven flow. The practical product of this work is a data-conditioned numerical tool capable of appropriately simulating the release of AFFF fluids into the vadose zone. Such a tool will find use where it is necessary or advantageous to simulate AFFF application history (i.e. rates and frequencies of application) in support of site characterization efforts aimed at determining the vertical and lateral extent of PFAS source areas. This model would be additionally useful in assessing the longevity of PFAS source areas to assist management decisions. The approach used to modify the HYDRUS model was described in Section 3.3.5.

4.4.1 HYDRUS Model Parameterization

The AFFF used in this preliminary work was a C6-based National Foam product (AER-O-Water® CEM^{C6}) that meets U.S. Military Specification MILPRF-24385F(SH). When the work scope shifted to evaluating AFFF flow, our objective was to include a legacy AFFF (i.e., 3M Light-Water product) for comparison. However, we were not able to secure a sample. Nonetheless, we were able to find surface tension data for a legacy 3M product that could be compared to the modern product (Dlugogorski et al., 2005).

Surface-tension isotherms measured for the National Foam AFFF used in this work (AFFF1), the legacy 3M product, and an additional National Foam MIL-SPEC product (AFFF2) are provided in [Figure 4-23](#). Note that the data for each of these of these AFFFs match closely, suggesting that because all were developed to meet the military specifications for AFFF, each

share similar surface-activity and surface-tension dependence on solution concentration. The surface-tension isotherm measured for IPA, which served as a non-reactive tension reducing solute, is also provided in Figure 4-23. The LS equation (Equation 3-1) was again used to fit the measured surface-tension data, providing model input parameters a and b that will be used to scale the concentration dependence on surface-tension reduction by Equation 3-18.

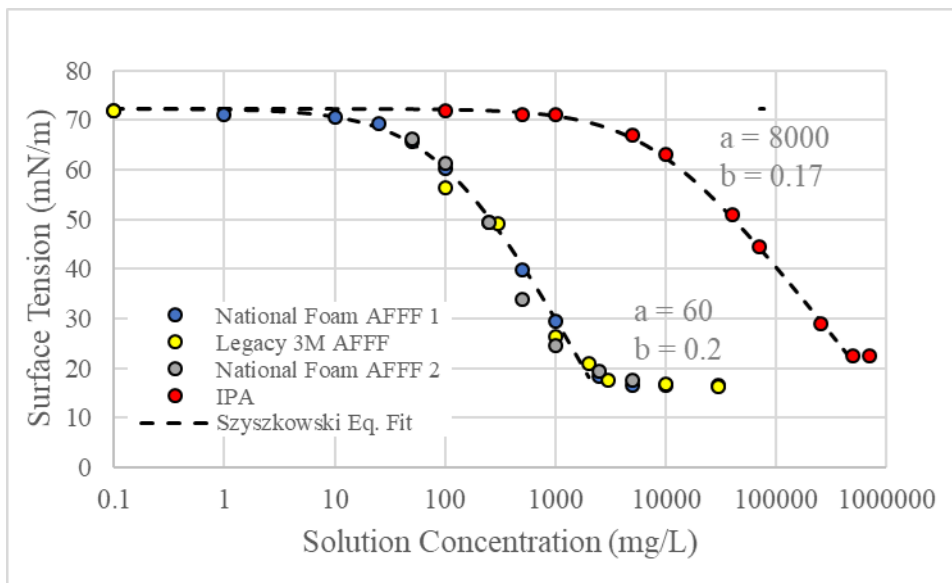


Figure 4-23. AFFF and IPA surface tension isotherms used to scale tension-driven flow simulations. a and b values are Szyszkowski equation parameters.

HYDRUS model initial conditions were specified as a uniform moisture content (18% in this case) throughout the domain. The solute concentration for the left-hand side (LHS) of the column was set to zero and the right-hand side (RHS) assigned the value used in a particular experiment. Zero-flux boundaries were assigned at both ends of the column. Hysteresis was not considered in this case and the input parameters for the VG were those determined for the main drainage curve. The model domain was 10 cm long, 4.5 cm wide, and a uniform nodal spacing of 0.1 cm was selected. Measured sand bulk density was input into the model as 1.7 g/cm³. The molecular diffusion coefficient for IPA was set as 0.036 cm²/hr and the dispersion coefficient was 2 cm, based on trial and error matching to the experimental IPA data.

A simulated example of the temporal change in the soil moisture profile provided for a 7 % v/v IPA concentration added to the RHS of the test column is presented in Figure 4-24 in terms of the actual moisture contents and percent change in moisture. Note the initial rapid movement of water from the RHS to the LHS. As reduced surface tension in the RHS of the core drives flow to the LHS of the core, the LHS gains moisture disproportionately as IPA-containing moisture adds to the existing IPA-free moisture. Concentration-dependent tension gradients continue to drive moisture from right to left where a pseudo-steady state condition is achieved at 1 – 10 hours. At longer times, diffusion leads to uniformity in the concentration distribution, resulting in a backflow of some pore-water within the core as tension-gradients stabilize.

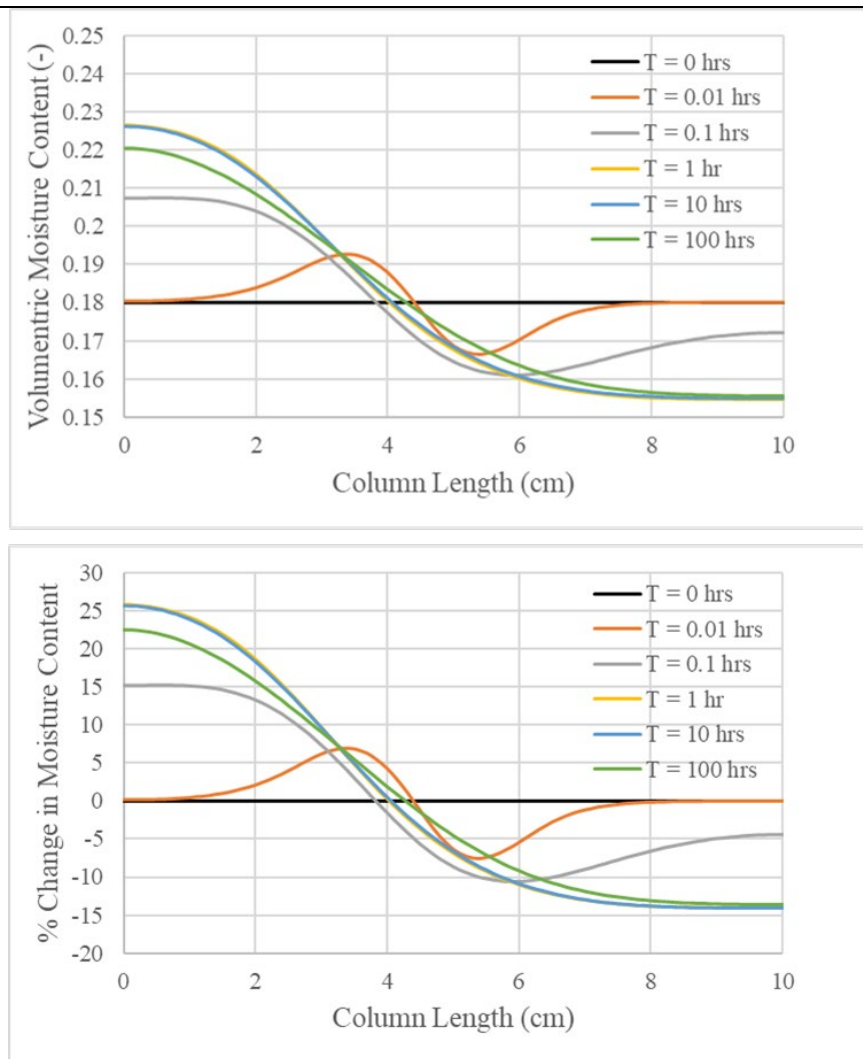


Figure 4-24. Example one-dimensional (1D) simulation results for IPA tension-driven flow.

4.4.2 Column Experiment Results and Model Conditioning

The HYDRUS model's moisture redistribution response to concentration-dependent surface tension changes was conditioned to the measured column test data for IPA solutions as a non-reactive (i.e., non-sorbing) tension-reducing solute. Experiments were performed utilizing two different IPA concentrations of 70% and 7% v/v. In both cases, a 12-hour moisture redistribution period was selected. Rather than evaluating the temporal responses at fixed concentration, which was previously done by Henry et al. (2001) using 1-butanol and a similar modification to HYDRUS, experiments were performed utilizing two different IPA concentrations of 70% and 7% v/v. The uniform moisture content was selected to be 18%, to provide enough initial moisture to observe the range of changes in moisture possible. This allowed a test of the model's ability to capture the magnitudes of moisture redistribution across an order of magnitude change of initial IPA concentration. The experimental results for the IPA experiments are provided as Figure 4-25 and include the corresponding modified HYDRUS model fits to the data.

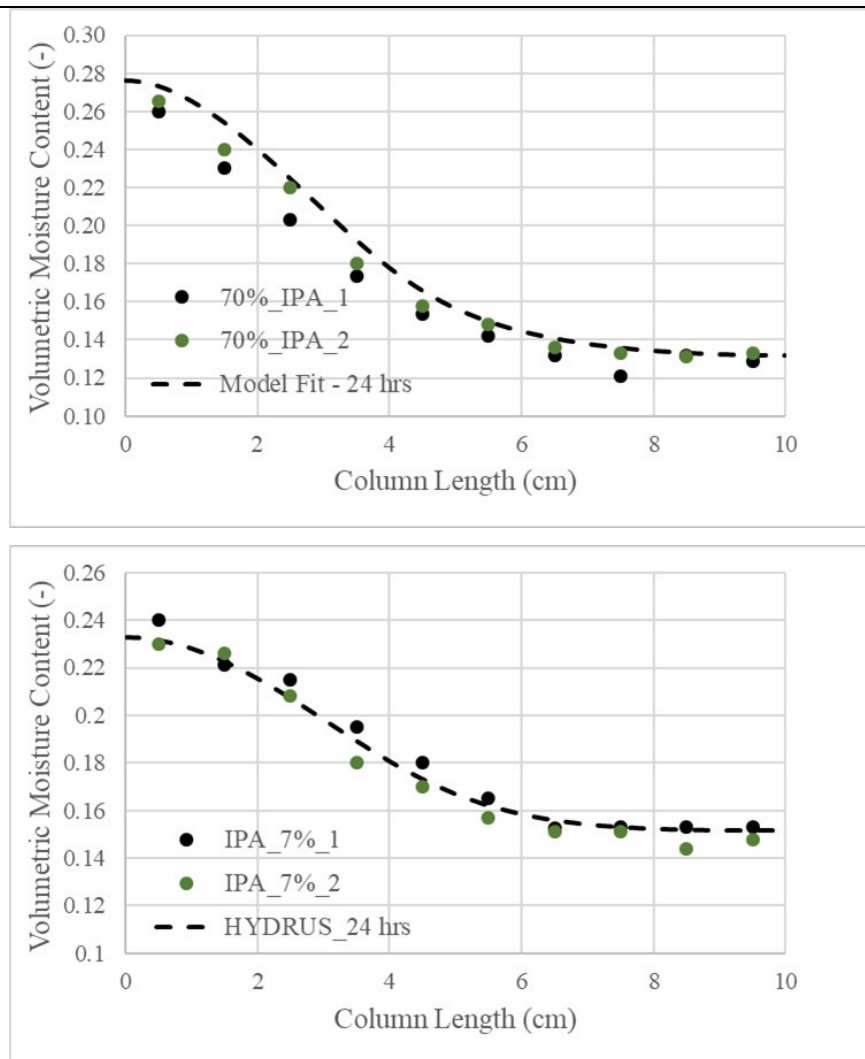


Figure 4-25. Experimental and simulated change in moisture contents for IPA solutions.

The modified HYDRUS model simulations matched the IPA experimental data well. The simulated results slightly over-predict the gain in moisture at 24 hours for the 70% solutions. One possible reason for this over-prediction could be related to the increased viscosity of the 70% IPA solution above that of the more dilute 7% solution. Solution viscosity and rheology measurements will be included in a future research proposal. Another possibility could be the differences in hydraulic dispersivities given the differences in rates of tension-driven flow provided at each initial concentration. Still, the model fit to the data was considered good enough to consider the model to be conditioned with respect to the concentration-dependent surface tension-driven flow condition under evaluation.

The tension-conditioned flow model was then applied to simulate the results of tension-driven moisture redistribution for AFFF. The experimental results for AFFF solutions at 2,500 mg/L and 10,000 mg/L (1% solution) are provided in [Figure 4-26](#).

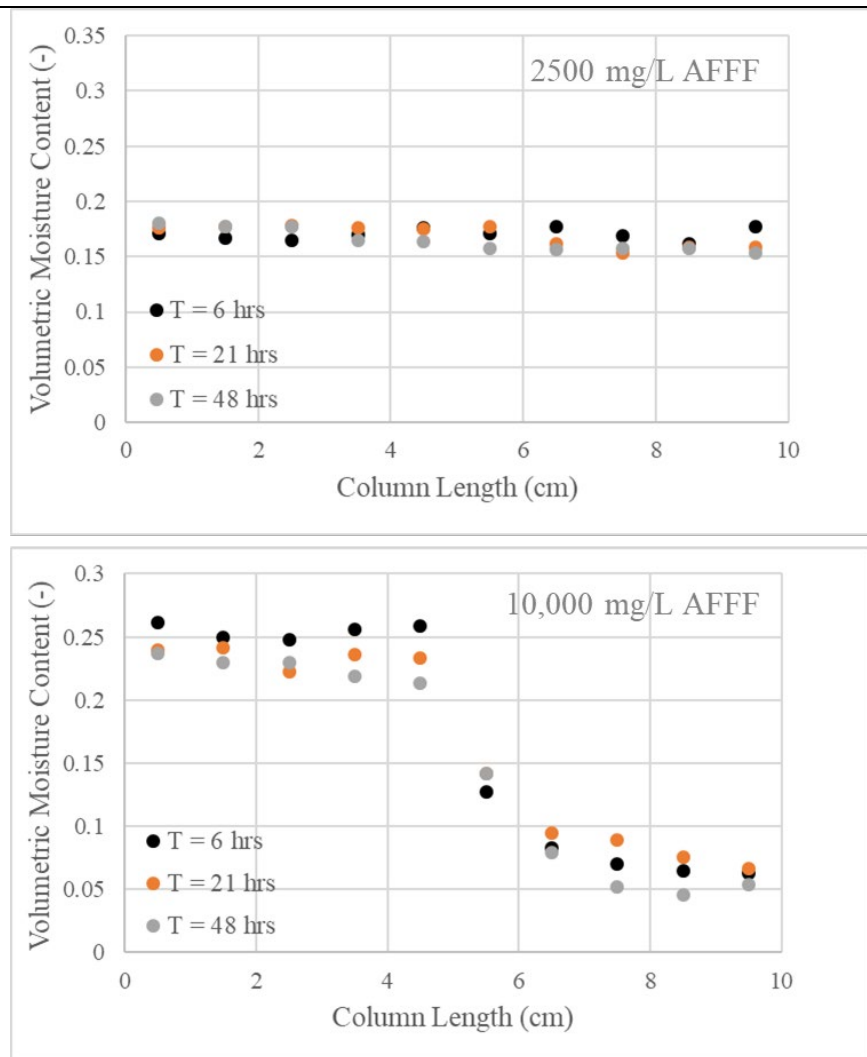


Figure 4-26. Change in moisture contents within experimental columns at 6, 21, and 48 hrs.

An AFFF solution concentration of 2,500 mg/L was initially selected because this was the concentration providing the greatest surface tension reduction, as demonstrated in [Figure 4-23](#). However, this solution did not mobilize and redistribute pore-water in our test columns. A similar result was observed when using a 5,000 mg/L AFFF solution (data not shown). Only when the AFFF solution concentration was increased to 1% (i.e. 10,000 mg/L) was tension-driven flow observed to a similar degree observed for IPA. However, the gradual increase in moisture content observed in the IPA result is absent. Rather, the LHS of the test column appears to have achieved a reasonably uniform moisture content. Given that the characteristics of the AFFF moisture redistribution profile are so different from that observed for a surface-active solute that does not interact with the solid phase, it is reasonable to consider that mineral adsorption of a component and/or components of the AFFF solution may have contributed to the experimental results.

As a part of column preparations, the AFFF solutions were added to a volume of dry sand to achieve a desired moisture content (17% in this case). When the 1%, and a 3%, AFFF solution was used, the sand was observed to lose cohesion, resulting in a loose and fluid-like consistency. This characteristic diminished with decreasing AFFF concentration and was essentially absent when the 2,500 mg/L solution was used. Further, when the 1% solution was used, the original cohesiveness of the unsaturated sand was largely restored.

Unlike IPA solutions, and the surface-active solutions utilized by the authors whose methodology was followed here (Kakare et al, 1993; Smith and Gillhan, 1999; Henry et al., 2001), AFFF solutions are mixtures of solvents and surface-active solutes. The material safety data sheet for the National Foam AER-O-Water® 3EM^{C6} product lists diethylene glycol monobutyl ether (butyl carbitol), ethylene glycol, and a proprietary combination of hydrocarbon and fluoroalkyl surfactants providing foaming agents and interfacial tension reducers. It is likely that a wetting-agent component like butyl carbitol that can alter the water-wettability of soils (e.g. ethylene glycol ethers have been used to characterize specific surface areas of geomaterials) contributed to the reduced cohesion observed at higher solution concentrations. Changing the wettability of the sand requires adsorption of the agent from solution. It is possible that at lower AFFF concentrations there was insufficient adsorbed wetting agent to cause an observable loss of cohesion.

However, the presence of the wetting agent alone does not explain the restoration of cohesivity for the sand containing the AFFF solution (i.e. the RHS of the test column) at the end of our experiments or the lack of tension-driven flow for lower AFFF solution concentrations. Perhaps the interaction between two or more components of the mixture are contributing to our experimental results. For example, butyl carbitol is also a coupling agent. As a bi-functional molecule the mineral adsorption of butyl carbitol could change the surface functionality of the sand to favor adsorption of other surface-active agents in the mixture. By this hypothesis, the results of column testing with elevated AFFF solution concentrations could be explained by the mere condition that solution concentrations of individual components were initially high enough to maintain sufficient solution surface activity and facilitate tension-driven flow, with the restoration of cohesivity of the sand in the RHS of the test column a result of dilution of the effect of interacting components as fluids redistributed. At lower concentration, this mechanism would result in insufficient solution surface activity to initiate and maintain tension-driven flow.

Regardless of the details of the actual mechanism, the net effect is that the surface-tension isotherm measured for the bulk AFFF solution used to scale pressure heads for changes in tension is not accurately describing tension-driven flow in porous media. Rather, the tension-driven flow process appears to be scaling along an alternative surface-tension isotherm of reduced strength (i.e., one that is shifted to the right of the bulk AFFF isotherms). An example of this hypothetical alternative tension isotherm is provided in [Figure 4-27](#) and the comparison between the experimental and simulated results utilizing the bulk solution AFFF surface-tension scaling and the hypothetical one is provided in [Figure 4-28](#).

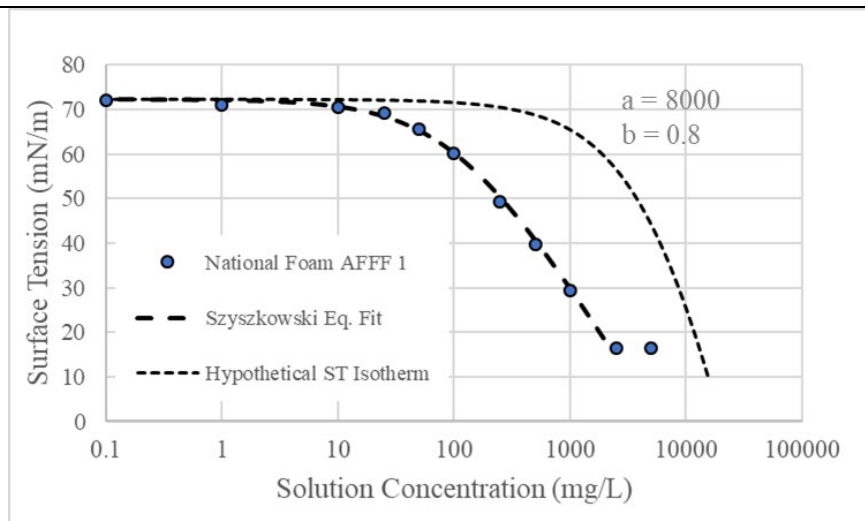


Figure 4-27. Bulk AFFF solution and alternative hypothetical surface-tension isotherm that best scales observed tension-driven flow in column tests.

Nonetheless, the use of the modified hypothetical isotherm scaling alone did not satisfactorily simulate the measured tension-driven flow results. As shown in [Figure 4-28](#), where the simulated change in moisture content is within the range of variability for the column tests, the simulated results for the 1% AFFF solution did not capture the sharp transition of moisture contents between the RHS and LHS of the test column. If the plateau is the result of an initially rapid spreading of a portion of the AFFF solution mixture and the subsequent removal of the more surface-active components via mineral sorption that truncates tension-driven flow, then sorption needs to be included in the simulations.

Our current work scope did not include physical measurement of solid-phase sorption isotherms from bulk aqueous solution. However, the contribution of mineral sorption was evaluated here numerically as a proof-of-principal exercise. Given the comparative lack of moisture movement observed in our experiments at lower AFFF concentrations and considerable redistribution at higher concentrations, it is likely that adsorption of AFFF components is not linear, but rather follows Langmuir adsorption. Langmuir adsorption, and the formation of mono-molecular layers on surfaces, is also a common behavior for surface-active solutes. By trial and error, a Langmuir constant (K_L) of 500 cm³/mg and a coefficient (n) of 2 were derived. This amount of sorption is considerable but within the range of K_L values observed for Triton X100 and mixtures of Triton X100 and SDoS on shale and sandstones (Muherei and Junin, 2009). However, as shown in [Figure 4-28](#), when Langmuir adsorption is coupled with the rescaled hypothetical surface tension response these modifications provided a reasonable level of control over these proposed mechanisms to more closely match the experimental data.

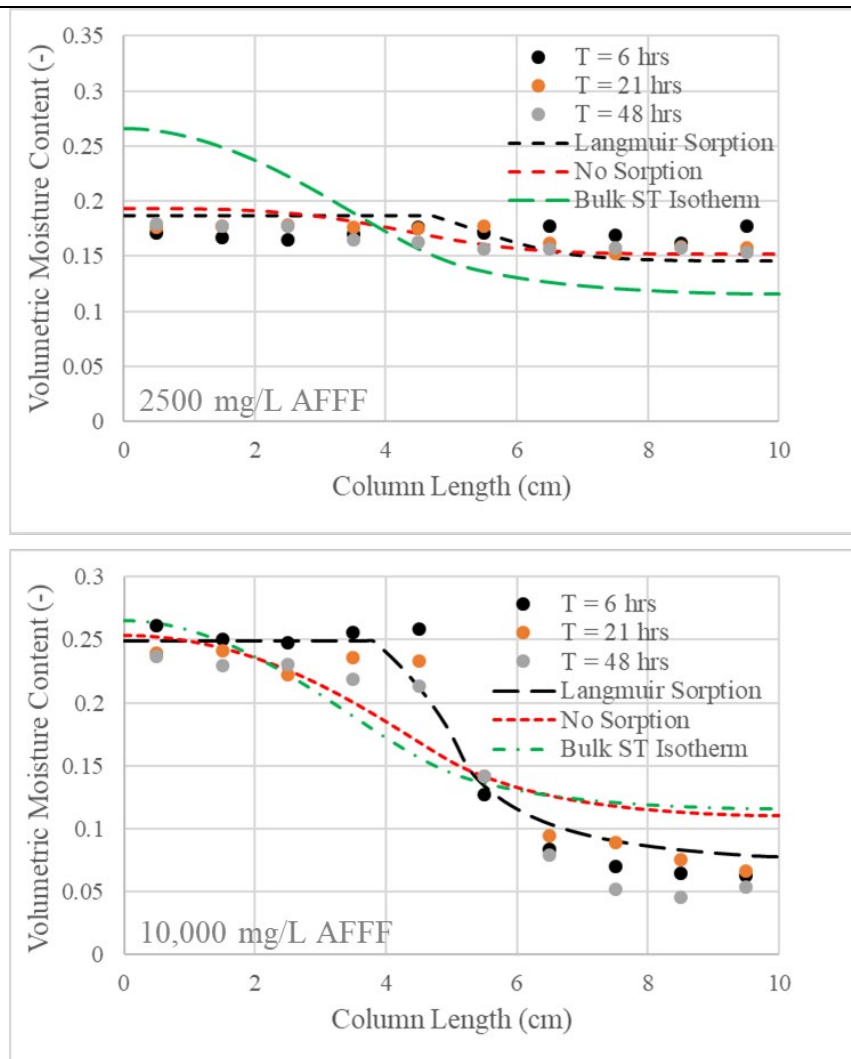


Figure 4-28. Experimental and simulated moisture redistributions for the National Foam AER-O-Water® 3EM^{C6} AFFF solutions used in this work. The “No Sorption” line is the simulated result utilizing the proposed hypothetical surface tension scaling alone. The “Langmuir Sorption” line combines both sorption and the hypothetical surface tension scaling.

The shape of the moisture redistribution profile shown in Figure 4-28, relative to the profile for IPA (Figure 4-25), demonstrates the effect of strong adsorption for AFFF as modeled. The simulated temporal evolution of moisture redistribution for AFFF, shown in Figure 4-29, further illustrates the effect. The surface tension induced capillary pressure gradient established when the contaminated sand contacts the uncontaminated sand initially drives rapid fluid movement from the RHS to the LHS. This is demonstrated by the drainage of water to the right of the line of contact and the gain in moisture to the left of the contact. Drainage within the AFFF-contaminated half of the column is accelerated by the change in the wettability of the sand, as evidenced by the significantly lower moisture condition achieved relative to the IPA case. However, this does not translate into a proportionate gain in moisture content on the LHS of the column. This is the result of mineral adsorption reducing pore-water concentrations and

mitigating the transfer of moisture resulting from the concentration-dependent capillary pressure gradient. Moisture transferring to the LHS of the domain would then be depleted of solute.

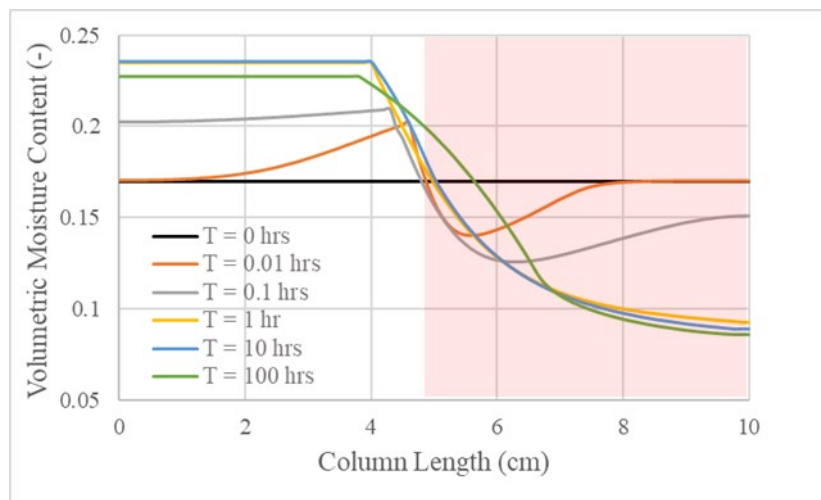


Figure 4-29. Simulated 1D results for AFFF tension-driven flow.

4.4.3 Example Forward Simulations for AFFF

1D simulations were performed to evaluate the general significance of tension-driven flow as a mechanism to enhance the transport of both surface-active solutes and non-surface-active co-solutes. The IPA-conditioned model was used and an additional solute (Solute 2) was added to the model that was not linked to the concentration-dependent surface tension model applied to Solute 1. The results of these simulations for the 10-cm column are provided in [Figure 4-30](#).

As anticipated, the tension-driven movement of water also drives the movement of the surface-active solute causing the movement of water. A co-dissolved non-reactive solute also spreads along with the surface-active solute and in the same proportion. A change in the initial concentration of the surface-active solute within the source area will change the rate of spreading. Likewise, as shown in [Figure 4-30](#), a decrease in the initial moisture content of the domain will also decrease the rate of spreading. Increasing the initial moisture content of the source area, a condition similar to a fresh release of surfactant solution, will increase the rate of spreading because gravity flow will assist tension-driven flow. Alternatively, decreasing the moisture content of the source area, relative to the adjacent media, will decrease the rate of spreading as gravity flow now works against tension-driven flow. These are all conditions for the tension-driven flow of non-sorbing fluids.

To assess the potential extent of fluid movement resulting from tension-driven flows, the same model was used while increasing the length of the 1D simulation domain. The results of these simulations are presented in [Figure 4-31](#). The extent of the spread of solutes driven by surface tension induced capillary pressure gradients alone is not particularly significant, having delivered a solute concentration of just 1 $\mu\text{g/L}$ to roughly a half meter in 100 hours.

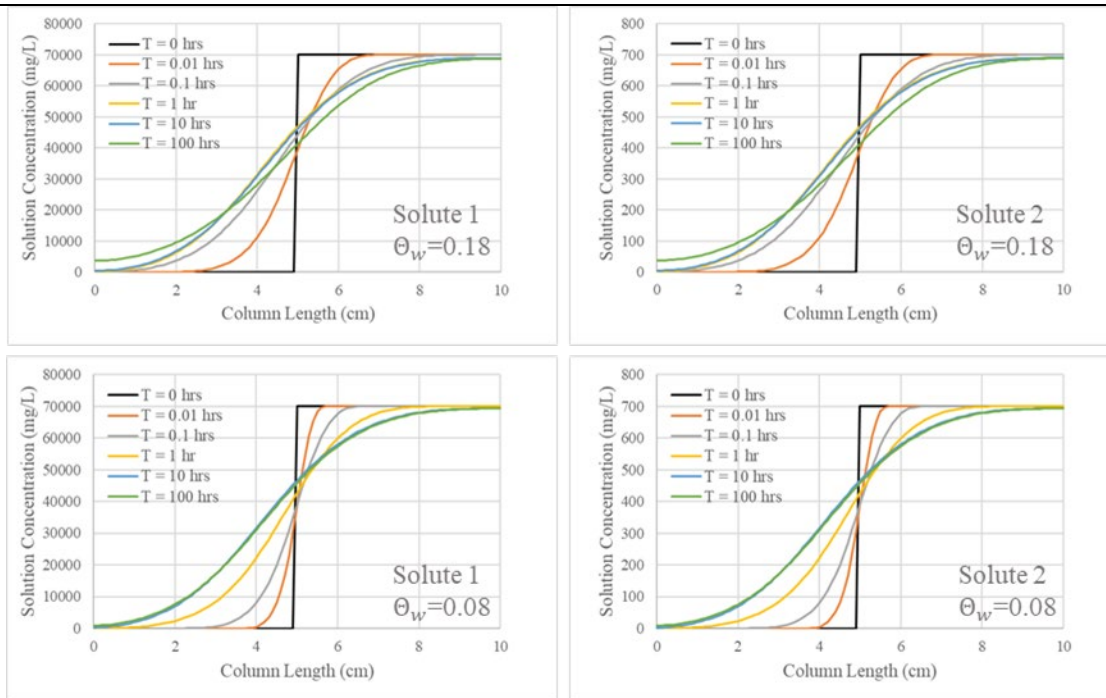


Figure 4-30. 1D Simulations demonstrating tension-driven solute transport.

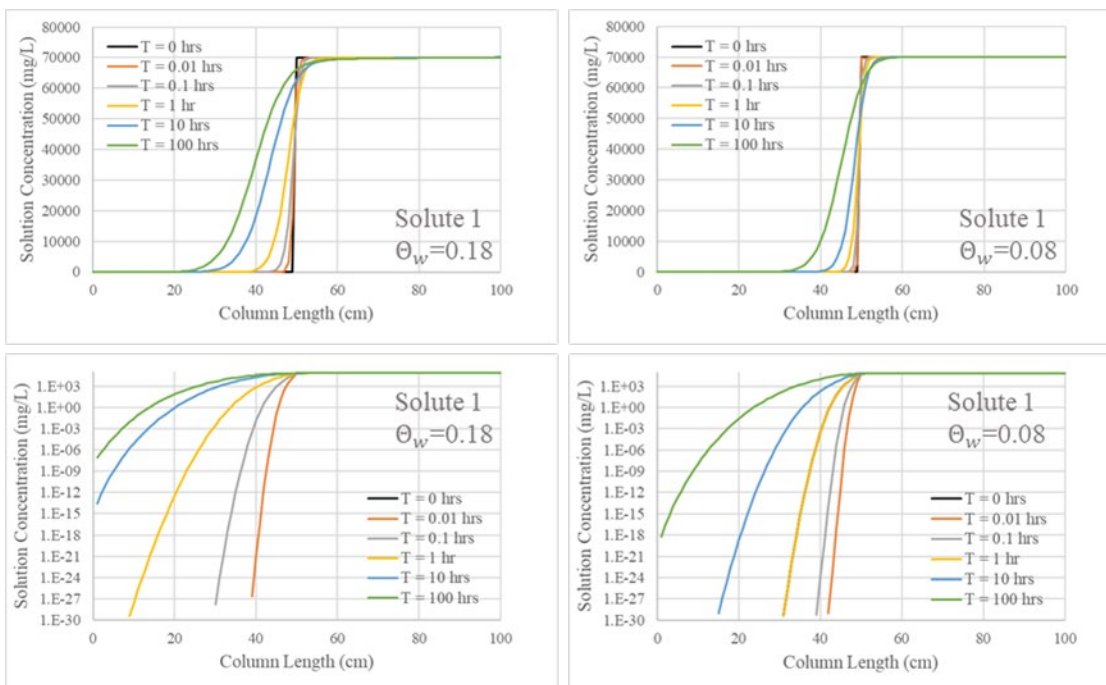


Figure 4-31. 1D simulations demonstrating extent of tension-driven solute transport.

However, where the process provides a more obvious contribution is during vertical drainage. The modified two-dimensional (2D) HYDRUS model was used to simulate the two drainage scenarios presented in [Figure 4-32](#). The initial moisture condition was set at field capacity ($\theta_w = 0.045$) for the system and a representative source area was established at the top and center of the homogeneous domain. The domain was 200 cm in height and width. The initial concentration of surface-active solute (Solute 1) was set at 10 mg/cm³ (or 1%) within the source area. The hypothetical surface tension isotherm developed for the AFFF solution ([Figure 4-24](#)) was used. Solute 1 and a non-surface-active solution (Solute 2) were simulated separately. Mineral sorption was not included in the simulations.

In these simulations surface-active fluids assist drainage by reducing capillary pressures at the solution front. Hydraulic conductivities also increase at the solution front as moisture contents increase. As shown previously, these fluids can also affect drainage by lateral spreading but are not particularly far-reaching. As shown in [Figure 4-29](#), the concentration of Solute 1 is greater at the leading edge of the drainage profile that observed for Solute 2, reflecting enhanced drainage within the source area. This is additionally demonstrated by the difference in soil moisture profiles. At 100 hours the solute concentrations begin to become more disperse as the moisture front moves downward through the domain and moisture contents decrease behind the front.

For simulations utilizing the adsorbing AFFF solution (results provided in [Figure 4-33](#)), the simulated conditions were changed slightly to allow gravity drainage within the entire domain by initially assigning a uniform moisture content of 0.1. The same degree of Langmuir adsorption used in conjunction with the rescaled hypothetical surface tension isotherm used to match the experimental AFFF moisture redistribution profile was implemented. Solute 1 is the surface-active and adsorbing solute and Solute 2 is a non-reactive solute. In this case, Solutes 1 and 2 were simulated simultaneously.

Contrary to the results of Solute 1 shown in [Figure 4-33](#), the modeled degree of mineral adsorption resulted in a complete lack of drainage of the AFFF solution out of the source area even after 30 days of free drainage. Drainage of fluids did occur within the simulated source area, as indicated by the change in moisture contents over time, but the bulk of the AFFF solution remained bound within the source area. These results could help explain the apparent longevity of PFAS source areas associated with AFFF application sites (Webber et al., 2017; Baduel et al., 2017; Anderson et al., 2019) and why the bulk of PFAS contamination within the vadose zone is often found within the first two meters below ground surface (Baduel et al., 2017).

As demonstrated in the 2D simulated results presented in [Figure 4-34](#), significant flushing of the source area is required to remove the AFFF-based solute from the implemented source area. Here the flushing of water occurred across the entire upper boundary (rate = 10 cm/hr) of the simulation domain and was simulated for 10 hours. During the flushing, removal of Solute 1 is observed within the source area. However, because the mineral adsorption is applied uniformly within the simulation domain, the bulk of Solute 1 flushed from the source area is again retained by the solid phase. The concentration scale was, by default, selected to describe the range of

values observed within the source area during the simulation. However, concentrations in the $\mu\text{g/L}$ and ng/L range were observed within the flow field just below the source area, again consistent with field observations.

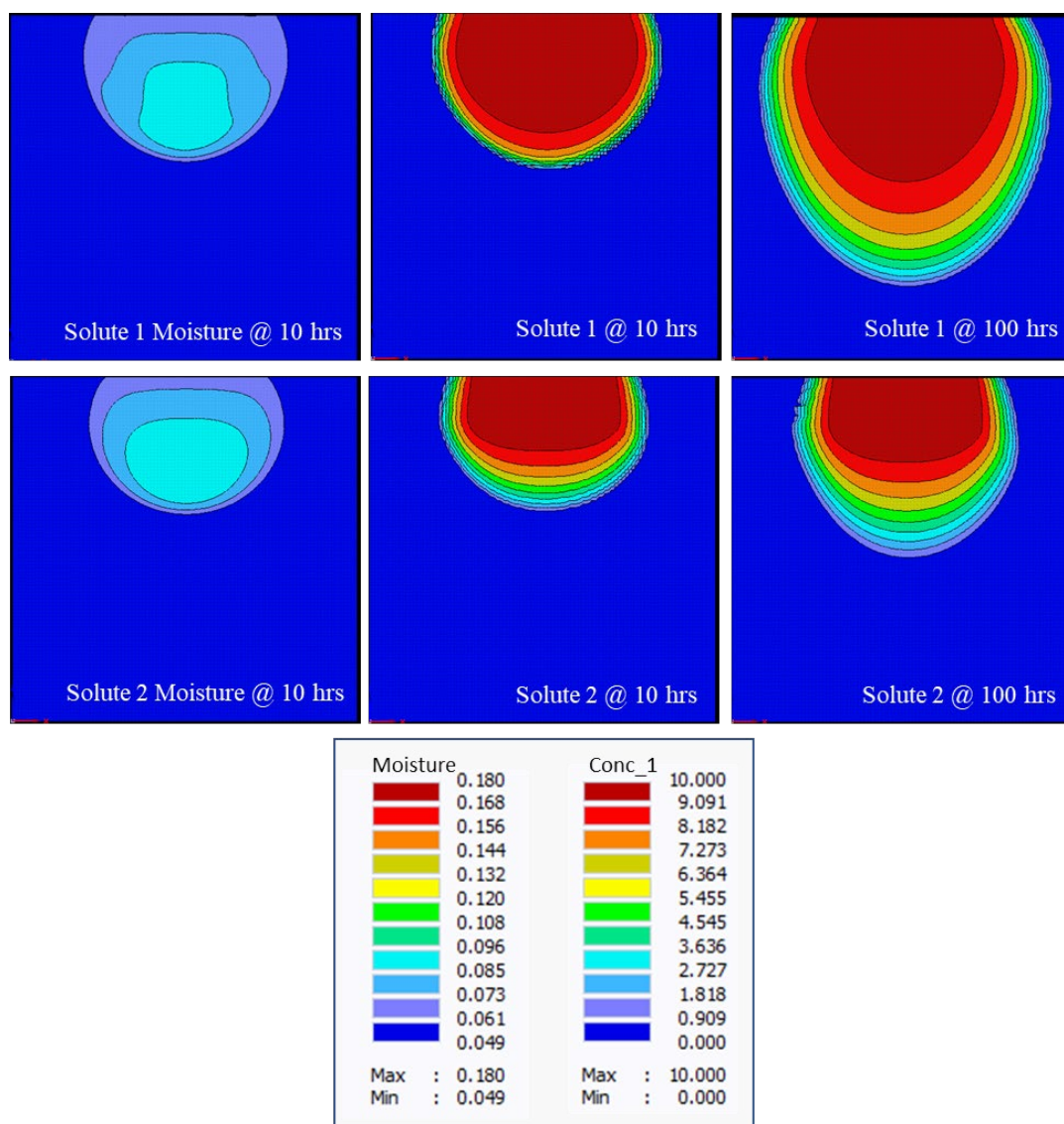


Figure 4-32. 2D simulated drainage scenarios showing the effects of tension-driven flow. Concentration units are in mg/m^3 . Solutes 1 and 2 were simulated separately.

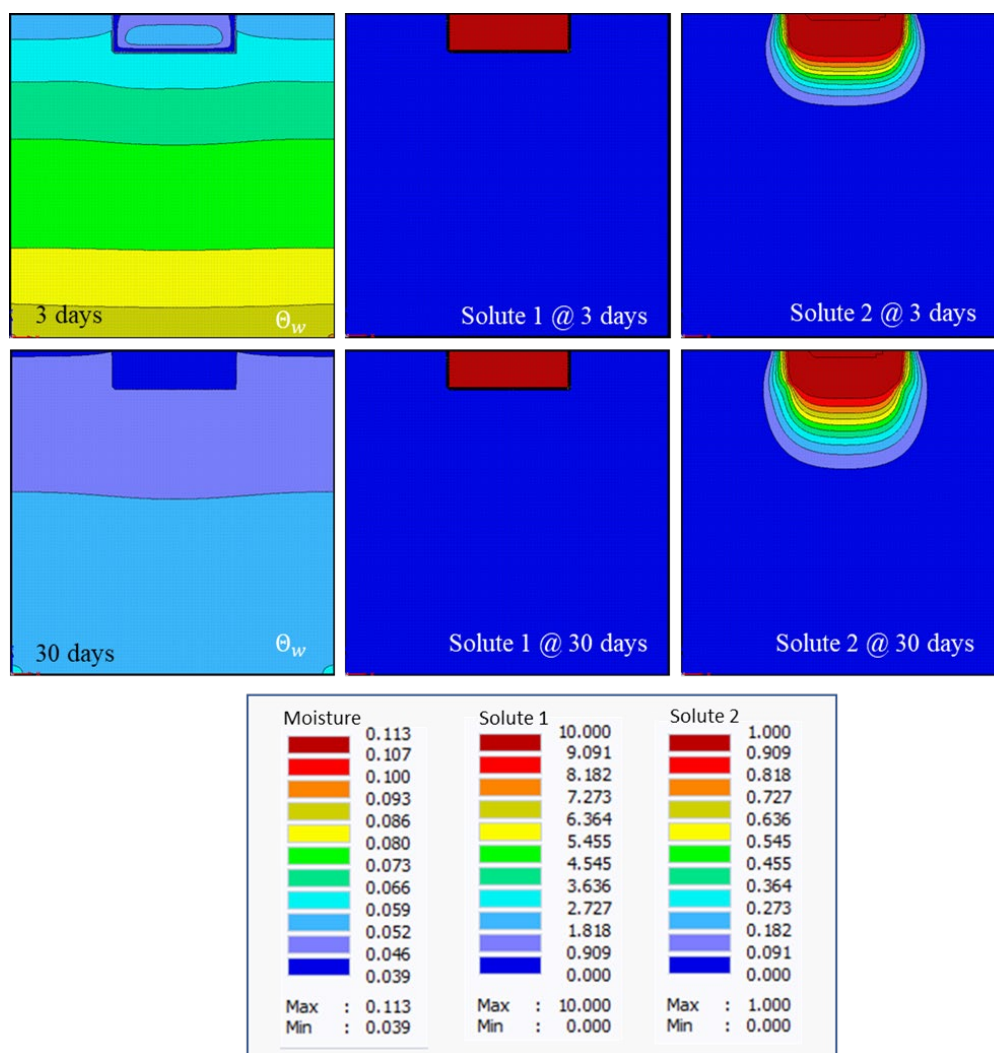


Figure 4-33. 2D simulated drainage of AFFF solution from an implemented source area. Solutes 1 and 2 were simulated simultaneously.

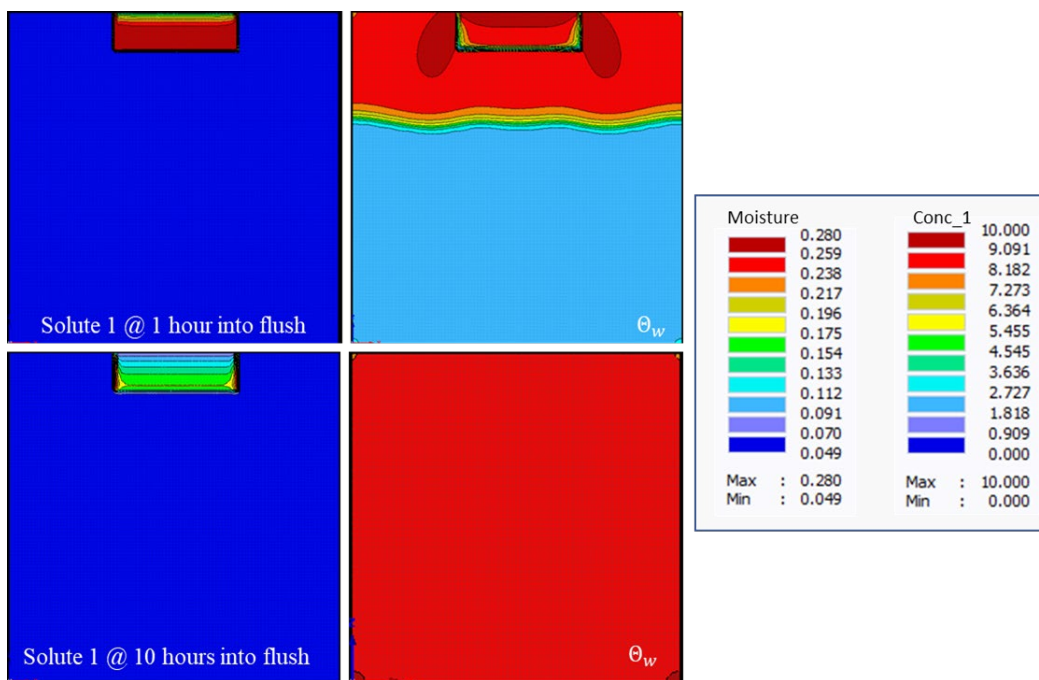


Figure 4-34. 2D flushing simulations for AFFF within an implemented source area.

4.4.4 Implications and Relevance (Task 2)

The degree of mineral adsorption of components of the AFFF solution to the test sands used in this research was not anticipated. Neither was the conclusion that surface-tension isotherms measured for bulk solutions of AFFF cannot be used directly to scale the water content-pressure head relationship in unsaturated flow models. However, we were still able to meet our stated objectives for this task and provide a modified unsaturated flow and transport model capable of simulating the release of AFFF and PFAS components from a source area. The existing model was useful to perform numerical experiments that provided additional insight into AFFF unsaturated transport.

Using the modified HYDRUS model, we have shown that the tension-driven flow mechanism, in and of itself, is not significant with respect to promoting lateral spreading of AFFF fluids and fluid components. However, the 2D simulated results demonstrate that the mechanism does contribute to the enhanced vertical drainage of tension held pore water when

mineral adsorption of that fluid is not significant. As a multicomponent mixture of independently surface-active components, each with their own potential affinity for solid surfaces, it is possible that one or more AFFF components would meet this criterion.

Ultimately, the use of the hypothetical rescaling of the surface-tension isotherm to represent AFFF solution transport is neither ideal nor mechanistically accurate but did allow us to perform simulations to test the modifications made to the HYDRUS code and draw conclusions relating to the effects of strong AFFF sorption. The flow of AFFF solutions in unsaturated porous media is affected by the viscosity of the solution, its surface-tension reducing power, and its ability to modify the contact angle of the solid media. As a part of this limited-scope project, the effects of concentration-dependent surface tension were the primary focus and this mechanism was incorporated into the HYDRUS flow and transport model. The effect of solution viscosity was also incorporated into the model but physical measurement of the concentration-dependence of solution viscosity was not a part of this initial work. However, the effects of changes in solution viscosity and changes in the wettability of the solid phase in the presence of AFFF solutions should be included as a component of future research to more accurately simulate AFFF solution transport in the vadose zone environment.

4.5 Initial Simulations of PFAS Transport in the Vadose Zone

The final objective of this limited-scope project was to modify the HYDRUS unsaturated flow and transport model to include AWI adsorption as a retention mechanism for simulating PFAS transport within water-unsaturated porous media. The approach used to accomplish this was described in Section 3.3.5.

4.5.1 Model Validation (Θ_w - Dependence)

At present, there is very little published transport data for PFAS that could be used to validate the performance of the modified model. One such publication is Lyu et al., (2018) who performed 1D unsaturated transport experiments using PFOA, of which water saturation and solution concentration were experimental variables. Beginning with the water saturation (or Θ_w) dependence, Lyu et al. (2018) employed the following linear model to describe the $A_{ia}(S_w)$ dependence: $A_{ia} = (1 - S_w)A_{max}$, where a A_{max} is the assigned maximum A_{ia} value for the 0.35 mm sand (i.e., 216 cm²/cm³) used in this comparison.

To match this linear $A_{ia}(S_w)$ dependence VG equation parameters (specifically α and n) were adjusted along with K_{sat} , to match the water flux used in the experiment. The simulation was performed as a constant Θ_w upper and lower flow boundary conditions and a concentration flux and zero concentration gradient upper and lower transport boundary conditions, respectively. Additional relevant flow and transport parameters used are provided in [Figure 4-35](#).

The simulated results matched the experimental data quite well for all moisture conditions considered. The early arrival and odd tailing observed in the $\Theta_w=0.28$ dataset provided by Lyu et al. (2018) is likely the result of experimental errors in this published data, as this did not occur at the other moisture conditions. The transport of PFOA at lower moisture conditions were also simulated. The increased retention reflects the increase in interfacial area with decreasing soil

moisture, consistent with the moisture-dependence model used. The increased dispersion observed with increasing moisture reflects the effects of the $0.7 \text{ cm}^2/\text{hour}$ value for longitudinal dispersivity that was determined by fitting the higher moisture cases.

Matching the $A_{ia}(S_w)$ dependence model assumed by Lyu et al. (2018) required modification of the VG equation parameters because the current model calculates A_{ia} based on the specific water characteristic curve (WCC) for the media being considered, after Bradford and Leij (1997) (cf. Section 3.35). The magnitude of the A_{ia} calculated increases with decreasing S_w and approaches the geometric surface area of the porous media as S_w approaches zero (Leverett, 1941). Example $A_{ia}(S_w)$ prediction models are presented in [Figure 4-36](#) for a few of the soil textural categories from Carsel and Parrish (1988) and the linear models used in this comparison. These plots demonstrate the variability in predicted A_{ia} values depending on the model selected. The linear model used by Lyu et al. (2018) was developed from unsaturated miscible-displacement 1D column experiments that used lower concentrations of surface-active AWI adsorbing tracers. These models have been shown to be more consistent with A_{ia} values calculated from assuming the porous media is a collection of smooth spheres (Constanza-Robinson and Brusseau, 2002). More recent investigations utilizing x-ray tomography to estimate the $A_{ia}(S_w)$ function in water unsaturated porous media have also provided linear $A_{ia}(S_w)$ relationships (Constanza-Robinson et al., 2008). Which $A_{ia}(S_w)$ model is most appropriate is still a matter of ongoing debate. However, the linear $A_{ia}(S_w)$ seem to be more predictive for 1D unsaturated flow and AWI adsorption in column studies. Fortunately, the current form of the modified HYDRUS model has the flexibility to represent both WCC-dependent and linear $A_{ia}(S_w)$ model predictions, by a simple modification of the VG equation parameters.

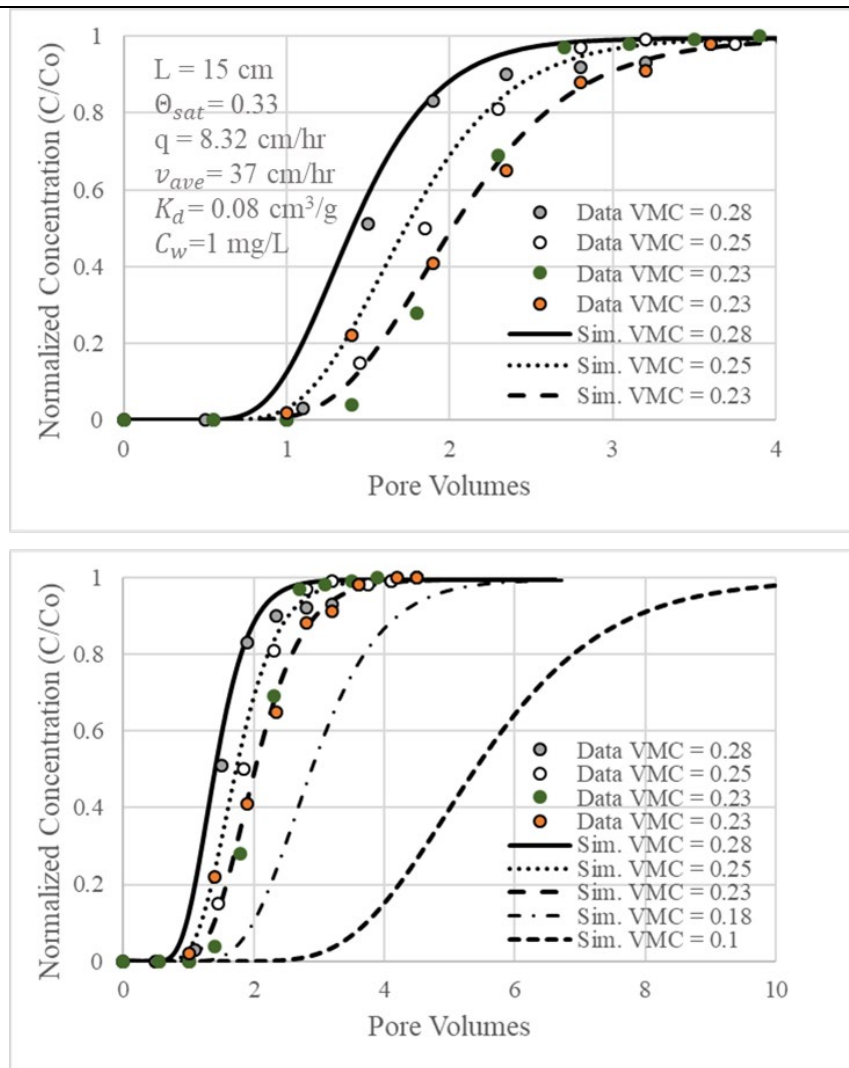


Figure 4-35. Experimental and simulated PFOA breakthrough profiles showing validation of the θ_w dependence on retention due to AWI adsorption.

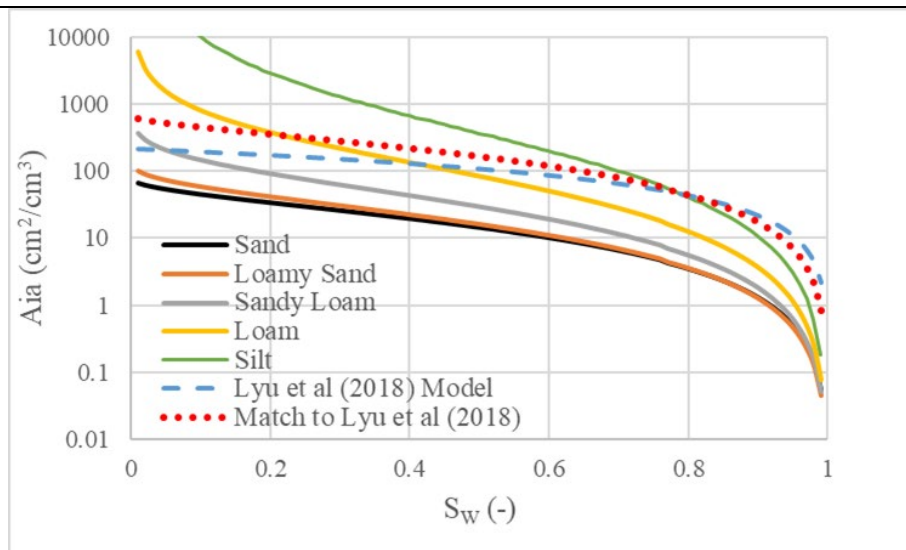


Figure 4-36. Comparison of $A_{ia}(S_w)$ functions.

4.5.2 Model Validation (C_w -Dependence)

At the time of this report, Lyu et al. (2018) had presented the only experimental transport data for PFAS in which C_w is a test variable. This general lack of physical transport data speaks to the need for further experimental research in this area. The Lyu et al. (2018) data is reproduced here in Figure 4-37(a) and represents the results of PFOA transport in unsaturated sand columns ($S_w = 0.68$) for $C_w = 1$ mg/L, 0.1 mg/L, and 0.01 mg/L. The experimental data shows increased retention of PFOA with decreasing C_w , within this range of values.

However, the simulated results using the modified HYDRUS model did not exhibit a change in retention within this range of concentrations. As shown in Figure 4-37(b), this is because the $k_{ia}(C_w)$ relationship, calculated from the surface tension isotherms produced in this work, is not dependent on concentration within this lower range of C_w . The $k_{ia}(C_w)$ relationship provided by Lyu et al. (2018) does not exhibit this lack of dependence on C_w , which is questionable given that the surface tension isotherms produced here and by Lyu et al. (2018) coincide within this lower range of C_w (Figure 4-37(c)). The slope of the surface tension isotherm in both cases are essentially the same and should therefore provide the same k_{ia} values and $k_{ia}(C_w)$ dependence. The accuracy of the transport data itself is questionable, in that breakthrough profiles for the same moisture condition and C_w exhibit different PFOA retention. In Figure 4-37(a) this variability in retention is shown for the two $C_w = 1$ mg/L datasets (one presented as Experiment #10 by Lyu et al. (2018) from the C_w -dependence data and the other for the results of Experiment #3, from the Θ_w -dependence experiments). Both experiments were reported to have been performed at the same moisture condition and both exhibit a similar degree variability in retention as is observed between the $C_w = 0.1$ mg/L and $C_w = 0.01$ mg/L datasets. AWI adsorption and retention of PFAS is highly dependent on the $A_{ia}(\Theta_w)$ relationship and it can be difficult to maintain a constant A_{ia} within a column of unsaturated sand throughout a given transport experiment, even when Θ_w is determined to be constant gravimetrically.

In the present work, we observe that the simulated retention of PFOA is accurately tracking the $k_{ia}(C_w)$ dependence for that solute as provided by the LS equation fit to the measured surface tension data. This is demonstrated in Figure 4-37(d) where, under the condition of a constant Θ_w and A_{ia} , PFOA retention is shown to decrease with increasing C_w in response to the decrease in k_{ia} . As shown in the $k_{ia}(C_w)$ relationships previously presented in Figure 4-18 and 4-19, retention of many of the PFAS components could exhibit a similar lack of sensitivity to changes in C_w for $C_w < 1$ mg/L.

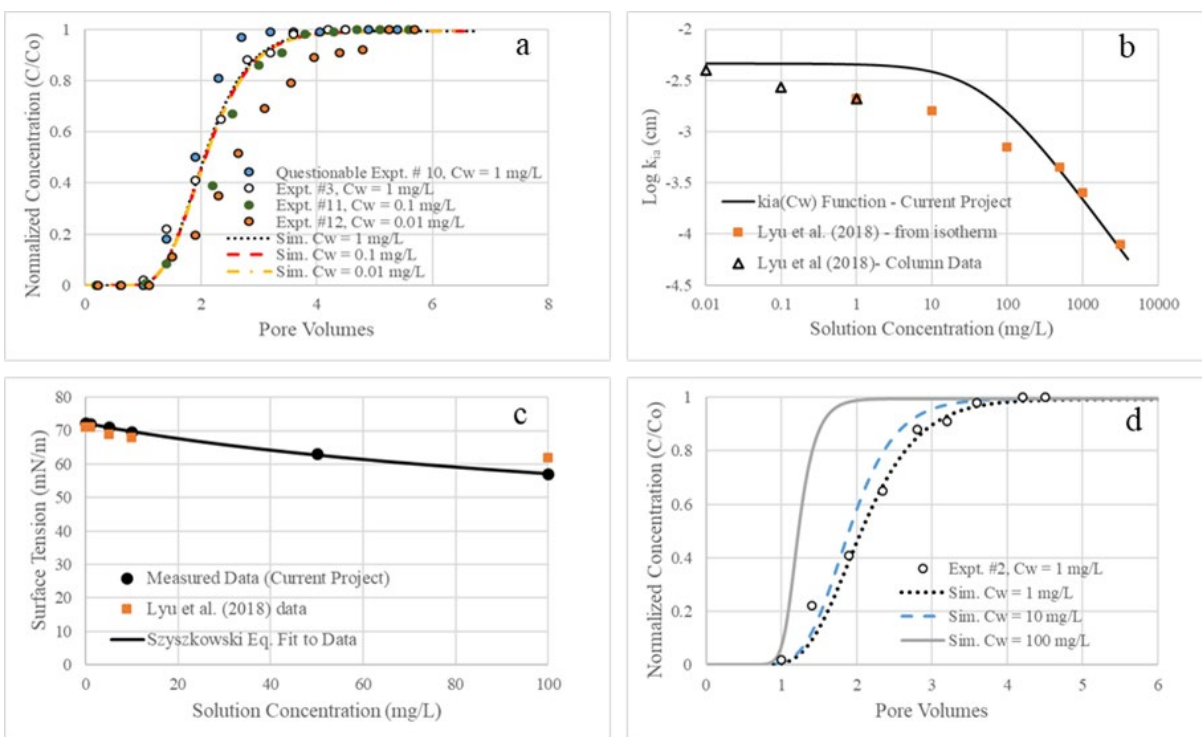


Figure 4-37. Experimental and simulated results for PFOA transport in water-unsaturated sand: (a) Experimental and simulated breakthrough profiles at different C_w , (b) comparison of $k_{ia}(C_w)$ relationships, (c) comparison of PFOA surface tension isotherms, (d) retention dependence on C_w provided by the modified HYDRUS simulator. All experimental data reproduced from the work of Lyu et al. (2018).

4.5.3 Ionic Strength Dependence

Transport data for PFAS under different IS conditions is not available in the existing literature, and therefore a similar model validation for this variable could not be performed. However, as this capability was added to the HYDRUS model as a part of this work, it was reasonable to include a simulated demonstration of this capability nonetheless. The effect of ionic strength on the transport of PFOA in unsaturated sand is presented in Figure 4-38. These simulated results utilized the same flow conditions and sand properties used in the previous model validation work, and Θ_w and the input C_w were 0.23 and 1 mg/L, respectively. K_L and Γ_{max} values for each PFOA IS-condition were taken from Table 4-1. Ionic strength values are those for the SGW's used earlier in this work.

As discussed in Section 4.1.5, the effect of increasing the ionic strength results in an increase in the PFAS solute k_{ia} value. k_{ia} was observed to increase sharply from its value for DI water, but the rate of increase thereafter was observed to diminish with increasing ionic strength. The simulated results presented in Figure 4-38 capture this same trend, in that the incremental increases in the retention of PFOA diminish with increasing ionic strength.

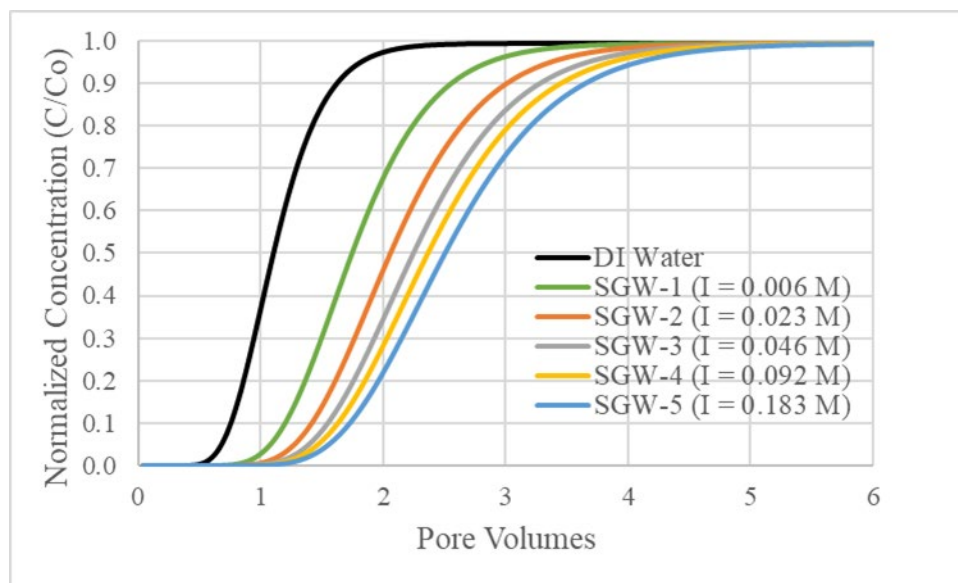


Figure 4-38. Simulated breakthrough profiles for PFOA as a function of increasing ionic strength.

4.5.4 Example PFAS Transport Simulations

Having successfully implemented AWI adsorption within the HYDRUS unsaturated flow and transport model as an additional retention mechanism, a few example simulations were performed to demonstrate the capability of the model. Until now, PFOA was the only PFAS included in the simulations and was introduced as a single-solute. Using the same flow conditions used previously, the 1D model was prepared to simulate the transport of PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA using the K_L and Γ_{max} values presented in Table 4-1 (SGW-2). Porous media hydraulic properties were changed to that of the “Loam” textural category (Carsel and Parish, 1988) that is built into the model to allow the model to calculate A_{ia} values as implemented (cf. Figure 4-36).

The results shown in Figure 4-39 demonstrate the variability in PFCA retention possible when soil moisture conditions change. Decreasing S_w by half results in roughly a factor of 100 increase in retention in the case of PFOA and PFNA. Simulated retention increases with increasing PFCA C_N , in keeping with the k_{ia} values. It is important to note that effects of solute-solute interactions at the AWI (i.e., the effects of preferential or competitive adsorption demonstrated for PFCA mixtures in Section 4.3.2) are not yet included in the model. Incorporating the effects of PFAS preferential adsorption at the AWI is being proposed as a part of future work.

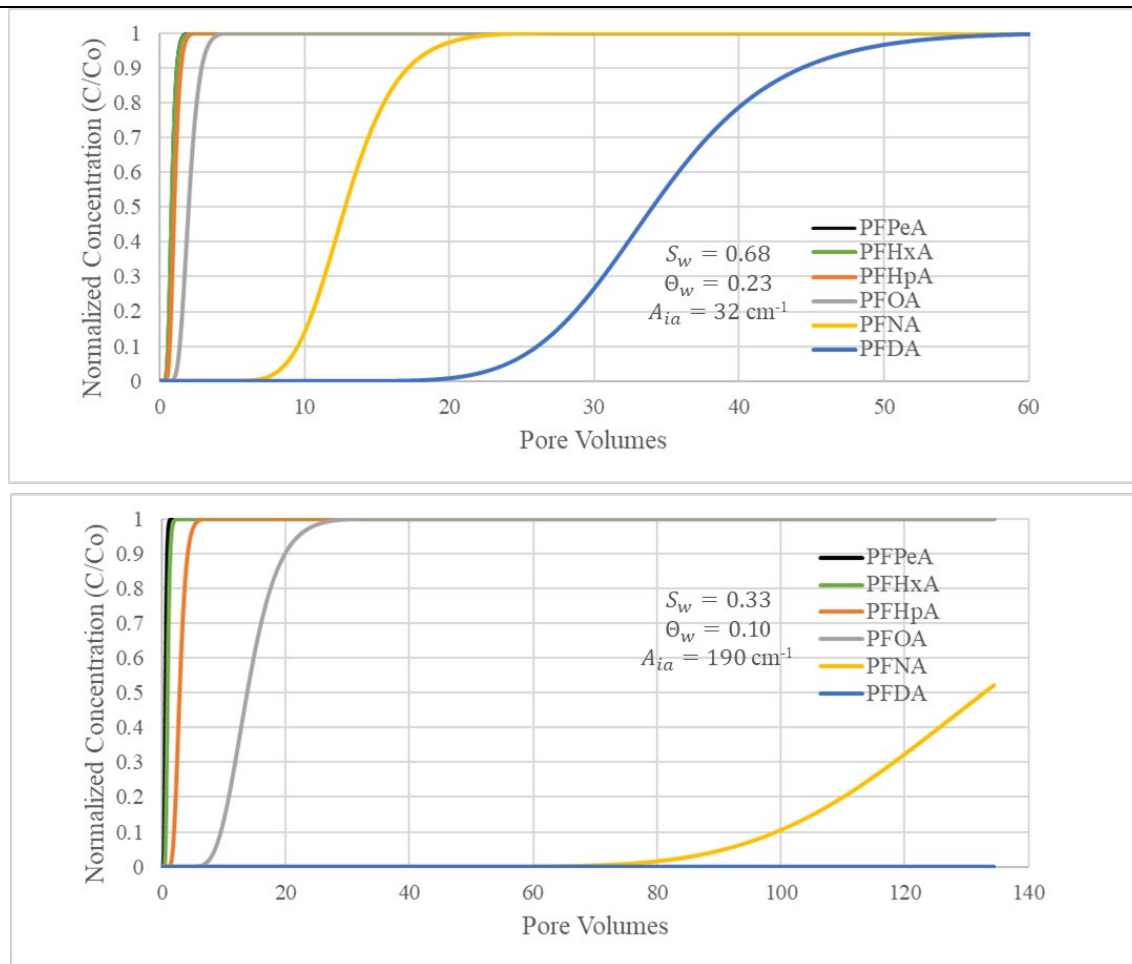


Figure 4-39. Comparative PFCA transport in water-unsaturated porous media for two soil moisture conditions. Hydraulic parameters used were those for the “Loam” textural classification from Carsel and Parish (1988). C_w in all cases was 0.001 mg/L.

AWI adsorption was also incorporated into the 2D HYDRUS model. As shown in Figure 4-40, a simple 2D simulation domain was constructed to simulate PFAS transport as drainage from a surficial source. Hydraulic properties for five different porous media categories were selected, each adhering to a separate $A_{ia}(\theta_w)$ function (cf. Figure 4-36) determined by the model. VG model parameters for the porous media categories are provided in Table 4-13. The initial moisture content in the “source” area was assigned a value of 0.35 ($S_w = 0.83$) to mimic a surface spill, and fluids drain into a uniform moisture condition below. C_w was assigned an equivalent value of 1 mg/L for PFHpA, PFOA, PFNA, and a non-reactive tracer.

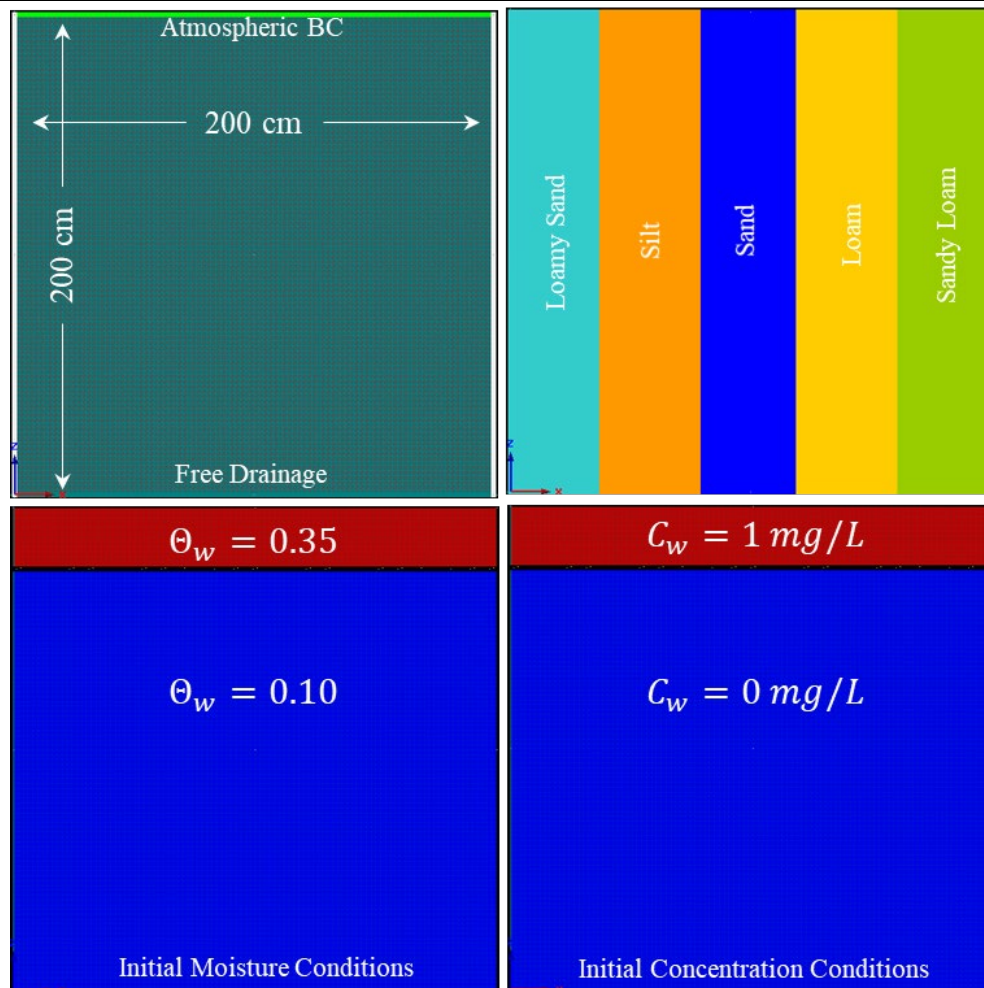


Figure 4-40. Boundary and initial conditions for the 2D simulations.

Table 4-13. VG Parameters for porous media categories used in example simulations.

Media	Qr	Qs	α	n	Ks	l
Sand	0.045	0.43	0.145	2.68	29.7	0.5
Loamy Sand	0.057	0.41	0.124	2.28	14.6	0.5
Sandy Loam	0.065	0.41	0.075	1.89	4.42	0.5
Loam	0.078	0.43	0.036	1.56	1.04	0.5
Silt	0.034	0.46	0.016	1.37	0.5	0.5

As shown in Figure 4-41, water drainage within the simulated domain occurred at different rates, depending on the hydraulic properties of the individual porous media categories. At each simulated time-step, a new A_{ia} distribution is being calculated in response to the changes in moisture, according to the $A_{ia}(\theta_w)$ relationships shown in Figure 4-36. In this way, the model is accounting for changes in PFAS AWI adsorption in response to the dynamic and transient nature of unsaturated flow.

The transport results of this simulation are presented in Figure 4-42. Again, these results demonstrate the effects of increased transport retardation with increasing PFCA C_N . The relative depth of transport is greater within the more conductive porous media. However, the overall depth of transport is limited, in addition to AWI adsorption, in this simulated example by reductions in hydraulic conductivity as Θ_w decreases behind the wetting front as it moves on through the domain.

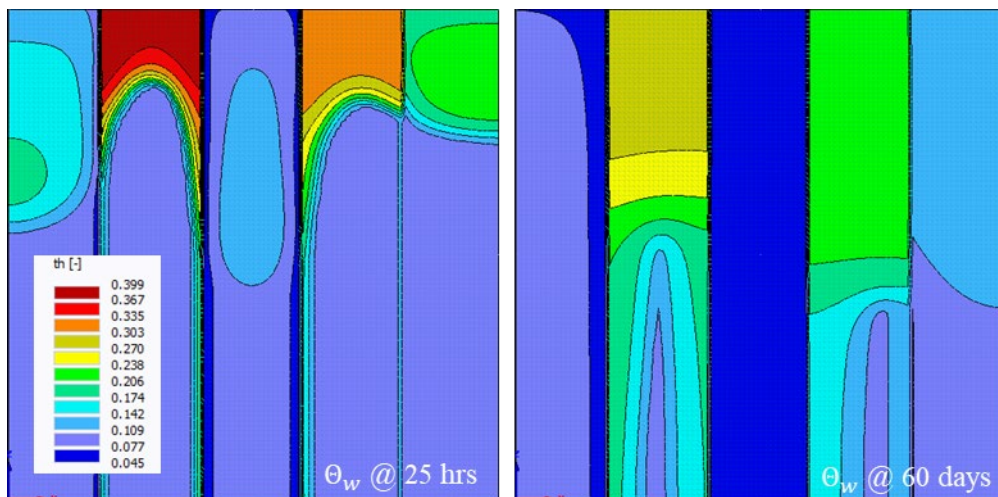


Figure 4-41. Simulated moisture redistribution for example 2D AWI adsorption runs.

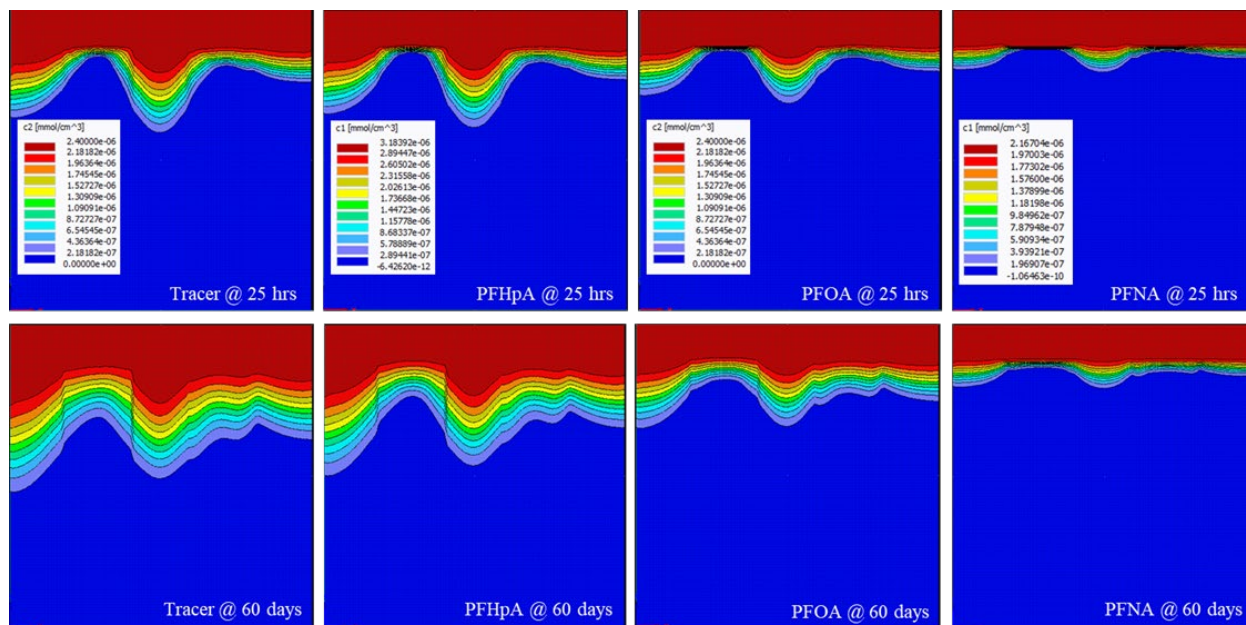


Figure 4-42. Simulated AWI adsorption of PFCAs during drainage from a surficial-applied source. Initial concentrations were 1 mg/L for each PFCA. Concentrations in the legends are the 1 mg/L concentration converted to units of mmol/cm³, in keeping with the units established in the model and those used in calculating K_L and Γ_{max} .

Taking this example further, a simulation was performed using the same initial conditions but including water infiltration events, introduced at the upper boundary of the domain in a series of 0.5 cm/hour water application events, each lasting 5-hours. A total of 7 events were simulated starting at 100 hours into the simulation and reoccurring every 300 hours thereafter. The total simulation time was 2880 hours or 120 days. The results of this simulation are presented in [Figure 4-43](#).

The purpose of this second transport simulation was to demonstrate that the modified HYDRUS model can in fact simulate the vertical migration of PFAS contaminants beyond their point of initial application. Water application rates in this example were purposely selected to be low enough to not exceed the capacity of the silt column to accept infiltrating moisture and is therefore not exactly representing the degree of vertical migration achieved for application rates typical of atmospheric precipitation. However, the number of application events were sufficient to move the contaminant downward within the unsaturated flow domain, in proportion to their individual K_L values.

One key takeaway from these simulated results is that the movement of AWI-adsorbing contaminants is generally not rapid, compared to saturated flow cases, because of the increase and decrease in unsaturated hydraulic conductivities as moisture fronts move down through the system and the corresponding increase and decrease of A_{ia} values. For the coarser sands, the water application rate is much lower than the saturated hydraulic conductivity (K_{sat}). θ_w does not change considerably during the infiltration events which limits the rate of infiltration. A_{ia} values are lower for these coarser media. However, the rate of infiltration of water and contaminant is ultimately hydraulically limited.

For the finer-grained media categories, the water application rate is closer to their respective K_{sat} values. The magnitude of K_{sat} is lower for these finer media but the rate of infiltration of water is similar to the coarsest media categories in this example. A_{ia} values are greater for the finer-grained media and increase more rapidly as moisture contents decrease behind the wetting fronts, which restricts the transport of these surface-active contaminants within the finest media categories. The loam appears to have the right combination of unsaturated hydraulic conductivity and range of A_{ia} values that combine to enhance the rate of infiltration of water and surface-active contaminant relative to the other porous media categories used in this example. That an optimal conductivity- A_{ia} condition exists suggests that this modified simulator could be potentially used to develop site screening metrics based on soil textural classifications to support PFAS contaminant risk assessments. To our knowledge, this is the first 2D representation of PFAS transport that includes the effects of solid-phase sorption and AWI adsorption within unsaturated porous media.

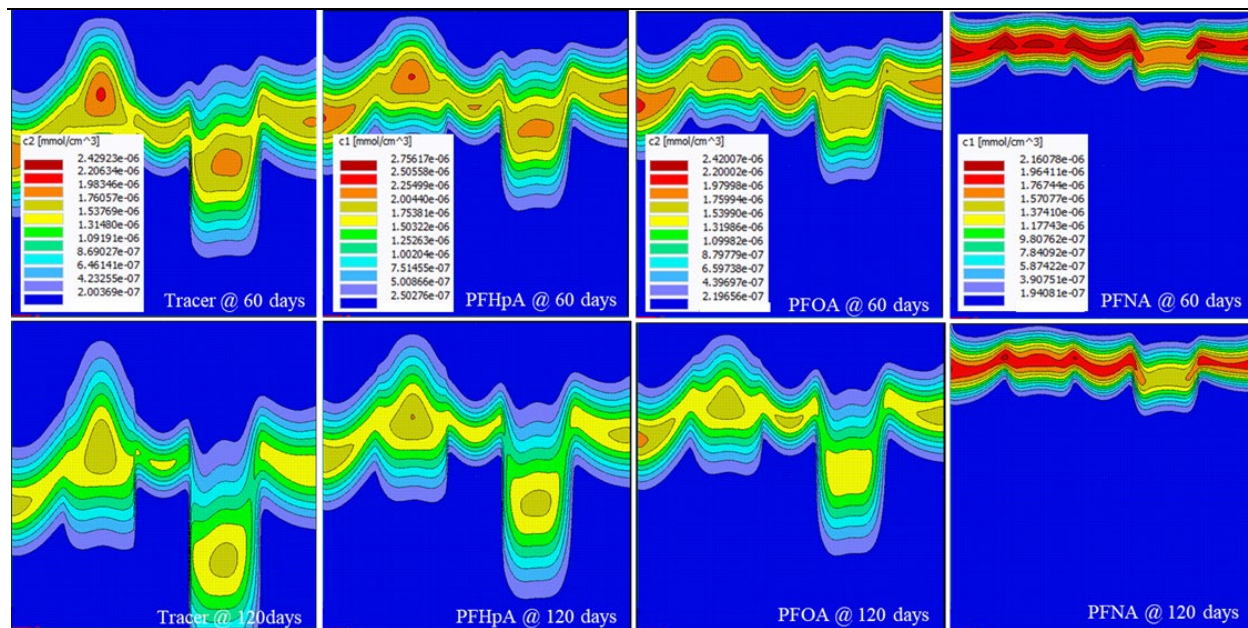


Figure 4-43. Simulated transport of PFCAs under periodic water application at the upper boundary. AWI adsorption is only source of retention. Initial concentrations were 1 mg/L for each PFCA. Concentrations in the legends are the 1 mg/L concentration converted to units of mmol/cm³, in keeping with the units established in the model and those used in calculating K_L and Γ_{max} .

4.5.5 Implications and Relevance (Modeling AWI Adsorption)

At the completion of this project, we have successfully modified the HYDRUS unsaturated flow and contaminant transport model to include AWI adsorption of PFAS and its dependence on solution concentration. The dependence of PFAS AWI adsorption on A_{ia} was modeled using an approach in which A_{ia} is calculated directly from the pressure head-saturation relationship. This approach allows the model to accommodate different $A_{ia}(\theta_w)$ functions for different soil types. In this way, the model captures the dynamic and transient nature of the $A_{ia}(\theta_w)$ function and its effect on PFAS AWI adsorption in the presence of soil textural heterogeneity. The model was also modified to account for changes in solution ionic strength, utilizing additional data generated as a result of this research. These capabilities were implemented in HYDRUS but could also be implemented in other unsaturated flow and transport models.

The modified model retains its original capabilities with regard to simulating the effects of solid-phase sorption (i.e. linear and non-linear sorption models) as a concurrent source of PFAS retention. The modified model also retains its original nonequilibrium contaminant flow and transport capabilities (e.g., mobile/immobile water, dual porosity, dual permeability models) and soil sorption kinetics modeling capabilities (e.g., one- and two-site kinetics and two-site sorption models)(Simunek and van Genuchten, 2008). To our knowledge, the current modified model is the first to account for the effects of AWI adsorption of PFAS (and its dependencies on solution concentration, the area of the AWI as it changes with soil moisture conditions, and changes in solution ionic strength) while providing enough computational flexibility to simulate

complexities of PFAS adsorption in 1D and 2D. Incorporating AWI adsorption into a 3D version of HYDRUS is the ultimate end goal of this research.

Utilizing the PFAS-specific data generated to date, the current modified model treats AWI adsorption as a non-linear equilibrium process with adsorption and desorption at the AWI occurring instantaneously (i.e. no kinetic effects). However, it is well known that surfactant interactions with the AWI can be rate-limiting. Kinetic effects were observed in our current research during surface tension measurements for PFAS mixtures where equilibrium tension values were achieved over the course of several hours. As described in Section 5, incorporating nonequilibrium AWI adsorption/desorption kinetics is being proposed in a future project which will further improve the accuracy of PFAS transport simulations.

The current modified model can simulate the transport of multiple PFAS components. However, the modified model does not currently account for interactions between individual PFAS components and its effect on adsorption at the AWI. As demonstrated in Section 4.3, the adsorbed composition of PFAS at the AWI is dependent on the dissolved solution composition and can change as the more surface-active PFAS components are preferentially retained during transport in the vadose zone. Developing mathematical relationships to describe this phenomenon and incorporating these relationships into the simulator is an additionally being proposed in as a component of a future project.

The objectives of Task 3 have been met as described in Section 1.3 of this report. Within the proposed limits of this preliminary research, we have successfully developed and incorporated mathematical relationships needed to implement AWI adsorption as a source of retention in HYDRUS for simulating PFAS transport in the vadose zone. We have also validated the model against available PFAS transport data and have highlighted the need for additional transport data that could be used to further validate the model against a wider range of physical conditions. We have also identified additional model modifications that would improve the accuracy of model predictions and provide a robust and comprehensive simulator for PFAS transport in the vadose zone. Finally, the utility and capability of the modified model was demonstrated in 1D and 2D example simulations. Implementing AWI adsorption in a 3D version of HYDRUS is the end goal of this work, which would provide a useful tool in supporting DoD efforts to characterize the PFAS source term in the vadose zone. Such a model would also improve hydrogeological risk assessments and evaluation of remedial alternatives and/or monitoring strategies.

5.0 Conclusions and Implications for Future Research

5.1 AWI Adsorption and Retention (Tasks 1 and 3)

At the completion of this limited-scope project, our fundamental understanding of PFAS adsorption at AWIs within the vadose zone environment has greatly improved. AWI adsorption is a significant source of retention of PFAS within water-unsaturated media and therefore should be included in fate and transport calculations for cases where the PFAS source area is in the vadose zone. Retardation factors for AWI interfacial adsorption alone were found to be in excess of 100 for PFCAs with $C_N > 8$, and decreased with increasing soil moisture content and with decreasing C_N . The significance of PFAS retention is highlighted when considering that retardation factors for many common regulated organic pollutants (e.g., TCE, PCE, TCA, BTEX) are often in the range from 1-3. AWI adsorption was also shown to increase with increasing groundwater ionic strength. The ionic strength dependence was not linear but was observed to level off with increasing ionic strength. A Langmuir-like model was used to accurately describe the ionic strength dependence on k_{ia} values.

It is important to consider that AWI adsorption and desorption (i.e. rehydration by the aqueous phase) is a dynamic process, with molecules being exchanged at the interface in response to changes in bulk solution concentrations, other solution composition changes, and changes in interfacial area. Based on the results of this limited-scope project we have developed a framework methodology that requires testing but could provide a more comprehensive predictive model for AWI adsorption, incorporating each of the aforementioned processes and could be implemented into existing numerical simulators.

NAPL-Water interfacial (NWI) adsorption was also evaluated in this work and was found to be a less significant contributor to PFAS retention, for the PFAS employed. NAPLs used were TCE and kerosene (as a surrogate for jet fuels) which are two NAPLs commonly found at AFFF-related PFAS source areas. NWI adsorption is likely dependent on PFAS carbon number and solution composition, but being a lower energy surface for PFAS adsorption, the dependence is also likely to be of a lesser degree.

During this 1-year scoping project, other researchers published data further demonstrating log-linear relationships for predicting PFAS AWI adsorption k_{ia} values based on structural characteristics of the hydrophobe (e.g. carbon number, molar volume, molecular connectivity indices). While it is true that measuring k_{ia} values for the hundreds of PFAS of environmental concern is not practical, these relationships are based on the size of the molecules and therefore largely depend on the hydrophobic effect, or water's tendency to push large hydrophobic molecules out of the bulk fluid phase as the principal contributing factor. These relationships are derived from literature data for deionized water. Our data suggests electrostatic contributions to AWI adsorption can impact the validity of these relationships, particularly as PFAS C_N increases beyond values of 9. Furthermore, these predictive relationships are based on the AWI adsorption of PFAS as individual components. Environmental PFAS contamination exists as a complex multi-component mixture. Our research demonstrates that k_{ia} values for individual PFAS in

mixtures can differ considerably from those determined as a single component k_{ia} values when solution concentrations increase and approach monolayer coverage for the mixture.

Finally, as demonstrated in Section 4.5, AWI adsorption was successfully incorporated into the HYDRUS unsaturated flow and transport model. The model was validated against experimental PFAS transport data derived from literature sources. However, there is a need for additional transport experiments to provide data with which to validate the model against a wider range of physical conditions. We have also identified additional model modifications that would improve the accuracy of model predictions and provide a robust and comprehensive simulator for PFAS transport in the vadose zone. Current model modifications have been applied to the 1D and 2D versions of HYDRUS to support development. However, implementing AWI adsorption in a 3D version of HYDRUS is the end goal of this work, which would provide a useful tool in supporting DoD efforts to characterize the PFAS source term in the vadose zone. Such a model would also improve hydrogeological risk assessments and evaluation of remedial alternatives and/or monitoring strategies.

5.2 Tension-Driven Flow (Tasks 2 and 3)

Experiments were performed to condition the HYDRUS unsaturated flow model to measured data. Modifications to the HYDRUS code were made to incorporate the effects of solution viscosity and concentration-dependent surface tension on the flow and transport of surface-active solutes in unsaturated porous media.

The lateral spreading and redistribution of solutes driven by surface-tension induced capillary pressure gradients alone was not found to be particularly impactful, with simulated results indicating lateral transport of solutes by just a half meter in 100 hours. Initial rapid movement of pore-waters is observed for this mechanism. However, flows are reduced by dilution at the drainage front and lowered unsaturated conductivity behind the front as a result of decreased moisture content.

Mineral sorption of the National Foam AFFF solution used in this work was considerable enough to greatly alter the steady-state moisture distribution in our sand column experiments, compared to a non-adsorbing surface-active solute (i.e. IPA). Surface-tension isotherms for the bulk AFFF fluid, used to scale tension-driven flow in our model, did not match the results of the physical column experiments. Only when Langmuir adsorption was included, and after re-scaling tension driven flow to an alternative surface-tension isotherm, did the simulated and experimental moisture distributions coincide. As a result of the adsorption observed, lateral spreading of AFFF solutions as a result of tension-driven flow mechanism alone is not significant.

However, observations during preparation of the AFFF column experiment indicated that a change in the wettability of the test sand occurred when the AFFF solutions were added to the sands. The sands were observed to take on a loose and fluid-like consistency when the AFFF solutions were added at concentrations greater than 5000 mg/L and was not observed for lower applied AFFF solution concentrations. We concluded that one or more of the components in the

mixture of surface-active solvents and surfactants were altering the wettability of the sand. Evaluating the effect of changes in wettability due to mineral adsorption of the AFFF solution was not considered under this limited-scope project, largely because the original proposed work scope did not include AFFF solutions as a test fluid.

Additional work is needed to characterize the concentration-dependence of the bulk AFFF solution on changes in media wettability (i.e. contact angles for same test sand used in this preliminary work, and perhaps natural aquifer media from a AFFF release area), solution viscosities, and surface tension. Each of these dependencies can be used to scale the pressure head term in the numerical model to more accurately represent AFFF solution transport. Additionally, characterizing these same properties for the major components the AFFF solutions is warranted. Doing so will allow the pressure head term to be appropriately scaled with respect to these primary concentration-dependent variables and allow each component, and its effect on unsaturated flow, to be represented independently.

The importance of continuing this proposed work centers on developing an ability to simulate historic AFFF release scenarios. As was the case for NAPL contamination during the 1990's and early 2000's, simulating the known or assumed release history of contaminants can be a valuable tool to ascertain a preliminary estimate of the lateral and vertical extent of the contaminant source area, which is useful in guiding site characterization efforts and to quantify the source term. For AFFF source areas, this can be accomplished rather easily using a properly conditioned model like that proposed here.

Likewise, a properly conditioned unsaturated flow and transport model would be useful to simulate the mass flux of PFAS components from historic AFFF source areas over the long term. This numerical tool could also serve as a site management tool with which to base remedial decision making or the design of long-term monitoring strategies. An unsaturated flow and transport model coupled to a groundwater flow simulator would further enhance the utility of this approach. However, decoupling and better understanding processes is the crucial first step to develop new theory that better explains the mechanisms of transport within vadose zone PFAS source areas.

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6.0 References

- 3M, 1991. Study summary of environmental effects of light water brand AFFF and its components. 3M Environmental Laboratory Technical Report: 3M MN01657098.
- Anderson, R.H., Long, G.C., Porter, R.C., Anderson, J.K., 2016. Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sited other than fire-training areas: Field-validation of critical fate and transport properties. *Chemosphere*, 150, 678-685.
- Anderson, R.H., Adamson, D.T., Stroo, H.F., 2019. Partitioning of poly- and perfluoroalkyl substances from soil to groundwater within aqueous film-forming foam source zones. *J. Contam. Hydrol.* 220, 59–65.
- ASTM Standard D1331, 1989. Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface-Active Agents. ASTM International, West Conshohocken, PA.
- Aveyard, B. Surfactants: In solution, at Interfaces, and in Colloidal Dispersions. Oxford University Press, Oxford, UK, 2019.
- Batista, M.M., Guirardello, R., Krahenbuhl, M.A., 2015. Determination of Hansen solubility parameters of vegetable oils, biodiesel, diesel, and biodiesel-diesel blends. *J. Am. Oil Chem. Soc.*, 92, 95-109.
- Baduel, C., Mueller, J.F., Rotander, A., Corfield, J., Gomez-Ramos, M.J., 2017. Discovery of novel per-and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility. *Chemosphere*, 185, 1030-1038.
- Bear, J., 1972. Dynamics of Fluids in Porous Media, Dover, New York.
- Bradford, S.A., Leij, F.J., 1997. Estimating interfacial areas for multi-fluid soil systems, *J. Contam. Hydrol.*, 27:83-105.
- Bradford, S.A., Wang, Y., Torkzaban, S., Šimůnek, J., Modeling the release of E. coli D21g with transients in water content, *Water Resources Research*, 51(5), 3303-3316, doi: 10.1002/2014WR016566, 2015.
- Brusseau, M.L., 1992. Rate-limited mass transfer and transport of organic solutes in porous media that contain immobile immiscible organic liquid. *Water Resour. Res.* 28, 33–45.
- Brusseau, M.L., Popovicova, J., Silva, J. A. K., 1997. Characterizing gas-water interfacial and bulk water partitioning for transport of gas-phase contaminants in unsaturated porous media. *Environ. Sci. Technol.*, 31 (6), 1645–1649.
- Brusseau, M.L., 2018. Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface. *Sci. Total Environ.* 613-614, 176-185.

- Brusseau, M.L., 2019. The influence of molecular structure on the adsorption of PFAS to fluid-fluid interfaces: Using QSPR to predict interfacial adsorption coefficients. *Water Res.* 152, 148-158.
- Brusseau, M.L., Yan, N., Van Glubt, S., Wang, Y., Chen, W., Lyu, Y., Dungan, B., Carroll, K.C., Holguin, F.O., 2019. Comprehensive retention model for PFAS transport in subsurface systems. *Water Res.* 148, 41-50.
- Carsel, R.F.; Parrish, R.S., 1988. Developing joint probability distributions of soil water retention characteristics. *Water Resour. Res.*, 24(5), 755-769.
- Costanza, M.S., Brusseau, M.L., 2000. Influence of adsorption at the air-water interface on the transport of volatile contaminants in unsaturated porous media. *Environ. Sci. Technol.* 34, 1–11.
- Costanza-Robinson, M. S., Brusseau, M. L., 2002. Air-water interfacial areas in unsaturated soils: Evaluation of interfacial domains. *Water Resour. Res.*, 38, 1195–1211.
- Costanza-Robinson, M.S., Harrold, K.H., Lieb-Lappen, R.M., 2008. X-ray microtomography determination of air-water interfacial area-water saturation relationships in sandy porous media. *Environ. Sci. Technol.*, 42(8), 2949-2956.
- Cui, Z.-G., Canselier, J.P., 2000. Interfacial and micellar properties of some anionic/cationic binary surfactant systems. 1. Surface properties and prediction of surface tension. *Colloid Polym. Sci.*, 278(1), 22-29.
- Cui, A.-G., Canselier, J.P.; Zhou, X.-Q, 2005. Mixed adsorption and surface tension prediction of nonideal ternary surfactant systems. *Colloid Polym. Sci.*, 283(5), 539-550.
- Downes, N., Ottewill, G. A., Ottewill, R. H. An investigation of the behavior of ammonium perfluoro-octanoate at the air/water interface in the absence and presence of salts. *Colloids Surf., A* 1995, 102, 203–211.
- Dlugogorski, B.Z., Phiyanalinmat, S., Kennedy, E.M. (2005). Dynamic Surface and Interfacial Tension of AFFF and Fluorine-free Class B Foam Solutions. *Fire Safety Science – Proceedings of the Eighth International Symposium*, pp. 719-730.
- Gurkov, T.D., Dimitrova, D.T., Marinova, K.G., Bilke-Crause, C., Gerber, C., Ivanov, I.B., 2005. Ionic surfactants on fluid interfaces: determination of the adsorption; role of the salt and the type of the hydrophobic phase, *Colloids Surf A Physicochem Eng Asp.*, 261, 29-38.
- Hansen, C.M., 2007. *Hansen Solubility Parameters: A Users Handbook*. 2nd Ed.. CRC Press, Boca Raton, FL.
- Henry, E. J., Smith, J.E., Warrick, A.W., 1999. Solubility effects on surfactant induced unsaturated flow through porous media, *J. Hydrol.*, 223, 164–174.
- Henry, E.J., Smith, J.E., Warrick, A.W., 2001. Surfactant effects on unsaturated flow in porous media with hysteresis: Horizontal column experiments and numerical modeling. *J. Hydrol.*, 245, 73-88.

- Henry, E. H., Smith, J.E., 2006. Numerical demonstration of surfactant concentration-dependent capillarity and viscosity effects on infiltration from a constant flux line source, *J. Hydrol.*, 329, 63–74.
- Huang, L., Maltesh, C., Somasundaran, P., 1996. Adsorption behavior of cationic and nonionic surfactant mixtures at the alumina-water interface. *J. Colloid Interface Sci.*, 177(1), 222-228.
- Karagunduz, A., Pennell, K.D., Young, M.H., 2001. Influence of a nonionic surfactant on the water retention properties of unsaturated soils, *Soil Sci. Soc. Am. J.*, 65, 1392–1399.
- Karagunduz, A., Young, M.H., Pennell, K.D., 2015. Influence of surfactants on unsaturated water flow and solute transport. *Water Resour. Res.*, 51, 1977-1988.
- Karkare M.V., La, H.T., Fort, T., 1993. Criteria for effectiveness of surfactants as water-moving agents in -unsaturated. ' wet sand. *Langmuir*, 9, 1684-1690.
- Karkare, M. V., Fort, T., 1996. Determination of the air-water interfacial area in wet "unsaturated" porous media, *Langmuir*, 12, 2041–2044.
- Kim, H., Rao, P.S.C, Annable, M.D., 1997. Determination of effective air-water interfacial area in partially saturated porous media using surfactant adsorption. *Water Res. Research*, 33(12), 2705-2711.
- Kim, H., Annable, M. D., Rao, P. S., 1998. Influence of air-water interfacial adsorption and gas-phase partitioning on the transport of organic chemicals in unsaturated porous media. *Environ. Sci. Technol.*, 32 (9), 1253-1259.
- Kim, H., Rao, P. S. C., Annable, M. D., 1999. Gaseous tracer technique for estimating air-water interfacial areas and interface mobility. *Soil Sci. Soc. Am. J.*, 63(6), 1554–1560.
- Kim, H., Annable, M. D., Rao, P. S. C., 2001. Gaseous transport of volatile organic chemicals in unsaturated porous media: effect of water-partitioning and air-water interfacial adsorption. *Environ. Sci. Technol.*, 35(22), 4457–4462.
- Kissa, E. 2001. *Fluorinated Surfactants and Repellents*, Surfactant Science Series, 97. Marcel Dekker, New York.
- Kovalchuk, N. M., Trybala, A., Starov, V., Matar, O., Ivanova, N., 2014. Fluoro- vs hydrocarbon surfactants: Why do they differ in wetting performance? *Adv. Colloid Interface Sci.*, 210, 65-71.
- Leverett, M. C. (1941), Capillary behavior in porous solids, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 142, 152-169.
- Li, P.; Ma, K.; Thomas, R.K.; Penfold, J. (2016). Analysis of the asymmetric synergy in the adsorption of zwitterionic-ionic surfactant mixtures at the air-water interface below and above the critical micelle concentration. *J. Phys. Chem. B*, 120(15), 3677-3691.

- Lunkenheimer, K., Prescher, D., Hirte, R., Geggel, K., 2015. Adsorption properties of surface chemically pure sodium perfluoro n-alkanoates at the air/water interface: counterion effects within homologous series of 1:1 ionic surfactants. *Langmuir*, 31, 970–981.
- Lyu, Y., Brusseau, M.L., Chen, W., Yan, N., Fu, X., Lin, X., 2018. Adsorption of PFOA at the air-water interface during transport in unsaturated porous media. *Environ. Sci. Technol.* 52, 7745-7753.
- McGuire, M.E., Schaefer, C., Richards, T., Backe, W.J., Field, J.A., Houtz, E., Sedlak, D.L., Guelfo, J.L., Wunsch, A., Higgins, C.P., 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance (PFAS) distribution at a former firefighter training area, *Environ. Sci. Technol.* 48(12), 6644-6652.
- Meng, P., Deng, S. B., Deng, S., Lu, X., Du, Z., Wang, B., Huang, J., Wang, Y., Yu, G., Xing, B., 2014. Role of air bubbles overlooked in the adsorption of perfluorooctanesulfonate on hydrophobic carbonaceous adsorbents. *Environ. Sci. Technol.*, 48, 13785–13792.
- Moody, C.A., Field, J.A., 1999. Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity. *Environ. Sci. Technol.*, 33(16), 2800-2806.
- Muherei, M.A., Junin, R., 2009. Equilibrium adsorption isotherms of anionic, nonionic surfactants and their mixtures to Shale and Sandstone. *Mod. Appl. Sci.*, 3(2), 158-167.
- Mukerjee, P., Handa, T., 1981. Adsorption of fluorocarbon and hydrocarbon surfactants to air-water, hexane-water, and perfluorohexane-water interfaces. Relative affinities and fluorocarbon-hydrocarbon nonideality effects. *J. Phys. Chem.* 85, 2298e2303.
- Peng, S., Brusseau, M.L., 2005. Impact of soil texture on air-water interfacial areas in unsaturated sandy porous media. *Water Resour. Res.* 41, W03021. <http://dx.doi.org/10.1029/2004WR003233>.
- Psillakis, E., Cheng, J.; Hoffmann, M. R., Colussi, A. J., 2009. Enrichment factors of perfluoroalkyl oxoanions at the air/water interface. *J. Phys. Chem. A*, 113, 8826–8829.
- Rosen, M.J.; Hua, X-Y., 1982. Surface concentrations and molecular interactions in binary-mixtures of surfactants. *J. Colloid Interface Sci.* 86(1), 164-172.
- Rosen, M.J., 2012. *Surfactants and Interfacial Phenomena*. 4th Ed. John Wiley & Sons, New Jersey.
- Rubingh, D.N., 1979. Mixed Micelle Solutions. In: *Solution Chemistry of Surfactants*. K.L. Mittal, Ed.), Vol 1, p337. Plenum, New York.
- Saripalli, P. K., Rao, P. S. C., Annable, M. D., 1998. Determination of specific NAPL-water interfacial areas of residual NAPLs in porous media using the interfacial tracers technique. *J. Contam. Hydrol.*, 30, 375-391.
- Shinoda, K., Hato, M., Hayashi, T., 1972. The physicochemical properties of aqueous solutions of fluorinated surfactants. *J. Phys. Chem.* 76, 909-914.

- Silva, J. A. K., 1997. Retention processes affecting VOC vapor transport in water-unsaturated porous media. Master's Thesis. University of Arizona, Tucson, AZ.
- Silva, J. A. K., Bruant, R. G., Conklin, M. H., Corley, T. L., 2002. Equilibrium partitioning of chlorinated solvents in the vadose zone: Low foc geomedial. *Environ. Sci. Technol.* 2002, 36(7), 1613-1619.
- Simunek, J., van Genuchten, M.Th., 2008. Modeling nonequilibrium flow and transport processes using HYDRUS. *Vadose Zone J.*, 7(2), 787-797.
- Smith, J. E., and R. W. Gillham (1994), The effect of concentration-dependent surface tension on the flow of water and transport of dissolved organic compounds: A pressure head-based formulation and numerical model, *Water Resour. Res.*, 30, 343–352.
- Smith, J.E., 1995. The effect of solute concentration dependent surface tension on vadose zone flow and transport, PhD thesis, University of Waterloo, Canada.
- Smith, J.E., Gillham, R.W., 1999. Effects of solute-concentration-dependent surface tension on unsaturated flow: Laboratory sand column experiments. *Water Resour. Res.*, 35(4), 973-982.
- Svitova, T.F., Wetherbee, M.J., Radke, C.J., 2003. Dynamics of surfactant sorption at the air-water interface: continuous-flow tensiometry.
- Szymczyk, K., Janczuk, B., 2007. The adsorption at solution-air interface and volumetric properties of mixtures of cationic and nonionic surfactants. *Colloids Surf A Physicochem. Eng. Asp.*, 293(1-3), 39-50.
- Tschapek, M., Wasowski, C., Torres Sanchez, R.M., (1981), Tangential force and water migration in unsaturated disperse material, *Colloids Surf.*, 3, 295–298.
- Tschapek, M., Wasowski, C., Falasca, S., (1984), The Gibbs-Marangoni flow of water in quartz sand unsaturated with water, *Colloids Surf.*, 11, 69–80.
- Vecitis, C. D., Park, H., Cheng, J., Mader, B. T., Hoffmann, M. R., 2008. Enhancement of perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) activity at acoustic cavitation bubble interfaces. *J. Phys. Chem. C*, 112, 16850–16857.
- van Genuchten, M.Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, 44, 892–898.
- Wallach, R., Margolis, M., Graber, E.R., 2013. The role of contact angle on unstable flow formation during infiltration and drainage in wettable porous media. *Water Resour. Res.*, 49, 6508-6521.
- Weber, A.K., Barber, L.B., LeBlanc, D.R., Sunderland, E.M., Vecitis, C.D., 2017. Geochemical and hydrologic factors controlling subsurface transport of poly- and perfluoroalkyl substances, Cape Cod, Massachusetts. *Environ. Sci. Technol.* 51 (8), 4269–4279.

Yoda, K., Tamori, K., Esumi, K., Meguro, K., 1989. Critical micelle concentrations of fluorocarbon surfactant mixtures in aqueous solution. J. Colloid Interface Sci. 131, 282-283.

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