EXECUTIVE SUMMARY

Proof of Concept: 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.

Distribution Statement A
This document has been cleared for public release

SERDP
DOD ▪ EPA ▪ DOE

This report was prepared under contract to the Department of Defense Strategic Environmental Research and Development Program (SERDP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

EXECUTIVE SUMMARY

Project: ER18-1389

TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1
2.0 OBJECTIVES 2
3.0 TECHNICAL APPROACH 3
4.0 RESULTS AND DISCUSSION 3
5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS 10

LIST OF FIGURES

Page

Figure ES-1. PFCA $\boldsymbol{RfSw}$ Functions Calculated for AWI and NWI Adsorption as the Only Source of Retention. 4
Figure ES-2. Measured Data for a PFCA Ternary Mixture 6
Figure ES-3. $\boldsymbol{kia\ Cw}$ Function for a PFCA Ternary Mixture. 6
Figure ES-4. Experimental and Simulated Moisture Redistributions for the National Foam AER-O-Water® CEM^{C6} AFFF Solutions Used in This Work 7
Figure ES-5. Example Results of 1D HYDRUS Simulations 8
Figure ES-6. Initial and Boundary Conditions Used in the Example 2D Simulations. 9
Figure ES-7. 2D HYDRUS Simulation of PFCA AWI Adsorption During Transport in Unsaturated Porous Media. 9

ACRONYMS AND ABBREVIATIONS

<	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
°C	Degrees Celsius
µg/L	micrograms per liter
% v/v	Percent by volume
AFFF	Aqueous film forming foam

AWI	Air-water interface
cm	centimeter
cm/sec	centimeters per second
DoD	Department of Defense
g/cm	grams per centimeter
g/L	grams per liter
HYDRUS	Modeling Software
LS	Langmuir-Szyszkowski
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
NAPL	Non-aqueous phase liquid
ng/L	nanograms per liter
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
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 Agency

ACKNOWLEDGEMENT

This research was supported wholly (or in part) by the U.S. Department of Defense (DoD), through the Strategic Environmental Research and Development Program (SERDP) - Grant Number ER18-1389. The project team wishes to acknowledge Dr. Andrea Leeson and other members of the SERDP staff for their assistance with the project team's research.

Co-investigators:
John E. McCray, Ph.D. (Colorado School of Mines)
William. A. Martin, Ph.D. P.E. (U.S. Army Engineer Research and Development Center)

Co-performers:
Jiří Šimůnek, Ph.D. (University of California – Riverside)
Jared L. Johnson, P.E. (U.S. Army Engineer Research and Development Center)

1.0 INTRODUCTION

Per- and polyfluoroalkyl substances (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 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 the project team's 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 perfluorocarboxylic acids (PFCA) 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. 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 has met the first requirements toward achieving this goal. The project team has modified the HYDRUS modeling software 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.

2.0 OBJECTIVES

The project's specific objectives were the following:

1. Generate fundamental physicochemical properties data that can be used to 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.

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.

3.0 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 PFCAs 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 the full 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 the full 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 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.

4.0 RESULTS AND DISCUSSION

<u>Task 1: Evaluating the Significance of AWI Adsorption</u>

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 PFSAs used in this research, are largely present at concentrations in the sub-mg/L range. The project team's 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 perfluoroalkyl acids, 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, the project team proposes 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, which 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 Perfluoropentanoic acid (PFPeA) (k_{ia}= 5.35×10^{-5} cm), 10.9 for PFOA (k_{ia}= 3.68×10^{-3} cm), and 165 (k_{ia}= 8.81×10^{-2} cm) for perfluorodecanoic acid (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 (trichloroethylene [TCE], tetrachloroethylene, trichloroacetic acid, BTEZ, etc) are often in the range from 1-3, these PFAS R_f values are highly significant from a practical perspective.

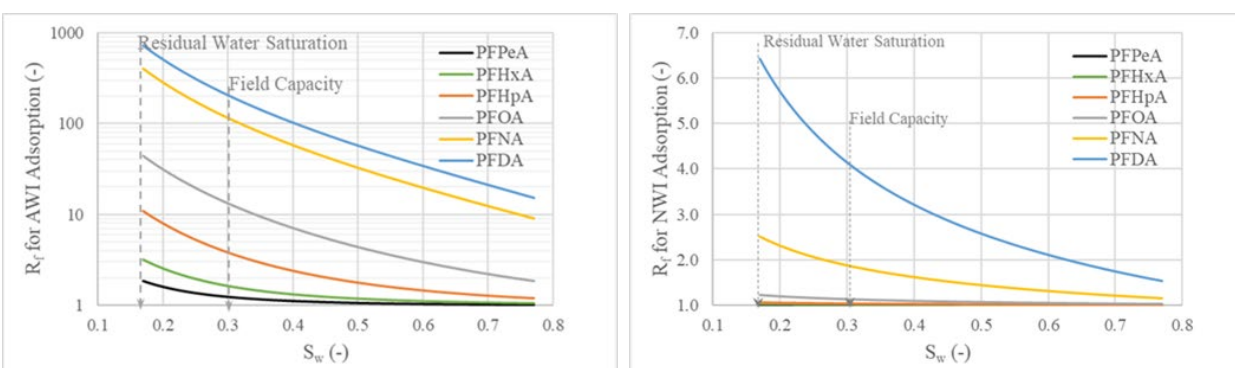

Figure ES-1. PFCA $R_f(S_w)$ Functions Calculated for AWI and NWI Adsorption as the Only Source of Retention.

- 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, assessment of 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. The project team's 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, it is thought to be the better approach to employ 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.

- 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, the project team concluded 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 for changes in 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) the project team's 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.

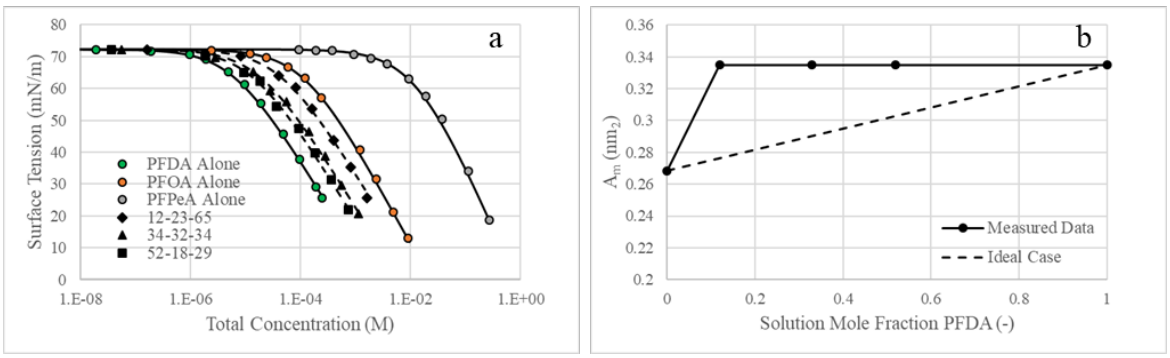

Figure ES-2. Measured Data for a PFCA Ternary Mixture: a) Surface Tension Isotherms for Each PFCA As a Single Component As Mixtures, b) Calculated Area of the Minimum Adsorbed Surface Areas Per Molecule (A_m) with Changes in the Solution Mole Fraction of the Most Surface-active Component of the Mixture.

- 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.

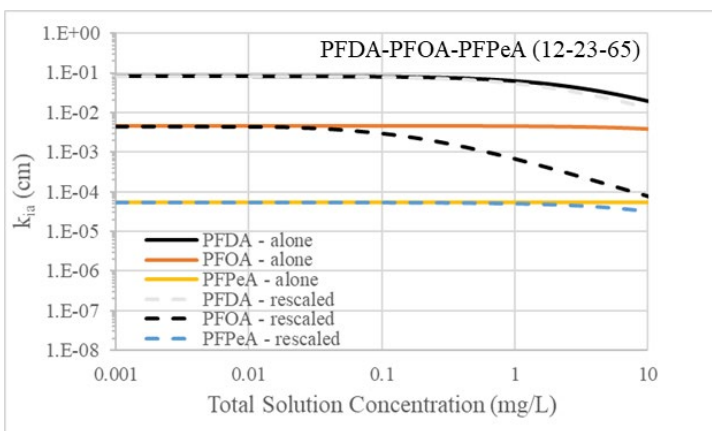

Figure ES-3. $k_{ia}(C_w)$ Function for a PFCA Ternary Mixture.

- 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-4, 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.

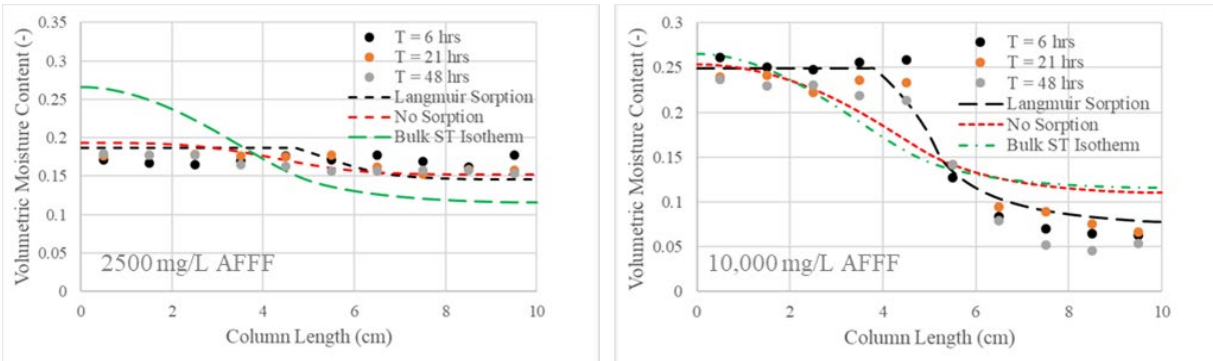

Figure ES-4. Experimental and Simulated Moisture Redistributions for the National Foam AER-O-Water® CEM^{C6} AFFF Solutions Used in This Work.

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 re-scaling of the surface tension isotherm.

The flow of 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, the project team has 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 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-5.

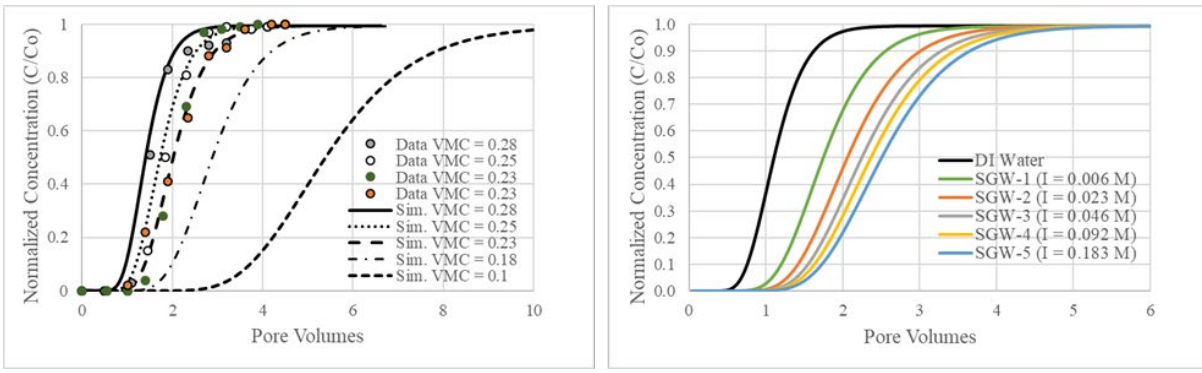

Figure ES-5. Example Results of 1D HYDRUS Simulations: a) Model Validation of Soil Moisture Content Dependence of PFOA AWI Adsorption and b) Demonstration of Ionic Strength (I) Dependence on PFOA AWI Adsorption.

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-6. 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 Θ_w = 0.35. Periodic simulated water applications were 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 Figure ES-7. To the project team's 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 that 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.

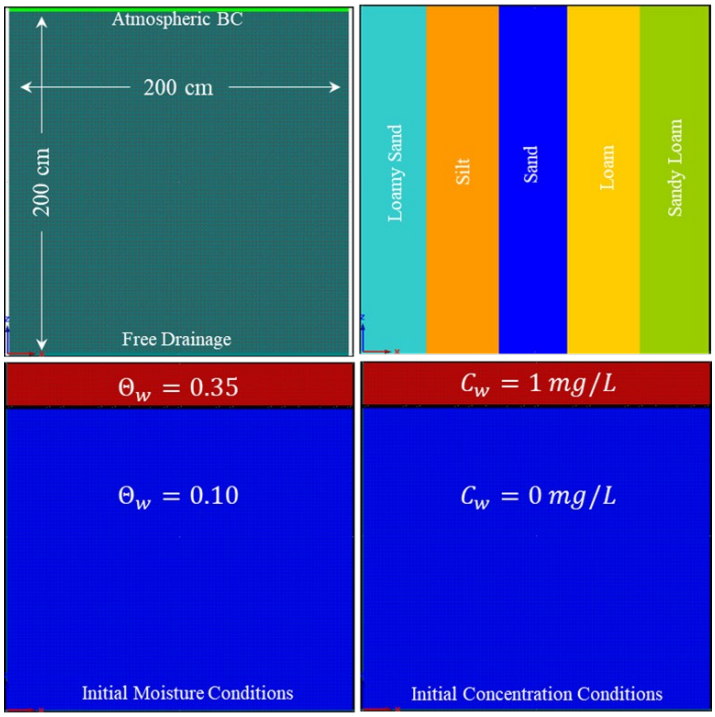

Figure ES-6. Initial and Boundary Conditions Used in the Example 2D Simulations.

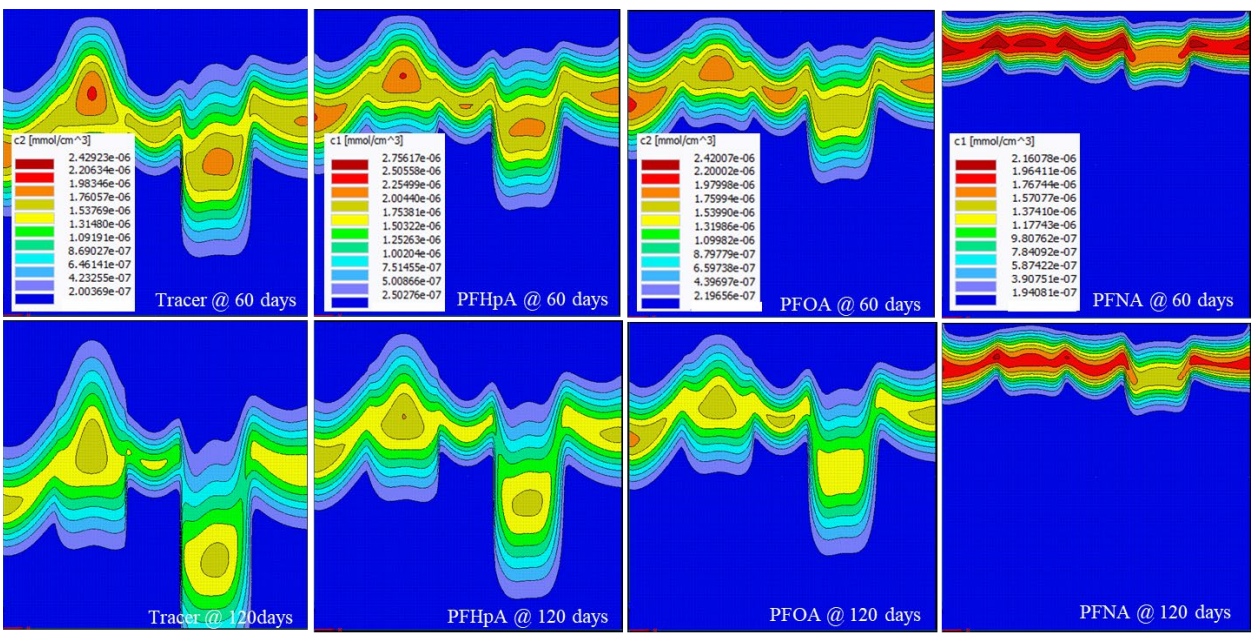

Figure ES-7. 2D HYDRUS Simulation of PFCA AWI Adsorption During Transport in Unsaturated Porous Media.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

At the completion of this limited-scope project, the project team has demonstrated the significance of AWI adsorption of PFAS as a source of retention within the vadose zone. The project team has 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. The project team has 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.