

**FINAL REPORT**

# Insights into the Long-Term Mass Discharge & Transformation of AFFF in the Unsaturated Zone

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Charles Schaefer  
Dung Nguyen  
**CDM Smith**

Christopher Higgins  
**Colorado School of Mines**

Jennifer Field  
**Oregon State University**

David Lippincott  
Paul Hatzinger  
**APTIM**

**June 2023**

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| <b>REPORT DOCUMENTATION PAGE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                               |                                             |                                                  |                                       | <i>Form Approved</i><br>OMB No. 0704-0188                        |  |
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| <b>1. REPORT DATE (DD-MM-YYYY)</b><br>15/06/2023                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                               | <b>2. REPORT TYPE</b><br>SERDP Final Report |                                                  |                                       | <b>3. DATES COVERED (From - To)</b><br>9/14/2018 - 9/13/2023     |  |
| <b>4. TITLE AND SUBTITLE</b><br><br>Insights into the Long-Term Mass Discharge & Transformation of AFFF in the Unsaturated Zone                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>5a. CONTRACT NUMBER</b><br>W912HQ18C0044                      |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>5b. GRANT NUMBER</b>                                          |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>5c. PROGRAM ELEMENT NUMBER</b>                                |  |
| <b>6. AUTHOR(S)</b><br>Charles Schaefer and Dung Nguyen: CDM Smith<br>Christopher Higgins: Colorado School of Mines<br>Jennifer Field: Oregon State University<br>David Lippincott and Paul Hatzinger: APTIM                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                               |                                             |                                                  |                                       | <b>5d. PROJECT NUMBER</b><br>ER18-1204                           |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>5e. TASK NUMBER</b>                                           |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>5f. WORK UNIT NUMBER</b>                                      |  |
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br>CDM Smith<br>CORPORATION 9200 WARD PKWY<br>STE 320<br>KANSAS CITY MO 64114-3372                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                               |                                             |                                                  |                                       | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b><br><br>ER18-1204 |  |
| <b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b><br>Strategic Environmental Research and Development Program (SERDP)<br>4800 Mark Center Drive, Suite 16F16<br>Alexandria, VA 22350-3605                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                               |                                             |                                                  |                                       | <b>10. SPONSOR/MONITOR'S ACRONYM(S)</b><br>SERDP                 |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       | <b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b><br>ER18-1204       |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                               |                                             |                                                  |                                       |                                                                  |  |
| <b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b><br>DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                               |                                             |                                                  |                                       |                                                                  |  |
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| <b>16. SECURITY CLASSIFICATION OF:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                               |                                             | <b>17. LIMITATION OF ABSTRACT</b><br><br>UNCLASS | <b>18. NUMBER OF PAGES</b><br><br>115 | <b>19a. NAME OF RESPONSIBLE PERSON</b><br>Dr. Charles Schaefer   |  |
| <b>a. REPORT</b><br><br>UNCLASS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | <b>b. ABSTRACT</b><br>UNCLASS | <b>c. THIS PAGE</b><br>UNCLASS              |                                                  |                                       | <b>19b. TELEPHONE NUMBER (Include area code)</b><br>732-590-4633 |  |

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## LIST OF ACRONYMS

|         |                                                   |
|---------|---------------------------------------------------|
| AFB     | Air Force Base                                    |
| AFFF    | aqueous film-forming foam                         |
| CEC     | cation exchange capacity                          |
| CSM     | Colorado School of Mines                          |
| DPT     | direct push technology                            |
| NAPL    | non-aqueous phase liquid                          |
| DO      | dissolved oxygen                                  |
| DOC     | dissolved organic carbon                          |
| DoD     | Department of Defense                             |
| EC      | electrical conductivity                           |
| ECF     | electrochemically formed                          |
| ESI     | electrospin ionization                            |
| ft bgs  | feet below ground surface                         |
| HDPE    | high density polyethylene                         |
| HPLC    | high pressure liquid chromatography               |
| IDW     | investigation derived waste                       |
| JBMDL   | Joint Base McGuire-Dix-Lakehurst                  |
| LC-QTOF | liquid chromatography quantitative time of flight |
| MS -    | mass spectrometry                                 |
| OSU     | Oregon State University                           |
| PFAS    | poly- and perfluoroalkyl substances               |
| PFCAs   | perfluoroalkyl carboxylates                       |
| PFSAs   | perfluoroalkyl sulfonates                         |
| SB      | soil boring                                       |
| TOC     | total organic carbon                              |
| TOP     | total oxidizable precursor                        |
| VOCs    | volatile organic compounds                        |
| VP      | vapor probe                                       |

*Specific PFAS abbreviations are provided in Appendix A1*

## LIST OF KEYWORDS

PFAS, AFFF, soil, leaching, desorption, flushing, lysimeter

## ACKNOWLEDGEMENTS

We gratefully acknowledge the efforts of both Stephanie Shea (Ph.D. candidate at the Colorado School of Mines) and Dr. Emerson Christie (recently graduated Ph.D. student at Oregon State University) in their support of the PFAS analyses and bench-scale testing. We also appreciate the field support provided by Sean O'Hare (CDM Smith) and Graig Lavorgna (APTIM). The support provided by Dung (Zoom) Nguyen (CDM Smith) throughout the project also is greatly appreciated. Finally, a special thanks also to the environmental staff at JBMDL for their support of this project.

## ABSTRACT

### **Introduction and Objectives**

Currently, there is little understanding of how PFAS sources in the unsaturated zone decay over time, and how PFAS mass discharge and composition vary as the sources decay. Furthermore, it remains unclear the extent to which equilibrium parameters that govern PFAS distribution (soil-water distribution and accumulation at the air-water interface) impact PFAS leaching *in situ*. This SERDP project focused on obtaining improved insights into the long-term mass discharge of PFAS from the unsaturated zone of a source area historically impacted by AFFFs. The overall goals of this project were 1) to attain insight into the transformation and mass discharge of PFAS from AFFF sources that reside in the unsaturated zone, and 2) to understand how these processes change over time and with AFFF composition and mass.

### **Technical Approach**

The overall approach employed in this study consisted of installing a highly instrumented test cell (approximately 14ft x 14ft) within an AFFF source area to monitor PFAS porewater concentrations as a function of moisture content, time, and depth within the unsaturated zone. An irrigation system was used to assess PFAS porewater concentrations during and after enhanced flushing, and to provide insight into the relationship between PFAS mass flux and mass removal. To provide insight into the mechanisms controlling the PFAS porewater concentrations, a parallel set of bench-scale experiments were performed using site soils to determine PFAS soil desorption kinetics and isotherms, and to determine the PFAS air-water interfacial sorption coefficient, and to evaluate leaching in a series of column experiments.

### **Results**

Results from the bench-scale soil desorption testing showed that desorption isotherms were reasonably described by a linear model, and that a fraction of the soil-bound PFAS mass was not readily desorbed (or, non-labile). The non-labile fraction of PFAS mass sorbed to the soil ranged from 0.17 g g<sup>-1</sup> for perfluorohexane sulfonamide in the deep soil to 0.87 g g<sup>-1</sup> for 8:2 fluorotelomer sulfonate in the shallow soil. PFAS porewater concentrations measured in the field lysimeters were well predicted using the soil isotherm data coupled with an estimate of the PFAS mass sorbed at the air-water interface, thereby demonstrating the role of air-water interfacial adsorption on PFAS mass flux during leaching. Enhanced flushing showed that, particularly for long-chained perfluorinated sulfonates such as PFOS, PFAS mass flux decreased much more rapidly than PFAS within the test cell; this was observed at both the bench-scale and in the field.

### **Benefits**

Overall, results from this study demonstrate that PFAS leaching can be reasonably predicted based on equilibrium-based parameters that can be readily quantified in the laboratory, particularly for longer-chained compounds. Furthermore, both the bench- and field-scale results suggest that elevated PFAS concentrations may persist in soils even after leaching has been substantially reduced. This observation can facilitate a scientifically-based justification for basing soil cleanup criteria based on site specific leaching/desorption values rather than generic regulatory limits.

## EXECUTIVE SUMMARY

### Introduction

This SERDP project was originally submitted in response to the SERDP Statement of Need ERSON-18-C1 that addressed the need for improved understanding of poly- and perfluoroalkyl substances (PFAS) source areas. Specific items of need included identifying source area characteristics that impact PFAS discharge to groundwater, filling critical data gaps with respect to PFAS transformation and transport, and development of tools to predict long-term PFAS release. This effort employed the use of both bench-scale and field-scale techniques to provide a balance of mechanistic and practical assessment of these processes to rapidly provide the DoD with scientifically-derived information and interpretation to facilitate improved site management of aqueous film forming foam (AFFF) source areas and their associated groundwater plumes. This project was a collaborative and multi-disciplinary effort among scientists and engineers at CDM Smith, the Colorado School of Mines (CSM), Oregon State University (OSU), and APTIM.

Currently, there is little understanding of how PFAS sources in the unsaturated zone decay over time, and how PFAS mass discharge and composition vary as the sources decay. This SERDP project focused on obtaining improved insights into the long-term mass discharge of PFAS from the unsaturated zone of a source area historically impacted by AFFFs. *Using a field test cell, coupled with mechanistic bench-scale experiments, the slow release and transformation of PFAS was evaluated over time.*

The aforementioned lack of knowledge is due, in part, to the complex nature of AFFF sources. *It is unclear how vadose processes such as wetting-drying cycles, aerobic/anaerobic cycling, and colloidal transport impact source decay, mass discharge and composition.* With respect to transformation, our focus was on the abundant range of precursor compounds that are present in AFFF (Barzen-Hanson et al., 2017), and those that are amenable to abiotic and/or biotic transformation processes.

Key fundamental questions related to the processes that control the long-term mass discharge of PFAS from AFFF-impacted source areas include:

- What is the nature of the long-term PFAS source loading from aged AFFF sources in the unsaturated zone?
- How do the PFAS composition and desorption kinetics vary with time?
- How do variably saturated conditions, including mobilization of natural colloids and changes in ionic strength, impact PFAS release and fate from sources?
- What information and understanding are critical for predicting long-term mass discharge from AFFF-impacted sites?

### Objectives

The overall goals of this project were 1) to attain insight into the transformation and mass discharge of PFAS from AFFF sources within the vadose zone and capillary fringe, and 2) to understand

how these processes change over time and with AFFF composition and mass. It is noted that the full range of AFFF-relevant PFAS, including perfluoroalkyl acids (PFAAs) and PFAA precursors, were monitored and assessed as part of this project. Specific objectives include the following:

1. ***Understand the nature of PFAS release into vadose zone and capillary fringe pore waters.*** This includes both understanding the nature of the PFAS (i.e., colloidal vs. dissolved) and the impacts of water geochemical conditions (pH, DOC, ionic strength) on their release from soil, and/or interfacial sources.
2. ***Determine the relationship between source removal (including comingled NAPL and hydrocarbon surfactants) and PFAS mass discharge.*** The overall rate of mass discharge is expected to change as both AFFF source mass becomes depleted, and the composition of the source changes due to transformation and preferential removal of more leachable components.
3. ***Attain insight into the role of variable saturation on PFAS fate and transport in the source area.*** This objective includes understanding both physical processes that may enhance or hinder the release of PFAS.

***Develop an approach to predict PFAS mass discharge from the unsaturated zone over time.*** Based on both laboratory and field data, the factors contributing to PFAS mass removal and discharge were mechanistically determined or empirically quantified over time. This information was used to develop a screening model to estimate PFAS mass discharge as a function of time and AFFF source mass remaining.

### **Technical Approach**

The overall approach for this project consisted of instrumenting a test cell (14 ft x 14 ft) in the unsaturated zone that had been historically impacted with AFFF. The former fire training area adjacent to Building 691 at the former Naval Air Training Technical Center at the Joint Base McGuire-Dix-Lakehurst (JBMDL) located in Burlington County, New Jersey was selected due to its relatively shallow depth to water [less than 10 feet below ground surface (bgs)], sandy vadose zone, and the presence of an aged AFFF source area. The test cell, which was hydraulically isolated with sheet piling, was instrumented with a network of porous cup suction lysimeters and moisture probes. A shallow monitoring well, rain gauge, and sprinklers (for enhanced flushing testing) also were installed (**Fig. ES1**). Lysimeters were connect to a vacuum manifold collection system for remote operation and monitoring. Lysimeters were sampled under ambient conditions, and also during/after enhanced flushing.

In addition to the field monitoring, soil samples were collected for site characterization. Collected soil samples were also used for bench-scale testing to determine PFAS desorption kinetics, determine PFAS equilibrium desorption isotherms, and to perform unsaturated column experiments.



**Figure ES1.** Installed 14 ft x 14 ft test cell.

### **Results and Discussion**

The initial soil investigation showed that elevated PFAS soil concentration were within the top foot of the surface (**Fig. ES2**). Also of note was the fact that several classes of precursors, despite nearly 20 years since the last reported AFFF release, persisted in the soil (**Fig. ES3**). The presence of electrochemically-formed (ECF) precursors and fluorotelomer precursors suggests multiple types of AFFF were used at this site. No NAPL or hydrocarbons were detected in the source area, so potential impacts of these co-contaminants on PFAS leaching could not be evaluated.

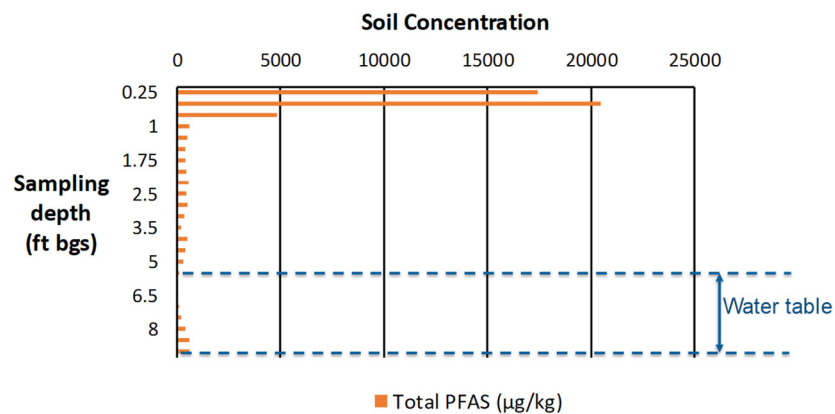


**Figure ES2.** PFAS (target + suspect analytes) soil concentrations measured in the test plot.

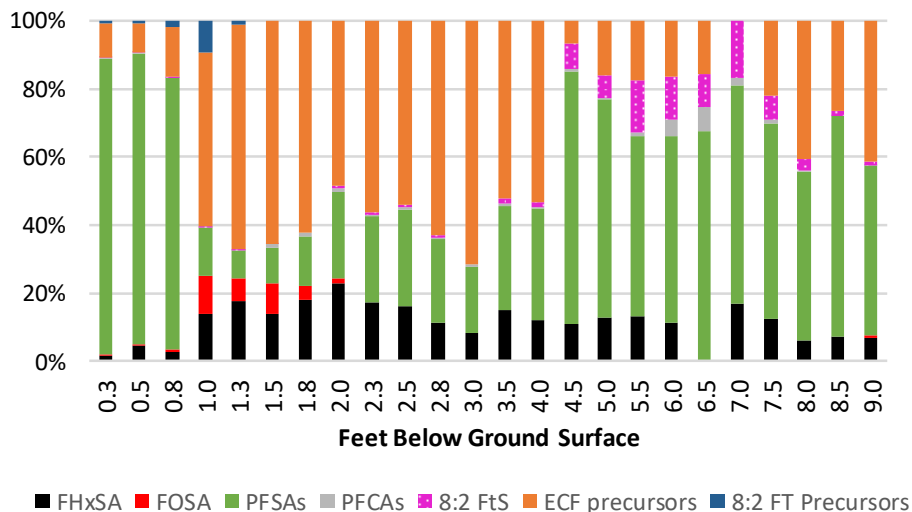


**Fig. ES3.** PFAS composition as a function of depth in SB02. ECF precursors represent polyfluorinated compounds associated with electrochemical fluorination processes, PFSA are perfluorinated sulfonic acids, PFC are perfluorinated carboxylic acids, FHxSA is perfluorohexane sulfonamide, and FOSA is perfluorooctane sulfonamide. ECF=electrochemically formed.

Batch kinetic desorption tests showed that perfluoroalkyl acids (PFAAs) with shorter-chained perfluorinated tails ( $C < 9$  for the perfluorinated carboxylates, and  $C < 7$  for the perfluorinated sulfonates) generally exhibited rate-limited desorption taking greater than a week to reach equilibrium. However, longer-chained PFAAs (i.e., PFNA, PFHpS, PFOS) reached near-equilibrium within 48 hours. Perfluorinated sulfonamides and the fluorotelomer sulfonates exhibited a similar trend. Although these non-equilibrium trends with respect to PFAS perfluorinated chain length and hydrophobicity appear counterintuitive, as longer-chained compounds with greater hydrophobicity might be expected to exhibit mass transfer controlled desorption rather than the more mobile compounds, similar observations have been made for polyaromatic hydrocarbons (PAHs) in field aged soils (Shor et al., 2003). The reason for these observations is described by two-domain sorption models that consist of a rapid equilibrium domain (associated with soil surface uptake and/or rapid migration into mesopores), and a diffusion controlled non-equilibrium domain (associated with contaminant diffusion into micropores or soil organic matter (Shor et al., 2003). Over time, weakly sorbing (i.e., short-chained) PFAS become depleted from the equilibrium domain, and only PFAS sorbed within the kinetically-controlled domain remaining. This conceptual model explains why only the shorter-chained compounds showed kinetic limitations in the shallow soil desorption experiment. Finally, PFAS concentrations in centrifuged vs. non-centrifuged supernatant samples were approximately equal, suggesting that the fraction of PFAS associated with natural colloids was negligible.

Batch PFAS equilibrium desorption isotherms using AFFF-impacted field soils showed that PFAS exhibited linear desorption behavior, but with a significant fraction of the PFAS that was not

readily desorbed from the soil (e.g., **Fig. ES4**). The fraction of PFAS mass that was not readily desorbed from the soil generally increased with perfluorinated chain length. Extended desorption testing with approximately a 9 month equilibration period verified the general recalcitrance of this strongly sorbed fraction.

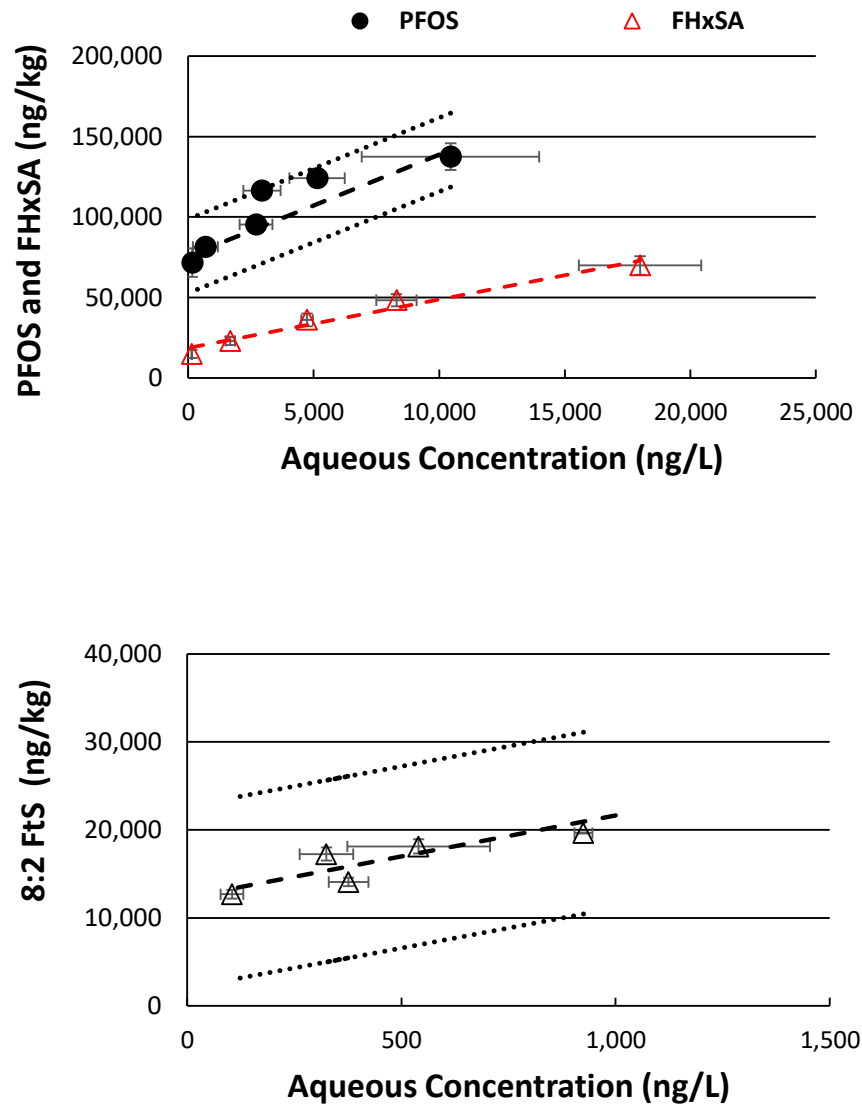


**Figure ES4.** PFAS desorption isotherms for soil collected at the site (homogenized deep soil interval). Average values are plotted. Large dashed lines represent linear regressions to the data. Error bars (x and y) represent 95% confidence intervals base on the desorption data. The dotted lines bracketing the data represent the 95% confidence intervals associated with the initial PFAS soil concentrations, and thus represent the uncertainty associated with the y-intercept and ultimately the non-labile soil concentration. Dotted lines are not shown for clarity when they reside within 10% of the dashed-line regression curves.

Measured PFAS porewater concentrations based on lysimeter samples collected in the field test plot (**Fig. ES1**) are summarized in **Fig. ES5**. Results show that PFAS concentrations were reasonably repeatable (within approximately a factor of 2) among the network of lysimeters. PFAS concentration were also similar for both the shallow and deep lysimeters. Using the PFAS equilibrium desorption isotherm data, along with an estimate of PFAS accumulation at the air-water interface, a model was developed that provided a reasonable prediction of the PFAS porewater concentrations measured in the field (**Fig. ES6**). Of note is that the model predictions were improved for PFOS and PFHpS when PFAS adsorption to the air-water interface was included. The elevated natural organic carbon levels in the porewater did not appear to adversely impact PFAS accumulation at the air-water interface when compared to electrolyte solutions of similar ionic strength.

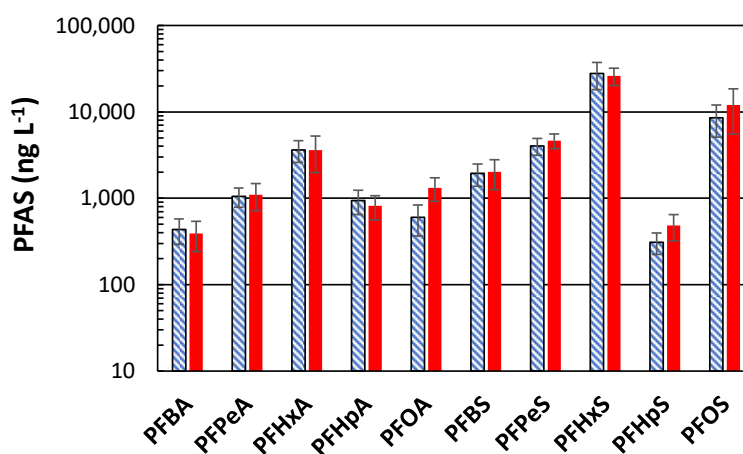


**Figure ES5.** Average PFAS porewater concentrations measured using the field-deployed lysimeters over three rounds of sampling. The blue-hatched bars are from the 4 deep (1.2 to 1.5 m bgs) lysimeters, and the red bars are from 4 shallow (0.61 m bgs) lysimeters. As described in the text, the first round of sampling from L-5 and outliers ( $> 3$  standard deviations from the mean) from the second and third rounds of sampling at L-1 were excluded from calculation of the averages shown in this figure. Error bars represent 95% confidence intervals. PFBA =perfluorobutanoic acid, PFPeA = perfluoropentanoic acid, PFHxA = perfluorohexanoic acid, PFHpA =perfluoroheptanoic acid, PFOA = perfluorooctanoic acid, PFBS =perfluorobutanesulfonate, PFPeS=perfluoropentanesulfonate, PFHxS = perfluorohexanesulfonate, PFHpS= perfluoroheptanesulfonate, and PFOS = perfluorooctanesulfonate.

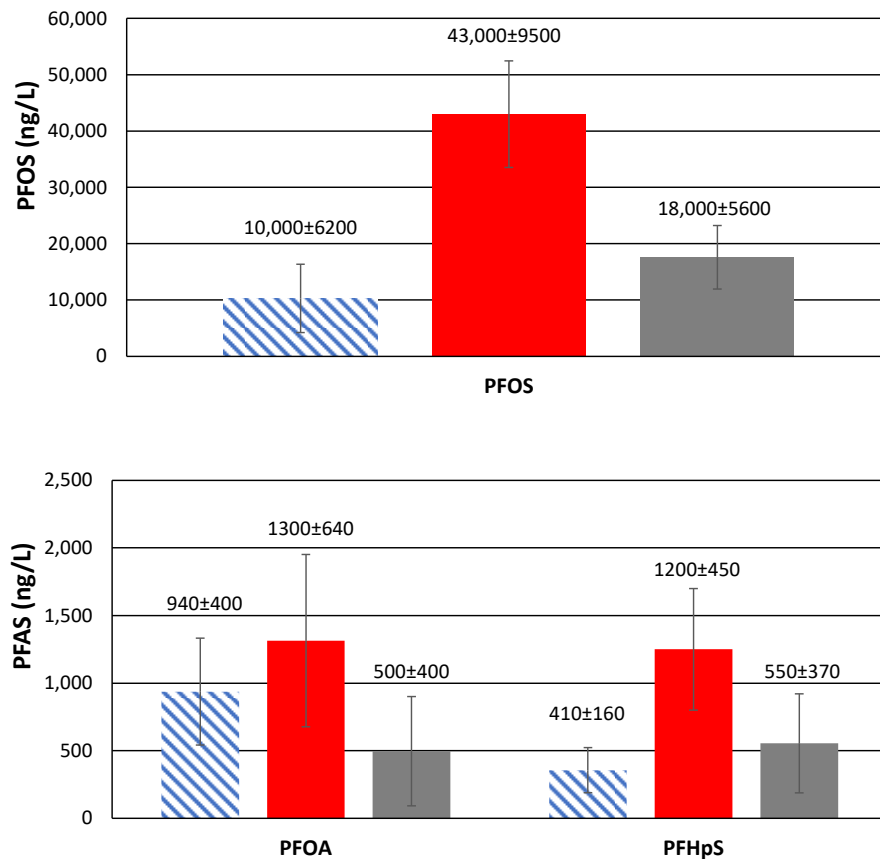


**Figure ES6.** PFAS average porewater concentrations for PFOS, PFHpS, and PFOA over all three rounds of sampling (blue hatched bars). Results are compared to predicted porewater PFAS concentrations that exclude (red bars) or include (gray bars) PFAS sorption to the air-water interface. Error bars for the measured porewater concentrations represent 95% confidence intervals using the shallow (0.61 m bgs) lysimeters over all three sampling rounds. Error bars for the predicted values represent 95% confidence intervals, which are calculated based on propagation of the error (95% confidence intervals) associated with the measured soil and air-water interface sorption coefficients, and the estimated value of the air-water interfacial area. Values shown above bars are the aqueous concentration  $\pm$  95% confidence intervals.

An irrigation system was used to enhance flushing of the PFAS from the unsaturated soils. The irrigation was intermittently paused to assess rebound and to evaluate the changes in PFAS mass discharge to underlying groundwater as a function of overall PFAS mass removal from the AFFF-impacted soil. Results (**Fig. ES7**) for the perfluorinated sulfonates showed that mass porewater concentrations (and thus mass discharge) decreased more rapidly than PFAS soil concentrations, particularly for the longer-chained compounds. This observation is consistent with the batch desorption data, where PFAS aqueous concentrations decreased more rapidly than the soil concentrations (**Fig. ES4**), particularly for the longer-chained PFAS. These results suggest that batch desorption experiments can be useful for predicting field leaching behavior, and that

substantial decreases in PFAS leaching may be obtained with relatively small decreases in soil concentrations.

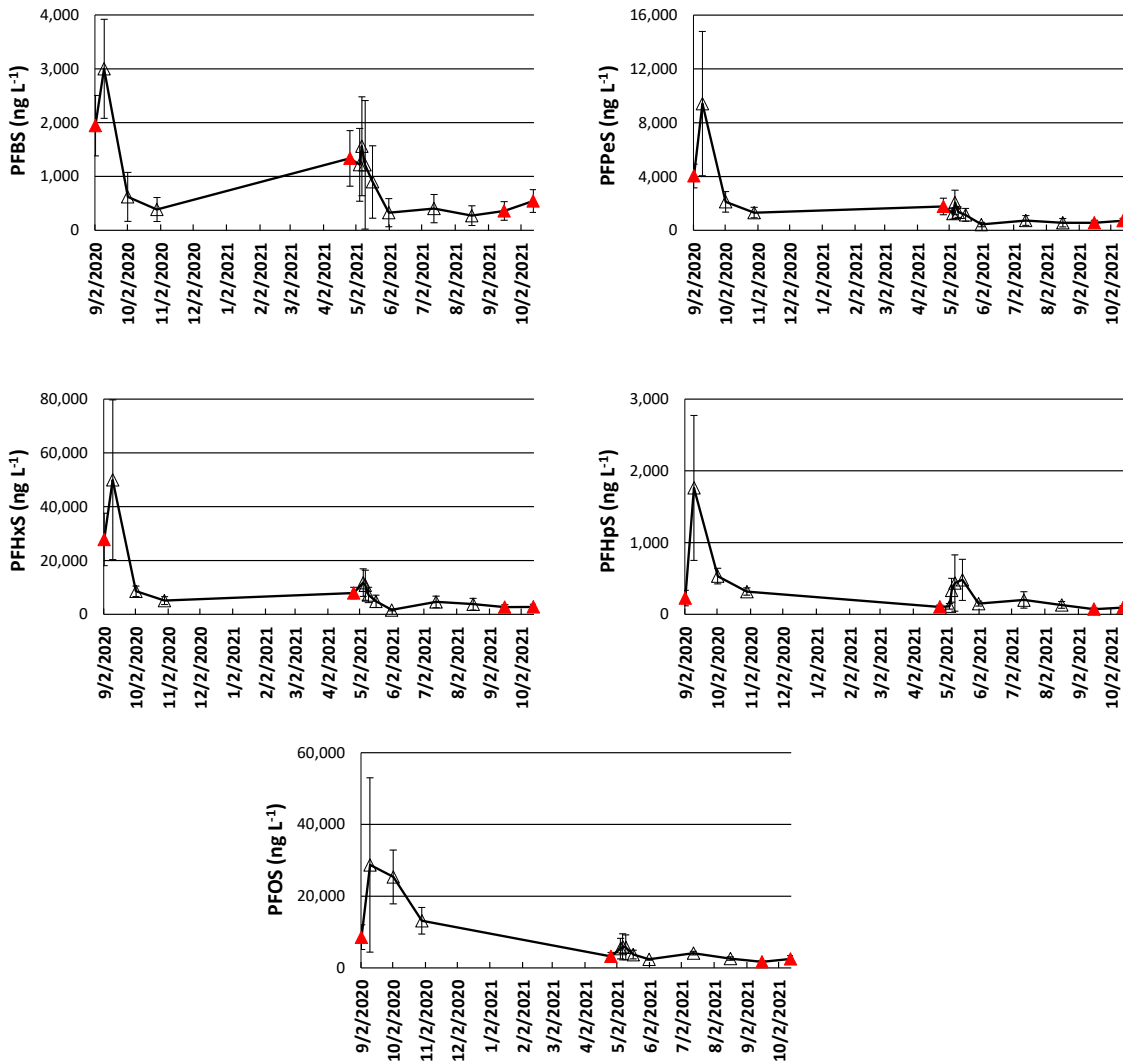


**Figure ES7.** PFSA concentrations measured in the 4 deep lysimeters. Average values are shown, with error bars representing the 95% confidence intervals. For the baseline and intermediate ambient (i.e., no flushing) data, a single average datapoint over the 3 temporal rounds of data is shown for clarity.  $\triangle$  = lysimeter sample collected during active flushing;  $\blacktriangle$  = lysimeter sample collected under ambient (no flushing) conditions.

### **Implications for Future Research and Benefits**

Results from this study showed reasonable temporal and spatial repeatability among the field lysimeters, that field-measured porewater concentrations were well-predicted using equilibrium-based parameters measured independently at the bench scale (using collected soil and porewater samples), and that leaching behavior during long-term flushing was described by batch desorption experiments with respect to the relationship between mass discharge versus mass removal. These findings hold promise that reasonable screening-level predictions of PFAS leaching can be made at the DoD's AFFF impacted sites. While this is quite encouraging, such equilibrium relationships may not be appropriate for all DoD sites.

While the clayey sand, ample rainfall, and shallow depth to water at the test location (JBMDL) is likely typical of many of the DoD's AFFF-impacted source areas on the east coast, conditions at other sites may be much more complex. Soil heterogeneity, arid conditions with large depths to groundwater (which may magnify the impacts of evapotranspiration), and the presence of residual NAPL may not be suitable for the equilibrium modeling applied for this study. Additional research efforts are needed to assess PFAS leaching, and the relationship between measured porewater concentrations and soil concentrations, under a greater range of site conditions. While some efforts with respect to these challenges are currently underway, the data and insight needed to develop and validate predictive long term leaching models likely will require substantial additional laboratory and field efforts.

## 1.0 Objectives

This SERDP project was originally submitted in response to the SERDP Statement of Need ERSON-18-C1 that addressed the need for improved understanding of poly- and perfluoroalkyl substance (PFAS) source areas. Specific items of need included identifying source area characteristics that impact PFAS discharge to groundwater, filling critical data gaps with respect to PFAS transformation and transport, and development of tools to predict long-term PFAS release. This effort employed the use of both bench-scale and field-scale techniques to provide a balance of mechanistic and practical assessment of these processes to rapidly provide the DoD with scientifically-derived information and interpretation to facilitate improved site management of aqueous film forming foam (AFFF) source areas and their associated groundwater plumes. This project was a collaborative and multi-disciplinary effort among scientists and engineers at CDM Smith, the Colorado School of Mines (CSM), Oregon State University (OSU), and APTIM.

Currently, there is little understanding of how PFAS sources in the unsaturated zone decay over time, and how PFAS mass discharge and composition vary as the sources decay. This SERDP project focused on obtaining improved insights into the long-term mass discharge of PFAS from the unsaturated zone of a source area historically impacted by AFFFs. *Using a field test cell, coupled with mechanistic bench-scale experiments, the slow release and transformation of PFAS was evaluated over time.*

The aforementioned lack of knowledge is due, in part, to the complex nature of AFFF sources. AFFF sources are often co-mingled with non-aqueous phase liquid (NAPL) hydrocarbons, and the fluorinated and hydrocarbon mixtures present in AFFF can create complex interfacial and phase behavior. *Furthermore, it is unclear how vadose processes such as wetting-drying cycles, aerobic/anaerobic cycling, and colloidal transport impact source decay, mass discharge and composition.* With respect to transformation, our focus was on the abundant range of precursor compounds that are present in AFFF (Barzen-Hanson et al., 2017), and those that are amenable to abiotic and/or biotic transformation processes.

Key fundamental questions related to the processes that control the long-term mass discharge of PFAS from AFFF-impacted source areas include:

- What is the nature of the long-term PFAS source loading from aged AFFF sources in the unsaturated zone?
- How do the PFAS composition and desorption kinetics vary with time?
- How do variably saturated conditions, including mobilization of natural colloids and changes in ionic strength, impact PFAS release and fate from sources?
- What information and understanding are critical for predicting long-term mass discharge from AFFF-impacted sites?

The overall goals of this project were 1) to attain insight into the transformation and mass discharge of PFAS from AFFF sources that reside in the vadose zone and capillary fringe, and 2) to understand how these processes change over time and with AFFF composition and mass. It is noted that the full range of AFFF-relevant PFAS, including perfluoroalkyl acids (PFAAs) and

PFAS precursors, will be monitored and assessed as part of this project. Specific objectives include the following:

4. ***Understand the nature of PFAS release into vadose zone and capillary fringe pore waters.*** This includes both understanding the nature of the PFAS (i.e., colloidal vs. dissolved) and the impacts of water geochemical conditions (pH, DOC, ionic strength) on their release from soil, and/or interfacial sources.
5. ***Determine the relationship between source removal (including comingled NAPL and hydrocarbon surfactants) and PFAS mass discharge.*** The overall rate of mass discharge is expected to change as both AFFF source mass becomes depleted, and the composition of the source changes due to transformation and preferential removal of more leachable components.
6. ***Attain insight into the role of variable saturation on PFAS fate and transport in the source area.*** This objective includes understanding both physical processes that may enhance or hinder the release of PFAS.
7. ***Develop an approach to predict PFAS mass discharge from the unsaturated zone over time.*** Based on both laboratory and field data, the factors contributing to PFAS mass removal and discharge were mechanistically determined or empirically quantified over time. This information was used to develop a screening model to estimate PFAS mass discharge as a function of time and AFFF source mass remaining.

Collectively, these objectives provided the DoD with the improved insight needed to make scientifically based management decisions for AFFF-impacted sites.

## 2.0 Background

### Source Strength Function.

The relationship between contaminant mass removal and contaminant mass discharge from a source is termed the *source strength function*, and has been a useful tool for assessing and managing source areas for non-aqueous phase liquid (NAPL) sources. For single component NAPL systems, numerous studies have been performed examining the source strength function, with results showing that both field-scale mass transfer processes and phase partitioning contribute to the contaminant mass discharge. The source strength function applied to field data typically takes a form that can be reasonably described using a simple empirical function relating mass discharge to mass removal (Falta et al., 2005; DiFilippo and Brusseau, 2008):

$$1 - \frac{J}{J_0} = \left(1 - \frac{M}{M_0}\right)^{1/n} \quad \text{Eq. 2.1.}$$

where J is the contaminant mass discharge (or flux), M is the contaminant mass, and the subscript 0 refers to the initial value (t=0) of either the discharge or mass.

For multicomponent systems with more complex phase behavior, changes in contaminant composition must be considered when determining the source strength function over the long-term (Eberhardt and Grathwohl, 2002; Christ et al., 2006; Mobile et al., 2012). In such cases, a more mechanistic model is needed to describe the long term mass transfer between the relevant phases. ***Such considerations likely will be needed to assess the source strength function in AFFF source areas.***

Numerous enhanced dissolution studies, where contaminant mass was rapidly removed by physical, chemical, or biological methods to rapidly determine the impact on mass discharge, have been performed for chlorinated solvent systems. Results of these studies have provided mechanistic insights into the processes sustaining chlorinated solvent source areas (Fure et al., 2006; Wang et al., 2014; Schaefer et al., 2016, 2017). By measuring both water and contaminant flux at locations with known contaminant mass (determined by high resolution investigation techniques), mechanistic insight was attained regarding the local source strength function that was independent of field scale flow heterogeneities (e.g., preferential flow). Although such studies have provided great value in management of chlorinated solvent sites, similar studies have not been performed for PFAS emanating from complex AFFF sources. ***This lack of information for PFAS source areas is a critical data gap, as the relationship between AFFF source mass removal and PFAS mass discharge is completely unknown.*** Figure 2.1 provides some hypothetical results for PFAS-enhanced release from the unsaturated zone at a particular test site, and the mechanistic insight that could be attained and used to assess PFAS source areas at other AFFF-impacted sites.

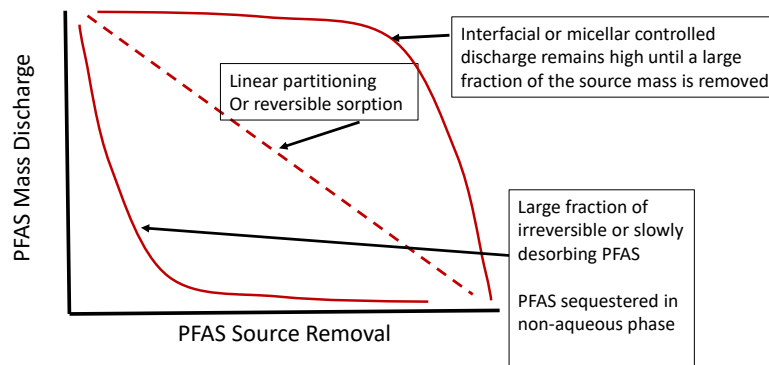


**Figure 2.1.** Three hypothetical cases for the PFAS source strength function, each of which are based on the nature of the unsaturated zone PFAS source. Insight into this functionality will provide the basis for determining plume stability, the potential need for source mitigation, and provide guidance on the extent of treatment needed.

### PFAS Sources

The nature of PFAS in AFFF-impacted source areas is poorly understood. Several studies have suggested that PFAS sources residing in the unsaturated zone are impacting groundwater (e.g., Xiao et al., 2014), thus improved insight regarding the nature and rates of the processes controlling both the long- and short-term mass discharge to groundwater are needed to improve management of these sites. While much of the attention on PFAS has focused on PFAAs, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), release and migration of PFAA precursors from AFFF sources from the unsaturated zone are of equal importance. Transformation of PFAA precursors in the unsaturated zone or after subsequent migration into underlying groundwater can result in increased PFAA groundwater impacts and adversely impact groundwater plumes (Backe et al., 2013). Thus, the nature, fate, and discharge of both PFAAs and PFAA precursors in the unsaturated zone must be understood.

Our recent work investigating an AFFF-impacted source area at Ellsworth AFB showed that PFAS sources are likely comingled with NAPL in the unsaturated zone (McGuire et al., 2014). The combination of NAPL with AFFF could lead to complex phase and partitioning behavior, including interfacial sorption. Because the NAPL (fuel hydrocarbons) and the AFFF (fluoro- and hydrocarbon surfactants) composition changes over time, mass discharge will likely vary over the lifetime of the source. This complex phase behavior could dictate the shape of the source strength function for AFFF sources comingled with NAPLs.

In addition, AFFF-impacted soils and sediments are relatively enriched over groundwater in the anionic long-chain PFSAs and PFCAs as indicated by measurements of individual PFAS (Anderson et al., 2016) and by the total oxidizable (TOP) assay (Houtz et al., 2013). It is plausible to assume that cationic and zwitterionic PFAS are more strongly associated with soil phases, thereby serving as a long term source via slow desorption and/or transformation; alternately,

cationic surfactants might be essentially irreversibly sorbed in vadose zone soils and thus not serve as a significant PFAS source to groundwater. Such behavior could result in a source strength function associated with the bottom curve shown in Figure 2.

Sorption of surfactants to soils is further complicated by the formation of hemimicelles or other monomer interactions, which may form at elevated concentration. The region of hemimicelle formation (Region II) can result in large decreases in sorbed surfactant mass with relatively small changes in aqueous concentration (Adamson and Gast, 1997). For AFFF source areas, this would mean that PFAS mass removal could be large, with little impact on overall PFAS mass discharge (resulting in a source strength function similar to the top curve in Figure 2.1).

These complexities highlight the importance of attaining a fundamental understanding of long-term PFAS release from unsaturated zone sources, and the need to assess PFAS transformation and discharge from an actual field source to ensure that pore scale phase distribution at the relevant scale is preserved.

### Vadose Zone Processes

Vadose zone processes associated with precipitation-induced variably saturated conditions have been well studied. Many of these processes affect the pore water in the vadose zone and capillary fringe, and are likely to impact the release of PFAS from AFFF-impacted source areas. Specifically, naturally-present colloidal levels have been shown to increase during drainage, resulting in a significant enhancement of contaminant migration (Ryan et al., 1998; Cheng and Sayers, 2010). This process occurs as immobile (due to sorption and/or partitioning to immobile solids or non-aqueous phases) contaminants attach to mobile colloids that have a relatively high affinity for the contaminants. Investigations of this process for PFAS have been limited. Rádi et al. (2014) showed that cationic surfactants were substantially bound to colloidal humic materials; studies by Ahrens et al. (2010) and Jia et al. (2010) suggest that natural colloidal and particulate materials increase the apparent solubility of some PFAS. Together, these findings point to the likelihood that the transport of hydrophobic and/or cationic PFAS may be significantly enhanced by natural colloids mobilized during transient wetting phases in the vadose zone. Thus, the source strength function shown in **Figure 2.1** may need to be defined in terms of both total and dissolved PFAS mass discharge.

Variably saturated conditions in the vadose zone also lead to biogeochemical cycling (Hansen et al., 2011), changes in dissolved organic carbon (De Troyer et al., 2014), and potentially changes in ionic strength (Simunek and Suarez, 1994). Numerous studies have been performed to investigate how these processes impact the fate and transport of various compounds in the vadose zone. However, the impacts of these processes on PFAS have received minimal attention. Recent studies (Carmosini and Lee, 2008; Tang et al., 2010; Jeon et al., 2011; Wang et al., 2012) have shown that increases in dissolved organic matter and ionic strength impact sorption of PFAS to solids, and that redox conditions can impact the sorption of PFOS (Ololade et al., 2016). Thus,

these studies suggest that the naturally occurring saturation variability in AFFF-impacted vadose zones will have a significant impact on PFAS partitioning and mass discharge. Improved insight into these processes may also provide means to engineer PFAS mass discharge from the vadose zone, by either enhancing conditions to increase mass discharge (for remedial purposes) or to limit mass discharge for source control.

Finally, the transient wetting and drying due to precipitation events in the vadose zone likely lead to substantial changes in fluid-fluid (water-air or water-NAPL) interfacial area (Schaefer et al., 2000a, 2000b). The surfactant nature of PFAS suggests that fluid-fluid interfacial sorption will occur; recent studies (Psillakis et al., 2009; Enami et al., 2016) have verified water-air sorption for both perfluorinated carboxylates and sulfonates. Given the large values of water-air interfacial areas ( $>100 \text{ cm}^2/\text{cm}^3$ ) present in even coarse-grained vadose zone materials (Schaefer et al., 2000a), as well as the reduction in water-air interfacial tension reduction measured for AFFF solutions (Dlugogorski et al., 2005), PFAS sorption at water-air interfaces in the vadose zone likely will be significant. Previous research has shown that species sorbed at the air-water interface are readily mobilized upon re-wetting of the unsaturated media (e.g., during to a heavy rainfall event) (Sirivithayapakorn and Keller, 2003), thus the water-air sorption of PFAS may enhance mass discharge to the underlying groundwater during rain infiltration.

### 3.0 Materials and Methods

#### 3.1 Site Selection and Detailed Characterization

##### *Site Selection and Preliminary Field Testing*

The former fire training area at the former Naval Air Training Technical Center at the Joint Base McGuire-Dix-Lakehurst (JBMDL, shown in **Figure 3.1**) located in Burlington County, New Jersey was considered to be an ideal candidate for field testing in support of SERDP project ER18-1204 due to its relatively shallow depth to water [less than 10 feet below ground surface (bgs)], sandy vadose zone, and the presence of an aged AFFF source area. To further evaluate the potential viability of the Site for field testing, characterization work was performed in November 2018 to verify adequate percolation through the vadose zone using the Cased Borehole Infiltrometer Testing methodology (Hvorlev 1951; ASTM 2006). Specifically, a series of boreholes were advanced through the vadose zone at the Site using a 4-inch inner diameter (ID) augers. Materials obtained during the hand augering process were subject to lithologic logging. Upon reaching the target depth, a 2-inch ID carbon steel pipe was placed centrally within each open borehole. The annular space was filled with approximately 2 to 3 inches of bentonite chips which were allowed to properly hydrate and native soil. Several inches of 10/20 silica sand were also emplaced inside the carbon steel pipe to protect the soil surface prior to commencement of the percolation test. Following setup, water was added to the borehole and changes in water level at varying initial heads were monitored as a function of time using a water level indicator.

Results from these simple percolation tests showed that a clayey sand zone was present at approximately 6 ft bgs at the initial percolation area (testing location on the right in **Figure 3.2**). However, two percolation test locations within the demonstration area shown in **Figure 3.2** showed that this clayey sand zone was absent, and water percolated freely and rapidly through the vadose zone; this zone was selected for further characterization.



**Figure 3.1.** Test site location – JBMDL.

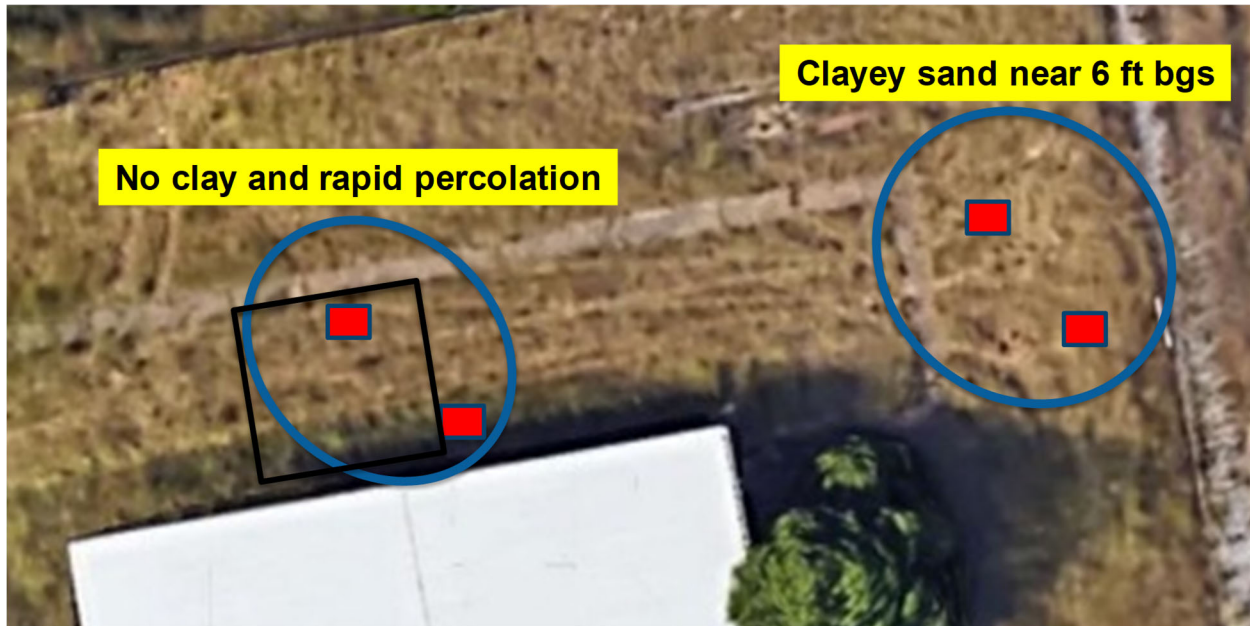


**Figure 3.2.** Approximate locations of the preliminary percolation tests (red squares), with the selected 15 ft x 15 ft test plot indicated by the black square.

#### Detailed Site Characterization

The following field activities were performed at the Site during First Quarter 2019:

- Electrical conductivity (EC) logging was performed at two locations including EC-01 and EC-02 to approximately 15 ft bgs (**Figure 3.3**)
- Lithologic logging and soil sample collection were performed at 5 soil borings (SB-01 through SB-05) within the 14 ft by 14 ft test area of interest using a Geoprobe 7822DT DPT drill rig to approximately 12 ft bgs as shown in **Figure 3.3**. Depth-discrete samples were collected at select boreholes for PFAS analyses (performed at CSM), volatile organic compounds (VOCs) (EMAX Laboratory), total organic carbon (TOC) (EMAX Laboratory), cation exchange capacity (CEC) (EMAX Laboratory), and grain size distribution (CDM Smith Geotechnical Laboratory). A list of samples collected for laboratory analyses is summarized below in **Table 3.1**.
- Seven soil borings in the vicinity of SB-01 (clustered just outside the test area) were advanced to approximately 10 ft bgs to facilitate collection of intact, 2.25-inch ID soil cores in plastic liners for bench-scale laboratory testing. Following collection, each soil core was measured for recovery, cut to appropriate lengths, capped, labeled, and placed in coolers for shipment to Oregon State University, CDM Smith, and CSM.

- One shallow and one deep vapor probe were installed using DPT. Each vapor probe was constructed of 0.75-inch ID PVC casing. A 6-inch sump was constructed at the bottom of each vapor probe. The shallow vapor probe was installed to a total depth of 4 ft bgs and screened from between 1 and 3.5 ft bgs. The deep vapor probe was installed to a total depth of 6.5 ft bgs and screened from between 3 and 5.5 ft bgs. Following installation within the drill rods, 10/20 sands were placed in and around the screen and up to 3 feet above the top of the screen. Bentonite chips were placed above the filter pack and up to the ground surface. Each vapor probe was completed with a 12-inch stickup. ***The sumps of these vapor probes are designed to serve as lysimeters, focusing on water collection during high flow events (positive pore pressure), but water was typically not recovered in these sumps during the field study.***
- Monitoring well MW-01 was installed at SB-02 using the same DPT rig with augering capability in 6-inch ID borehole to a total depth of approximately 15 ft bgs. The monitoring well was constructed of 2-inch ID, Schedule 40 PVC casing and screened between 10 and 15 ft bgs with Schedule 40 PVC, 10-slot screen. The filter pack was constructed of 10/20 sand from the bottom of screen to approximately 2 feet above the top of screen. A 2-foot thick bentonite seal was installed using medium-sized bentonite chips on top of the filter pack; the bentonite chips were allowed to hydrate prior to installation of the grout seal. The remainder of the borehole annulus was filled with Portland cement grout to the ground surface. Similar to the vapor probes, monitoring well MW-01 was completed with a 12-inch stickup. MW-01 was properly developed via a combination of surging and pumping approximately 48 hours following well installation. Following development, groundwater samples were collected and submitted for laboratory analyses of VOCs (EMAX) and PFAS (CSM).
- All investigation boreholes with no planned future use were abandoned via grouting with Portland cement.
- All aqueous IDW generated as part of this field investigation were containerized in 55-gallon drums. A sample of the IDW was collected and submitted for laboratory analyses of VOCs and RCRA metals in accordance with SW-846 8260B and SW-846 6010, respectively. Following proper waste profiling and waste manifest preparation, the waste was transported offsite for disposal as non-hazardous waste via incineration (as per the Base request) on April 11, 2019.

*A detailed description of the methods used for both target and suspect PFAS analyses in soil and water is provided in **Appendix A1**. **Appendix A1** also includes the target analyte list. These PFAS analytical methods were used for the PFAS analyses for all the experiments described in Section 3.*

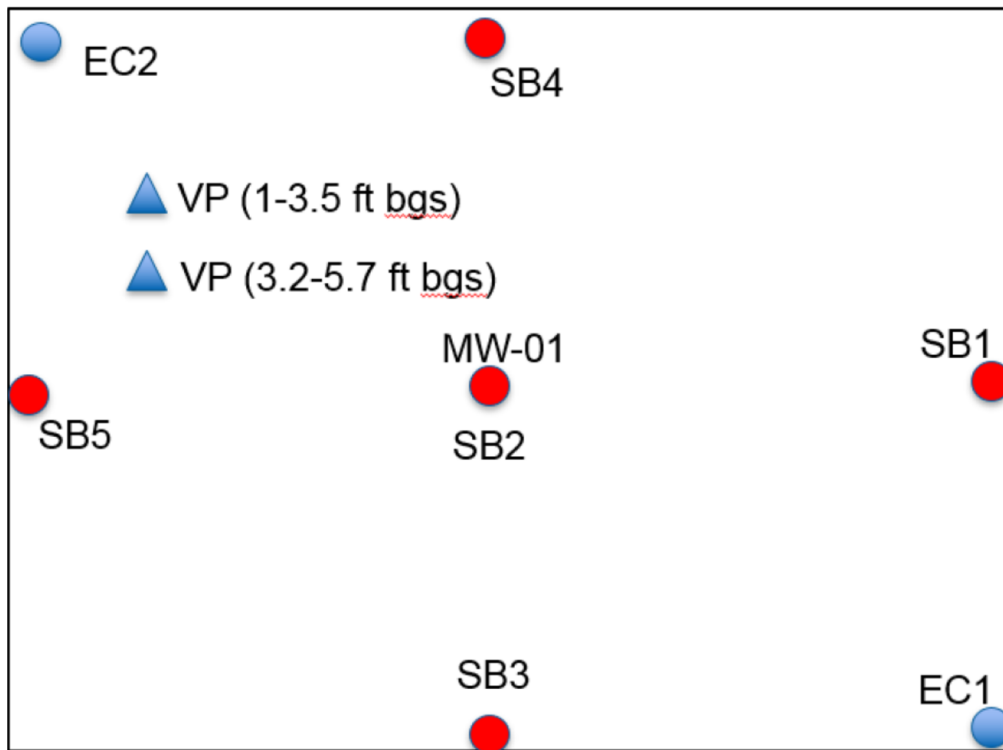


**Figure 3.3.** Investigation locations, and installation of vapor probes (used as lysimeters) and a groundwater monitoring well.

**Table 3.1.** List of Soil Samples Collected

| Soil boring ID | Sampling depth | Samples collected                                                            |
|----------------|----------------|------------------------------------------------------------------------------|
| SB-01          | 0-5 ft bgs     | VOC at 1.8 ft bgs<br>TOC at 1, 2, and 3 ft bgs                               |
|                | 5-10 ft bgs    | VOC at 4.5 ft bgs<br>TOC at 5, 6, 7, 8, 9, 10 ft bgs                         |
|                | 10-12 ft bgs   | VOC at 7.6 ft bgs<br>TOC at 7, 8, and 9 ft bgs<br>PFAS at 7, 8, and 9 ft bgs |
| SB-02          | 0-5 ft bgs     | TOC every 0.25 ft<br>PFAS every 0.25 ft                                      |
|                | 5-10 ft bgs    | TOC every 6 inches<br>PFAS every 6 inches                                    |
|                | 10-12 ft bgs   | VOC at 7.7 ft bgs<br>TOC every 6 inches<br>PFAS every 6 inches               |
| SB-03          | 0-5 ft bgs     | PFAS at 1, 2, 3, and 4 ft bgs<br>CEC at 1, 2, 3, and 4 ft bgs                |
|                | 5-10 ft bgs    | PFAS at 5 and 6 ft bgs<br>CEC at 5, 6, 7, and 8 ft bgs                       |
|                | 10-12 ft bgs   | PFAS at 7, 8 ft bgs                                                          |
| SB-04          | 0-5 ft bgs     | TOC at 2 and 3 ft bgs<br>PFAS at 1, 2, and 3 ft bgs                          |
|                | 5-10 ft bgs    | TOC at 4.25 ft bgs<br>PFAS at 4.25 ft bgs                                    |
|                | 10-12 ft bgs   | TOC at 5 ft bgs<br>PFAS at 5 ft bgs                                          |
| SB-05          | 0-5 ft bgs     | TOC at 1, 2, and 3 ft bgs                                                    |
|                | 5-10 ft bgs    | TOC at 4, 5, and 6 ft bgs<br>PFAS at 4, 5, and 6 ft bgs                      |
|                | 10-12 ft bgs   | TOC at 7, 8, and 9 ft bgs<br>PFAS at 7, 8, and 9 ft bgs                      |

### 3.2 PFAS Desorption and Partitioning to Natural Colloids

#### Desorption Kinetic Experiments

Desorption kinetic experiments were performed to determine the duration required to attain PFAS desorption equilibrium from the collected soils. This information was needed prior to performing the batch experiments focused on attaining the equilibrium desorption isotherms.

The desorption batch kinetic testing was performed using source area soils collected from the AFFF-impacted site at Joint Base McGuire-Dix-Lakehurst (JBMDL), as described in Section 2.1. Shallow soil (0 – 3 ft bgs) and deep soil (3 – 8 ft bgs) were used for testing. Before proceeding with the experiment, all mixing utensils, labware, bottles, and collection vessels were pre-rinsed with analytical grade methanol and deionized water, and then air-dried. Shallow soil was homogenized in a 1-gallon HDPE bottle, capped and shaken to mix, and then mixed again using a stainless-steel spoon. This homogenization procedure was repeated for the deep soil. A minimum of two 10-g samples of the homogenized soil from each zone (shallow and deep) were collected in 50-mL polypropylene conical tubes and sent to the Colorado School of Mines to determine the PFAS levels (target and suspect analytes) in the homogenized soils.

The kinetic batch desorption tests were performed using 1-L high density polyethylene bottles (Figure 3.4). For each soil (shallow and deep), duplicate bottles were prepared. 200 g of homogenized soil (either shallow or deep) and 500 mL of 0.01 M NaCl aqueous solution were added to each bottle. After capping, bottles were vigorously hand shaken, and were then incubated and automatically at 20°C. At each sampling event, after settling for approximately 1 hour, the supernatant was sampled. These aqueous samples were subsequently analyzed for PFAS (target and suspect analytes) by OSU. Details of the PFAS analytical are provided in (Schaefer et al., 2020). Bottles were prepared in duplicate for each soil (shallow and deep).



**Figure 3.4.** Batch desorption tests.

*Testing to assess potential PFAS adsorption to natural colloidal material is described in Appendix A3.*

### Desorption Equilibrium Isotherm Experiments

Using the information attained from the desorption kinetic experiments, equilibrium desorption isotherm experiments were performed for both the shallow and deep soils. This desorption isotherm testing was performed to obtain key insight into the release of PFAS during leaching, and potentially identify the fraction of PFAS that was not readily desorbed from the soil.

Equilibrium (or, near equilibrium) soil desorption isotherm experiments were performed using batch soil-water slurries (similar to that employed for the kinetic testing) and employing a serial dilution approach. Experiments were performed using both the homogenized shallow (0-3 ft bgs) and deep (3-8 ft bgs) soils. Approximately 10 g of soil and 26 mL of 0.01 M NaCl were initially added into each 250-mL HDPE bottle that was pre-rinsed with methanol and deionized water. Control conditions containing no soil were also prepared to evaluate cross-contamination potential. All experimental conditions were prepared in triplicate. Following initial set-up, all bottles were placed on a temperature-controlled shaker table at 20°C and agitated at 80 rpm.

An equilibration time of approximately 200 hours was targeted for the shallow soil, and 96 hours for the deep soil; these equilibration times were based on the results of the kinetic desorption experiments. Seven dilution events were performed for each soil, accompanied by a sampling event for each dilution step. At each sampling event, the bottles were removed from the shaker to allow for settling (4 hours), after which the supernatant was sampled. After sampling, the bottles were replaced with a fresh volume of 0.01 M NaCl. The volume replaced ranged from 26 to 208 mL, as the dilution volume was increased as the experiment progressed. Collected samples were analyzed for PFAS (target and suspect analytes) by OSU. Triplicate bottles were prepared for both the shallow and deep soils.

The PFAS mass remaining in the soil after each sequential dilution step was calculated as the difference between the PFAS mass initially in the soil (directly measured via soil analysis and based on the soil concentrations presented in **Table 4.2**) and the cumulative PFAS mass desorbed into the aqueous phase for each dilution step. Applying approaches used by others (Chen et al., 2016, Kan et al., 1998), a linear desorption isotherm was employed to determine both the desorption  $K_d$  value (slope of the regressed curve, and applied to the labile PFAS mass sorbed to the soil) and the non-labile soil concentration (y-intercept of the regressed line). This is described in Eq. 1 as follows:

$$C_s = K_d C + S^{NL} \quad \text{Eq. 3.1}$$

where  $C_s$  is the total (labile and non-labile) PFAS soil concentration,  $C$  is the PFAS aqueous concentration, and  $S^{NL}$  is the non-labile PFAS soil concentration. Eq. 3.1 was applied to each of the PFAS examined in this study. It is noted that the  $K_d$  in Eq. 3.1 describes the aqueous-solid partitioning associated with the labile fraction only.

### 3.3 Unsaturated Column Experiments

Historically AFFF-impacted sandy soil was collected from 0 to 8 feet below ground surface (bgs) and divided into shallow (0-3 ft bgs) and deep (3-8 ft bgs) intervals. Each interval was air-dried, sieved to 2 mm, and homogenized. The shallow and deep soils had organic carbon contents of 0.00068 g/g and 0.0034 g/g, respectively. The synthetic rainwater used was a solution of  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{HCl}$  in deionized water (pH 5).

The soil columns were constructed with 1-inch diameter clear schedule 40 PVC pipes and caps. Each column was 10.2 inches in length and all fittings were sealed using silicone-based sealant. All tubing was 1/16" diameter Tygon® transfer tubing.

#### *Constant Saturation Conditions*

Four columns were packed with the shallow interval soil and six columns were packed with the deep interval soil. The columns were dry packed in 1 cm lifts and manually compressed between lifts. One centimeter of clean coarse silica sand was placed on top of the packed soil to encourage even flow distribution.

Four of the columns (1 shallow, 3 deep) were operated under saturated conditions. Prior to filling, the columns were purged with carbon dioxide to ensure 100% saturation. The saturated columns were filled with bottom-to-top flow. The other 6 columns (3 shallow, 3 deep) were operated under unsaturated conditions using top-to-bottom flow and a manifold vacuum pump attached at the bottom. The degree of saturation in the unsaturated columns was controlled by the vacuum and monitored gravimetrically.

Initially, the soil columns were operated under constant saturation conditions. Synthetic rainwater was applied to the columns at a rate of 0.166 mL/ minute and the effluent was collected at 15- and 30-minute intervals. The unsaturated soil columns were operated at approximately 65% saturated. Flow events occurred 6 hours a day for 5 consecutive days and were followed by 7-12 days of no-flow. The soil did not undergo drying during the no-flow events. This process was repeated 3 times.

#### *Variable Saturation Conditions*

Following the constant saturation condition experiments, the unsaturated columns were operated under variable saturation conditions. During the variable saturation experiments, the unsaturated columns were dried to approximately 30% saturated then 25.7 mL of artificial rainwater was applied to each column at a rate of 0.166 mL/ minute. The columns reached a maximum saturation of approximately 80-85%. To facilitate drainage, the vacuum pressure at the bottom of the column was gradually increased and the column effluent was collected at regular time intervals. Drainage

took 4-6 hours after each wetting event. The variable saturation cycles of drying, wetting, and draining were repeated 5 times.

#### *PFAS Analysis*

The soils and column effluents were analyzed for PFAS using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) using negative (ESI-) and positive (ESI+) mode electrospray ionization. All soil samples were extracted using the method published by Nickerson et. al. (2020). For PFAS without appropriate reference standards available, suspect analysis was used to identify and semi-quantify the compounds.

### **3.4 Biotic and Abiotic Transformation of AFFF Source Materials**

Two soil cores, SB09 and SB10 (collected adjacent to SB-1 in **Figure 2.3**), were homogenized via mixing according to depth: shallow (0-5 ft bgs) and deep (5-10 ft bgs), resulting in a total of four homogenized blocks (SB09 0-5', SB09 5-10', SB10 0-5', and SB10 5-10'). After homogenization, approximately 300 g of each soil type was subsampled and transferred to a glass bottle for sterilization via gamma irradiation. Gamma irradiation was performed to keep the temperature of sterilization as low as possible in order to avoid potential thermal impacts to PFAS and retain as much similarity as possible between sterilized and unsterilized samples (Buchan et. al., 2012). Sterilization was performed at the Oregon State University Radiation Center with each bottle subject to gamma irradiation for 10 hours and receiving a total of 5 MegaRads.

Batch transformation experiments were prepared by placing 1 g of unsterilized soil sample in 50 mL polypropylene tubes (VWR, Radnor, PA, USA). For each soil core and depth (shallow and deep), the following conditions were prepared: abiotic aerobic, biotic aerobic, and biotic anaerobic (**Figure 3.5**). Abiotic tubes consisted of soil from the gamma irradiated sub samples described above. Aerobic conditions are maintained by purging the tubes with air every 2-3 days. To ensure that aerobic soil samples did not dry out during the experiment, 200  $\mu$ L of water was applied at 17 weeks to aerobic tubes and, if necessary, an additional water amendment will be made. Anaerobic conditions were achieved by flushing the tube with nitrogen gas for 20 seconds, capping, and storing in a nitrogen flushed heat sealed Mylar bag. All tubes are incubated in the dark at 22 °C. Bottles were sampled sacrificially.



**Figure 3.5.** Experimental set-up for the batch transformation experiments.

The experimental design is presented below in **Table 3.2**. All control conditions (time = 0) were prepared as n=4 replicates. Each four week time point for both cores includes an n=4 replicate to allow for %RSD to be calculated for the corresponding analytical sequence. Core SB09 contains n=3 replicates for all four week time points. All other samples in each time point are individual. A total of 504 soil samples have been prepared for the time course.

**Table 3.2.** Experimental design with number of samples for each block

|           |       |                  | Total Samples Prepared (#) |    |    |    |    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|-----------|-------|------------------|----------------------------|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|           |       |                  | t0                         | t2 | t4 | t6 | t8 | t10 | t12 | t14 | t16 | t18 | t20 | t22 | t24 | t26 | t28 | t30 | t32 | t34 | t36 | t38 | t40 | t42 | t44 | t46 | t48 |
| SB 09     | 0-5'  | Abiotic Aerobic  | 4                          | 1  | 4  | 1  | 3  | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
|           |       | Biotic Aerobic   | 4                          | 1  | 3  | 1  | 4  | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
|           |       | Biotic Anaerobic | 4                          | 1  | 3  | 1  | 3  | 1   | 4   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
|           | 5-10' | Abiotic Aerobic  | 4                          | 1  | 3  | 1  | 3  | 1   | 3   | 1   | 4   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
|           |       | Biotic Aerobic   | 4                          | 1  | 3  | 1  | 3  | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 4   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
|           |       | Biotic Anaerobic | 4                          | 1  | 3  | 1  | 3  | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 4   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   | 1   | 3   |
| Sub-Total |       |                  | 24                         | 6  | 19 | 6  | 19 | 6   | 19  | 6   | 19  | 6   | 19  | 6   | 19  | 6   | 18  | 6   | 18  | 6   | 18  | 6   | 18  | 6   | 18  | 6   | 18  |

|           |       |                  |    |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|-----------|-------|------------------|----|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SB 10     | 0-5'  | Abiotic Aerobic  | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|           |       | Biotic Aerobic   | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
|           |       | Biotic Anaerobic | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 |
|           | 5-10' | Abiotic Aerobic  | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 | 1 |
|           |       | Biotic Aerobic   | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 | 1 | 1 |
|           |       | Biotic Anaerobic | 4  | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 4 | 1 |
| Sub-Total |       |                  | 24 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 6 | 9 | 6 | 9 | 6 | 9 | 6 | 9 | 6 | 9 | 6 | 9 |

The soil extraction procedure was performed as described in Nickerson et. al. 2020. Briefly, 0.5g of soil was spiked with 4 ng of isotopically labeled surrogate standards. The soil sample was then exposed to two rounds of basic extraction and two rounds of acidic extraction. The resulting extracts were passed through dispersive SPE, neutralized, blown to dryness under nitrogen gas, reconstituted in 1.5 mL of solvent, and combined to produce a final 3 mL extract. A 937.5  $\mu$ L aliquot of extract was combined with 25  $\mu$ L of isotopically labeled internal standards and 537.5  $\mu$ L of HPLC grade methanol to produce a 1500  $\mu$ L sample. Concentrations were determined via LC MS/MS according to Backe et. al. 2013. Briefly a 900  $\mu$ L large volume injection was loaded onto two Zorbax amino propyl and one Zorbax sil guard column for ion exchange under a gradient of HPLC grade water. The gradient was shifted to 10mM ammonium acetate in HPLC grade methanol to exchange the analytes off of the guard columns and undergo reverse phase separation on a C18 analytical column.

Comparison between control groups (time zero) and the final time point were done via two tail T-tests. Concentrations that were reported as <LOD or <LOQ were substituted with their theoretical maximum values, 0.06 and 0.2  $\mu$ g/kg respectively, to improve the accuracy of the statistics. Without these substitutions the statistical analysis would ignore these concentrations, however, we need to ensure that we capture all concentration losses within the statistics even if they decreased below instrument sensitivity.

### 3.5 Field Test Cell

*Please note that portions of Section 3.5 have been reprinted (adapted) with permission from {Leaching of perfluoroalkyl acids during unsaturated zone flushing at a field site impacted with aqueous film forming foam. Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R. et al., Environ. Sci. Technol., 57, 1940-1948}. Copyright 2023. American Chemical Society, and from {A field study to assess the role of air-water interfacial sorption on PFAS leaching in an AFFF source area. Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R. et al., J. Contam. Hydrol. 248} Copyright 2022. Elsevier.*

#### 3.5.1 Installation

Using the 14 ft x 14 ft (4.3 m x 4.3 m) test plot described in Section 3.1, a field test cell to assess PFAS leaching from the unsaturated zone under both ambient and enhanced flushing conditions. Sheet-piling was installed to isolate the test cell with respect to water migration in the unsaturated zone. Approximately 1.5 years following the soil core collection and site investigation activities described in Section 3.1, porous cup suction lysimeters (Soil Moisture Equipment Corp., Goleta, CA) were installed at various depths to monitor porewater. **Table 3.3** summarizes the lysimeter installation depths. A two-inch layer of sand was placed on the test cell to serve as a contact barrier between the PFAS-impacted soil surface, and to facilitate even flow of percolating water during the enhanced flushing (described in Section 3.5.2).

The lysimeters used were constructed of PVC and had a diameter of 4.8 cm. The ceramic porous cup was 3.8 cm long with a 2 bar bubbling pressure; lysimeter lengths ranged from 0.3 m to 1.5 m.

Lysimeters were installed using hand augers. A silica flour (200 mesh) slurry was used in the lysimeter boreholes such that the annular space was filled with the silica flour several centimeters above the porous cup. A few centimeters of coarse sand was layered on top of the silica flour, and the remaining annular space was filled with medium-size bentonite chips to the ground surface. Lysimeters were connected to a vacuum manifold system for sample collection.

A bromide tracer was included with the silica flour slurry. After collecting an initial round of porewater samples to flush the system, the initial round of samples for PFAS analysis was collected. This initial round of samples for PFAS analysis also was analyzed for bromide. These measured bromide concentrations were less than 10% of initial bromide concentrations, indicating that the water captured in the lysimeters was representative of natural porewater that was not artificially diluted by the slurry water. Parallel laboratory testing with both the lysimeters and silica flour showed that PFOS sorption to the silica flour and lysimeter was negligible.

Three moisture probes (PR2/6 probes, manufactured by Delta-T Devices) were installed in the unsaturated zone. A sprinkler system also was installed to facilitate flushing. Finally, a shallow monitoring well was installed in the center of the test cell, which was used to monitor the water table elevation (which remained below the deepest lysimeters). The test cell, lysimeters, moisture probes, and other components of the test cell are shown in **Figure 3.6**. Additional details of the test cell installation, including details of the lysimeter installation, are provided in Schaefer et al. (2022).

**Table 3.3.** Lysimeter depths. Lysimeters L-2 and L-8, installed at the very shallow depth below ground surface of 0.15 m, also were not used in this study. This shallow depth, coupled with rapid water infiltration into the sandy soil, likely were not representative of equilibrium conditions and PFAS porewaters impacting underlying groundwater.

| Lysimeter | Depth<br>(m below ground surface) |
|-----------|-----------------------------------|
| L-1       | 0.61                              |
| L-2       | 0.15                              |
| L-3       | 0.61                              |
| L-4       | 1.5                               |
| L-5       | 0.61                              |
| L-6       | 1.5                               |
| L-7       | 1.2                               |
| L-8       | 0.15                              |
| L-9       | 0.61                              |
| L-10      | 1.2                               |
| L-11      | 0.61                              |

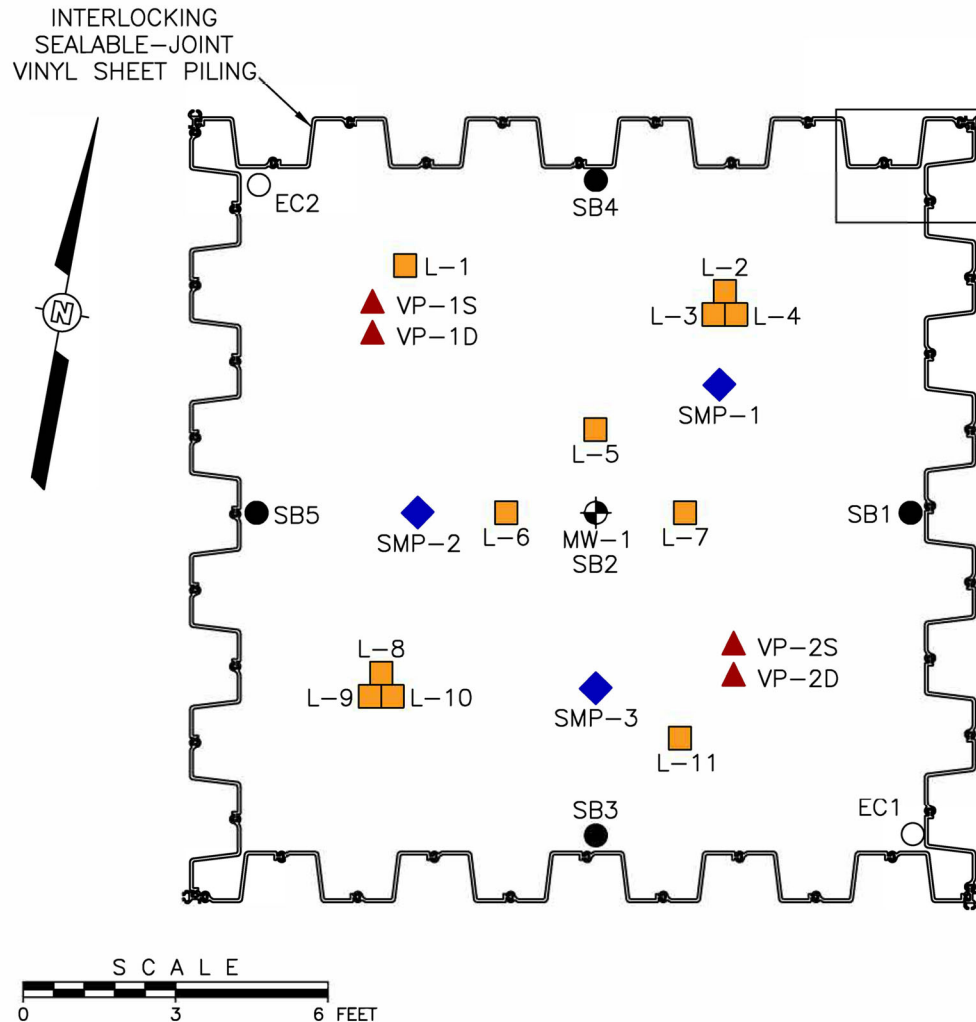


**Figure 3.6** Details of installed system components. L-1 through L-11 are the lysimeters. SMP-1 through SMP-3 are the soil moisture probe locations. VP indicates locations for vapor probes. EC1 and EC2 indicate locations where electrical conductivity probes were used, and SB1 through SB5 are soil bore locations. MW-1 is a shallow monitoring well used to monitor the water table elevation.

### 3.5.2 Sampling and Flushing

Lysimeter sampling occurred using a vacuum manifold system, where a vacuum of approximately 30 to 45 cb was applied over a set time interval of approximately 18 hours to 5 days for each sampling event. Purging of the initial porewater collected within each lysimeter was performed to ensure that PFAS concentrations measured in the collected samples were representative of porewater and not moisture added during the lysimeter installation.

Three rounds of sampling were performed over a 49 day period (July 15, 2020 to September 2, 2020), where the lysimeters shown in **Table 3.3** were sampled. Samples were collected in 1 L glass bottles for each lysimeter within the manifold system. Collected porewater volumes in each glass bottle typically ranged from 5 to 300 mL per sampling event. Collected lysimeter porewater samples were transferred to 50 mL polypropylene centrifuge tubes for PFAS analysis. Select samples were also analyzed for TOC via combustion analysis, pH, and electrical conductivity. PFAS analyses on the collected aqueous porewater samples was performed using an Agilent 1260 series HPLC (Santa Clara, CA) and a SCIEX QTOF X500R (Framingham, MA) using positive and negative mode electrospray ionization for analysis of cationic/zwitterionic and anionic/zwitterionic compounds (respectively) via orthogonal chromatography, as previously described in Barzen-Hansen et al (2015). Additional details of the PFAS analyses, including screening and semiquantitation of suspect analytes, are described in Schaefer et al. (2022).

Irrigation was performed using a network of sprinklers set to deliver a determined volume of water over a pre-determined time interval each day. Care was taken to ensure that the irrigation rate did not exceed the rate of water uptake into the subsurface (i.e., minimal ponding observed visually), and that the water distribution was uniform over the surface. The two-inch layer of clean sand placed on the soil surface of the test plot was intended to improve flow uniformity into the native soil. A summary of system operation and monitoring is provided in **Table 3.4**. Baseline PFAS porewater concentrations prior to flushing were initially measured (three rounds) under ambient conditions, as described in the previous paragraph. These baseline rounds were followed by 51 days of flushing/irrigation prior to 5 months of non-flushing (ambient conditions) until the following spring. After collecting three rounds of porewater measurements under ambient (no flushing) conditions in the spring, flushing was resumed; flushing intensity was increased after the first 13 days of flushing in the spring. After 103 days of total flushing in the spring/summer of 2021, porewater samples were collected after one and two months of non-flushing (ambient) conditions.

**Table 3.4.** Summary of system operation and monitoring during both active flushing and ambient (no-flushing) conditions.

| Phase                                   | Dates                                | Flushing Rate (m <sup>3</sup> d <sup>-1</sup> ) | Lysimeter Monitoring |
|-----------------------------------------|--------------------------------------|-------------------------------------------------|----------------------|
| <b>Baseline ambient</b>                 | July 14, 2020 – September 2, 2020    | 0                                               | 3 rounds             |
| <b>Phase 1 flushing</b>                 | September 2, 2020 – October 29, 2020 | 1.2 <sup>1</sup>                                | 3 rounds             |
| <b>Intermediate ambient<sup>2</sup></b> | April 7, 2021- April 26, 2021        | 0                                               | 3 rounds             |
| <b>Phase 2 flushing</b>                 | May 4, 2021 – May 17, 2021           | 1.2 <sup>1</sup>                                | 4 rounds             |
| <b>Phase 3 flushing</b>                 | May 18, 2021-August 17, 2021         | 3.7 <sup>3</sup>                                | 3 rounds             |
| <b>Final Ambient</b>                    | August 17, 2021- October 13, 2021    | 0                                               | 2 rounds             |

<sup>1</sup> Water volume delivered over an approximate 2-hour interval each day.

<sup>2</sup> intermediate ambient monitoring initiated approximately 5 months after cessation of Phase 1 flushing

<sup>3</sup> Water volume delivered over a 10 hour interval each day.

Porewater samples were prepared using a micro liquid-liquid extraction method modified from that previously described in Backe et al. (2013). Analysis of anionic PFAS were performed on an Agilent 1260 Infinity II HPLC (Santa Clara, CA) coupled to a Sciex X500R QTOF (Framingham, MA). Detailed descriptions of the extraction and analysis are provided in Schaefer et al. (2022, 2023).

## 4.0 Results and Discussion

### 4.1 Detailed Characterization

Key findings from the detailed site characterization performed in January, 2019 are as follows:

- No VOCs were detected in any of the soil or groundwater samples collected, which is consistent with the fact that this location was only used for foam testing, but not any fire fighting activities.
- Soil TOC results are graphically illustrated in **Figure 3.1**. In all four borings (SB-01, SB-02, SB-04, and SB-05) where depth-discrete TOC samples were collected, elevated TOC measurements (greater than 1,000 mg/kg) were limited to samples collected between 0 and 2 ft bgs. Note that high resolution sampling was performed in SB-02.

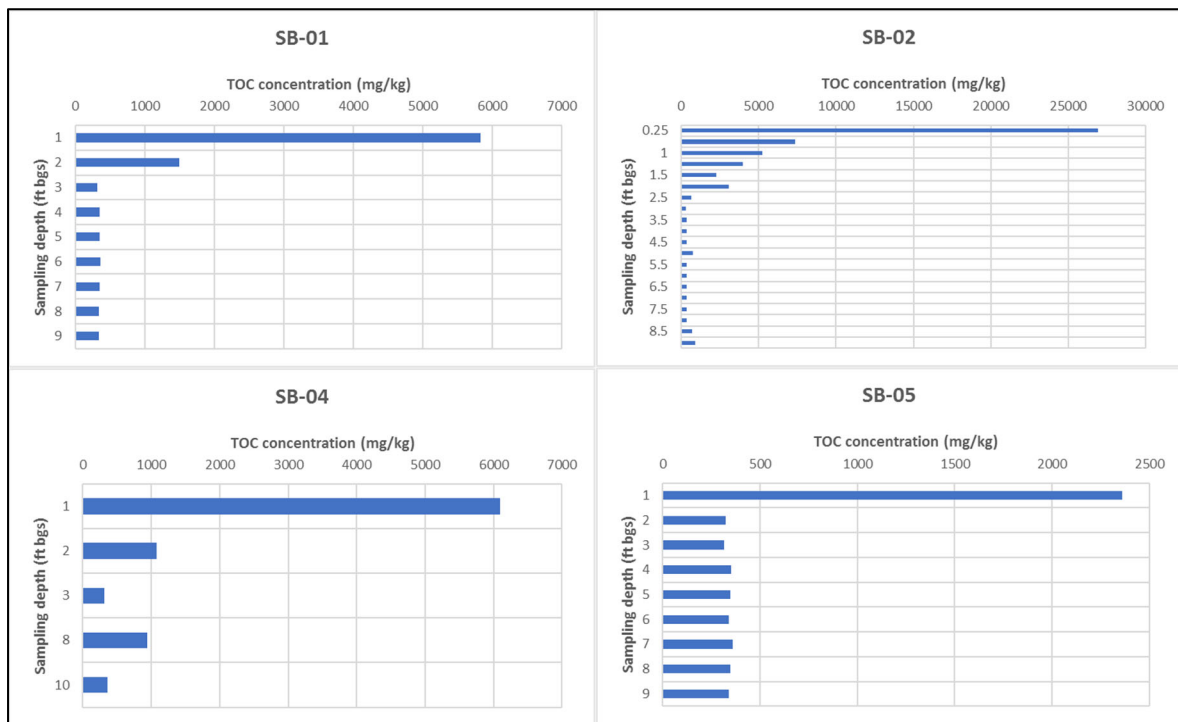


**Figure 4.1.** TOC results in collected soil borings.

- Cation exchange capacity (CEC) results for depth-discrete soil samples collected at soil boring SB-03 are graphically depicted in **Figure 4.2**. Relatively high CEC values are likely attributable to the presence of clay in site soil.

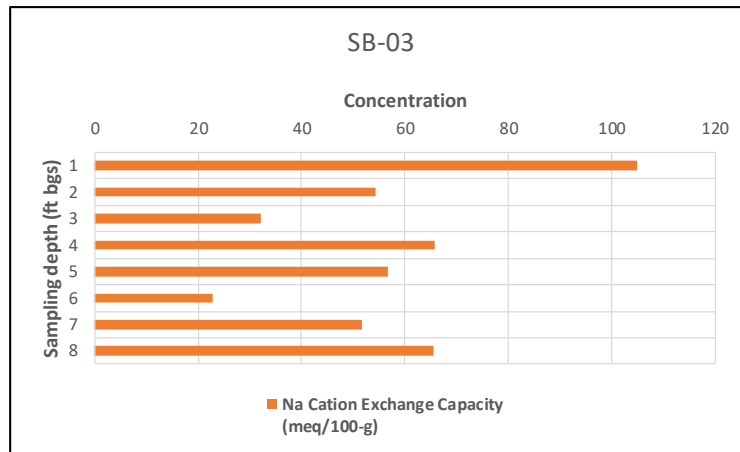


**Figure 4.2.** CEC results for soil collected in borehole SB-03

- As shown in **Figure 4.3**, total PFAS (target + suspect) concentrations are most abundant in the shallow soil within 1 foot of the ground surface. PFAS concentrations below 1 ft bgs are approximately 20-times less than these highly concentrated shallow soils. Also, there is no apparent decreasing trend in PFAS soil concentration below approximately 1 ft bgs to the water table.
- PFAS concentrations show a clear correlation with both TOC and CEC levels, as shown in **Figure 4.4**. These correlations suggest that the elevated PFAS concentrations within 1 ft of the ground surface may be attributable to elevated sorption related to the high TOC/CEC content of these shallow soils.

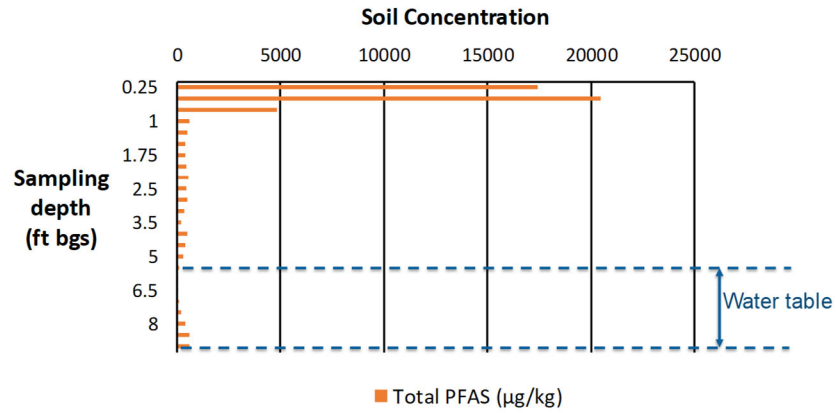


**Figure 4.3** PFAS (target + suspect analytes) soil concentrations measured in soil bore SB02. Results from other soil boring, which were attained at a significantly lower sampling density, were consistent with the results observed in SB02.

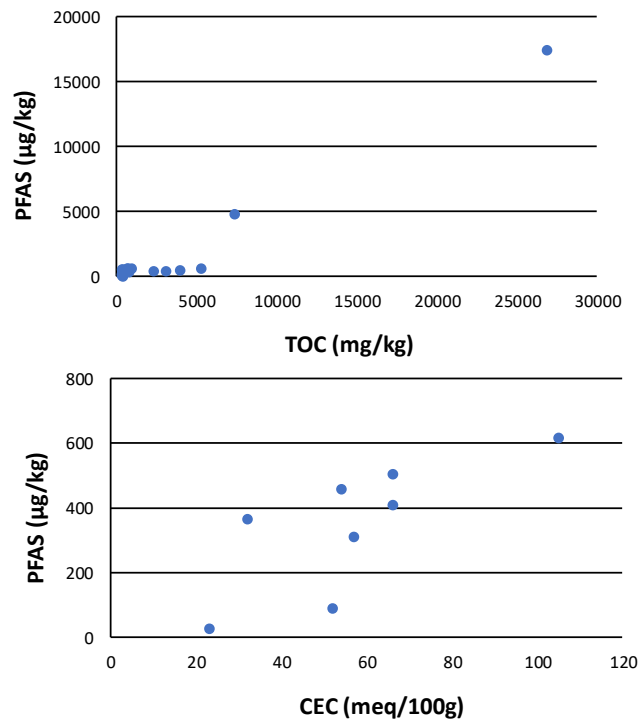


**Figure 4.4** PFAS concentrations as a function of soil TOC (top) and soil CEC (bottom).

- As shown in **Figure 4.5**, PFOS is the most abundant PFAA (and, target analyte) present in the soil. Thus, PFOS is likely a key PFAS at this site.
- **Figure 4.6** shows the PFAS composition as a function of depth. These data show that PFASs (primarily PFOS) abound near the surface, but polyfluorinated precursors become most abundant from approximately 1 to 4 ft bgs. The data also suggest precursor transformation has occurred, as indicated by the appearance of PFCAs and 8:2 FtS with depth, presumably from the transformation of the overlying polyfluorinated compounds (ECF precursors and 8:2 FtS precursors, respectively). It is also important to note that the ECF precursors are dominated by 6-carbon perfluorinated chain compounds, which may explain the abundance of the PFHxA relative to FOSA.

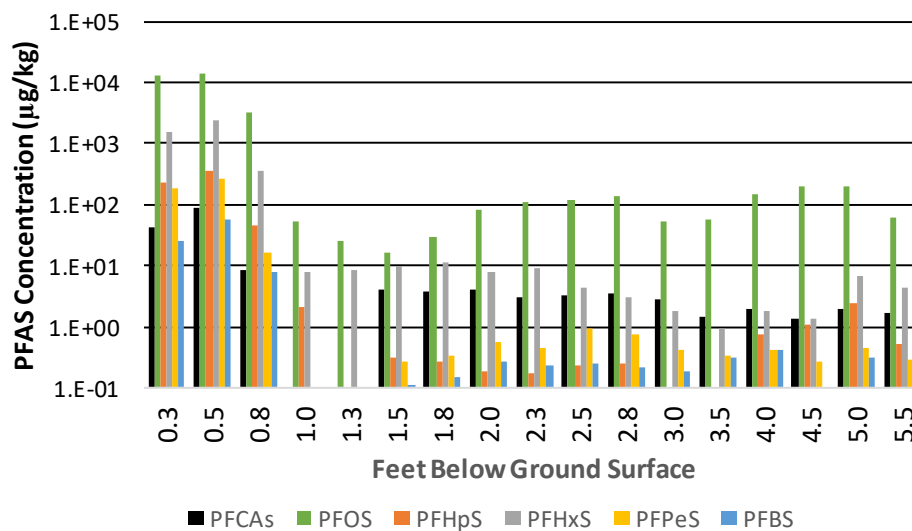


**Figure 4.5** PFAAs present at the site, as measured in borehole SB02. PFCA represents the sum of the perfluorinated carboxylic acids. PFOS is the most abundant PFAS present.

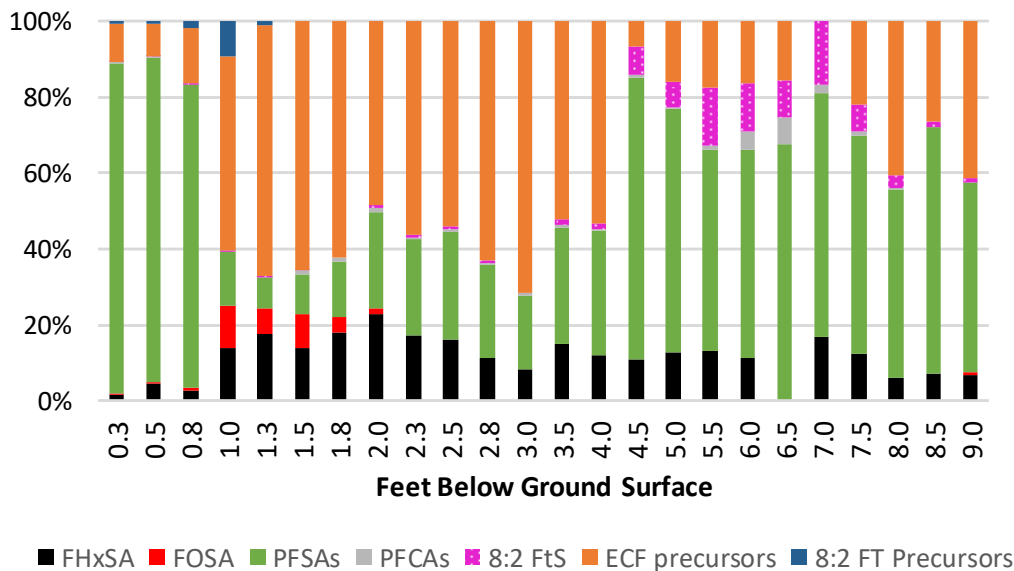


**Figure 4.6.** PFAS composition as a function of depth in SB02. ECF precursors represent polyfluorinated compounds associated with electrochemical fluorination processes, PFSA are perfluorinated sulfonic acids, PFC are perfluorinated carboxylic acids, FHxSA is perfluorohexane sulfonamide, and FOSA is perfluorooctane sulfonamide.

## 4.2 PFAS Desorption

### 4.2.1 Desorption Kinetics

#### *Deep Soil*

A summary of the target PFAS, along with their acronym and chemical formula, is provided in **Appendix A1**. Changes in PFAA aqueous concentrations as a function of time during the kinetic desorption test in the deep soil are shown in **Figure 4.7**. Corresponding results for the other identified PFAS are plotted in **Figure 4.8**. Results show that, with the exception of 6:2 FtS, PFPeS, PFHxS and PFHxSi, apparent equilibrium is attained within 48 hours for all PFAS. These results are consistent with a conceptual model where PFAS are desorbed from equilibrium-controlled domains that are not kinetically controlled, and are not in mass transfer controlled domains that might include soil micropores (Li and Werth, 2004; Qin et al., 2017) and/or organic matter (Xing and Pignatello, 1996). The comparatively slow desorption of 6:2 FtS, PFPeS, PFHxS and PFHxSi is not readily explained.

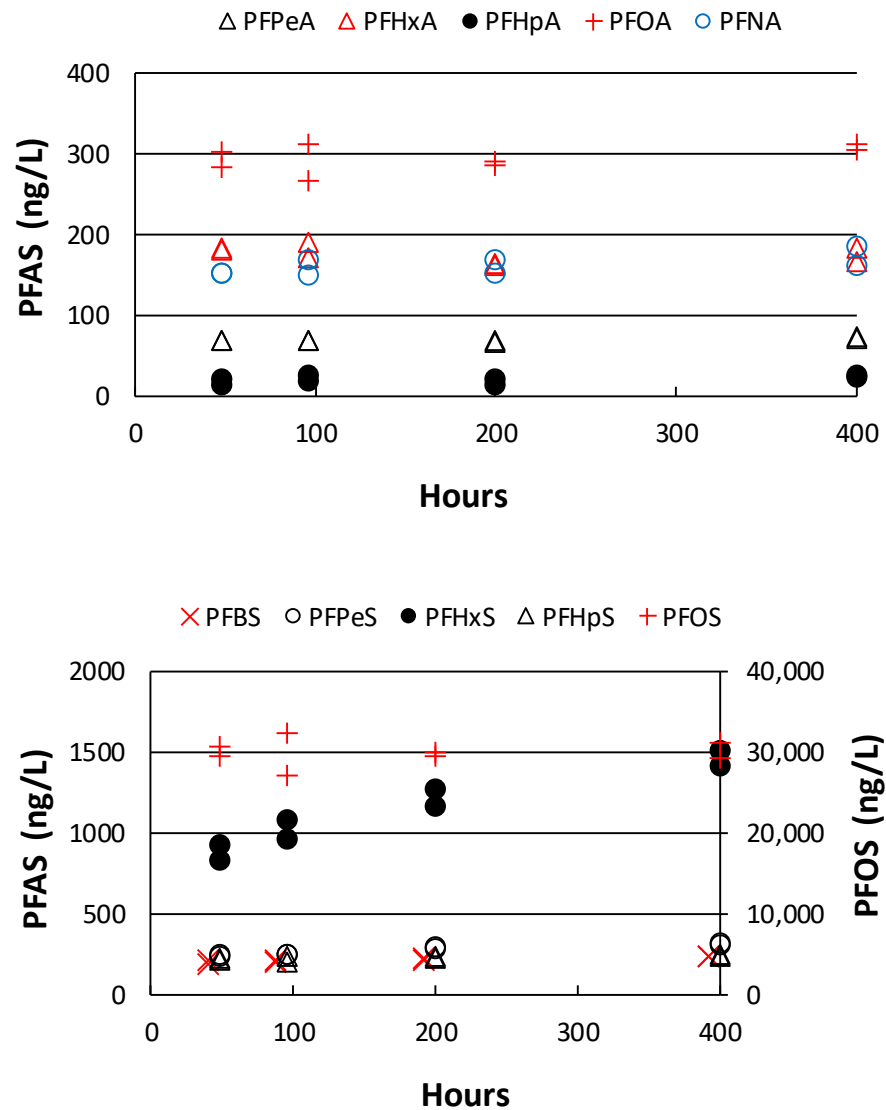


**Figure 4.7.** Measured aqueous perfluorinated carboxylate (top) and perfluorinated sulfonate (bottom) concentrations for the deep soil desorption experiments. With the exception of PFHxS, approximate equilibration was attained with 48 hours. Duplicate values are plotted for each compound; in many cases, symbols for the duplicate experiments overlap. PFOS is plotted on the secondary y-axis. The PFBS times are plotted with an 8-hours offset to improve clarity.

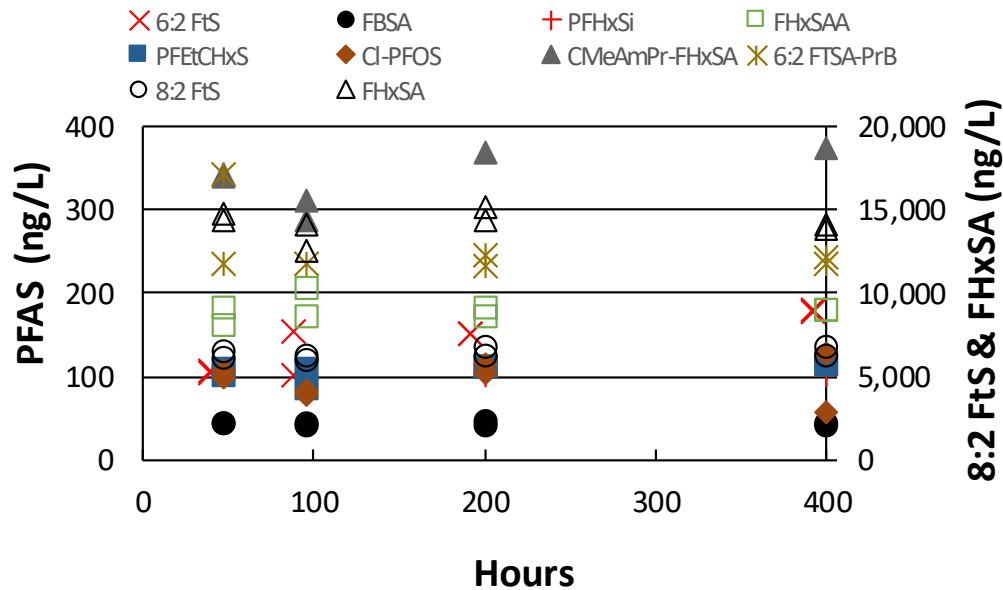


**Figure 4.8.** Measured aqueous PFAS concentrations for the deep soil desorption experiments. With the exception of PFHxSi, approximate equilibration was attained with 48 hours. Duplicate values are plotted for each compound; in many cases, symbols for the duplicate experiments overlap. 8:2 FtS and FHxSA are plotted on the secondary y-axis. The 6:2 FtS times are plotted with an 8-hours offset to improve clarity.

#### Shallow Soil

PFAS desorption kinetics for the shallow, which contains a comparatively elevated organic carbon content (0.0034 g/g) compared to the deep soil (<0.00068 g/g), soil are provided in **Figure 4.9**. Desorption kinetics for PFAS precursors are provided in **Figure 4.10**. In contrast to the results observed for the deep soil, kinetic limitations on desorption were observed for many PFAS., with no clear indication that equilibrium had been attained within the 400 hr desorption timeframe. Short-chained (C<7) PFAS typically exhibited kinetically controlled behavior, while the longer chained compounds typically achieved comparatively rapid equilibrium.

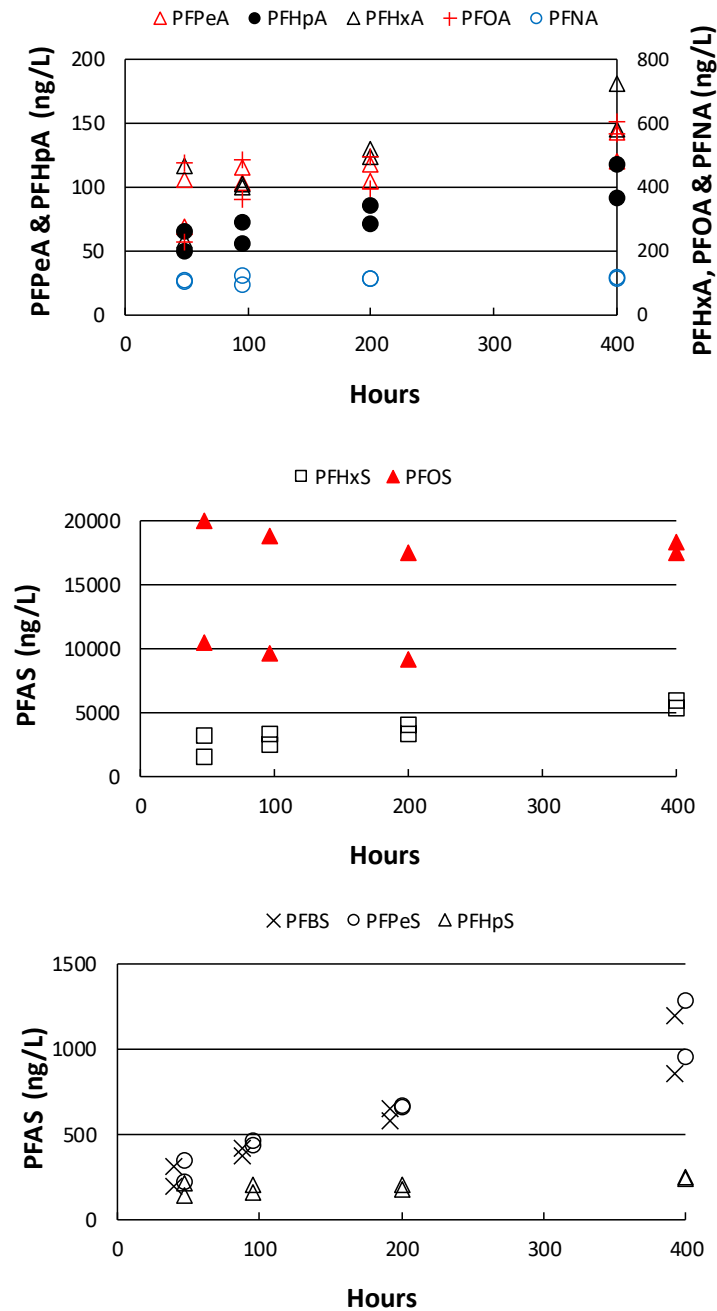


**Figure 4.9.** Measured aqueous perfluorinated carboxylate (top) and perfluorinated sulfonate (middle and bottom) concentrations for the shallow soil desorption experiments. With the exception of PFOS and PFHpS, equilibration was not attained within 400 hours. Duplicate values are plotted for each compound; in many cases, symbols for the duplicate experiments overlap.

PFOS is plotted on the secondary y-axis. The PFBS times are plotted with an 8-hour offset to improve clarity.

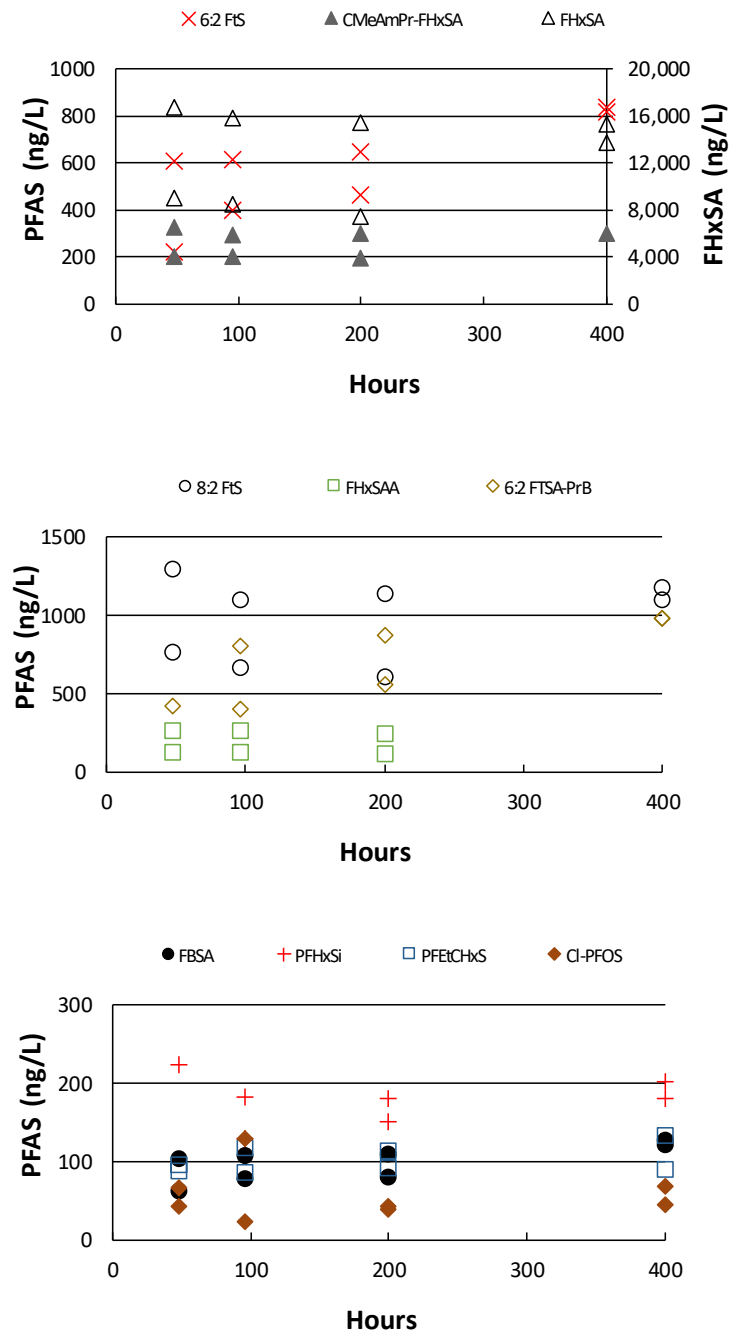


**Figure 4.10.** Measured aqueous PFAS concentrations for the shallow soil. With the exception 6:2 FtS, 6:2 FTSA-PrB, and FBSA, equilibration was attained within 400 hours. Duplicate values are

plotted for each compound; in many cases, symbols for the duplicate experiments overlap. For PFHxSAA, the final timepoint was omitted because the results increased by 50 to 100%, which likely was due to analytical error as levels had previously stabilized through 200 hours.

Less hydrophobic PFAS with shorter-chained perfluorinated tails ( $C < 9$  for the perfluorinated carboxylates, and  $C < 7$  for the perfluorinated sulfonates) generally exhibited this non-equilibrium behavior, while longer-chained and more hydrophobic PFAAs (i.e., PFNA, PFHpS, PFOS) reached near-equilibrium within 48 hours. Perfluorinated sulfonamides and the fluorotelomer sulfonates exhibited a similar trend.

Although these non-equilibrium trends with respect to PFAS perfluorinated chain length and hydrophobicity appear counterintuitive, as longer-chained compounds with greater hydrophobicity might be expected to exhibit mass transfer controlled desorption rather than the more mobile compounds, similar observations have been made for polyaromatic hydrocarbons (PAHs) in field aged soils (Shor et al., 2003). The reason for these observations is described by two-domain sorption models that consist of a rapid equilibrium domain (associated with soil surface uptake and/or rapid migration into mesopores), and a diffusion controlled non-equilibrium domain (associated with contaminant diffusion into micropores or soil organic matter (Shor et al., 2003). Over time, weakly sorbing (i.e., short-chained) PFAS become depleted from the equilibrium domain, and only PFAS sorbed within the kinetically-controlled domain remaining. This conceptual model explains why only the shorter-chained compounds showed kinetic limitations in the shallow soil desorption experiment.

To attain a screening level assessment of the PFAA desorption kinetics from the shallow soil, to assess the relative desorption behavior among the PFAAs, and to assess the plausibility of this conceptual desorption model for soils historically impacted with AFFF, a dual-site sorption model consisting of rapid equilibrium sites and mass transfer-controlled sites was employed (Leij et al., 1993; Wehrhan et al., 2010). The details of this model and application to the shallow soil are provided in **Appendix A2**. Simulation results (**Figure A2.1**) show that the desorption data are reasonably described by the model, with a normalized (to the mean) root-mean square error typically less than 10%. The only regressed parameter, the desorption rate coefficient  $\alpha$  ( $\text{h}^{-1}$ ), generally scales with the aqueous diffusivity (Schaefer et al., 2019) (**Figure 4.11**), which is consistent with a diffusion-controlled desorption mechanism. Together, these observations support the conceptual model of diffusion-controlled desorption of shorter-chained PFAS from field-aged soils.

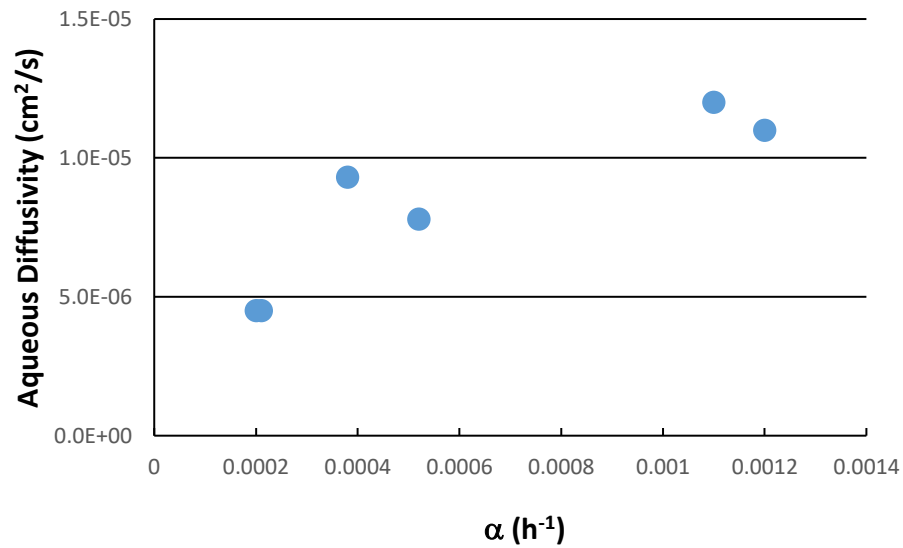


**Figure 4.11.** Aqueous diffusivity as a function of the regressed desorption rate constant  $\alpha$  for each PFAA where non-equilibrium was observed. PFPeS is omitted because aqueous diffusivity data were not available for this compound.

#### 4.2.2 Desorption Isotherms

Properties of the shallow and deep soils and PFAS soil concentrations using in the desorption testing are provided in **Table 4.1** and **Table 4.2**, respectively.

**Table 4.1.** Soil properties for the shallow and deep soils used in the desorption studies.

| Soil    | Average Grain Size <sup>1</sup> (mm) | Silt/Clay <sup>1</sup> (%) | Total Organic Carbon <sup>2</sup> (g/g) | Cation Exchange Capacity (meq/100g) | pH <sup>3</sup> |
|---------|--------------------------------------|----------------------------|-----------------------------------------|-------------------------------------|-----------------|
| Shallow | 0.4                                  | 5 / 0                      | 0.0034                                  | 80                                  | 5.8             |
| Deep    | 0.3                                  | 5 / 0                      | < 0.00068                               | 46                                  | 6.3             |

<sup>1</sup> via sieve analysis

<sup>2</sup> via combustion analysis

<sup>3</sup> as prepared in the laboratory desorption experiments

**Table 4.2.** PFAS soil concentrations in the shallow and deep soils used for the desorption studies. Average of 2 to 4 samples are shown with 95% confidence intervals. The < values indicate that the sample was below the limit of quantification. Results are shown on a dry weight basis (moisture content of the soil was 8% prior to desorption testing).

| PFAS Acronym   | Name                                                                 | Deep Soil Concentration (µg/kg) | Shallow Soil Concentration (µg/kg) |
|----------------|----------------------------------------------------------------------|---------------------------------|------------------------------------|
| PFBS           | perfluorobutane sulfonic acid                                        | 1.2 ± 0.08                      | 5.4 ± 3.2                          |
| PFPeS          | perfluoropentane sulfonic acid                                       | 1.9 ± 0.19                      | 23 ± 5.6                           |
| PFHxS          | perfluorohexane sulfonic acid                                        | 15 ± 2.1                        | 210 ± 37                           |
| PFHpS          | perfluoroheptane sulfonic acid                                       | 2.1 ± 0.4                       | 21 ± 6.0                           |
| PFOS           | perfluorooctane sulfonic acid                                        | 170 ± 23                        | 1300 ± 330                         |
| PFBA           | perfluorobutanoic acid                                               | <6.0                            | <2.4                               |
| PFPeA          | perfluoropentanoic acid                                              | 0.42*                           | 0.80*                              |
| PFHxA          | perfluorohexanoic acid                                               | <0.06                           | 5.5 ± 0.91                         |
| PFHpA          | perfluoroheptanoic acid                                              | <0.60                           | 1.5 ± 0.35                         |
| PFOA           | perfluorooctanoic acid                                               | 1.1 ± 0.1                       | 6.4 ± 1.1                          |
| FOSA           | perfluorooctane sulfonamide                                          | < 1.3                           | 11 ± 2.4                           |
| FHxSA          | perfluorohexane sulfonamide                                          | 110 ± 2.2                       | 250 ± 60                           |
| 8:2 FtS        | 8:2 fluorotelomer sulfonate                                          | 23 ± 10                         | 22 ± 5.0                           |
| 6:2 FtS        | 6:2 fluorotelomer sulfonate                                          | 3.1 ± 0.07                      | 19 ± 8.0                           |
| 8Cl-PFOS       | chloro-perfluorooctane sulfonic acid                                 | 1.1 ± 0.05                      | 3.1 ± 1.9                          |
| CMeAmPr-FHxSA  | N-Carboxymethyldimethylammoniopropyl-perfluorohexanesulfonamide      | 8.4 ± 8.2                       | 46 ± 2.0                           |
| PFEtCHxS       | perfluoro-4-ethylcyclohexane sulfonate                               | <0.49                           | 12 ± 6.4                           |
| AmPr-FHxSA-Pra | N-dimethyl ammonio propyl perfluorohexane sulfonamido propanoic acid | 4.5 ± 1.0                       | 70 ± 0.0                           |

\* estimated based on detection in collected soils cores

**NOTE:** Two shallow soil samples showed 10:2 FtS was <0.24 µg/kg. Two additional shallow soil samples showed 10:2 FtS at 1.1 and 1.2 µg/kg.

Desorption isotherms for the shallow and deep soils are provided in **Figures 4.12** and **4.13**, respectively. Linear regressions (Eq. 3.1) were performed on the desorption data (regressions performed using the triplicate data, not the averages of the triplicate data), with regression parameters provided in **Table 4.3**. The relatively low  $R^2$  values for some of the PFAS are primarily due to scatter among the triplicate desorption data;  $R^2$  values based on linear correlation to the average of the triplicate values (shown in parentheses in Table 1) were typically greater than 0.82. The use of an alternate isotherm model (i.e., Freundlich) resulted in lower  $R^2$  values when regressed to the data, compared to the linear model presented in Eq. 3.1. The exception was PFOA in the shallow soil, which with a regressed Freundlich exponent of  $0.23 \pm 0.13$  yielded a slightly better  $R^2$  value (0.57) using a Freundlich isotherm than that which was obtained using Eq. 1 ( $R^2 = 0.53$ ).

Parallel testing was performed to evaluate the extent to which natural colloidal material were impacting measurements of (apparently) dissolved PFAS concentrations in the supernatant. As shown in Appendix A3, dissolved PFAS concentrations were nearly identical when comparing centrifuged versus non-centrifuged samples. Thus, it is unlikely that colloidal impacts were causing any bias as the batch systems were sequentially diluted, and that the behavior observed in **Figures 4.12** and **4.13** were due to desorption behavior.

Using soils spiked with PFAS and incubated 5 days prior to initiation of desorption, Chen et al. (2016) also observed linear desorption isotherms consistent with Eq. 3.1 for PFOS from sediments. In experiments similar to those performed by Chen et al. (2016), Pan et al. (2009) applied the Freundlich model to describe their PFOS desorption isotherm. However, upon re-regressing the Pan et al. PFOS soil desorption data to Eq. 1, the desorption isotherm was well-described by the linear model, with an  $R^2$  of 0.94. In addition, similar to observations herein, both Chen et al. (2016) and Pan et al. (2009) observed desorption hysteresis, as both studies showed that a fraction of the PFAS sorbed to the soil appeared resistant to desorption when compared to the corresponding adsorption isotherm.

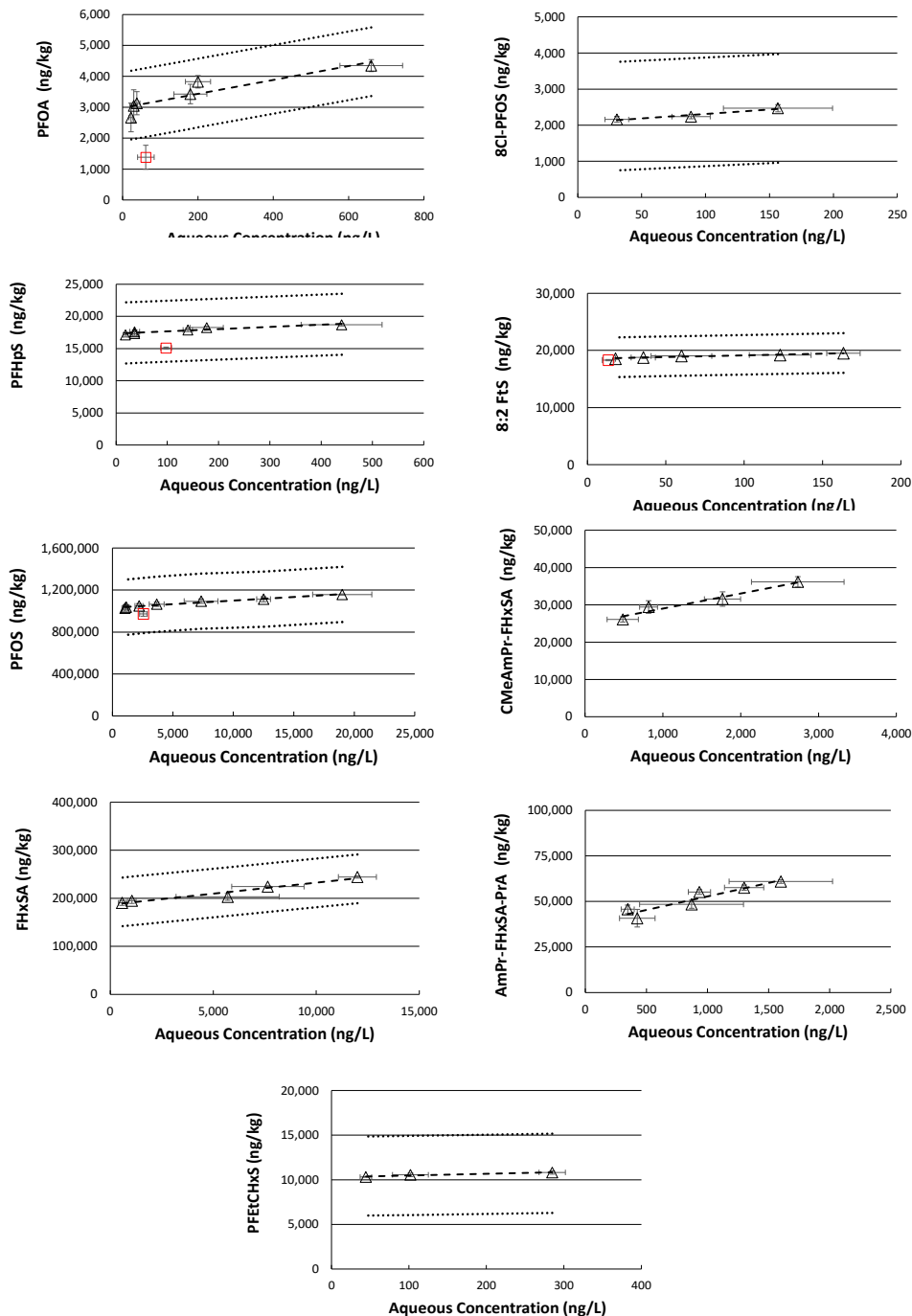


**Figure 4.12.** PFAS shallow soil concentrations as a function of PFAS aqueous concentrations. Average values are plotted. Large dashed lines represent regression of Eq. 3.1 to the data. The red squares on the PFOA, PFHpS, PFOS, and 8:2 FtS plots represent the 9-month equilibrated desorption timepoint. Error bars (x and y) represent 95% confidence intervals base on the desorption data. The dotted lines bracketing the data represent the 95% confidence intervals associated with the initial PFAS soil concentrations, and thus represent the uncertainty associated with the y-intercept and ultimately the non-labile soil concentration ( $S^{NL}$ ). Dotted lines are not shown for clarity when they reside within 10% of the dashed-line regression curves.

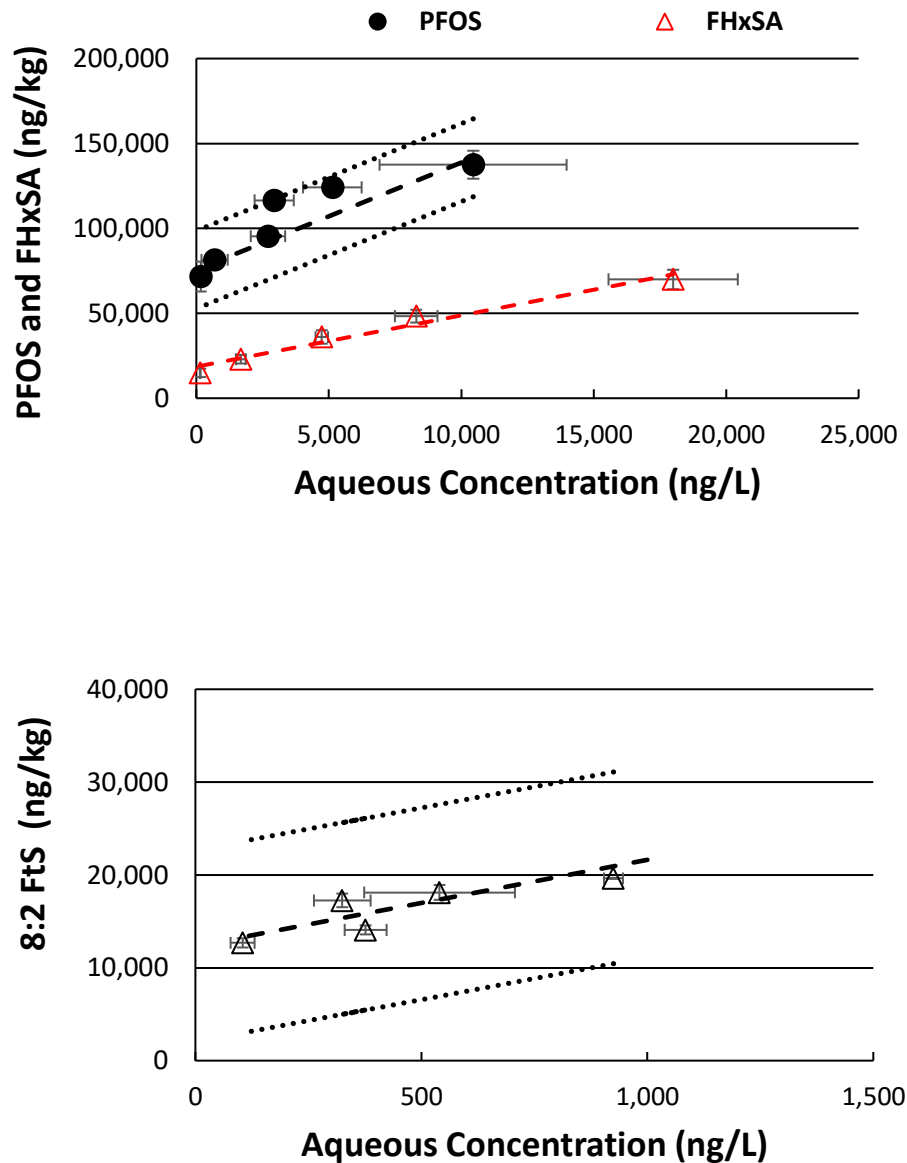


**Figure 4.13.** PFAS deep soil concentrations as a function of PFAS aqueous concentrations. Average values are plotted. Large dashed lines represent regression of Eq. 3.1 to the data. Error bars (x and y) represent 95% confidence intervals base on the desorption data. The dotted lines bracketing the data represent the 95% confidence intervals associated with the initial PFAS soil concentrations, and thus represent the uncertainty associated with the y-intercept and ultimately the non-labile soil concentration ( $S^{NL}$ ). Dotted lines are not shown for clarity when they reside within 10% of the dashed-line regression curves.

### Desorption $K_d$ Values

The regressed slopes in **Figures 4.12 and 4.13** were used to determine the desorption  $K_d$  values (Eq. 3.1). Regressed  $K_d$  values are provided in **Table 4.3**. Despite differences in soil organic carbon content, PFAS headgroup, and PFAS charge, all regressed  $K_d$  values were within approximately one order of magnitude of each other. This observation likely is due to the relative importance of the perfluorinated chain length in controlling desorption from the labile fraction in the model soils used herein, as the perfluorinated chain length only varied between 6 and 8 for all compounds evaluated in this study. In addition, the acidic soil pH (**Table 4.1**) likely resulted in protonation of negatively charged soil surface moieties that might have otherwise (under neutral or alkaline pH conditions) enhanced the sorption of positively charged moieties of the zwitterionic PFAS present in the shallow soil, thus serving as a plausible explanation as to why anionic and zwitterionic PFAS show similar desorption behavior with respect to the regressed  $K_d$  values.

**Table 4.3.** Regressed values of  $K_d$  and  $S^{NL}$  using Eq. 3.1 and the desorption isotherm data. The  $\pm$  values represent the 95% confidence intervals. The  $R^2$  values of the regression to the raw data are provided; the values in parentheses represent the  $R^2$  data when Eq. 3.1 is fit to the average values rather than the raw triplicate data. The  $K_{oc}$  values are the average values obtained from Nguyen et al. (2020) with 95% confidence intervals.

| PFAS                | $K_d$ (L kg <sup>-1</sup> ) | $S^{NL}$ (ng kg <sup>-1</sup> ) | $R^2$       | $K_{oc}$ (L kg <sup>-1</sup> ) |
|---------------------|-----------------------------|---------------------------------|-------------|--------------------------------|
| <b>Shallow Soil</b> |                             |                                 |             |                                |
| PFOA                | 2.2 $\pm$ 1.1               | 3,000 $\pm$ 1,100               | 0.52 (0.82) | 350 $\pm$ 230                  |
| PFHpS               | 3.2 $\pm$ 1.2               | 17,000 $\pm$ 6,000              | 0.63 (0.87) | 550 $\pm$ 290                  |
| PFOS                | 6.9 $\pm$ 1.5               | 1,000,000 $\pm$<br>330,000      | 0.82 (0.97) | 1600 $\pm$ 750                 |
| 8:2 FtS             | 5.2 $\pm$ 1.7               | 19,000 $\pm$ 5,000              | 0.76 (0.94) | 3800 $\pm$ 2300                |
| FHxSA               | 4.2 $\pm$ 1.1               | 190,000 $\pm$ 60,000            | 0.83 (0.94) | 470 $\pm$ 340                  |
| 8Cl-PFOS            | 1.7 $\pm$ 1.5               | 2,200 $\pm$ 1,900               | 0.43 (0.95) | NA                             |
| CMeAmPr-FHxSA       | 3.3 $\pm$ 1.7               | 27,000 $\pm$ 2,000              | 0.63 (0.96) | NA                             |
| PFEtCHxS            | 1.3 $\pm$ 1.3               | 10,000 $\pm$ 6,400              | 0.43 (0.93) | 470 $\pm$ 250                  |
| AmPr-FHxSA-Pra      | 10 $\pm$ 1.4                | 45,000 $\pm$ 0                  | 0.75 (0.88) | NA                             |
| <b>Deep Soil</b>    |                             |                                 |             |                                |
| PFOS                | 6.3 $\pm$ 1.8               | 76,000 $\pm$ 23,000             | 0.77 (0.82) | 1600 $\pm$ 750                 |
| FHxSA               | 2.8 $\pm$ .64               | 20,000 $\pm$ 2,200              | 0.86 (0.97) | 470 $\pm$ 340                  |
| 8:2 FtS             | 9.1 $\pm$ 2.3               | 12,000 $\pm$ 10,000             | 0.75 (0.74) | 3800 $\pm$ 2300                |

NA = not available

As an alternate explanation for the similarity in  $K_d$  values among the compounds shown in **Table 4.3**, CMeAmPr-FOSA (which has 2 more perfluorinated carbons in its tail than the CMeAmPr-FHxSA examined herein) is considered. CMeAmPr-FOSA also is assigned the nomenclature of perfluorooctane sulfonamidoalkyl betaine (Mejia-Avendaño et al., 2020). Mejia-Avendaño et al. (2020) postulated that, based on observation of sorption behavior to soil as a function of pH, CMeAmPr-FOSA transitioned from predominantly zwitterionic to predominantly anionic between a pH of 5 and 6, and that the SPARC-predicted pH value for this transition was too high. Following this postulation (Mejia-Avendaño et al., 2020), the assumption that CMeAmPr-FHxSA also transitions from predominantly zwitterionic to predominantly anionic between a pH of 5 and 6 provides a plausible explanation as to why CMeAmPr-FHxSA has similar  $K_d$  values to the anionic PFAS examined herein, as soil pH values herein ranged from 5.8 to 6.3. Similar speciation (i.e., transition from zwitterionic to predominantly anionic) might occur for AmPr-FHxSA-PrA due to the presence of the carboxylate and ammonium groups. Thus, the similarity observed in the desorption  $K_d$  values among the various headgroups observed herein (Table 1) may be due to the fact that all PFAS examined are primarily anionic under the experimental conditions tested.

In contrast, Xiao et al. (2019) showed that anionic PFOA and zwitterionic perfluorooctaneamido betaine showed substantially different desorption behavior on the five soils they examined, with the perfluorooctaneamido betaine showing enhanced retention to the soil compared to PFOA. The soils used by Xiao et al. (2019) all had pH values varying between 8.2 and 8.4, which is higher than the soil pH values examined herein or by Mejia-Avendaño et al. These results, along with those observed herein and by Mejia-Avendaño et al. (2020), suggest the possibility that pH could be an important factor in PFAS desorption from historically AFFF-impacted soils. Further detailed investigations of this process and the impacts of pH for various soils types and PFAS is warranted.

Desorption  $K_d$  values, based on the labile fraction (Eq. 3.1), for PFOS and FHxSA were measured in both the shallow and deep soils, thus providing a comparison of PFAS desorption behavior between the soils collected from the two depth intervals. As shown in **Table 4.3**, the desorption  $K_d$  values for these PFAS are statistically identical for these two soil intervals, despite the fact that the organic carbon content in the shallow soil is at least 5-times greater than in the deep soil. This result is consistent with data presented for PFAS adsorption by Nguyen et al. (2020), who show that  $K_d$  values typically did not decrease with decreasing soil organic carbon content for soils below a soil organic carbon content of 0.003 to 0.004 g g<sup>-1</sup>. Overall, for the low organic carbon deep soil studied herein, this suggests the possibility that PFAS release (i.e., the  $K_d$  value) is not controlled by soil organic carbon, but rather by other non-hydrophobic interactions. The controlling role of non-hydrophobic interactions for PFAS have been previously observed for low organic content soils (Zhang et al., 2014).

To further assess the PFAS desorption  $K_d$  values (based on the labile fraction) measured for the shallow soil herein, desorption  $K_d$  values are compared to predicted  $K_d$  values based on soil adsorption data. Predicted  $K_d$  values are determined by multiplying the mass fraction of organic carbon in the shallow soil ( $f_{oc} = 0.0034$  g g<sup>-1</sup>) by the PFAS organic carbon partition coefficient

( $K_{oc}$ ).  $K_{oc}$  values for several PFAS were determined by Nguyen et al. (2020) based on PFAS adsorption studies using a wide range of soil types, and are listed in **Table 4.3**. **Figure 4.14** shows the desorption  $K_d$  values measured herein compared to predicted  $K_d$  values based on adsorption-based  $f_{oc}$   $K_{oc}$  values; only those PFAS for which corresponding  $K_{oc}$  values were reported are shown in Figure 1. While it is recognized, based on the work of Nguyen et al. (2020), that PFAS soil sorption is not solely based on organic carbon content, Figure 1 suggests that adsorption-based  $K_{oc}$  values provide a reasonable (within a factor of approximately 3) estimate of the desorption  $K_d$  values when normalized to the shallow soil organic carbon content. This observation is consistent with results of a dual domain sorption model, consisting of an “instantaneous” sorption domain that with reversible sorption (the  $K_d$  domain herein), and a kinetically controlled sorption domain (associated with the non-labile portion herein), as discussed in Section 4.2.1.

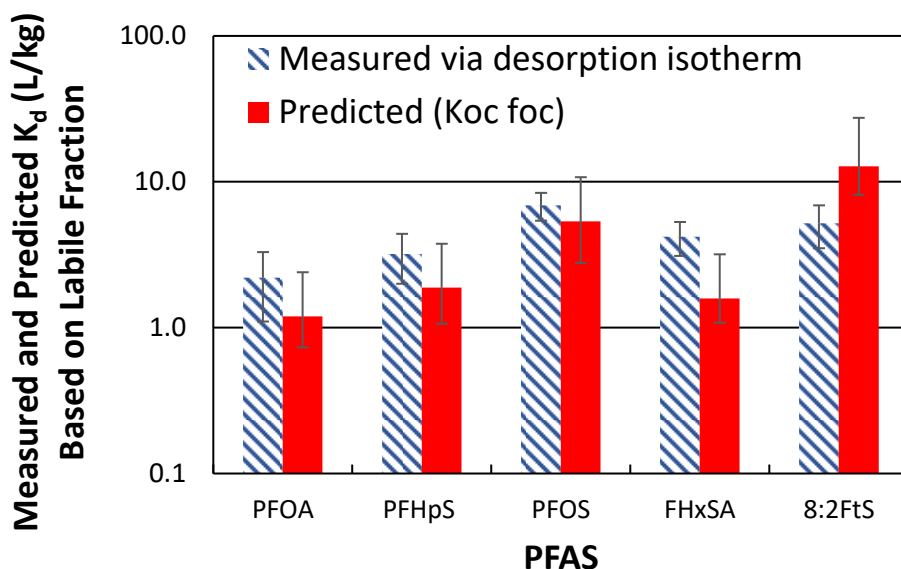


**Figure 4.14.** Desorption  $K_d$  values for PFAS measured herein for the shallow soil compared to predictions based on adsorption-derived  $K_{oc}$  values determined by Nguyen et al. (2020). The  $K_{oc}$  values were multiplied by the fraction of organic carbon ( $f_{oc}$ ) for the shallow soil ( $0.0034 \text{ g g}^{-1}$ ) to provide prediction of the desorption  $K_d$  values. Error bars for the values measured herein represent 95% confidence intervals on the regressed desorption  $K_d$  values (**Table 4.3**). Error bars on the predicted values are the 95% confidence intervals based on the  $K_{oc}$  values determined by Nguyen et al. (2020).

Because  $f_{oc}$  values were below the analytical detection limit for the deep soil (**Table 4.1**), specific  $f_{oc} K_{oc}$  based predictions could not be made for the deep soil. However, predicted values would be at least 5-times less than those obtained for the shallow soil (based on the  $f_{oc}$  detection limit shown in **Table 4.1**), which would mean that  $f_{oc} K_{oc}$  based predictions would underestimate the  $K_d$  values in the deep soil by approximately an order of magnitude. Thus, consistent with previous observations for PFAS adsorption on to soils,  $f_{oc} K_{oc}$  approaches are not appropriate for predicting PFAS sorption in soils with low  $f_{oc}$  (Nguyen et al., 2020).

It is noteworthy that the PFHxA mass desorbed from the soil over the 9-month duration ranged as high as 13-times the mass of PFHxA initially measured in the soil; for PFHpA, the mass desorbed was 1.3-times the mass of PFHpA initially measured in the soil. No such discrepancies in mass balance occurred for the other PFAAs in the desorption study. It is plausible that these discrepancies were due to precursor transformation, as known precursors were present in the soil.

#### *Evaluating the Non-Labile PFAS Fraction in the Soils*

As expressed in Eq. 3.1, the y-intercepts of the linear regressions represent the (effectively) non-labile sorbed PFAS concentrations. The dashed lines bracketing the desorption data and linear regressions in **Figures 4.12 and 4.13** represent the 95% confidence intervals associated with the initial soil concentration (based on the measured PFAS soil concentrations provided in **Table 4.2**), which ultimately control the uncertainty on the regressed y-intercepts and non-labile PFAS soil concentrations ( $S^{NL}$ ). For all PFAS examined in **Figures 4.12 and 4.13**, these non-labile sorbed PFAS concentrations were significantly greater than zero (**Table 4.3**).

The fraction of sorbed PFAS that is non-labile, defined as the non-labile soil concentration ( $S^{NL}$ ) divided by the initial soil concentration, is plotted as a function of the PFAS  $K_{oc}$  value in **Figure 4.15**. The non-labile fraction ranges from 0.17 for FHxSA in the deep soil, to 0.87 for 8:2 FtS in the shallow soil. In general, the non-labile fraction is greater in the shallow soil for a given  $K_{oc}$  value than in the deep soil, suggesting that the non-labile sorbed mass likely is associated with soil organic matter, and that organic matter in the shallow soil may be hindering overall PFAS desorption. The non-labile fraction also increases with  $K_{oc}$  (increasing trend with  $p=0.03$  determined using Mann-Kendall test for the shallow soil). This possible role of soil organic matter controlling the non-labile fraction is consistent with non-PFAS studies showing that soil organic matter can facilitate desorption hysteresis and sorption “irreversibility” due to alteration of the organic matter structure (Sander et al., 2006; Sander and Pignatello, 2009).

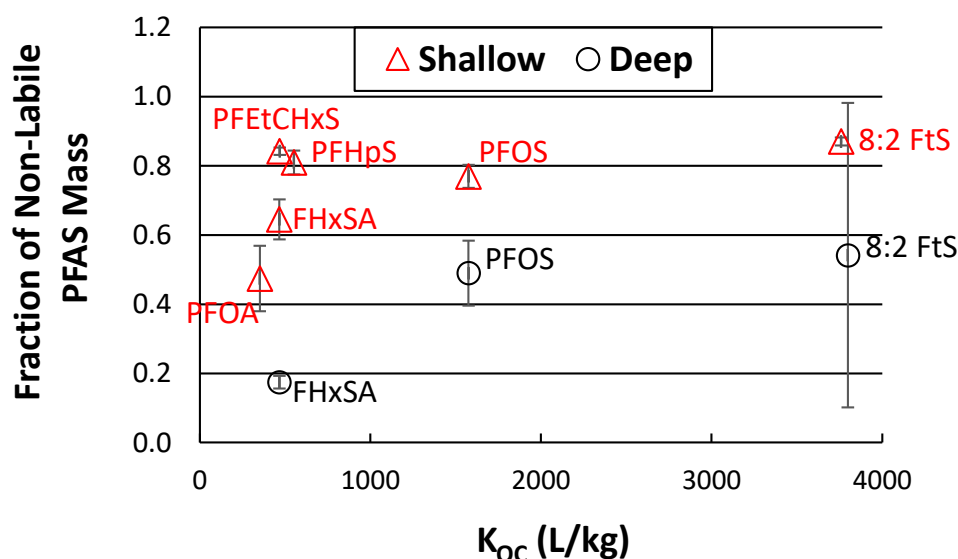


**Figure 4.15.** Fraction of non-labile PFAS mass (non-labile mass divided by the total mass) sorbed to the soil (shallow and deep) as a function of PFAS  $K_{oc}$ . Error bars represent the 95% confidence intervals. The marker for 8:2 FtS in the shallow soil ( $K_{oc} = 3800 \text{ L kg}^{-1}$ ) is plotted with a slight offset for clarity. The large error bar associated with 8:2 FtS in the deep soil is reflective of the error associated with the initial concentration measured in the soil (Table 4.2).  $K_{oc}$  values are from Nguyen et al. (2020), and are presented in Table 4.3.

To further assess the extent to which the non-labile fraction may be slowly released from the soil, PFAS concentrations for the shallow soil were measured in the supernatant water after approximately 9 months of incubation following the last sequentially diluted desorption point; results of this screening test (where analyses were performed on target analytes by the commercial laboratory) are shown as the red squares in Figure 4.12. For each of the 4 PFAS evaluated (PFOA, PFHpS, PFOS, and 8:2 FtS), aqueous concentrations increased between the last desorption time point and the 9-month sampling event, indicating that very slow desorption processes were occurring. However, the fraction of PFAS soil mass removed during this 9-month incubation period was typically small ( $< 13\%$  of the mass remaining in the soil following the last desorption isotherm point), with a negligible impact on the estimated soil non-labile fraction. The exception was PFOA, where approximately 48% of the soil mass remaining after the last desorption point was released after 9 months incubation. Thus, the non-labile fraction estimated for PFOA is only applicable to timescales of days to weeks rather than months, which still may be sufficient to effectively sequester PFOA during precipitation induced vadose zone infiltration/drainage events that occur over timescales of several days in near-surface permeable soils. Interestingly, the previously performed kinetic desorption data for PFOA noted that (despite demonstrating

relatively constant concentrations through 8 days) PFOA concentrations increased between 8 and 16 days. Thus, the PFOA desorption data may not have been at quasi equilibrium following the 8-day desorption timeframe employed in this current study. It is also possible that the increases observed for PFOA were due, at least in part, to slow biotransformation of polyfluorinated precursors over the 9-month incubation period. Previous study on these soils (Schaefer et al., 2020) suggests that such biotic transformation is unlikely over the time scale of 2 to 3 weeks, but the possibility of biotic transformations over this extended 9-month period cannot be excluded. In fact, for PFHxA and PFHpA, the mass of PFAS desorbed exceeded that of PFAS mass initially present in the soil, suggesting the possibility of precursor transformation.

Kan et al. (1998) developed a model to predict the non-labile soil concentration ( $S^{NL}$ ) associated with soil organic matter for non-PFAS organic compounds:

$$S^{NL} = 0.044f_{oc}C^{max}\exp[0.048\alpha] \quad \text{Eq. 4.1}$$

where  $f_{oc}$  is the fraction of natural organic carbon in the soil ( $f_{oc} = 0.0034 \text{ g g}^{-1}$  for the shallow soil),  $C^{max}$  is the maximum aqueous phase PFAS concentration to which the soil was historically exposed, and  $\alpha$  is the hydrophobic area per PFAS molecule. Herein Eq. 4.1 is modified slightly from that of Kan et al., in that  $C^{max}$  is used instead of the aqueous solubility that was originally used by Kan et al., as Kan et al. performed their initial adsorption experiments at solute concentrations within approximately a factor of 3 of the aqueous solubility. As discussed below, the maximum PFAS concentrations exposed to the soil were likely much ( $>10$ -times) less than their aqueous solubilities. Also, herein  $S^{NL}$  is operationally defined as the PFAS which is non-labile through the 8-day desorption timeframe for the shallow soil, which is consistent with the 3 to 14 day desorption timeframe generally applied by Kan et al. (1998).

The value for  $\alpha$ , as described by Silva et al. (2021), can be determined based on air-water interfacial tension measurements and application of the Langmuir-based Szyszkowski equation. Employing this approach, and based on measurements of PFOS and PFOA air-water interfacial tensions in 0.01 M ionic strength aqueous solution, reported  $\alpha$  values are 30 and 66  $\text{\AA}^2$  per molecule for PFOA and PFOS, respectively (Silva et al., 2021, Schaefer et al., 2019b; Schaefer et al., 2020b). The maximum aqueous PFOA and PFOS concentrations to which the soil was exposed ( $C^{max}$ ) are estimated based on a 3% dilution of 3M AFFF (this dilution was often used in US Department of Defense applications, and is used herein to provide a screening level approximation of PFAS concentrations to which the shallow soil was likely exposed). The  $C^{max}$  values for PFOA and PFOS based on 3% dilutions of measured PFOA and PFOS concentrations in 3M AFFF formulations (Backe et al., 2013) are therefore  $3.3 \pm 0.78 \times 10^6$  and  $2.8 \pm 0.89 \times 10^8 \text{ ng L}^{-1}$ , respectively.

As shown in **Figure 4.16**, the predicted non-labile soil concentrations ( $S^{NL}$ ) based on Eq. 4.1 are within 40% of the values measured in the shallow soil desorption isotherms (**Table 4.3**). This agreement is consistent with the data presented in **Figure 4.15**, which suggests that the non-labile fraction is related to PFAS hydrophobicity (for which  $K_{oc}$  serves as an approximate surrogate for

hydrophobicity). The agreement between measured and predicted values in **Figure 4.16** also is consistent with soil organic matter serving as the domain responsible for  $S^{NL}$ , as Eq. 2 is based on soil  $f_{oc}$  levels. However, while these results suggest that Eq. 4.1 may be appropriate for estimating  $S^{NL}$  values, a more systematic assessment is needed covering a much wider range of PFAS and site conditions to demonstrate the general validity and usefulness of Eq. 4.1 for PFAS.

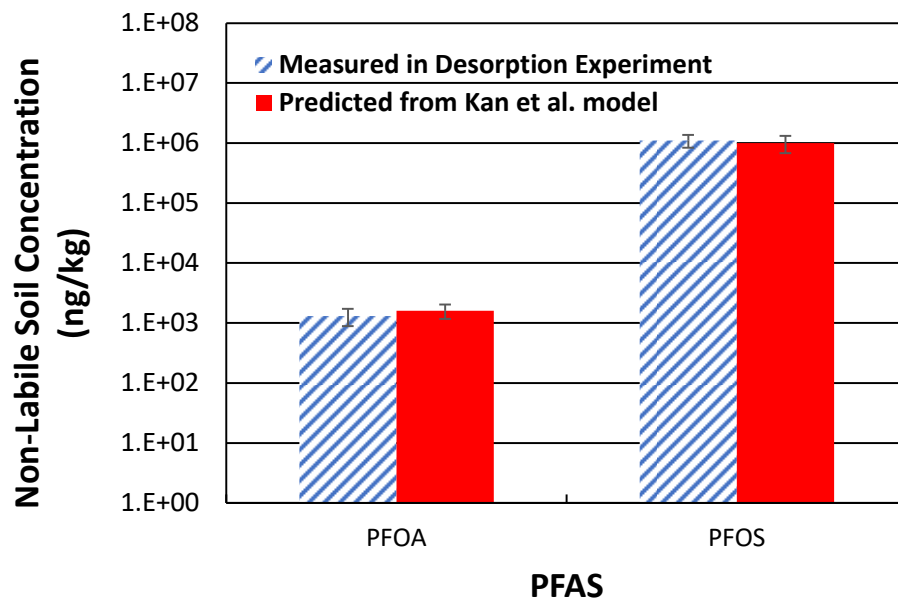


**Figure 4.16.** Comparison of measured \ and predicted (Eq. 4.1) values of the non-labile concentration ( $S^{NL}$ ) for both PFOA and PFOS in the shallow soil. Error bars represent 95% confidence intervals.

### 4.3 Unsaturated Column Experiments and Additional Investigation of Colloids

#### *PFAS Mass Release – Saturated Conditions*

The soils from both intervals were characterized prior to the start of the column experiments. The quantified or semi-quantified concentrations of compounds found in the soils are presented in **Appendix A.4**. The shallow soil had more PFAS mass and more identified compounds than the deep soil.

Peak concentrations of the perfluorinated carboxylates and sulfonates from the saturated columns were observed in the first 250 mL eluted (**Figure 4.17**). Within a homologous series, longer chain length compounds peaked in concentration later than the shorter chained compounds. This observation is likely due to the collapse of air-water interfaces upon initial wetting of the dry soil in the columns, and the subsequent PFAS pulse that migrated through the columns. Several stop-flow events occurred during the experiment and many of the concentration profiles show an increase in concentration eluted from the columns after flow resumed. This suggests the soil-water systems are in non-equilibrium. Concentration perturbations following soil column flow interruptions in AFFF- impacted soils were also observed by Maizel et al. (2022). These increases in concentrations are observed in both the shallow and deep soil columns, but the response is more pronounced in the shallow soils. This is likely due to the differences in organic carbon content between the two soils. The desorption kinetic experiments (Section 4.2.1) showed that the deep soil reached equilibrium rather quickly but many compounds did not reach equilibrium in the shallow soil, which was attributed to the increased organic carbon content in the shallow soil. Additionally, peak concentrations for the same compound appear later from the shallow soils than the deep soils. This further supports that the PFAS mass release from the shallow soil is more kinetically controlled than the deep soil.

#### *PFAS Mass Release – Constant Unsaturated Conditions*

The PFAS mass released under saturated conditions was compared to the mass released under unsaturated conditions for both soil intervals (**Figure 4.18**). In the deep soil columns, generally more mass was released under saturated conditions than unsaturated conditions. The differences in mass eluted in the deep soil columns is likely due to the retention of the PFAS at the air-water interfaces in the unsaturated columns. Opposite trends were observed from the mass eluted from the shallow soil columns. For almost all identified compounds, more mass was eluted from the unsaturated soil. The mechanisms responsible for increased mass to be released from the unsaturated soil are not immediately clear, but it is likely that the higher organic carbon content in the shallow soil is contributing to the observed trends.

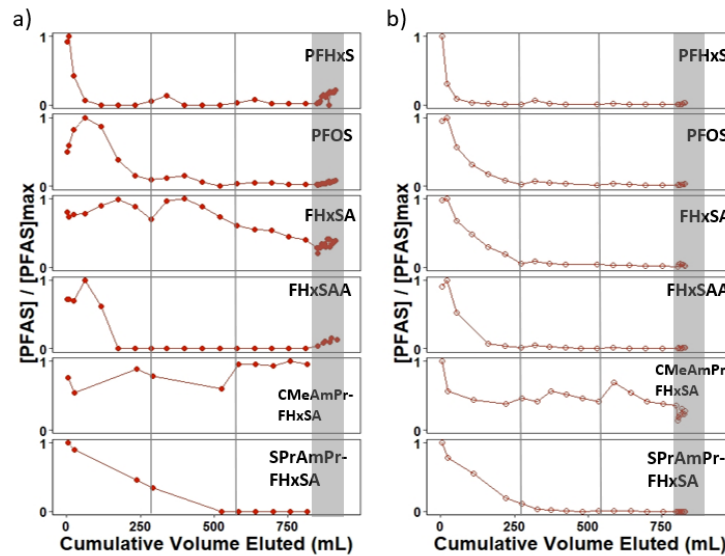


**Figure 4.17.** Normalized concentrations of select PFAAs and PFAA precursors eluted from shallow (a) and deep (b) soil columns. The gray lines indicate stop-flow events that lasted for 7-12 days during the constant saturation condition experiments. The gray bars indicate the 5 wetting and drying events that occurred during the variable saturation condition experiments.

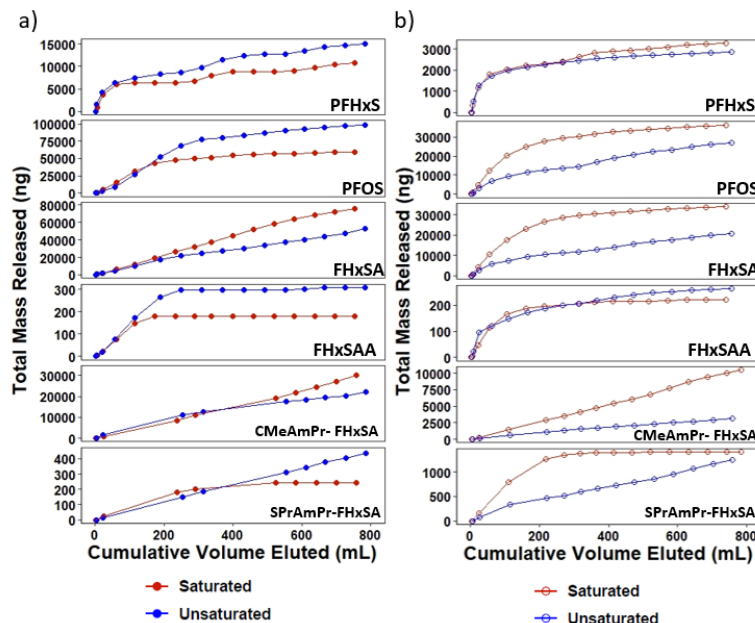


**Figure 4.18.** Cumulative mass of select PFAAs and PFAA precursors eluted from shallow (a) and deep (b) soil columns under constant saturation conditions.

The organic matter content in the shallow soil may be retaining more PFAS in the saturated system when compared to the unsaturated soil system. The immobile water and air in the unsaturated system means there is also organic carbon that is inaccessible to the mobile water. More organic carbon is accessible in the saturated soil because there is less immobile water and no air in the system, which could result in more PFAS mass being retained in the soil.

#### *PFAS Mass Release – Variably Unsaturated Conditions*

Following the constant saturation conditions experiments, the unsaturated columns underwent variable saturation experiments. The concentrations of PFAS in the column effluent varied over each wetting/ drying event (**Figure 4.19**). In the shallow soil columns, the concentrations generally spiked in the first sample eluted in each cycle. Concentrations then decreased during drainage. As seen in the other saturation conditions presented, the PFAS mass released in the shallow soil system appears to be controlled by desorption kinetics that are influenced by the presence of organic matter. During the drying phase, residual water was left in the unsaturated columns and PFAS were able to desorb from the organic matter in the soil into the water during this time (approximately 7 days). When the wetting phase began, the PFAS were already in the aqueous phase and were eluted from the column with the added water. Concentration fluctuations were also observed from the deep soil systems, but peak concentrations are generally in the last sample eluted from each cycle. The PFAS mass release from the deep soil system is likely a result of collapsing air-water interfaces within the soil when the water is added. Greater increases in concentration eluted during each cycle are seen in compounds with greater hydrophobicity (PFOS, FHxSA), which further supports that collapsing air-water interfaces are responsible for the increased mass released from the deep soil as it drains.

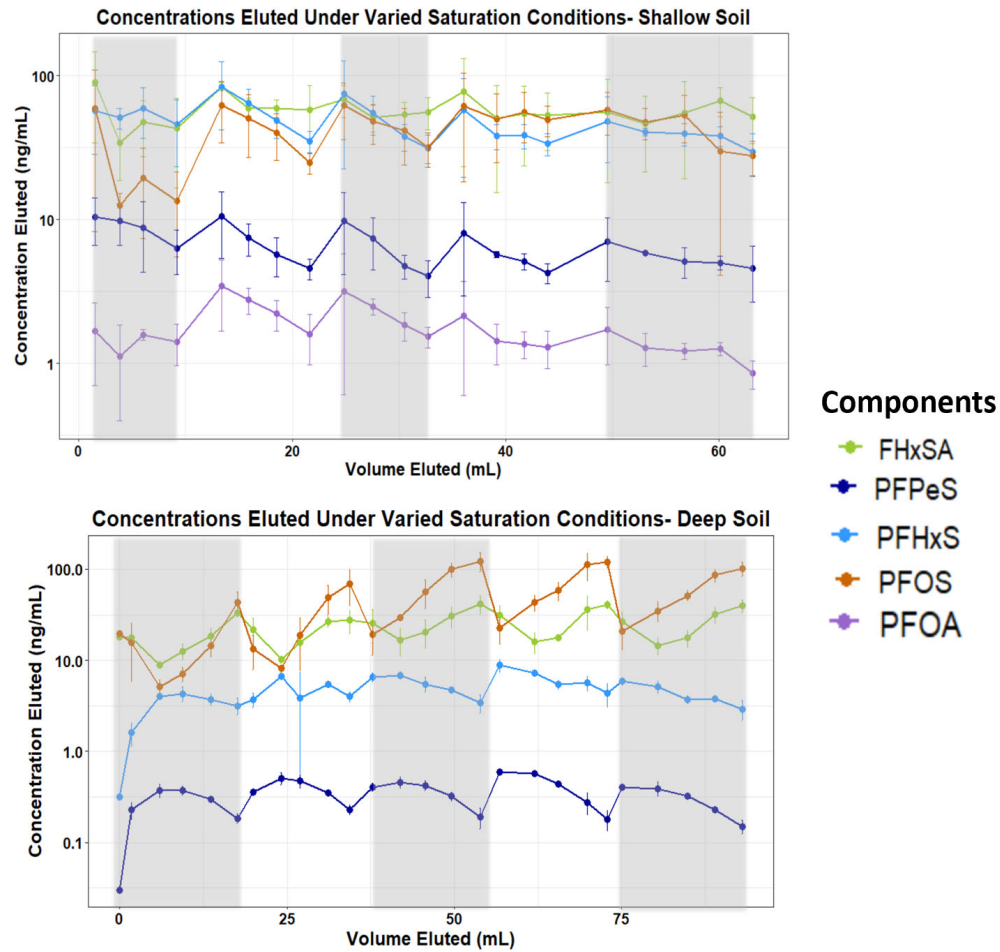


**Figure 4.19:** Concentrations eluted from unsaturated shallow and deep soil columns under variable unsaturated conditions. The gray bars indicate wetting cycles.

#### 4.4 Biotic and Abiotic Transformation of AFFF Source Materials

Overall, large uncertainty (typically 25% to 75% of the average value) among replicate soil samples precluded any sort of quantitative assessment of precursor transformation. As an example, results for soil in the 0-5 ft bgs interval are provided in **Figure 4.20**. Thus, this subtask did not yield any meaningful insight with respect to precursor transformation in these historically AFFF-impacted soils. However, as discussed in Section 4.5.2, PFAS desorption/leaching results suggest that biotic precursor transformation, resulting in formation of PFHxA and PFHpA, was occurring in site soils.

|            |                     | Initial Soil   |       |       |      |       | Soil (48 weeks aerobic) |        |       |      |       |        | Soil (48 weeks anaerobic) |       |       |      |       |        |      |
|------------|---------------------|----------------|-------|-------|------|-------|-------------------------|--------|-------|------|-------|--------|---------------------------|-------|-------|------|-------|--------|------|
|            |                     | AVG [C]        | S DEV | #Obs  | SE   | RSE   | AVG                     | S DEV  | #Obs  | SE   | RSE   | T TEST | AVG                       | S DEV | #Obs  | SE   | RSE   | T TEST |      |
| Semi-quant | Isomers<br>(557 mz) | PFBA           | 0.18  | 0.05  | 8.00 | 0.02  | 10%                     | 0.20   | 0.00  | 3.00 | 0.00  | 0%     | 0.35                      | 0.20  | 0.00  | 3.00 | 0.00  | 0%     | 0.35 |
|            |                     | PFPeA          | 0.18  | 0.09  | 8.00 | 0.03  | 17%                     | 0.20   | 0.00  | 3.00 | 0.00  | 0%     | 0.54                      | 0.20  | 0.00  | 3.00 | 0.00  | 0%     | 0.54 |
|            |                     | PFHxA          | 30.51 | 42.92 | 8.00 | 15.17 | 50%                     | 1.35   | 1.12  | 3.00 | 0.65  | 48%    | 0.10                      | 0.80  | 0.52  | 3.00 | 0.30  | 38%    | 0.09 |
|            |                     | PFOA           | 1.05  | 1.25  | 8.00 | 0.44  | 42%                     | 0.66   | 0.49  | 3.00 | 0.29  | 43%    | 0.48                      | 0.33  | 0.12  | 3.00 | 0.07  | 20%    | 0.15 |
|            |                     | PFBS           | 0.41  | 0.19  | 8.00 | 0.07  | 16%                     | 1.21   | 1.74  | 3.00 | 1.01  | 83%    | 0.51                      | 0.20  | 0.00  | 3.00 | 0.00  | 0%     | 0.02 |
|            |                     | PFPeS          | 2.49  | 3.80  | 8.00 | 1.35  | 54%                     | 9.99   | 7.75  | 3.00 | 4.47  | 45%    | 0.23                      | 5.88  | 9.28  | 3.00 | 5.36  | 91%    | 0.59 |
|            |                     | PFHxS          | 34.39 | 29.89 | 8.00 | 10.57 | 31%                     | 38.18  | 24.77 | 3.00 | 14.30 | 37%    | 0.84                      | 9.34  | 9.03  | 3.00 | 5.22  | 56%    | 0.06 |
|            |                     | PFHpS          | 7.47  | 5.51  | 8.00 | 1.95  | 26%                     | 7.21   | 4.32  | 3.00 | 2.49  | 35%    | 0.94                      | 1.85  | 2.86  | 3.00 | 1.65  | 89%    | 0.06 |
|            |                     | PFOS           | 91.64 | 23.64 | 8.00 | 8.36  | 9%                      | 100.00 | 0.00  | 3.00 | 0.00  | 0%     | 0.35                      | 53.71 | 33.06 | 3.00 | 19.09 | 36%    | 0.17 |
|            |                     | PFNS           | 3.29  | 2.10  | 8.00 | 0.74  | 23%                     | 2.67   | 0.77  | 3.00 | 0.44  | 17%    | 0.49                      | 1.49  | 0.19  | 3.00 | 0.11  | 7%     | 0.05 |
|            |                     | FHxSA          | 5.81  | 1.65  | 8.00 | 0.58  | 10%                     | 8.68   | 1.38  | 3.00 | 0.79  | 9%     | 0.04                      | 3.21  | 3.62  | 3.00 | 2.09  | 65%    | 0.34 |
|            |                     | 8Cl - PFOS     | 2.92  | 2.74  | 8.00 | 0.97  | 33%                     | 1.09   | 0.69  | 3.00 | 0.40  | 36%    | 0.12                      | 0.24  | 0.07  | 3.00 | 0.04  | 16%    | 0.03 |
|            |                     | 6:2 FtS        | 2.25  | 1.17  | 8.00 | 0.41  | 18%                     | 2.52   | 1.77  | 3.00 | 1.02  | 41%    | 0.83                      | 1.68  | 0.55  | 3.00 | 0.31  | 19%    | 0.30 |
|            |                     | 8:2 FtS        | 4.01  | 1.35  | 8.00 | 0.48  | 12%                     | 2.54   | 1.16  | 3.00 | 0.67  | 26%    | 0.14                      | 2.49  | 1.50  | 3.00 | 0.86  | 35%    | 0.21 |
|            |                     | 6:2 FtSO2AoS   | 1.14  | 1.97  | 8.00 | 0.70  | 61%                     | 0.92   | 0.59  | 3.00 | 0.34  | 37%    | 0.78                      | 0.11  | 0.08  | 3.00 | 0.05  | 44%    | 0.18 |
|            |                     | 8:2 FtSO2AoS   | 2.13  | 0.74  | 8.00 | 0.26  | 12%                     | 0.59   | 0.45  | 3.00 | 0.26  | 45%    | 0.01                      | 1.05  | 0.42  | 3.00 | 0.24  | 23%    | 0.02 |
|            | Other               | AmPr-FBSA      | 1.10  | 1.19  | 8.00 | 0.42  | 38%                     | 0.69   | 0.48  | 3.00 | 0.28  | 40%    | 0.43                      | 2.55  | 2.88  | 3.00 | 1.66  | 65%    | 0.48 |
|            |                     | CETAmPr-FBSA   | 0.31  | 0.22  | 8.00 | 0.08  | 25%                     | 0.51   | 0.55  | 3.00 | 0.31  | 61%    | 0.58                      | 0.36  | 0.27  | 3.00 | 0.16  | 44%    | 0.79 |
|            |                     | AmPr-FPeSA     | 0.74  | 0.82  | 8.00 | 0.29  | 39%                     | 0.20   | 0.00  | 3.00 | 0.00  | 0%     | 0.10                      | 3.01  | 4.57  | 3.00 | 2.64  | 88%    | 0.48 |
|            |                     | CETAmPr-FPeSA  | 0.54  | 0.38  | 8.00 | 0.14  | 25%                     | 0.42   | 0.38  | 3.00 | 0.22  | 52%    | 0.68                      | 0.99  | 1.49  | 3.00 | 0.86  | 87%    | 0.65 |
|            |                     | CMeAmPr-FHxSA  | 2.02  | 1.19  | 8.00 | 0.42  | 21%                     | 0.51   | 0.53  | 3.00 | 0.31  | 61%    | 0.02                      | 1.95  | 1.54  | 3.00 | 0.89  | 46%    | 0.95 |
|            |                     | AmPr-FHxSA-PrA | 9.17  | 3.30  | 8.00 | 1.17  | 13%                     | 10.15  | 3.78  | 3.00 | 2.18  | 22%    | 0.72                      | 43.85 | 49.45 | 3.00 | 28.55 | 65%    | 0.35 |
|            |                     | CETAmPr-FHxSA  | 15.20 | 8.52  | 8.00 | 3.01  | 20%                     | 19.70  | 7.97  | 3.00 | 4.60  | 23%    | 0.46                      | 55.93 | 42.34 | 3.00 | 24.45 | 44%    | 0.24 |
|            |                     | SPrAmPr-FPeSA  | 1.79  | 1.05  | 8.00 | 0.37  | 21%                     | 1.99   | 0.79  | 3.00 | 0.46  | 23%    | 0.74                      | 19.37 | 29.49 | 3.00 | 17.02 | 88%    | 0.41 |
|            |                     | AmPr-FHxSA     | 9.55  | 8.33  | 8.00 | 2.95  | 31%                     | 11.58  | 8.11  | 3.00 | 4.68  | 40%    | 0.73                      | 37.23 | 54.38 | 3.00 | 31.40 | 84%    | 0.47 |
|            |                     | CETAmPr-FOSA   | 1.90  | 1.86  | 8.00 | 0.66  | 35%                     | 1.58   | 1.01  | 3.00 | 0.58  | 37%    | 0.72                      | 13.59 | 20.84 | 3.00 | 12.03 | 89%    | 0.43 |

**Figure 4.20.** Initial soil PFAS concentrations compared to those measure 48 weeks of either aerobic or anaerobic incubation. Results are shown for soil collected and homogenized in the 0 to 5 ft bgs interval.

#### 4.5 Test Cell – PFAS Leaching

Please note that portions of Section 4.5 have been reprinted (adapted) with permission from {Leaching of perfluoroalkyl acids during unsaturated zone flushing at a field site impacted with aqueous film forming foam. Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R. et al., Environ. Sci. Technol., 57, 1940-1948}. Copyright 2023. American Chemical Society, and from {A field study to assess the role of air-water interfacial sorption on PFAS leaching in an AFFF source area. Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R. et al., J. Contam. Hydrol. 248} Copyright 2022. Elsevier.

#### 4.5.1 PFAS Leaching under Ambient Conditions

##### *Sample Collection and Porewater Characteristics*

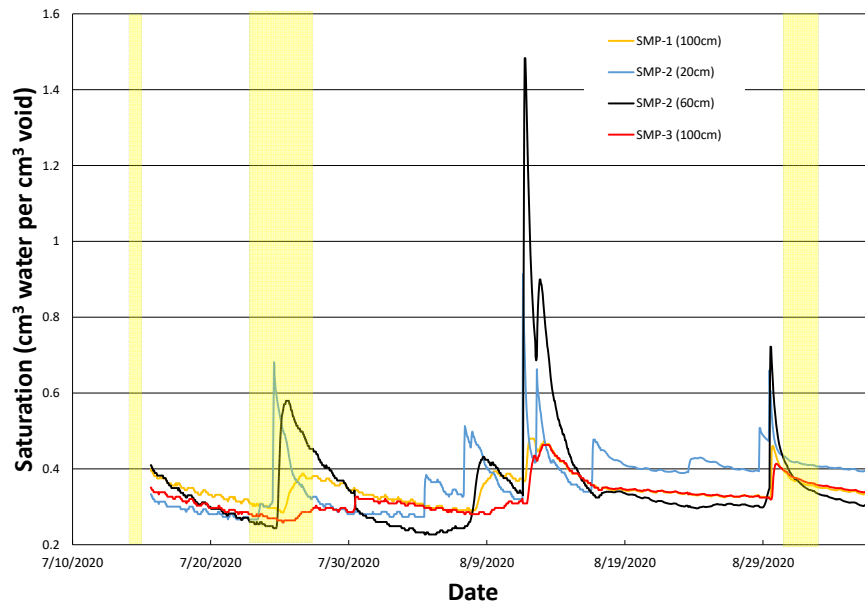
The porewater saturations ( $S$ , in  $\text{cm}^3$  per  $\text{cm}^3$ ) and the three lysimeter temporal sampling intervals over which porewater was collected are shown in **Figure 4.21**; corresponding cumulative precipitation is also shown in **Figure 4.21**. Porewater TOC, conductivity, and pH levels are summarized in **Table 4.4**. Porewater samples were collected during a precipitation event, or within 3 days of a precipitation event. In all cases, evidence of water flux through the vadose zone was noted during sample collection by decreases in soil moisture as a function of time. It is unclear why a saturation reading of approximately 1.5 was measured at SMP-2(60 cm) during a severe storm event on August 11, 2020.

The water flux thorough the test cell was conservatively estimated for the well-drained sandy soils at the site by using the rainfall flux. As shown in **Figure 4.21**, 0.184 m of rainfall occurred over the 49 day monitoring period, resulting in an average water flux of  $3.4 \times 10^{-3} \text{ m d}^{-1}$  through the test cell (assuming 100% recharge – evaluation of the actual recharge is discussed in Section 4.5.2).

##### *PFAS Porewater Concentrations and Mass Flux*

Average PFAS concentrations over all 3 sampling events measured among the 5 lysimeters at a depth of 0.61 m bgs and also among the 4 lysimeters at a depth of 1.2 to 1.5 m bgs are shown in **Figure 4.22**. Lysimeters L-2 and L-8, installed at the very shallow depth below ground surface of 0.15 m, were not included in **Figure 4.22** because the shallow depth coupled with rapid water infiltration into the sandy soil likely were not representative of equilibrium conditions and PFAS porewaters impacting underlying groundwater; average PFAS concentrations in L-2 and L-8 over the 3 sampling events were approximately 4 standard deviations greater than the mean calculated among the deeper lysimeters shown in **Figure 4.22**, suggesting these data were outliers compared to the lysimeter data measured at depths of 0.61 m and 1.2 to 1.5 m bgs. For example, the average PFOS concentration at 0.15 m over the 3 sampling events was  $45,000 \pm 25,000 \text{ ng/L}$ , which is more than 4 time greater than that measured in the deeper lysimeters. In addition, lysimeter L-5 from the first round of sampling was excluded because only a very limited volume of porewater ( $6.5 \text{ cm}^3$  of porewater versus  $> 60 \text{ cm}^3$  for all other lysimeters) had been initially flushed through the lysimeter prior to and including porewater collection associated with the first sampling event, and PFAS concentrations were 5-times lower in L-5 than the average observed among the other lysimeters. The subsequent round of sampling in L-5 yielded greater than  $200 \text{ cm}^3$  of porewater. Finally, for L-1, several PFAS results for the second and third rounds of sampling (including results for PFOS, PFHpS, and PFOA) were excluded from the averages shown in **Figure 4.22** because measured PFAS concentrations were at least 3 standard deviations greater than then average calculated among the other lysimeters for most of the PFAS detected. Overall, with these exceptions, results show that PFAS concentrations measured in the porewater at depths of at least 0.61 m bgs were generally repeatable among the lysimeters and over the 3 sampling events, as indicated by 95% confidence intervals that were typically less than 50% of the average for the shallow (0.61 m bgs) lysimeters, and less than 40% of the average for the deep (1.2 to 1.5 m bgs) lysimeters.

a.



b.

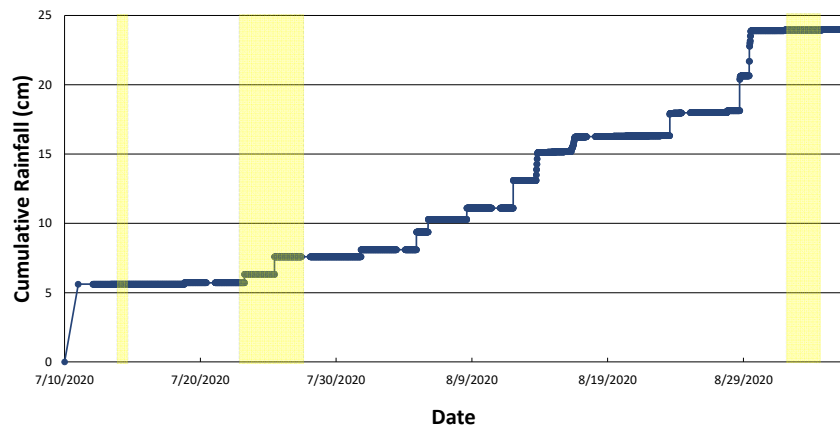


**Figure 4.21. a.** Lysimeter sampling intervals and corresponding water saturations (measured using the moisture probes) over the study period. The three shaded bars indicate the sampling intervals over which lysimeter samples were collected via an applied vacuum. Lysimeter samples were collected during or shortly after rainfall events where the soil moisture and vertical water flow remained elevated. Saturation values were calculated based on calibration to soil moisture contents obtained via direct collection of soil samples.

**b.** Lysimeter sampling intervals and cumulative precipitation over the study period. The installed rain gauge was only operational after 8/16/20; a local weather station (data provided at <https://www.cocorahs.org/>) was used to monitor rainfall prior to this date.

**Table 4.4.** Total organic carbon (TOC), conductivity, and pH results for select lysimeters measured during the 3<sup>rd</sup> sampling event. NM=not measured.

| Lysimeter | TOC<br>(mg/L) | Conductivity<br>( $\mu$ S/cm) | pH<br>(SU) |
|-----------|---------------|-------------------------------|------------|
| L-1       | 80            | 650                           | 8.2        |
| L-4       | 34            | 810                           | 7.6        |
| L-9       | 52            | 820                           | NM         |
| L-10      | 96            | 1100                          | 8.4        |
| L-11      | 67            | 1600                          | 8.5        |

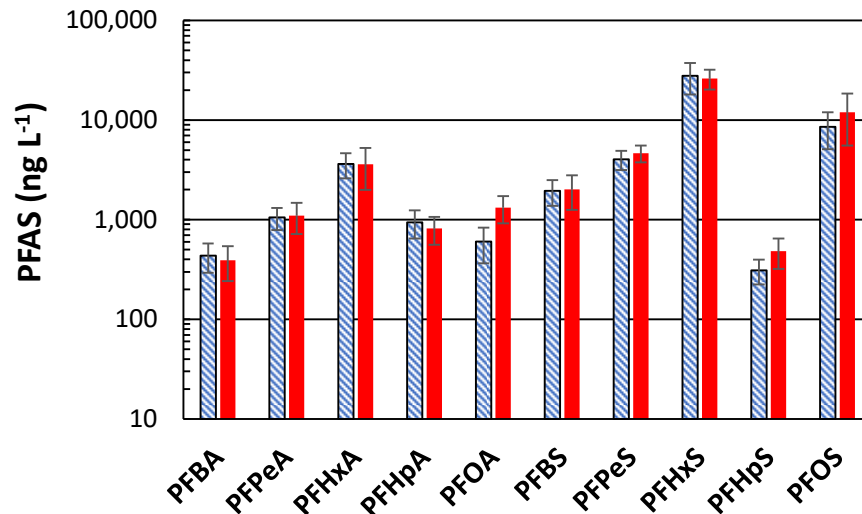


**Figure 4.22.** Average PFAS porewater concentrations measured using the field-deployed lysimeters over three rounds of sampling. The blue-hatched bars are from the 4 deep (1.2 to 1.5 m bgs) lysimeters, and the red bars are from 4 shallow (0.61 m bgs) lysimeters. As described in the text, the first round of sampling from L-5 and outliers ( $> 3$  standard deviations from the mean) from the second and third rounds of sampling at L-1 were excluded from calculation of the averages shown in this figure. Error bars represent 95% confidence intervals. PFBA =perfluorobutanoic acid, PFPeA = perfluoropentanoic acid, PFHxA = perfluorohexanoic acid, PFHpA =perfluoroheptanoic acid, PFOA = perfluorooctanoic acid, PFBS =perfluorobutanesulfonate, PFPeS=perfluoropentanesulfonate, PFHxS = perfluorohexanesulfonate, PFHpS= perfluoroheptanesulfonate, and PFOS = perfluorooctanesulfonate.

Results show that the PFAS concentrations measured in the shallow lysimeters located at 0.61 m bgs were typically statistically identical (overlapping 95% confidence intervals) to those measured at 1.2 to 1.5 m bgs, indicating that PFAS concentrations were at an apparent equilibrium in the percolating porewater within the interrogated depth interval of the vadose zone (i.e., PFAS concentrations in porewater not changing with depth). Thus, despite the comparatively higher organic carbon and PFAS concentrations associated with the shallow soil, PFAS concentrations in the porewater are in local equilibrium with the soil throughout the interrogated interval. This apparent local equilibrium suggests that independently determined equilibrium partitioning parameters may be useful for predicting PFAS porewater concentrations, as discussed in the following section.

PFOS and perfluorohexane sulfonate (PFHxS) were the PFAS that showed the highest average porewater concentrations in **Figure 4.22** of approximately 10,000 and 25,000 ng L<sup>-1</sup>, respectively, for the depths of 0.61 m and 1.2 – 1.5 m. PFOS and PFHxS were also the PFAS that had the highest concentrations in the soil (**Table 4.2**). The perfluoroalkyl acid (PFAA) mass flux through the test cell during the 49 day monitoring period is shown in **Table 4.5** (*note: this mass flux assume 100% recharge; actual recharge rates are estimate in Section 4.5.2*). Extrapolated over the course of a year, the total mass of PFAAs leached from the unsaturated soil within a year would be 1.1 ± 0.37 g. Based on PFAA soil concentrations measured within the test cell (**Table 4.2**), this total annually leached PFAA mass represents only 2% of the total PFAS mass present in the unsaturated zone. These results suggest that PFAAs will persist in the unsaturated soils for decades to come, although it is currently unclear how PFAA mass flux will diminish over time due to thermodynamic and/or kinetic limitations.

**Table 4.5.** Calculated PFAS mass flux through the vadose zone towards underlying groundwater based on an average water flux of  $3.4 \times 10^{-3}$  m d<sup>-1</sup>, 100% recharge, and the average PFAS concentrations for the deep lysimeters at 1.2 to 1.5 m bgs.

| PFAS  | Mass Flux (ng m <sup>-2</sup> d <sup>-1</sup> ) |
|-------|-------------------------------------------------|
| PFBS  | 6,400 ± 1,800                                   |
| PFPeS | 13,000 ± 2,900                                  |
| PFHxS | 92,000 ± 32,000                                 |
| PFHpS | 750 ± 360                                       |
| PFOS  | 28,000 ± 11,000                                 |
| PFBA  | 1,400 ± 470                                     |
| PFPeA | 3,500 ± 860                                     |
| PFHxA | 12,000 ± 3,300                                  |
| PFHpA | 3,100 ± 980                                     |
| PFOA  | 1,800 ± 805                                     |

Sporadic (<35% of lysimeter samples) detections of perfluorohexane sulfonamide (FHxSA) were observed, but results were typically below the analytical method quantification limit of 2,000 ng L<sup>-1</sup>, which was much greater than the 200 ng L<sup>-1</sup> method quantification limit for most PFAAs. When detected, FHxSA concentrations ranged from 5,000 to 10,000 ng L<sup>-1</sup>. 6:2 Fluorotelomer sulfonate (6:2 FtS) was only sporadically detected during the first 2 sampling events, but was measured at an average concentration of approximately 2,000 ng L<sup>-1</sup> in the third round. It is currently unclear why these two compounds were not detected on a more consistent level. No suspect PFAS analytes were detected in the porewater, though this is likely due to the high degree of dilution required for aqueous analysis due to the high PFHxS and PFOS levels.

### *PFAS Mass Balance and Role of the Air-Water Interface*

As described in **Appendix A5**, results of the film experiments yielded values of the air-water interfacial adsorption coefficient ( $K_{aw}$ ) of  $0.18 \pm 0.029$  cm,  $0.071 \pm 0.061$  cm,  $0.064 \pm 0.048$  cm for PFOS, PFHpS, and PFOA, respectively (average  $\pm$  95% confidence intervals shown). The elevated  $K_{aw}$  values for PFOS are expected due to its increased perfluorinated chain length relative to PFHpS and PFOA (Schaefer et al., 2019b).  $K_{aw}$  values for the other PFAS present in porewater were below that which could be measured using the film method.

**Figure 4.23** shows the average PFAS porewater concentrations measured in the field lysimeters compared to predicted values of the PFAS porewater concentrations. Only PFAS that were both consistently detected in the lysimeters samples (**Figure 4.22**), and also shown to be at equilibrium in the batch kinetic desorption testing (Section 4.2.1), were evaluated. Predicted PFAS porewater concentrations are based conceptually on the PFAS mass balance model developed by Brusseau et al. (2019b), which considers PFAS distribution among the soil, aqueous phase, and air-water interface. The application of the model is based on two key parameters: a desorption  $K_d$  value to describe PFAS soil-water partitioning and a PFAS interfacial partition coefficient ( $K_{aw}$ ) to describe PFAS partitioning to the air-water interface. The following 3 equations were used to describe PFAS phase behavior among the soil, aqueous, and air-water interfacial phases in a 10 g unit mass of shallow soil (50% saturation based on moisture probe and soil moisture data):

$$K_{aw} = \frac{\Gamma}{C} \quad \text{Eq. 4.2}$$

$$K_d = \frac{C_s - b}{C} \quad \text{Eq. 4.3}$$

$$M_T = \text{Mass at interface} + \text{Mass in soil} = V\Gamma a_{aw} + C_s m \quad \text{Eq. 4.4}$$

where  $C$  is the aqueous concentration (ng cm<sup>-3</sup>),  $C_s$  is the sorbed soil concentration (ng kg<sup>-1</sup>),  $M_T$  is the total PFAS mass used in a  $10 \times 10^{-3}$  kg mass of soil (ng, determined on a dry soil basis by multiplying the total PFAS concentrations in the collected soil shown in **Table 4.2** by the  $10 \times 10^{-3}$

<sup>3</sup> kg of dry soil),  $V$  is the *in situ* soil bed volume associated with the  $10 \times 10^{-3}$  kg of dry soil ( $6.1 \text{ cm}^3$ , estimated assuming a dry bulk density of  $1.65 \text{ g cm}^{-3}$ ),  $a_{aw}$  is the air water interfacial area per bed volume ( $\text{cm}^2 \text{ per cm}^3$ ), and  $m$  is the mass of dry soil ( $10 \times 10^{-3}$  kg). Desorption isotherms using the shallow soil described herein were previously determined using a sequential batch dilution technique to determine  $K_d$  (PFAS soil sorption coefficient in  $\text{L kg}^{-1}$ ) and  $b$  (the y-intercept associated with the linear desorption isotherm in  $\text{L kg}^{-1}$  (Section 4.2.2)). It is noted that Eq. 4.4 neglects the mass contribution from the aqueous phase. Based on the measured soil concentration and PFAS porewater concentrations, the PFAS mass in the water accounts for less than 1% of the total mass, thus justifying this simplification. Based on the amount of rainfall between soil collection and the time lysimeter sampling was initiated (approximately 142 cm of rainfall over 18 months based on weather station data), and using the porewater concentrations in Figure 4.22, the mass of PFOS and PFHpS leached from the soil between the time of soil collection and the beginning of the lysimeter sample collection 18 months later is estimated at less than 1% and 2% of their mass present in the saturated zone, respectively. Thus, this small amount of mass removal was considered negligible for the model. For PFOA, using this same approach, the mass removal over this 18 month period is estimated at 15%. To account for this,  $M_T$  for PFOA in Eqs. 4.3 and 4.4 was decreased by 15% to provide a more appropriate value for the model.

The value for  $a_{aw}$  was determined based on the average soil grain size using the following equation (Lyu et al., 2018; Brusseau et al., 2019):

$$a_{aw} = 3.9d^{-1.2}(1 - S) \quad \text{Eq. 4.5}$$

where  $d$  is the mean particle diameter of the shallow soil (0.04 cm) and  $S$  is the pore saturation of the soil during lysimeter sample collection (estimated at  $0.5 \text{ cm}^3 \text{ cm}^{-3}$  based on moisture probe data). The resulting value for  $a_{aw}$  is  $93 \text{ cm}^{-1}$ . A discussion of the error associated with the model predictions is provided in **Appendix A6**.

As depicted in **Figure 4.23**, if PFAS sorption to the air-water interface is not considered, the predicted PFAS porewater concentrations are 1.4- to 4-times greater than the PFAS concentrations measured in porewater. PFOS shows the greatest discrepancy in aqueous concentration between the lysimeter-based and batch desorption-based results among the PFAS examined. PFOS is the most surface active among the three PFAS shown in **Figure 4.23** (Costanza et al., 2019; Schaefer et al., 2019b). These observations suggest the possibility that the discrepancy between lysimeter and batch desorption results is due to PFAS accumulation at air-water interfaces, which are present in the unsaturated soils within the test cell.

**Figure 4.23** also shows that including PFAS retention at the air-water interface results in a substantial improvement in the prediction of PFAS porewater concentrations, most notably for PFOS where a 58% reduction in the predicted porewater concentration was observed. When considering uptake at the air-water interface, the predicted porewater PFOS concentration is within the 95% confidence interval of the measured PFOS porewater concentration. PFOS showed a much greater measured interfacial partition coefficient ( $K_{aw}=0.18 \text{ cm}$ ) than PFHpS (0.071 cm) and

PFOA (0.064 cm) in porewater, thus inclusion of air-water interfacial sorption expectedly had the most notable effect on PFOS.

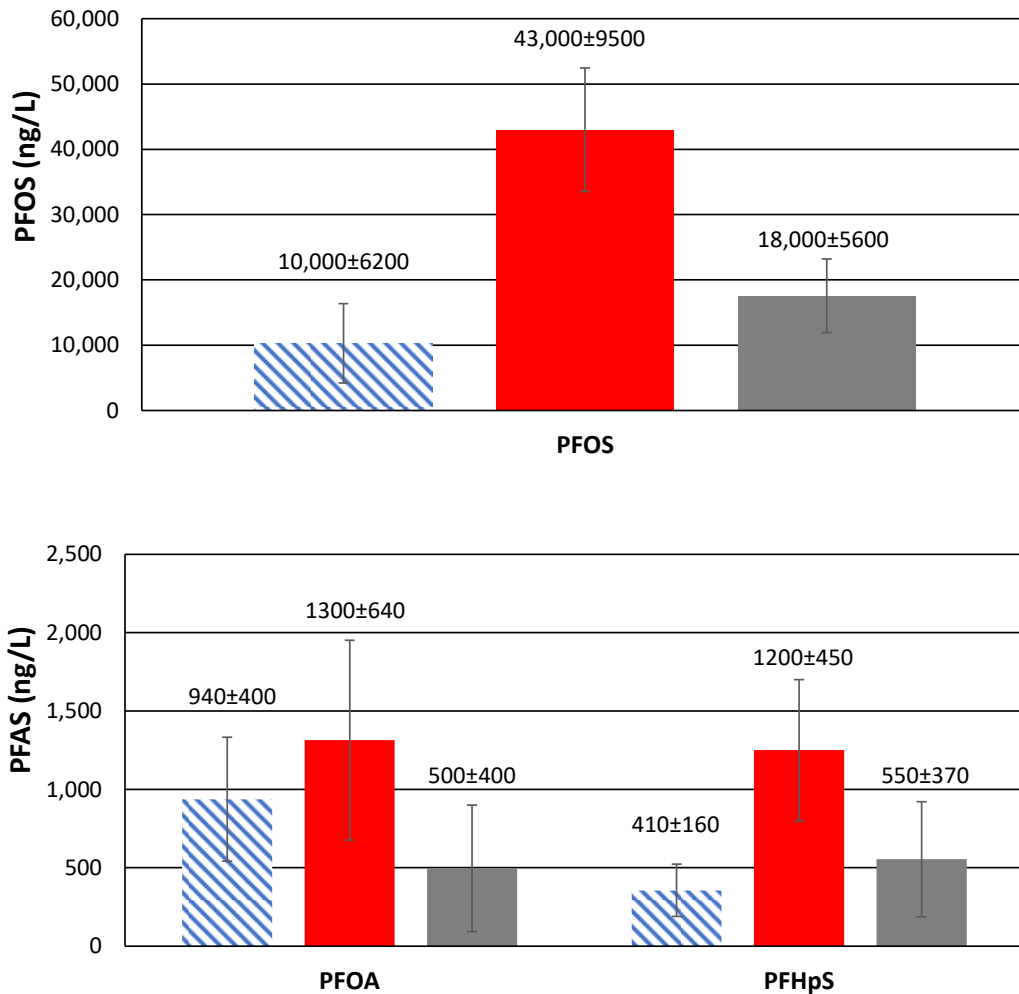


**Figure 4.23.** PFAS average porewater concentrations for PFOS, PFHpS, and PFOA over all three rounds of sampling (blue hatched bars). Results are compared to predicted porewater PFAS concentrations that exclude (red bars) or include (gray bars) PFAS sorption to the air-water interface. Error bars for the measured porewater concentrations represent 95% confidence intervals using the shallow (0.61 m bgs) lysimeters over all three sampling rounds. Error bars for the predicted values represent 95% confidence intervals, which are calculated based on propagation of the error (95% confidence intervals) associated with the measured  $K_d$  and  $K_{aw}$  values, and the estimated  $a_{aw}$  value. Values shown above bars are the aqueous concentration  $\pm$  95% confidence intervals.

For PFHpS, inclusion of air-water interfacial sorption also resulted in a predicted value that was within the 95% confidence interval of the measured porewater value, whereas exclusion of air-water interfacial sorption resulted in a significant overprediction of the measure porewater value. For PFOA, the relatively large uncertainty associated with the soil-water partitioning ( $K_d$  value) limited the ability to conclusively assess any improvement in porewater prediction by including sorption at the air-water interface.

Together, these measured values and calculations provide a line of evidence for the relevance of PFAS air-water interfacial sorption *in situ*. To our knowledge, these are the first field data that demonstrate the impact of PFAS air-water interfacial sorption on PFAS leaching, thereby validating bench-scale studies that suggest air-water interfacial sorption is an important mechanism to consider at AFFF-impacted sites.

While, particularly for PFOS and PFHpS, inclusion of the air-water interfacial sorption resulted in improved predictions of *in situ* porewater concentration, it is possible that factors besides sorption at the air-water interface could have played a role in the overpredictions shown in **Figure 4.23**. These factors include flow heterogeneity and other mass transfer limitations. However, given the similarity in PFAS concentrations between the shallow and deep lysimeters (which suggests mass transfer effects were limited), as well as the fact that the most surface active compound examined (PFOS) showed the greatest improvement when the model included interfacial sorption, it is likely that air-water interfacial sorption was the primary factor responsible for the discrepancy between the measured porewater values and the  $K_d$ -only partitioning model shown in Figure 5. Additional studies at a variety of sites are needed to further validate the role of interfacial sorption on PFAS concentrations in porewater.

### *Environmental Implications*

Results presented herein show that PFAS mass flux to underlying groundwater is likely being reduced by 1.5- to 4-times for PFOS, PFHxS, and PFOA due to accumulation at the air water interface, as highlighted by the impact of air-water retention on PFAS porewater concentrations. Thus, consistent with previously performed unsaturated column experiments (e.g., Lyu et al., 2018), air-water interfacial uptake plays an important role in PFAS transport through the unsaturated zone. While the overall PFAS mass flux from the AFFF-impacted soils remains largely controlled by desorption from the soil, accounting for PFAS accumulation at the air-water interface is required to estimate overall PFAS mass flux. Further study is needed to more closely examine the impacts of variable saturation and water flux on PFAS mass flux through the vadose zone. Further study also is needed to assess PFAS mass flux under differing soil, hydraulic, and PFAS loading conditions.

#### 4.5.2 PFAS Leaching during Flushing

##### *Water Migration and PFAA Leaching*

Irrigation water was collected prior to flushing to verify that PFAS concentrations were below the limits of quantification. Implementation of soil flushing expectedly resulted in the rapid infiltration of water through the permeable sandy soil, as indicated in the moisture probe data. With the exception of lysimeter L6 on May 10, 2021, where only 1 mL was collected within the lysimeter, collected lysimeter sample volumes during and after flushing were in excess of 20 mL.

Perfluorinated sulfonic acid (PFSA) and perfluorinated carboxylic acid (PFCA) concentrations measured in the lysimeters are summarized in **Figures 4.24 and 4.25**, respectively. In general, measured PFAA porewater concentrations showed increased variability (as indicated by the increased size of the 95% confidence intervals) immediately after flushing was initiated, which may have been the result of transient flow and percolation pathways resulting from the rapid water infiltration and elevated pore saturations. Based on prior batch testing performed on site soils that showed negligible colloidally-bound PFAS (9), it is unlikely that this variability was due to any colloid-facilitated transport from the change in flow conditions.

The longer-chained and more surface active PFSAs, particularly PFOS, showed a comparatively greater extent of elevated porewater concentrations following the initial flushing event than the shorter-chained compounds (first three flushing sampling events compared to the baseline ambient data in **Figure 4.24**). This may be due to the increased pore saturations following flushing, and the subsequent collapse and release of PFAS from the air-water interface. While this is less apparent after initiation of the second flushing phase due to scatter in the data, comparison of the PFOS and PFBS data at each of the 4 lysimeters shows no significant increase for PFBS over the first three sampling events following initiation of the Phase 2 flushing, but a  $73 \pm 26\%$  increase for PFOS over this same interval.

Overall, PFAA porewater concentrations typically decreased by at least a factor of two between the initial (baseline) rounds of ambient sampling and the final (post flushing) rounds of ambient sampling collected in September and October of 2021. For the PFSAs, porewater concentrations measured through each of the last three monitoring events only increased for PFBS, suggesting the possibility that PFBS concentrations may still have been rebounding following flushing. For the PFCAs, PFPeA, PFHxA, and PFHpA all show increasing concentrations through the last three monitoring events, suggesting the possibility that these compounds did not reach pseudo-equilibrium conditions following flushing; a potential explanation for the behavior of these PFCAs is discussed below.

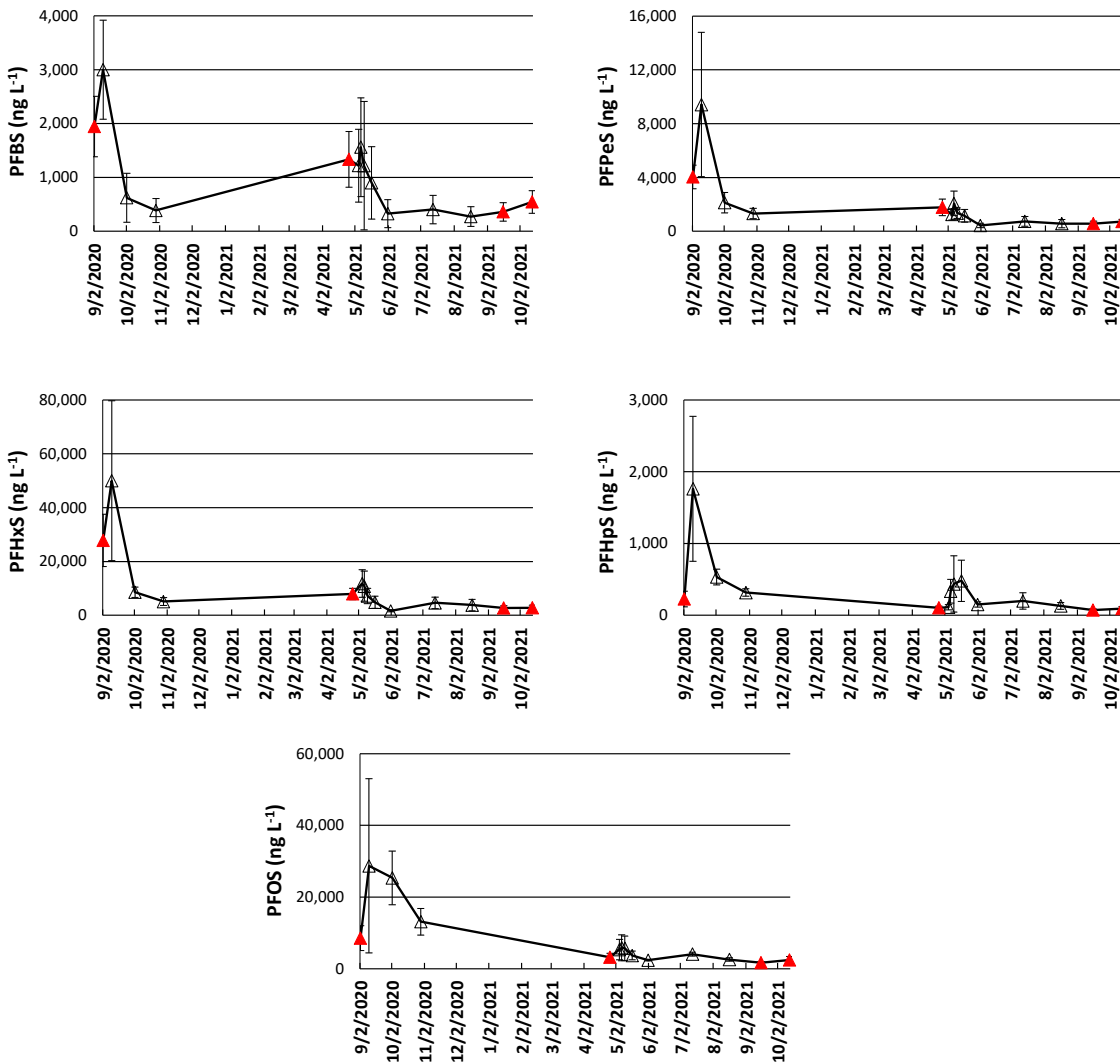


**Figure 4.24.** PFSA concentrations measured in the 4 deep lysimeters (Table S1). Average values are shown, with error bars representing the 95% confidence intervals. For the baseline and intermediate ambient data, a single average datapoint over the 3 temporal rounds of data is shown for clarity.  $\triangle$  = lysimeter sample collected during active flushing;  $\blacktriangle$  = lysimeter sample collected under ambient (no flushing) conditions.

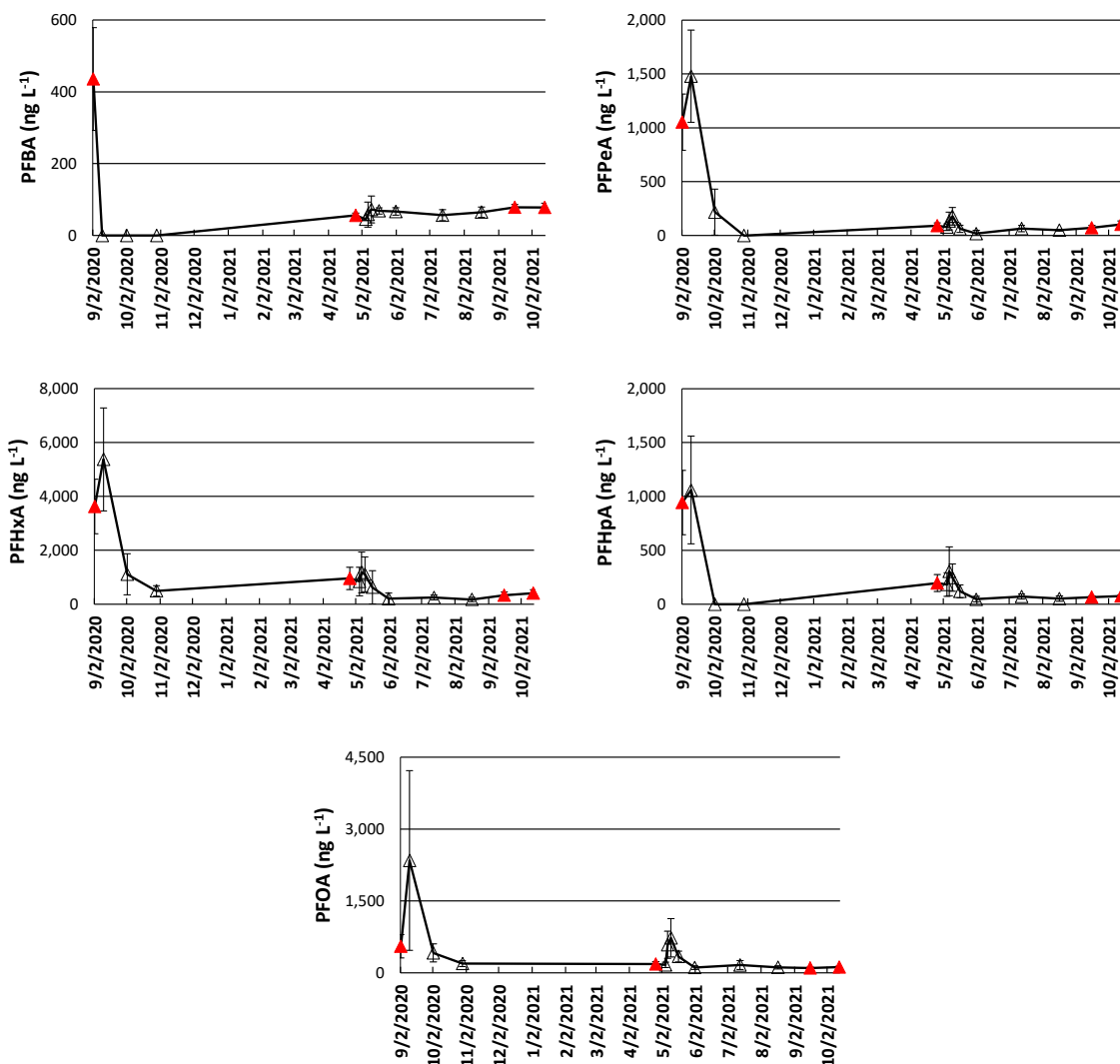


**Figure 4.25.** PFCA concentrations measured in the 4 deep lysimeters (Table S1). Average values are shown, with error bars representing the 95% confidence intervals. For the baseline and intermediate ambient data, a single average datapoint over the 3 temporal rounds of data is shown for clarity.  $\triangle$  = lysimeter sample collected during active flushing;  $\blacktriangle$  = lysimeter sample collected under ambient (no flushing) conditions.

### *PFAA Mass Removal and Mass Balance*

The initial PFAA mass in the unsaturated test plot (to a depth of 1.5 m bgs, similar to that of the deepest lysimeters) can be readily estimated based on the soil data provided in Table S3 and assuming a soil bulk density of  $1.6 \text{ kg m}^{-3}$ . However, the flushing experiment was initiated approximately 20 months after the soil data shown in **Table 4.2** was collected (soil data collected in January 2019), and PFAA leaching and mass removal occurred during the 20 month time period between January 2019 and September 2020 due to ambient rainfall and subsequent percolation through the unsaturated zone. To account for this, the mass of each PFAA in the test plot immediately prior to the September 2020 flushing (Table 1) was therefore calculated as follows:

$$M_0 = M_i - (F A t I_w) \quad \text{Eq. 4.6}$$

where  $M_0$  is the PFAA mass immediately prior to flushing [mg],  $M_i$  is the PFAA mass in the test plot based on the January 2019 soil data (**Table 4.2**) [mg],  $F$  is the PFAA mass flux under ambient conditions (assuming 100% recharge) previously measured (20) [ $\text{mg m}^{-2} \text{ d}^{-1}$ ],  $A$  is the area of the test plot [ $18.5 \text{ m}^2$ ],  $t$  is the time [600 d], and  $I_w$  is the fraction of rainfall (or, water flux) that infiltrates through the top 1.5 m of the unsaturated zone; thus,  $I_w$  is effectively the fraction of rainfall that recharges to groundwater.  $I_w$  is estimated at 0.49 based on estimated rainfall and evapotranspiration values as described in **Appendix A7**.

Values of  $M_i$  and  $M_0$  for the PFAAs evaluated in this study are presented in **Table 4.6**. For several of the PFAAs, a substantial percentage (>20%) of the PFAS mass present in the test plot during the initial soil investigation performed in January 2019 had leached from the source area prior to initiation of the flushing experiment. For PFBS, PFHxA, and PFHpA, the coupled uncertainty for the initial soil mass and ambient leaching flux resulted in large uncertainties in estimated soil mass ( $M_0$ ) mass prior to initiation of flushing. For PFBS and PFHpA, relatively large uncertainty in the mass initially present in the test plot (59% and 47%, respectively) and the mass leached inhibits a quantitative assessment of the mass balance. Thus, PFBS and PFHpA are excluded from subsequent discussion on PFAS mass removal. PFHxA, despite the large uncertainty, was retained for discussion purposes related to potential precursor transformation, as discussed later in this section. The persistence of PFAS such as PFHxA and PFHpA for over 20 years, despite their relatively substantial removal between January 2019 and September 2020, suggests that their soil concentrations were initially much greater than those initially measured in 2019, that precursor transformation has effectively sustained their concentrations, and/or non-linear desorption behavior at historically elevated PFAS concentrations inhibited leaching.

**Table 4.6.** PFAS mass in the test plot (0 to 1.5 m below ground surface) based on the time of initial soil collection ( $M_i$  - January 2019) and then immediately before flushing ( $M_0$  - September 2020), as described in Eq. 1.  $\pm$  values represent the 95% confidence interval.

| PFAS               | Estimated Mass ( $M_i$ )<br>Based on January 2019<br>Soil Data [mg] | Estimated Mass ( $M_0$ )<br>Immediately Prior to<br>Flushing [mg] <sup>2</sup> | % Decrease |
|--------------------|---------------------------------------------------------------------|--------------------------------------------------------------------------------|------------|
| PFBA <sup>1</sup>  | -                                                                   | -                                                                              | -          |
| PFPeA <sup>1</sup> | -                                                                   | -                                                                              | -          |
| PFHxA              | 150 $\pm$ 46                                                        | 71 $\pm$ 67                                                                    | 52         |
| PFHpA              | 44 $\pm$ 21                                                         | 24 $\pm$ 28                                                                    | 45         |
| PFOA               | 180 $\pm$ 31                                                        | 170 $\pm$ 40                                                                   | 5.5        |
| PFBS               | 160 $\pm$ 95                                                        | 120 $\pm$ 110                                                                  | 25         |
| PFPeS              | 630 $\pm$ 150                                                       | 540 $\pm$ 170                                                                  | 14         |
| PFHxS              | 5700 $\pm$ 1000                                                     | 5100 $\pm$ 1400                                                                | 11         |
| PFHpS              | 580 $\pm$ 170                                                       | 570 $\pm$ 171                                                                  | 1.8        |
| PFOS               | 37000 $\pm$ 9400                                                    | 36000 $\pm$ 11000                                                              | 2.7        |

NOTES:

<sup>1</sup> Soil mass not estimated due to analytical results below the quantification level. The lower quantification level for PFBA and PFPeA were 2.4 and 6  $\mu\text{g/kg}$ , respectively.

<sup>2</sup> the 95% confidence interval for the calculated  $M_0$  values includes the sum of the errors associated with  $M_i$ , with the ambient mass flux, and an estimated 20% error associated with the recharge fraction ( $I_w$ ).

Values of  $F$  used to determine  $M_0$ , are as follows:

PFBS 7,400  $\pm$  2,100  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFPeS 15,000  $\pm$  3,300  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFHxS 110,000  $\pm$  37,000  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFHpS 860  $\pm$  410  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFOS 32,000  $\pm$  13,000  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFBA 1,700  $\pm$  540  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFPeA 4,000  $\pm$  1,000  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFHxA 14,000  $\pm$  3,800  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFHpA 3,600  $\pm$  1,100  $\text{ng m}^{-2} \text{d}^{-1}$   
 PFOA 2,100  $\pm$  930  $\text{ng m}^{-2} \text{d}^{-1}$

The mass of each PFAS initially (based on 2019 soil data; **Table 4.6**) present in the test cell compared to the mass of PFAS removed during leaching (combined ambient and enhanced flushing from January 2019 through October 2021) is summarized in **Figure 4.26**. The total mass removed from the test cell (20 month ambient period + active flushing) for each PFAS was calculated as follows:

$$M_T = (M_i - M_0) + \sum_{\text{each stage}} V_f C \quad \text{Eq. 4.7}$$

where  $V_f$  is the total flushing volume [L] and  $C$  is the volume-averaged PFAS porewater concentration [ $\text{mg L}^{-1}$ ] for each flushing stage (**Table 3.4**), which is summed for each active

flushing stage. With the exception of the most hydrophobic compounds (i.e., PFOS and PFHpS), the mass leached from the test plot exceeded 50% of the initial mass present. For PFHxA, the average mass leached exceeded the initial mass estimated in the test cell.

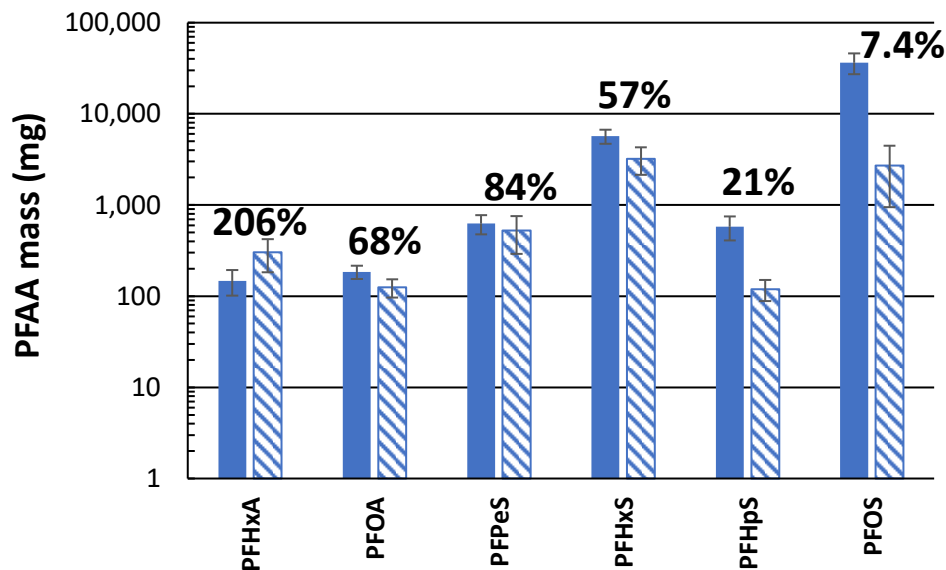


**Figure 4.26.** Mass initially present in the test cell (solid bars) compared to the mass leached from the test cell following the 20 months of ambient leaching and the active flushing (hatched bars). Error bars represent 95% confidence intervals. Values shown above the bars represent the average percentage of mass removed due to combined ambient and active flushing compared to the initial mass in the test cell.

While uncertainty in the mass initially present and the mass leached for PFHxA precludes a definitive assessment with respect to mass balance, it is plausible that the mass leached from the test cell for PFHxA did actually exceed the mass of this compound initially present (January 2019) in the test cell. Previous soil analysis showed that 6:2 and 8:2 fluorotelomer sulfonates, and 6:2 fluorotelomer sulfonamido propyl betaine, were present in the soil at concentrations that together exceeded that of PFHxA by approximately 8-times; these polyfluoroalkyl substances can all be biotransformed to PFHpA and/or PFHxA (Harding-Marjanovic et al., 2015; Zhang et al., 2016; D’Agostino and Mabury, 2017; Choi et al., 2022). In addition, previously performed desorption isotherms performed on the test cell soils showed that the PFHxA mass desorbed from the soil over a 9-month duration ranged as high as 13-times the mass of PFHxA initially measured in the soil, and 1.3-times the mass of PFHpA measured in the soil. No such discrepancies in mass balance occurred for the other PFAAs in the desorption study. Thus, it is plausible that the discrepancy in mass balance for PFHxA in **Figure 4.26** is due, in part, to precursor transformation, although heterogeneity in PFHxA distribution in the test cell may also have been the primary cause of this

observation. Such biotransformation may also explain the increasing trends (or, apparent rebound) for PFHpA and PFHxA shown in **Figure 4.25**. While these results point to the potential for PFHxA precursor transformation in the vadose zone, additional studies are needed to verify that the *in situ* transformation of precursors to PFHxA is occurring. At least one recent study (Adamson et al., 2022) presented evidence for the *in situ* formation of PFHxA biological transformation of precursors.

#### *Decreases in Porewater Concentrations versus Fractional Mass Removal*

The relative decreases in PFAA pore water concentrations were calculated by dividing the porewater concentrations measured during the intermediate and final ambient (i.e., no active flushing, as shown in **Table 3.4**) lysimeter sampling events by the porewater concentration measured at the baseline ambient sampling events. For each PFAA, and for the concentrations measured at either the baseline, intermediate, or final ambient porewater sampling events, the fraction of the porewater concentration relative to baseline ( $F_C$ ) was calculated as follows:

$$F_C = \frac{C_A}{C_0} \quad \text{Eq. 4.8}$$

where  $C_A$  is the average PFAA concentration measured at either the baseline, intermediate, or final ambient porewater sampling events, and  $C_0$  is the average PFAA concentration measured at the baseline (just prior to flushing) sampling events.

The fractional PFAA mass removal ( $F_m$ ) for each stage of flushing (**Table 3.4**) was calculated as follows:

$$F_m = \frac{V_f C}{M_0} \quad \text{Eq. 4.9}$$

$F_m$  for each stage is added to provide the cumulative fractional mass removal for each PFAA. The fractional decrease in PFAA porewater concentration ( $F_C$ ) as a function of the fractional PFAA mass removal ( $F_m$ ) is provided in **Figure 4.27** for each PFAA.

For all PFAAs, the fractional decrease in porewater concentration exceeded the fractional decrease in mass removal. The exception was PFHxA which, as previously discussed, may be due to formation of this compound from precursors that are present in the soil. A linear relationship indicated by the dashed lines in **Figure 4.27** is expected if leaching is controlled by a linear equilibrium desorption isotherm that intercepts zero. Larger decreases in porewater concentrations as compared to mass removal has typically been explained by either mass transfer limitations (e.g., Brusseau et al., 2013; Borden and Cha, 2021) or non-linearity in the desorption isotherm (e.g., Schlebaum et al., 1999). Herein we consider both possibilities.

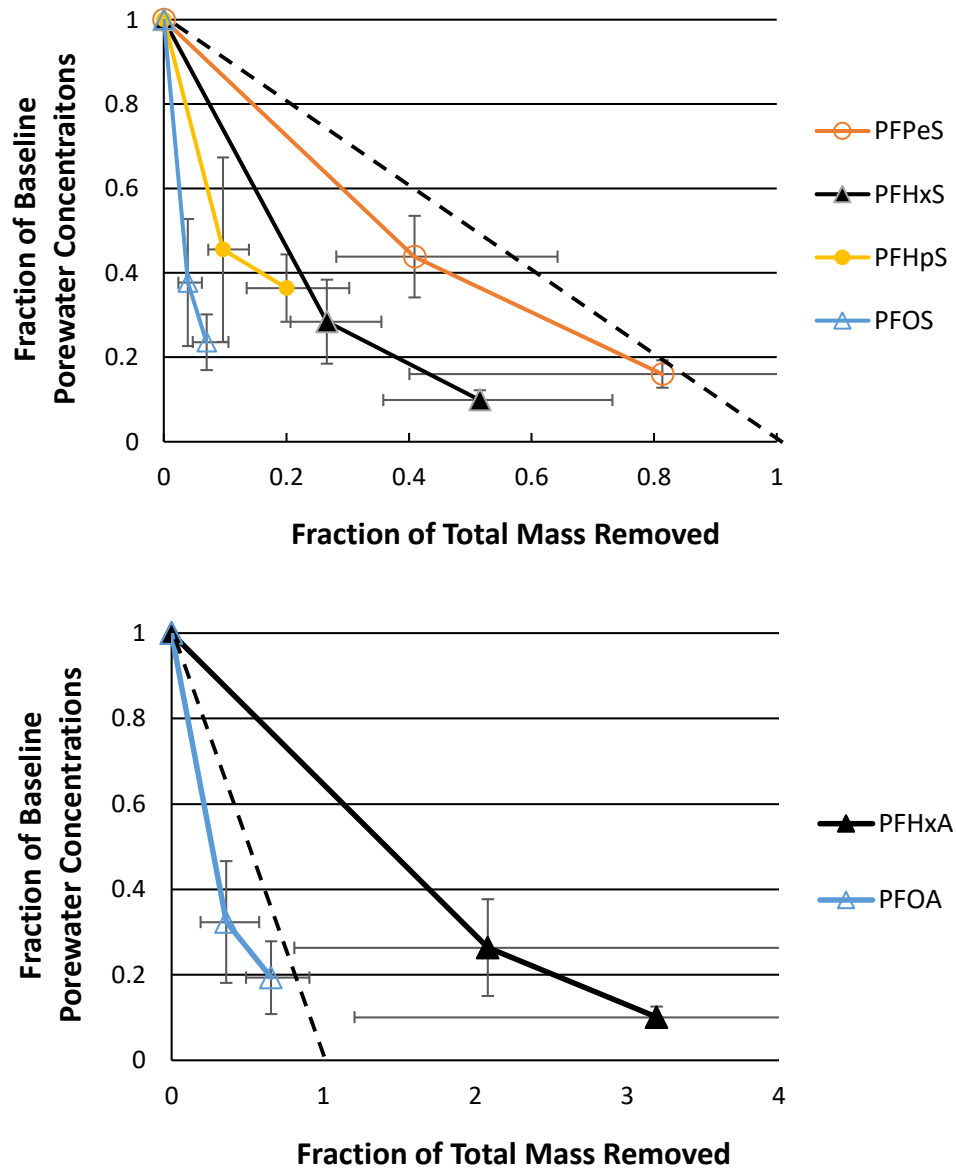


**Figure 4.27.** Fraction relative to the baseline ambient porewater concentrations versus the fraction of total mass removed from the test cell for the PFSA and the PFCAs. Error bars represent 95% confidence intervals, where Fieller's Theorem (Motulsky, 2017) is applied to calculate the 95% confidence interval of the fraction of total mass removed because the error associated with the denominator is not small compared to the denominator. The dashed lines represent the expected relationship between porewater and mass removal if leaching is controlled by a linear desorption isotherm with an intercept of zero. The average of the final two post-flushing data points in **Figures 4.24 and 4.25** are used for the final point in **Figure 4.27**.

The potential for rate-limited release considering the rapid infiltration (on the order of approximately one hour based on the moisture probe responses during and after the flushing cycles) is plausible. To evaluate such rate limited dissolution/leaching, one common approach is to stop or reduce flow to observe any increase in dissolved contaminant concentrations (e.g., Maizel et al., 2021; Rivett et al., 2006). As previously discussed, with the exception of PFBS, PFSA rebound following flushing was negligible. Thus, rate limited desorption at the macro scale (i.e., preferential flow, migration from low permeability domains) does not appear to be the cause of the trends observed in **Figure 4.27**. The absence of such mass transfer-controlled leaching at the macroscale is consistent with the observed geology of the test plot, which was shown to be a relatively homogeneous silty sand through the targeted interval.

In contrast, previous examination of the desorption kinetics for the test cell soils using a bench-scale batch technique indicated that release of several of the less hydrophobic PFAAs (e.g., PFBS, PFPeS, PFHxS) was kinetically controlled at the grain scale, as both equilibrium and kinetic sorption domains controlled overall release (Section 4.2.1). The absence of such kinetically controlled desorption/leaching at the field scale, with the exceptions previously noted, is an apparent contradiction to these bench-scale results. However, the bench-scale kinetic testing was performed over a period of approximately 17 days at a liquid:solid ratio ( $L\ kg^{-1}$ ) of approximately 2.5:1, or a dilution rate factor (liquid:solid ratio divided by the time) of  $0.15\ d^{-1}$ . In comparison, active flushing performed at the field scale resulted in a final liquid:solid ratio of 9.3:1 over 154 days, or a dilution rate factor of  $0.060\ d^{-1}$ . Thus, the slower rate of dilution during in situ flushing may have masked the kinetically controlled desorption kinetics (relative to the fraction in relatively rapid equilibrium) observed at the bench-scale. It is recognized that the daily water pulse via flushing (up to  $3.7\ m^3$  per day) occurred on a time frame of several hours, resulting in a dilution rate factor as high as  $0.14\ d^{-1}$ , which is nearly identical to the rate observed in the bench-scale testing. However, it is plausible that this daily water pulse is largely mixed with the existing porewater ( $4.9\ m^3$  of porewater remaining in the test plot at the start of each pulse, based on the pore saturation data measured via moisture probes and an estimated porosity of 0.35). Thus, kinetic effects related to actual soil desorption are likely mitigated by porewater mixing effects during the individual water pulses, and the overall soil desorption kinetics are better evaluated over the aggregate 154 day flushing period.

Soil desorption testing (Section 4.2.2) showed that the PFAAs exhibited linear desorption behavior (excluding a sorbed fraction that was resistant to desorption even after nine months of incubation). Thus, desorption isotherm nonlinearity is likely not the apparent cause of the leaching results shown in **Figure 4.27**. However, several studies have shown that contaminant release/desorption from soil can be impacted by the presence of a sorbed fraction that is not readily desorbed (e.g., Braida et al., 2002; Shor et al., 2003). This fraction that is resistant to desorption could be attributable to extremely slow desorption kinetics and/or contaminant-induced matrix deformation that increases contaminant affinity to the soil once sorbed (Sander and Pignatello, 2009). The resultant effect of these processes would be apparent desorption isotherm behavior in which the sorbed concentration remains well above zero as the dissolved concentration approaches zero. Indeed, PFAA desorption isotherms for these test plot soils indicated a significant fraction of the

sorbed mass was resistant to desorption (despite linear desorption behavior for the fraction of PFAA mass that was readily desorbable), as dissolved concentrations approached zero with a comparatively small fractional decrease in soil concentrations (Section 4.2.2). Thus, the field-scale flushing results are consistent with the desorption behavior observed in the bench-scale study, as PFAA aqueous concentrations decrease more rapidly than the corresponding soil mass.

Given the above discussion, the trend observed for the PFSA's (**Fig. 4.27**) suggests that the fraction of desorption resistant PFAA mass increases with perfluorinated chain length/hydrophobicity, with the more hydrophobic compounds expectedly exhibiting a more rapid decrease in dissolved (porewater) concentration relative to decreases in soil concentration compared to less hydrophobic compounds. The fraction of PFAA mass that was shown to readily desorb from the soil (Section 4.2.2) is plotted as a function of the fractional decrease in porewater concentration divided by the fraction of mass removed (total after completion of flushing) (**Fig. 4.28**). The x-axis in **Fig. 4.28** is a measure of the negative deviation from the linear equilibrium desorption behavior indicated by the dashed lines in **Fig. 4.27**; an x-axis value of 1 corresponds to the dashed line in **Fig. 4.27**. An increasing trend is clearly observed in **Fig. 4.28**, which suggests that the relatively rapid decreases in PFAA porewater concentrations relative to overall mass removal are largely controlled by the desorption resistant fraction in the soil. The results shown in **Fig. 4.28** also suggest that the field scale behavior can also be described, at least qualitatively, by bench-scale batch desorption testing. Aggressive methods, such as cosolvent flushing (Senevirathna et al., 2021), might be needed to more rapidly removal PFAS from soil exhibiting such behavior.

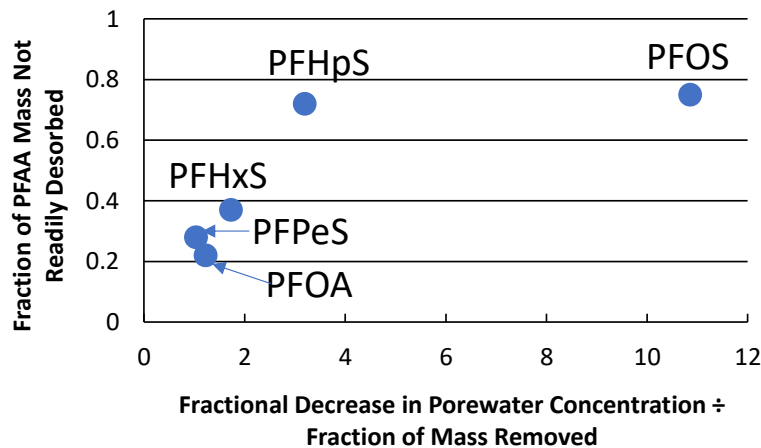


**Figure 4.28.** The fraction of PFAA mass not readily desorbed from soil based on 9-month desorption data (Section 4.2) versus the ratio the fractional decrease in porewater concentration ÷ fraction of mass removed measured herein.

### *Environmental and Treatment Implications*

The in situ flushing results herein show that, for many PFAAs, leaching/flushing resulted in a more rapid decrease in porewater concentrations than overall decreases in mass. This was shown to be particularly true for perfluorinated sulfonates with at least 6 carbons. Thus, PFAA mass discharge to underlying groundwater decreased more rapidly than the overall decrease in PFAA mass removal from the unsaturated soils. This behavior suggests that, when considering soil impacts to groundwater, less stringent soil cleanup criteria than those that consider an equivalent relationship between mass removal and mass discharge (i.e., PFAA soil-porewater distribution described by a linear  $K_d$  relationship with a y-intercept of zero) may be appropriate, though additional data from other sites are certainly needed before definitive conclusions can be drawn. In addition, remedial approaches that remove only a modest fraction of the PFAA mass in soil may be protective of underlying groundwater. Further study is needed to extend the findings herein to other sites, and to evaluate the relationship between PFAA mass removal and corresponding porewater concentrations with more aggressive flushing such that multi-log decreases in porewater concentrations relative to overall mass removal can be assessed. The extent to which precursor transformation impacts overall PFAA leaching also warrants further study.

## 5.0 Conclusions and Implications for Future Research

Primary findings and conclusions include the following:

- PFAS concentrations are greatest in the range of 0 to 1 ft bgs. Evaluation of the soil concentration profile with depth suggest that precursor transformation has occurred. Elevated PFAS levels in the shallow soil are associated with elevated organic carbon levels and (to a much lesser extent) elevated cation exchange capacity.
- For the shallow site soils investigated herein, desorption was kinetically controlled (particularly for the smaller-chained PFAS). This kinetically controlled desorption was observed in batch slurry systems, suggesting that the desorption was kinetically controlled at the grain scale. The kinetic desorption behavior was consistent with a dual-domain model that included an equilibrium domain and a kinetic domain.
- Desorption isotherms for most PFAS indicated that a significant fraction of the sorbed PFAS was not readily desorbed from the soil. The readily desorbable fraction exhibited linear desorption behavior.
- Both bench-scale and field data suggest that ongoing precursor transformation, with the formation of PFHxA and PFHpA, is occurring.
- Field lysimeter results showed that measured PFAS concentrations were reasonable repeatable (~ factor of 2). PFHxS was the most abundant PFAS measured in the unsaturated zone porewater, with an average concentration of approximately 25,000 ng/L measured during the baseline ambient conditions.
- PFAS field porewater concentration in the unsaturated zone were reasonably, typically within a factor of 2 to 4, predicted based on equilibrium soil-water partitioning data (measured independently at the bench-scale). For PFOS and PFHpS, this prediction was significantly improved if accumulation at the air-water interface was accounted for in the model. This model employed the use of collected porewater to determine a site-specific air-water interfacial partition coefficient.
- *In situ* flushing resulted in rapid decreases in PFAS concentrations relative to their corresponding decreases in mass removal, particularly for longer-chained (>C6) perfluorinated sulfonates. This observation was consistent with the bench-scale desorption testing, which showed that dissolved concentrations decreased more rapidly than the soil concentrations.

Practical implications of this research with respect to site investigation and evaluation include the following:

- Repeatability of lysimeter data. Results showed that PFAS concentrations in the porewater were reasonably (with approximately a factor of 2) repeatable among the lysimeters, and among the temporal sampling events. While these results are encouraging, evaluation at a larger number of sites and over a greater degree of moisture variability are needed to further assess repeatability.
- PFAS retention in the unsaturated zone. Results showed that both accumulation at the air-water interface and resistance to desorption can both play substantial roles in limiting PFAS leaching from soil to groundwater. Thus, conventional approaches to determine soil cleanup criteria based on impacts to groundwater may not be appropriate for many AFFF-impacted sites, and any leaching tests should be designed to consider these retention processes. Results of this study also suggest that PFAS impacts to underlying groundwater may be minimal despite there being elevated PFAS concentrations in the unsaturated zone soils. Further evaluation at a wider variety of sites is needed to verify and further assess PFAS leaching processes.
- Soil flushing to treat PFAS in the unsaturated zone. Results of this study showed that, particularly for longer-chained PFAS such as PFOS, PFAS porewater concentrations and flux to underlying groundwater decreased substantially during flushing with comparatively little PFAS mass removal. Thus, in situ soil flushing may be a reasonable treatment approach for sites if cleanup criteria are based on PFAS flux to groundwater and not soil concentrations. In theory, these same principles could apply to ex situ soil flushing.

Some key research questions based on the findings of this study include:

- Applicability to other AFFF-impacted sites: While repeatability of field lysimeter results, applicability of equilibrium partitioning for predicting PFAS porewater concentrations in situ, and the presence of a desorption-resistant PFAS fraction in the soil were key findings for this project, the extent to which these results are applicable to other AFFF-impacted sites remains unclear. While this question is being addressed in part via ongoing ESTCP Project ER20-5088, similar studies performed under a wider-range of site conditions is needed to provide further insight and to better apply results obtained herein to site management.
- Precursor transformation at sites historically impacted by AFFF: Data obtained herein, both at the bench-scale and field scale, suggest the likelihood that precursor transformation of PFAAs is occurring. Because of the abundance of potential precursor compounds that

are present in AFFF source areas, precursor transformation could have a significant impact on PFAS leaching. Further studies to assess such transformations at AFFF-impacted sites – particularly in unsaturated zone soils – is needed to improve conceptual site models.

- *Complex geologies and arid/semi-arid climates*: The site examined herein had a relatively shallow (< 10 ft) depth to water, received moderate rainfall, and had a geology consisting of relatively homogeneous sandy materials. While such characteristics may be somewhat representative of many of the DOD's AFFF-impacted source areas near the east coast, many sites have more complex geologies and are subject to greater contribution from evapotranspiration due to diminished rainfall. The applicability of field lysimeter-based approaches for evaluating PFAS leaching are not as clear for such sites, and approaches for predicting porewater concentrations may be more complex.
- *Long-term leaching behavior*: Results herein showed that longer-chain PFAS (e.g., PFOS) showed rapid decreases in porewater concentration (and correspondingly, rapid decreases in mass flux to underlying groundwater) with only a small decrease in mass removal. These observations were noted for close to a 1-log decrease in PFOS concentration in porewater. Longer term studies are needed to evaluate such behavior to assess multi-log reductions in PFAS porewater and/or soil concentrations.
- *Potential impacts of elevated PFAS concentrations in surface soils*. Elevated PFAS concentrations were observed in the top 9 inches of soil. It is currently unclear if removal of this surface soil would substantially decrease PFAS leaching. If so, and if such highly impacted surface soils are common at AFFF-impacted sites, excavation of such soils might prove to be an effective means of mitigating PFAS leaching to underlying groundwater. *Efforts to assess this are currently on-going to as part of add-on funding provided by SERDP.*

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## **APPENDIX A1: PFAS Analyses and Target PFAS Analytical Table**

### **PFAS Analytical Methods**

PFAS native and isotopically labeled analytical standards were purchased from Wellington Laboratories. Table S1 lists the anionic analytical standards used for analysis. The cationic analytical standards used for ESI<sup>+</sup> analysis were n-dimethyl ammonio propyl perfluorohexane sulfonamide (AmPr- FHxSA), n-trimethylammoniopropyl perfluorohexane sulfonamide (TAmPr- FHxSA), and 6:2 fluorotelomer sulfonamido propyl betaine (6:2 FTSA-PrB). Isotopically labeled cationic PFAS standards were not available at the time. The cationic injection standards used were methamphetamine for aqueous samples and atrazine-d5, diuron-d6, triphenyl phosphate-d15, metolachlor-d6, and carbamazepine-d10 (CDN Isotopes), and TCEP-d12 (Sigma Aldrich) for soil samples. A second source of PFAS standards (Absolute Standards, Hamden, CT) were used to determine accuracy and were required to be 70–130% for each analyte. All solvents used were high performance liquid chromatography (HPLC) Optima<sup>®</sup> grade from Fisher Scientific.

### ***Soil Analysis***

Soil PFAS analysis was performed using the methods described in Nickerson et al. (2020). The soil was air-dried, sieved to 2 mm and homogenized with a mortar and pestle. The dry weight of the soil was determined by drying overnight at 105 °C. Briefly, 0.5 g of each soil in a 50 mL polypropylene tube was spiked with isotopically labeled internal standards and then 4 mL of 0.1 M ammonium hydroxide in methanol (“basic methanol”) was added to each tube. The samples were sonicated for 15 minutes at 30 °C and then centrifuged at 2470 rcf for 20 minutes. The extract was decanted into a vial and the process was repeated once again. Following the 2 rounds of extraction with basic methanol, the process was repeated twice more using 0.5 M hydrochloric acid in methanol (“acidic methanol”). The acidic methanol extracts were decanted into a separate vial. The extracts were then passed through ENVI-Carb solid phase extraction (SPE) cartridges (Sigma Aldrich, 250 mg) and evaporated to dryness under nitrogen gas (N<sub>2</sub>) in a 30 °C water bath. Prior to evaporation, the acidic methanol extracts were neutralized with 7 M ammonium hydroxide in methanol. Finally, the extracts were reconstituted in 1.5 mL of 1% acetic acid in methanol and the acidic and basic extracts for each soil sample were combined. The extracts were centrifuged for 10 minutes at 17,000 rcf to remove precipitants. Aliquots of the extracts (10-100 µL) were diluted in 80% methanol and 20% water to 400 µL total volume in HPLC autosampler vials.

Analysis was completed using liquid chromatography quadrupole time of flight mass spectrometry (LC-QTOF-MS). The instruments used were a SCIEX ExionLC HPLC system and a SCIEX X500R QTOF MS (Framingham, MA). The soils were analyzed for anionic/ zwitterionic PFAS using negative mode electrospray (ESI<sup>-</sup>) and for cationic/zwitterionic PFAS using positive mode

electrospray (ESI<sup>+</sup>). For ESI<sup>-</sup> analysis, a Gemini C18 analytical column (3 mm × 100 mm × 5 μm; Phenomenex, Torrance, CA), one SecurityGuard C18 guard cartridge (4 mm × 2 mm I.D.; Phenomenex), and two Zorbax DIOL guard columns (4.6 mm × 12.5 mm × 6 μm; Agilent, Santa Clara, CA) were used in the LC. The same configuration was used for ESI<sup>+</sup> analysis, except the 2 Zorbax DIOL guard columns were replaced with a single Zorbax SIL guard column (4.6 mm × 12.5 mm × 5 μm; Agilent). A 20 minute gradient of 20 mM ammonium acetate (Fisher Scientific) in Optima<sup>®</sup> HPLC grade water and 100% Optima<sup>®</sup> HPLC grade methanol (Fisher Scientific) was used for analyte separation. The injection volume for both the positive and negative analyses was 100 μL. All data were collected via SWATH data-independent acquisition. The analytical sequence used a calibration curve over the range of 0.02 to 2000 pg (mass/100 μL) for all ESI<sup>-</sup> analytes and 0.02 to 1000 pg (mass/100 μL) for all ESI<sup>+</sup> analytes.

### ***Aqueous Analysis***

Aqueous desorption samples were vortexed for 30 seconds and diluted 1:10 into methanol and spiked with 25 μL of isotopically labeled internal standards (Wellington Laboratories, Guelph, ON, Canada) for quantification prior to injection. Final sample volumes were 1.5 mL. Analysis was completed with an Agilent 1260 series HPLC (Santa Clara, CA) and a SCIEX QTOF X500R (Framingham, MA) using positive and negative mode electrospray ionization for analysis of cationic/zwitterionic and anionic/zwitterionic respectively via orthogonal chromatography previously described in Barzen Hansen et al (2015). In short, the HPLC was fitted with three Zorbax diol (Agilent, Santa Clara, CA; 4.6 x 12.5 mm x 6 μm) and one Zorbax silica (Agilent; 4.6 x 12.5 mm x 5 μm) guard columns connected to a Zorbax Eclipse Plus C18 analytical column (Agilent; 4.6 x 100 mm x 3.5 μm). The injection volume for each analysis was 900 μL. A 27 minute gradient of 3% methanol in water and 10 mM ammonium acetate in methanol was used for analyte separation.

All data were collected via SWATH data-independent acquisition. Analyte identification and quantification have been described in Allred et al. (2014). Negative and positive mode analytical sequences utilized a 5-point calibration curve over the range of 20 -10,000 ng/L for all analytes. Precision was calculated, as relative standard deviation, from four replicate samples and ranged from 0-20%. The limit of detection (LOD, 6 ng/L) was calculated by normalized-weighted regression (1/X), from which the LOQ (20 ng/L) was calculated as 3.3 x the LOD (Vial and Jardy, 1999).

### ***Suspect Screening and Semi-quantitation of soil and aqueous samples.***

PFAS that did not have analytical standards available to be quantified in the soil and aqueous samples were screened against a custom extracted ion chromatogram (XIC) list to identify suspect matches. The XIC list used is presented in the supplemental information of Nickerson et al. (2020).

When compared to the XIC list, compounds were considered suspect matches when they met the following criteria:

- 1) Sample area count to blank area count ratio  $\geq 2$  (aqueous), 3 (soil)
- 2) Mass error  $< 5$  ppm
- 3) Difference ion ratio  $< 10\%$
- 4) Relative retention time

The concentrations of compounds identified through suspect screening were estimated using a semi-quantitation procedure described in Nickerson et al. The procedure associates each compound on the XIC list with a compound for which analytical standards are available (“targeted calibrant”). This associated calibrant is used to estimate the concentration of the XIC list compound that had been identified as a suspect match in the sample. The concentration estimation of the suspect analyte is a function of the response factor of the targeted calibrant and its internal standard, the molar masses of both the target calibrant and the suspect compound, the peak areas of both compounds, and the nominal spiked mass of the internal standard. The LOQ for all semi-quant analytes was the same as the corresponding calibrant LOQ. Acronyms and structures of suspect analytes are provided in **Figure A1.1**.

### ***Analytical References***

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**Table A1.1 Target PFAS Analytical Table.** Targeted analytes for ESI- PFAS analysis. All standards were obtained from Wellington Labs.

| Chemical Name                                                      | Acronym    | Neutral<br>Molecular Formula                       |
|--------------------------------------------------------------------|------------|----------------------------------------------------|
| <b>Perfluoroalkanoic acids</b>                                     |            |                                                    |
| Perfluoro-n-butanoic acid                                          | PFBA       | C <sub>4</sub> H <sub>0</sub> F <sub>7</sub>       |
| Perfluoro-n-pentanoic acid                                         | PFPeA      | C <sub>5</sub> H <sub>0</sub> F <sub>9</sub>       |
| Perfluoro-n-hexanoic acid                                          | PFHxA      | C <sub>6</sub> H <sub>0</sub> F <sub>11</sub>      |
| Perfluoro-n-heptanoic acid                                         | PFHpA      | C <sub>7</sub> H <sub>0</sub> F <sub>13</sub>      |
| Perfluoro-n-octanoic acid                                          | PFOA       | C <sub>8</sub> H <sub>0</sub> F <sub>15</sub>      |
| Perfluoro-n-nonanoic acid                                          | PFNA       | C <sub>9</sub> H <sub>0</sub> F <sub>17</sub>      |
| Perfluoro-n-decanoic acid                                          | PFDA       | C <sub>10</sub> H <sub>0</sub> F <sub>19</sub>     |
| Perfluoro-n-undecanoic acid                                        | PFUdA      | C <sub>11</sub> H <sub>0</sub> F <sub>21</sub>     |
| Perfluoro-n-dodecanoic acid                                        | PFDoA      | C <sub>12</sub> H <sub>0</sub> F <sub>23</sub>     |
| Perfluoro-n-tridecanoic acid                                       | PFTTrDA    | C <sub>13</sub> H <sub>0</sub> F <sub>25</sub>     |
| Perfluoro-n-tetradecanoic acid                                     | PFTeDA     | C <sub>14</sub> H <sub>0</sub> F <sub>27</sub>     |
| Perfluoro-n-hexadecanoic acid <sup>iii</sup>                       | PFHxDA     | C <sub>16</sub> H <sub>0</sub> F <sub>31</sub>     |
| <b>Perfluoroalkane sulfonates</b>                                  |            |                                                    |
| Perfluoropropane sulfonate                                         | PFPrS      | C <sub>3</sub> H <sub>0</sub> 3SF <sub>7</sub>     |
| Perfluorobutane sulfonate                                          | PFBS       | C <sub>4</sub> H <sub>0</sub> 3SF <sub>9</sub>     |
| Perfluoropentane sulfonate                                         | PFPeS      | C <sub>5</sub> H <sub>0</sub> 3SF <sub>11</sub>    |
| Perfluorohexane sulfonate <sup>i</sup>                             | PFHxS      | C <sub>6</sub> H <sub>0</sub> 3SF <sub>13</sub>    |
| Perfluoroheptane sulfonate                                         | PFHpS      | C <sub>7</sub> H <sub>0</sub> 3SF <sub>15</sub>    |
| Perfluorooctane sulfonate <sup>i</sup>                             | PFOS       | C <sub>8</sub> H <sub>0</sub> 3SF <sub>17</sub>    |
| Perfluorononane sulfonate                                          | PFNS       | C <sub>9</sub> H <sub>0</sub> 3SF <sub>19</sub>    |
| Perfluorodecane sulfonate                                          | PFDS       | C <sub>10</sub> H <sub>0</sub> 3SF <sub>21</sub>   |
| Perfluoroundecane sulfonate                                        | PFUdS      | C <sub>11</sub> H <sub>0</sub> 3SF <sub>23</sub>   |
| Perfluorododecane sulfonate                                        | PFDoS      | C <sub>12</sub> H <sub>0</sub> 3SF <sub>25</sub>   |
| <b>Chlorinated perfluoroalkane sulfonates and ether sulfonates</b> |            |                                                    |
| 8-chloro-perfluorooctane sulfonate                                 | Cl-PFOS    | C <sub>8</sub> H <sub>0</sub> 3SClF <sub>16</sub>  |
| 9-chloro-3-oxa-perfluorononane sulfonate                           | Cl-O-PFNS  | C <sub>8</sub> H <sub>0</sub> 4SClF <sub>16</sub>  |
| 11-chloro-3-oxa-perfluoroundecane sulfonate                        | Cl-O-PFUdS | C <sub>10</sub> H <sub>0</sub> 4SClF <sub>20</sub> |

## Target PFAS Analytical Table(continued)

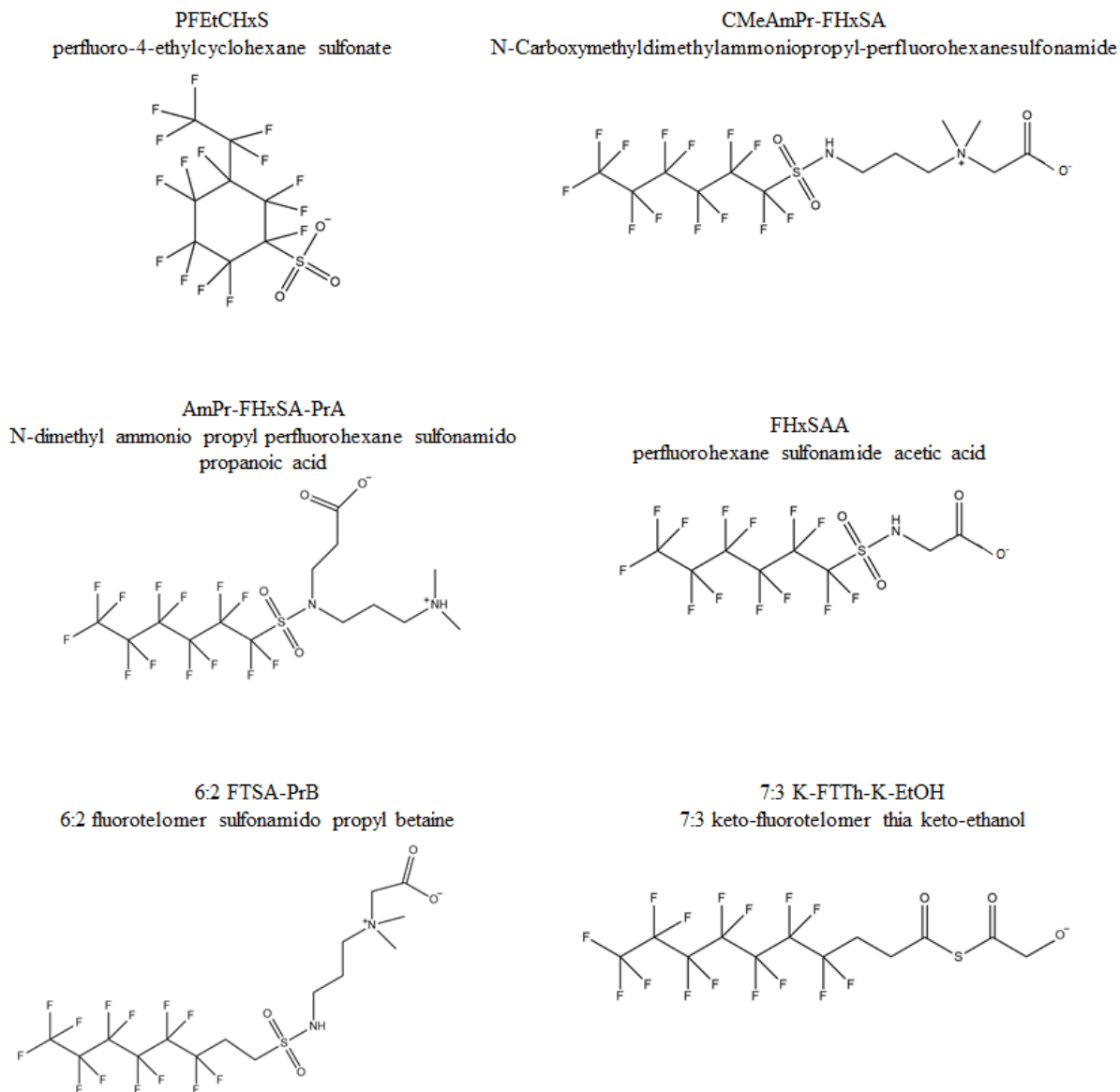
| PFAS Name                                                        | Abbreviation                       | Molecular Formula<br>(neutral)                                  |
|------------------------------------------------------------------|------------------------------------|-----------------------------------------------------------------|
| <b>Perfluoroalkane sulfonamides</b>                              |                                    |                                                                 |
| perfluorobutane sulfonamide                                      | FBSA                               | C <sub>4</sub> H <sub>2</sub> O <sub>2</sub> SNF <sub>9</sub>   |
| Perfluorohexane sulfonamide                                      | FHxSA                              | C <sub>6</sub> H <sub>2</sub> O <sub>2</sub> SNF <sub>13</sub>  |
| Perfluorooctane sulfonamide                                      | FOSA                               | C <sub>8</sub> H <sub>2</sub> O <sub>2</sub> SNF <sub>17</sub>  |
| N-methylperfluoro-1-octane sulfonamide                           | MeFOSA                             | C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> SNF <sub>17</sub>  |
| N-ethylperfluoro-1-octane sulfonamide                            | EtFOSA                             | C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> SNF <sub>17</sub> |
| <b>Perfluoroalkane sulfonamido acetic acids</b>                  |                                    |                                                                 |
| Perfluorooctane sulfonamido acetic acid <sup>ii</sup>            | FOSAA                              | C <sub>10</sub> H <sub>4</sub> O <sub>4</sub> SNF <sub>17</sub> |
| N-methylperfluorooctane sulfonamido acetic acid <sup>i, ii</sup> | MeFOSAA                            | C <sub>11</sub> H <sub>6</sub> O <sub>4</sub> SNF <sub>17</sub> |
| N-ethylperfluorooctane sulfonamido acetic acid <sup>i, ii</sup>  | EtFOSAA                            | C <sub>12</sub> H <sub>8</sub> O <sub>4</sub> SNF <sub>17</sub> |
| <b>Fluorotelomer sulfonates</b>                                  |                                    |                                                                 |
| 4:2 fluorotelomer sulfonate                                      | 4:2 FTS                            | C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> SF <sub>9</sub>    |
| 6:2 fluorotelomer sulfonate                                      | 6:2 FTS                            | C <sub>8</sub> H <sub>5</sub> F <sub>13</sub> SO <sub>3</sub>   |
| 8:2 fluorotelomer sulfonate                                      | 8:2 FTS                            | C <sub>10</sub> H <sub>5</sub> O <sub>3</sub> SF <sub>17</sub>  |
| 10:2 fluorotelomer sulfonate                                     | 10:2 FTS                           | C <sub>12</sub> H <sub>5</sub> O <sub>3</sub> SF <sub>21</sub>  |
| <b>Fluorotelomer alkanolic acids</b>                             |                                    |                                                                 |
| 6:2 fluorotelomer carboxylic acid <sup>iii</sup>                 | 6:2 FTCA                           | C <sub>8</sub> H <sub>3</sub> O <sub>2</sub> F <sub>13</sub>    |
| 8:2 fluorotelomer carboxylic acid <sup>iii</sup>                 | 8:2 FTCA                           | C <sub>10</sub> H <sub>3</sub> O <sub>2</sub> F <sub>17</sub>   |
| 10:2 fluorotelomer carboxylic acid <sup>iii</sup>                | 10:2 FTCA                          | C <sub>12</sub> H <sub>3</sub> O <sub>2</sub> F <sub>21</sub>   |
| 2H-Perfluoro-2-octenoic acid (6:2) <sup>iii</sup>                | 6:2 UFTCA                          | C <sub>8</sub> H <sub>2</sub> O <sub>2</sub> F <sub>12</sub>    |
| 2H-Perfluoro-2-decenoic acid (8:2) <sup>iii</sup>                | 8:2 UFTCA                          | C <sub>10</sub> H <sub>2</sub> O <sub>2</sub> F <sub>16</sub>   |
| 2H-Perfluoro-2-dodecenoic acid (10:2) <sup>iii</sup>             | 10:2 UFTCA                         | C <sub>12</sub> H <sub>2</sub> O <sub>2</sub> F <sub>20</sub>   |
| <b>Hydrido-perfluoro polyether alkanolic acids</b>               |                                    |                                                                 |
| 3-H-4, 8-dioxa-perfluorononanoic acid                            | ADONA                              | C <sub>7</sub> H <sub>2</sub> O <sub>4</sub> F <sub>12</sub>    |
| <b>Perfluorocycloalkyl sulfonic acids</b>                        |                                    |                                                                 |
| Perfluoro-4-ethylcyclohexane sulfonate                           | PF <sub>Et</sub> CH <sub>x</sub> S | C <sub>8</sub> H <sub>3</sub> O <sub>3</sub> SF <sub>15</sub>   |

i. Exist in the standard as the linear and branched isomers.

ii. PFHxDA, FOSAA, MeFOSAA, and EtFOSAA excluded from high -level (>3.85 ng/mL) calibration standards to prevent instrument carryover.

iii. Stored in 100% Optima HPLC-grade isopropanol (IPA) to limit potential degradation. (All other compounds stored in 100% HPLC-grade methanol.)

**Figure A1.1 Suspect Analytes: Acronyms and Structures**



## APPENDIX A2: Screening-Level PFAS Kinetic Leaching Model

### Desorption Model for PFAAs in the Shallow Soil

A two-site desorption model, consisting of rapid (equilibrium sites and slow (mass transfer controlled) sites is used (Leij et al., 1993; Wehrhan et al., 2010):

$$dC = \frac{\frac{-\alpha\rho}{\theta}[S-(1-f)K_{d,eq}C]}{1+\frac{f\rho K_{d,eq}}{\theta}} dt \quad \text{Eq. A2.1}$$

$$dS = \alpha[S - (1 - f)K_{d,eq}C]dt \quad \text{Eq. A2.2}$$

where C is the aqueous concentration (ng L<sup>-1</sup>), S is the soil concentration associated with the mass-transfer controlled sites (ng kg<sup>-1</sup>), f is the fraction of equilibrium soil sorption sites, K<sub>d,eq</sub> is the linear equilibrium adsorption coefficient (L kg<sup>-1</sup>), α is the desorption rate coefficient (h<sup>-1</sup>), ρ is the density of the batch system (1.2 kg L<sup>-1</sup>), and θ is the water volume fraction of the batch system (0.87). Eqs. A2.1 and A2.2 were solved assuming an initial rapid equilibration condition where C for each PFAA was equal to the aqueous concentration measured at 48 hours. Values for f were approximated for each PFAA as the fraction sorbed by 48 hours to that at equilibrium or 400 hours, and where f of unity was assumed for PFHpS, PFOS, PFOA and PFNA. Values for K<sub>d,eq</sub> were estimated based on the measured single-point K<sub>d</sub> for PFOS measured in the kinetic experiments (since PFOS was at equilibrium), then scaled based on reported K<sub>oc</sub> values for PFPeA, PFHxA, PFHpA, PFPeS, and PFHxS. Equations A2.1 and A2.2 were solved using a spreadsheet-based finite difference method with dt ranging from 0.5 to 2 hours. The mass transfer rate constant α was the only regressed parameter. *We note that application of this model is intended to provide a screening level evaluation of the desorption kinetics, and to provide insight into the relative behavior of the PFAAs in the field-aged shallow soil.* It is recognized that use of a linear K<sub>d,eq</sub> sorption model may not capture any non-linear behavior in PFAA sorption, but the extent of PFAA non-linearity observed is typically low (Freundlich exponent >0.85) (Higgins and Luthy, 2006; Guelfo and Higgins, 2013).

### References

- Guelfo, J.L.; Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.*, 47, 4164-4171.
- Higgins, C.P. and Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* 40, 7251-7256.

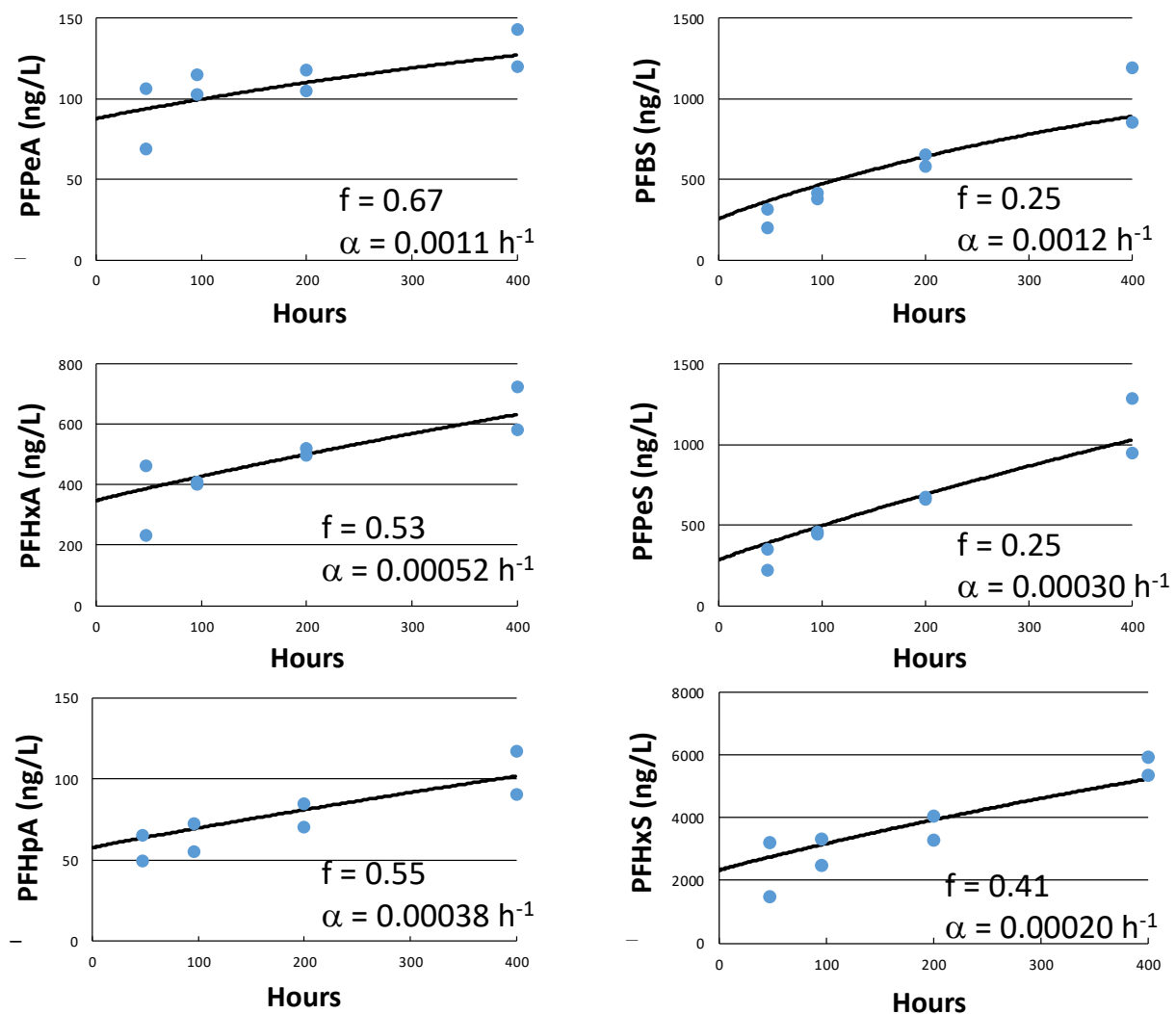


**Figure A2.1.** Desorption kinetic model descriptions (solids lines) of PFAS desorption. The model input parameter  $f$  is shown, as well as the regressed parameter  $\alpha$ .

## APPENDIX A3: Assessing Impacts of Natural Soil Colloids on Measured PFAS Aqueous Concentrations

Batch experiments were performed where deionized water was mixed with either the shallow or deep soil in a 2:1 liquid:solid ratio. After equilibrating for 48 hours, two aqueous supernatant samples were collected from each bottle. One set of aqueous samples was subject to centrifugation at 4,000 RCF for 30 minutes prior to sub-sampling the aqueous phase for PFAS analysis; the other set of aqueous samples were analyzed for PFAS without centrifugation. Comparison of PFAS results between the centrifuged and non-centrifuged samples was intended to assess the impacts of natural soil colloids (if present) on measured PFAS concentrations.

The difference in measured PFAS concentrations between the centrifuged and non-centrifuged samples were negligible (<15%), thus there were no substantial impacts of any colloidal-bound PFAS on measured aqueous concentrations (Exhibit A3). These results indicate that, for the sequential dilution desorption isotherms, dilution of the soil and any natural colloids likely did not result in any artificial dilution of measured PFAS concentrations.

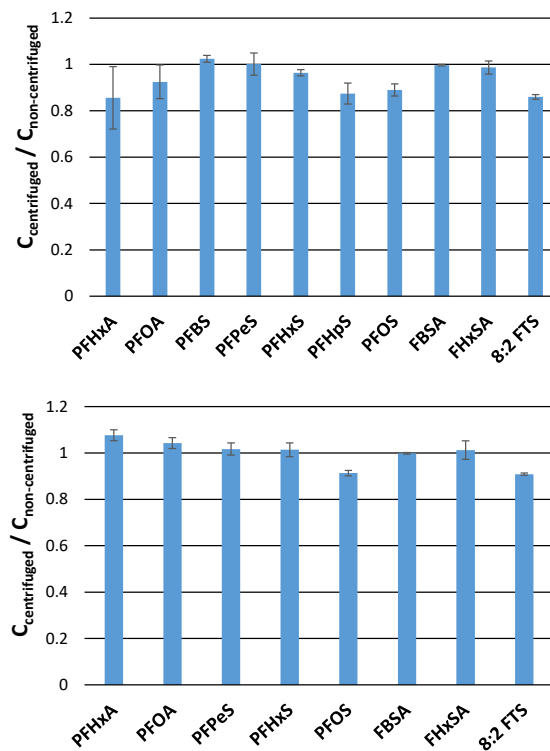


**Exhibit A3.** Comparison of PFAS levels in the collected supernatant from the shallow (top) and deep (bottom) soil samples, where PFAS analyses were performed with and without prior centrifugation. Average values for 5 replicates are shown. Error bars represent 95% confidence intervals.

## APPENDIX A4: PFAS Soil Concentrations in the Column Experiments

| Compound                                                                                                                  | Precursor Mass | Class      | Deep Soil<br>Concentration (ng/g) | Shallow Soil<br>Concentration (ng/g) |
|---------------------------------------------------------------------------------------------------------------------------|----------------|------------|-----------------------------------|--------------------------------------|
| <b>Perfluoroalkane sulfonic acids, Perfluoroalkane sulfinic acids</b>                                                     |                |            |                                   |                                      |
| PFPrS                                                                                                                     | 248.946        | PFAS       | 0.04±0.00                         | 0.09±0.04                            |
| PFBS                                                                                                                      | 298.943        | PFAS       | 2.71±1.04                         | 2.12±0.63                            |
| PFPeS                                                                                                                     | 348.940        | PFAS       | 2.07±1.38                         | 32.14±33.51                          |
| PFHxS                                                                                                                     | 398.937        | PFAS       | 27.22±19.66                       | 347.81±320.12                        |
| PFHpS                                                                                                                     | 448.933        | PFAS       | 3.62±2.16                         | 44.08±38.54                          |
| PFOS                                                                                                                      | 498.930        | PFAS       | 268.25±86.29                      | 2360±2022                            |
| PFNS                                                                                                                      | 548.927        | PFAS       | 5.26±0.43                         | 20.46±10.12                          |
| PFDS                                                                                                                      | 598.924        | PFAS       | 1.07±0.10                         | 7.60±2.45                            |
| PFDoS                                                                                                                     | 698.917        | PFAS       | 0.02±0.00                         | 0.40±0.10                            |
| PFHxSi                                                                                                                    | 382.942        | PFSai      |                                   | 1.26±0.14                            |
| <b>Perfluoroalkyl carboxylic acids</b>                                                                                    |                |            |                                   |                                      |
| PFBA                                                                                                                      | 212.979        | PFCA       | 0.65±0.16                         | 0.57±0.12                            |
| PFPeA                                                                                                                     | 262.976        | PFCA       | 0.50±0.08                         | 0.60±0.13                            |
| PFHxA                                                                                                                     | 312.973        | PFCA       | 1.35±0.39                         | 3.48±1.31                            |
| PFHpA                                                                                                                     | 362.970        | PFCA       | 0.43±0.07                         | 0.70±0.21                            |
| PFOA                                                                                                                      | 412.966        | PFCA       |                                   | 6.11±4.94                            |
| PFNA                                                                                                                      | 462.963        | PFCA       | 0.41±0.05                         | 0.43±0.06                            |
| PFDA                                                                                                                      | 512.960        | PFCA       | 0.47±0.05                         | 0.69±0.05                            |
| PFUdA                                                                                                                     | 562.957        | PFCA       |                                   | 0.50±0.03                            |
| PFDoA                                                                                                                     | 612.954        | PFCA       |                                   | 0.28±0.00                            |
| PFTeDA                                                                                                                    | 712.947        | PFCA       |                                   | 0.16±0.01                            |
| <b>Perfluoroalkane sulfonamides, Perfluoroalkane sulfonamido acetic acids, N-Sulfo Propyl perFluoroAlkaneSulfonAmides</b> |                |            |                                   |                                      |
| FBSA                                                                                                                      | 297.959        | FASA       |                                   | 1.48±0.13                            |
| FPeSA                                                                                                                     | 347.956        | FASA       | 0.88±0.02                         | 3.00±0.30                            |
| FHxSA                                                                                                                     | 397.953        | FASA       | 148.60±6.52                       | 297.10±30.54                         |
| FHpSA                                                                                                                     | 447.949        | FASA       | 1.23±0.06                         | 6.16±0.42                            |
| FOSA                                                                                                                      | 497.946        | FASA       | 1.79±0.22                         | 26.72±1.38                           |
| MeFHxSA                                                                                                                   | 411.968        | MeFASA     | 6.34±2.85                         | 11.93±6.97                           |
| MeFOSA                                                                                                                    | 511.962        | MeFASA     |                                   | 0.32±0.00                            |
| EtFHxSA                                                                                                                   | 425.984        | EtFASA     | 0.44±0.12                         | 0.65±0.29                            |
| EtFOSA                                                                                                                    | 525.978        | EtFASA     |                                   | 0.61±0.28                            |
| FHxSAA                                                                                                                    | 455.958        | FASAA      | 0.87±0.06                         | 1.65±0.13                            |
| FOSAA                                                                                                                     | 555.952        | FASAA      | 0.07±0.01                         | 0.43±0.05                            |
| MeFOSAA                                                                                                                   | 569.967        | MeFASAA    |                                   | 1.06±0.10                            |
| EtFHxSAA                                                                                                                  | 483.989        | EtFASAA    | 0.43±0.09                         | 2.99±0.68                            |
| SPr-FHxSA                                                                                                                 | 519.956        | SPr-FASA   | 1.70±0.00                         | 3.93±1.61                            |
| SPr-FOSA                                                                                                                  | 619.950        | SPr-FASA   | 1.25±0.42                         | 1.21±0.46                            |
| OAmPr-FHxSA                                                                                                               | 499.037        | OAmPr-FASA | 1.12±0.00                         | 6.29±1.84                            |
| <b>n:2 Fluorotelomer sulfonic acids, X:2 fluorotelomer sulfonates</b>                                                     |                |            |                                   |                                      |
| 4:2 FTS                                                                                                                   | 326.974        | X:2 FTS    | 0.06±0.01                         | 0.09±0.00                            |
| 6:2 FTS                                                                                                                   | 426.968        | X:2 FTS    | 2.18±0.19                         | 5.15±2.24                            |
| 8:2 FTS                                                                                                                   | 526.962        | X:2 FTS    | 17.16±0.88                        | 7.57±1.54                            |
| 10:2 FTS                                                                                                                  | 626.955        | X:2 FTS    |                                   | 0.06±0.01                            |
| 6:2 FTSi                                                                                                                  | 410.973        | X:2 FTSi   | 0.23±0.00                         |                                      |
| 8:2 FTSi                                                                                                                  | 510.967        | X:2 FTSi   | 0.31±0.02                         | 0.47±0.13                            |

| Compound                                                                   | Precursor Mass | Class            | Deep Soil<br>Concentration (ng/g) | Shallow Soil<br>Concentration (ng/g) |
|----------------------------------------------------------------------------|----------------|------------------|-----------------------------------|--------------------------------------|
| <b>Unsaturated, cyclic, and substituted perfluoroalkane sulfonic acids</b> |                |                  |                                   |                                      |
| F5S-PFPeS                                                                  | 456.905        | F5S-PFSA         |                                   | 0.21±0.17                            |
| F5S-PFHpS                                                                  | 556.899        | F5S-PFSA         |                                   | 0.74±0.55                            |
| F5S-PFOS                                                                   | 606.896        | F5S-PFSA         | 3.15±0.28                         | 21.58±8.74                           |
| F5S-PFNS                                                                   | 656.893        | F5S-PFSA         | 0.13±0.04                         | 2.46±0.68                            |
| F5S-PFDS                                                                   | 706.890        | F5S-PFSA         |                                   | 0.12±0.01                            |
| K-PFHxS                                                                    | 376.935        | K-PFSA           | 0.44±0.00                         | 0.67±0.68                            |
| K-PFOS                                                                     | 476.928        | K-PFSA           | 0.38±0.21                         | 3.90±3.09                            |
| K-PFDS                                                                     | 576.922        | K-PFSA           | 0.16±0.02                         | 0.76±0.33                            |
| K-PFUdS                                                                    | 626.919        | K-PFSA           |                                   | 0.51±0.15                            |
| Cl-PFOS                                                                    | 514.901        | Cl-PFAS          | 1.23±0.43                         | 8.87±3.14                            |
| UPFHxS                                                                     | 360.940        | UPFSA            |                                   | 0.88±0.81                            |
| UPFOS                                                                      | 460.933        | UPFSA            | 1.06±0.76                         | 13.09±10.58                          |
| UPFDS                                                                      | 560.927        | UPFSA            | 0.28±0.05                         | 1.05±0.63                            |
| UPFUdS                                                                     | 610.924        | UPFSA            | 0.33±0.03                         | 1.83±0.56                            |
| UPFDoS                                                                     | 660.921        | UPFSA            |                                   | 0.93±0.20                            |
| UPFTTrDS                                                                   | 710.917        | UPFSA            |                                   | 0.47±0.14                            |
| <b>Perfluoroalkane sulfates</b>                                            |                |                  |                                   |                                      |
| PFHp-OS                                                                    | 464.928        | PFA-OS           |                                   | 0.40±0.30                            |
| PFO-OS                                                                     | 514.925        | PFA-OS           | 0.45±0.00                         | 2.29±1.89                            |
| PFN-OS                                                                     | 564.922        | PFA-OS           | 1.00±0.07                         | 4.81±2.03                            |
| PFD-OS                                                                     | 614.919        | PFA-OS           |                                   | 0.49±0.16                            |
| PFUd-OS                                                                    | 664.916        | PFA-OS           |                                   | 0.19±0.07                            |
| <b>Other perfluoroalkane sulfonamido substances</b>                        |                |                  |                                   |                                      |
| CEtAmPr-FHxSA                                                              | 557.077        | CEtAmPr-FASA     | 28.30± 5.98                       | 300.10± 72.47                        |
| CEtAmPr-FHpSA                                                              | 607.074        | CEtAmPr-FASA     | 1.63± 0.56                        | 10.06± 6.67                          |
| CEtAmPr-FHxSA-PrA                                                          | 629.099        | CEtAmPr-FASA-PrA | 0.98± 0.24                        |                                      |
| CEtAmPr-N-EtFHxSA                                                          | 585.109        | CEtAmPr-N-EtFASA | 2.55± 0.54                        | 11.87± 2.17                          |
| CMeAmPr-FHxSA                                                              | 543.062        | CMeAmPr-FASA     | 40.29± 6.34                       | 145.25± 29.67                        |
| diOHBAmpPr-FPrSA                                                           | 423.118        | diOHBAmpPr-FASA  | 1.31± 0.23                        |                                      |
| diOHBAmpPr-FPeSA                                                           | 523.112        | diOHBAmpPr-FASA  | 1.06± 0.19                        |                                      |
| diOHBAmpPr-FHpSA                                                           | 623.106        | diOHBAmpPr-FASA  | 3.08± 0.58                        |                                      |
| AmPr-FHxSA                                                                 | 485.056        | AmPr-FASA        | 2.69± 0.42                        | 50.00± 9.71                          |
| Am-CPr-FHxSA                                                               | 529.046        | Am-CPr-FASA      | 1.26± 0.22                        | 5.22± 0.00                           |
| Am-CPr-FOSA                                                                | 629.040        | Am-CPr-FASA      | 0.70± 0.09                        |                                      |
| EtOH-AmPr-FHxSA                                                            | 529.083        | EtOH-AmPr-FASA   | 1.77± 0.37                        | 5.81± 1.06                           |
| SPrAmPr-FHxSA                                                              | 607.060        | SPrAmPr-FHxSA    | 2.40± 0.51                        |                                      |
| TAmPr-FHxSA                                                                | 499.072        | TAmPr-FASA       | 1.50± 0.25                        | 25.23± 3.69                          |
| TAmPr-FHxSAPrA                                                             | 571.093        | TAmPr-FASA-PrA   | 3.43± 0.63                        | 15.36± 2.82                          |
| TAmPr-FHpSAPrA                                                             | 621.090        | TAmPr-FASA-PrA   | 3.89± 1.09                        | 25.10± 17.08                         |
| <b>Miscellaneous</b>                                                       |                |                  |                                   |                                      |
| 8:2 FTCA                                                                   | 476.979        |                  | 2.93±0.47                         |                                      |
| 7:3 FTCA                                                                   | 440.998        |                  | 0.72±0.27                         | 0.55±0.06                            |
| diOHPrAm-MeOHPr-FHxSA                                                      | 587.089        |                  | 0.71±0.19                         | 2.54±1.01                            |
| 6:2 FTTh-EtAdPrAm                                                          | 523.108        |                  | 1.27± 0.28                        |                                      |
| 8:2 FTTh-EtAdPrAm                                                          | 623.102        |                  | 2.85± 0.49                        |                                      |

## **APPENDIX A5: Film Experiments to Determine PFAS $K_{aw}$ Values in Porewater at the Lakehurst, NJ DoD Site**

Laboratory bench-scale batch experiments were performed to determine values of the air-water interfacial partition coefficient  $K_{aw}$  (cm) for PFOS, PFHpS, and PFOA. Values of  $K_{aw}$  were directly measured using porewater collected from the lysimeters using the film method, which is described in detail in Schaefer et al. (2019b). Briefly, this method entails filling a 25 cm diameter HDPE pan with approximately 2.2 L of the collected porewater, allowing 3 days of equilibration, draining the bulk water (while collecting a sample of this bulk water for PFAS analysis), and collecting the film of water remaining in the pan (approximately 0.15 L) for PFAS analysis. PFOS, PFHpS, and PFOA concentrations measured in the bulk porewater sample collected were 9,800, 310, and 400 ng/L, respectively. Applying a mass balance, and knowing the geometric surface area of the air-water interface in the film residing in the pan, the PFAS mass per unit area at the air water interface ( $\Gamma$  in units of ng cm<sup>-2</sup>) is determined.  $K_{aw}$  is then calculated as  $\Gamma$  divided by the bulk water concentration. This experiment was performed in duplicate.

## APPENDIX A6: Determination of 95% Confidence Intervals for Predicted PFAS Porewater Concentrations

The errors associated with the model (Eqs. 4.2-4.5) predictions for PFOS, PFHpS, and PFOA concentrations, which are represented by the error bars (95% confidence intervals) in **Figure 4.23**, are based upon the generalized propagation of error formula (NIST/SEMATECH e-Handbook of Statistical Methods, <http://www.itl.nist.gov/div898/handbook/>, 2006). Three parameters used in the model are considered for the error propagation calculation:

- $K_{aw}$ . The 95% confidence intervals for these values were determined in duplicate batch film experiments, as described in the main text.  $K_{aw}$  values were  $0.18 \pm 0.029$  cm,  $0.071 \pm 0.061$  cm,  $0.064 \pm 0.048$  cm for PFOS, PFHpS, and PFOA, respectively (average  $\pm$  95% confidence intervals shown).
- $K_d$ . The 95% confidence intervals for  $K_d$  are provided in **Table 4.3**.
- $a_{aw}$  (the air-water interfacial area). Determination of this parameter is described by Eq. 4.5, and employs the use of the measured particle size distribution and estimated soil moisture saturation of 0.5. The  $a_{aw}$  value used in the model is  $93 \text{ cm}^{-1}$ . Here, we assume that an uncertainty of 40% (or, a 95% confidence interval of  $\pm 37 \text{ cm}^{-1}$ ) is a reasonable estimate. This error is driven by the fact that the particle diameter associated with  $d_{40}$  and  $d_{60}$  varies by only 25% from the  $d_{50}$  value used in the calculation of  $a_{aw}$ , and that the maximum moisture saturation ( $S$ ) measured during lysimeter sampling in the two most shallow moisture probes has an average value among the 3 sample events of  $0.5 \pm 0.2$  (the  $\pm 0.2$  represents the approximate range of  $S$  during porewater sample collection). The maximum moisture during lysimeter sampling is used because most of the water drawn into the lysimeters likely occurred during the peak pore saturation.

For the first sampling period, difficulties with equipment prevented us from having actual soil probe readings during the sample collection. However, **Figure 4.21** clearly shows that there was a substantial rainfall event approximately 3 days prior to the porewater sampling event. Projecting the linear slopes of the moisture probes observed during the first several hours of readings on July 15<sup>th</sup> backwards in time, the average peak saturations are approximately 0.45. If there is any non-linearity in these slopes, such as what is typically observed following rainfall event, values would be near, or perhaps even in excess, of 0.5.

It is also assumed that the 3 moisture probes, which are generally within 1 meter of the lysimeters, are representative of water saturation within the test plot.

The 95% confidence interval ( $CI_{\text{model}}$ ) for the model is then determined as follows based on the NIST/SEMATECH e-Handbook of Statistical Methods:

$$CI_{\text{model}} = \sqrt{\left(\frac{\partial C}{\partial K_{\text{aw}}}\right)^2 (CI_{K_{\text{aw}}})^2 + \left(\frac{\partial C}{\partial K_{\text{d}}}\right)^2 (CI_{K_{\text{d}}})^2 + \left(\frac{\partial C}{\partial a_{\text{aw}}}\right)^2 (CI_{a_{\text{aw}}})^2}$$

where  $CI_{K_{\text{aw}}}$ ,  $CI_{K_{\text{d}}}$ , and  $CI_{a_{\text{aw}}}$  refer to the 95% confidence intervals associated with the  $K_{\text{aw}}$ ,  $K_{\text{d}}$ , and  $a_{\text{aw}}$  values, respectively.  $CI_{\text{model}}$  is calculated for PFOS, PFHpS, and PFOA, and represented by the error bars associated with the model predictions in **Figure 4.23**.

It is also noted that uncertainty regarding the PFAS soil concentrations ( $C_s$  in Eq. 4.4) due to heterogeneity in the test plot is considered small compared to the error described above. This is based on the PFAS porewater concentrations, which were reasonably uniform across the test plot. If all of the variation (i.e., averages  $\pm$  95% confidence intervals) in the PFAS porewater concentrations shown in **Figure 4.23** were due to a variation in PFAS soil concentrations (which is likely not the case), then application of Eq. 4.4 coupled with the soil isotherm data indicates that the soil concentration varies very little. For example, the PFOS porewater concentration in **Figure 4.23** is shown as  $10,000 \pm 6,2000$  ng/L. Application of Eq. 4.4 shows that at 16,000 ng/L, the equilibrium PFOS soil concentration is only 3.7% greater than that in equilibrium with 10,000 ng/L porewater. Performing the same calculations for PFHpS and PFOA results in a soil variability of 6.9% and 17%, respectively.

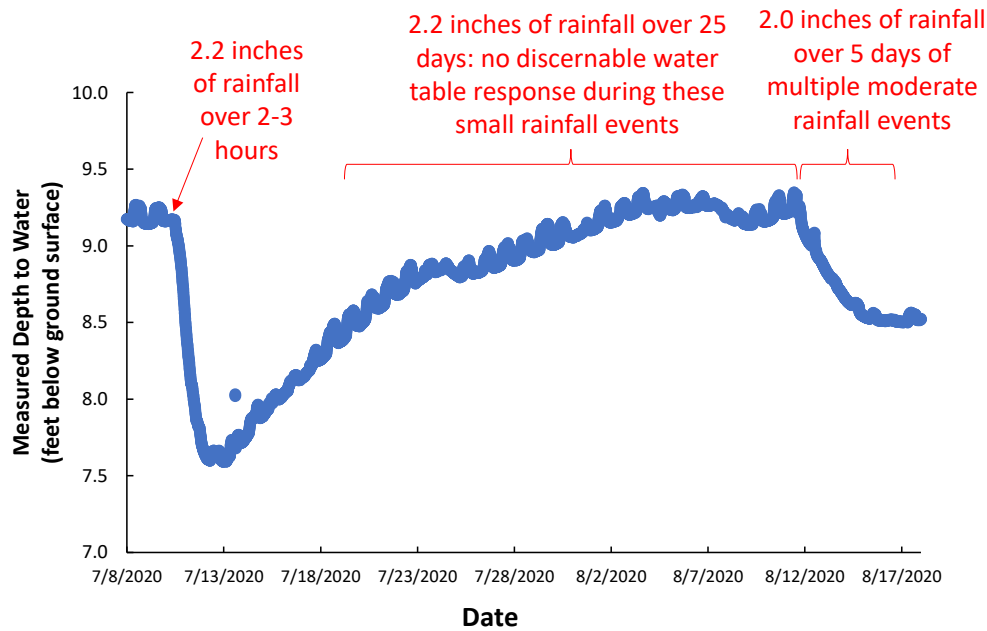
## **APPENDIX A7: Estimation of the fraction of rainfall reaching the water table ( $I_w$ )**

The amount of rainfall at the site during the 20 months prior to flushing, based on a local weather station with rain gauge data (data provided at wunderground.com), was approximately 92 inches. The potential evapotranspiration (PET) for this 20 month period is estimated at 47 inches, which is based on local evapotranspiration estimates provided by the Northeast Regional Climate Center (<https://www.nrcc.cornell.edu/wxstation/pet/pet.html>). Since the measured rainfall exceeded the PET for each month, the actual evapotranspiration (AET) was assumed equal to the PET, as discussed in Bakundukize et al. (2011). The resulting value of  $I_w$  is then calculated assuming that only 45 of the 92 inches of rainfall reach the water table (approximately 6 feet below ground surface), resulting in an  $I_w$  value of 0.49.

In addition, the value of  $I_w$  was estimated using the water table fluctuation method (WTF), as described in Gumuła-Kawęcka et al. (2022). Using the WTF,  $I_w$  is estimated as:

$$I_w = \frac{S\Delta H}{R} \quad \text{Eq. A7.1}$$

Where  $S$  is the specific yield,  $\Delta H$  is the change in water table elevation following rainfall events [inches], and  $R$  is amount of rainfall [inches]. For the test plot, all parameters were estimated using the combined rainfall ( $R$ ) and water table elevation data described in Section 4.5, and presented in the figure below. To determine  $S$ , it was assumed that a heavy rainstorm (2.2 inches of rainfall over 2 to 3 hours) that occurred on July 10, 2020 resulted in nearly complete recharge to the underlying groundwater ( $I_w=1$  for this storm event); the rapid infiltration of approximately 2.6 inches of flushing water over 2 hours used in the flushing experiments herein supports this assumption. The  $\Delta H$  measured in response to this event (measured in MW-1, which was screened across the water table, and where water table elevation was recorded using a datalogger) was 18 inches. Inserting these values into Eq. A7.1, the resulting value for the specific yield ( $S$ ) is 0.1, which is in the range expected for a fine sand (Johnson, 1967). To determine  $I_w$  for conditions of “moderate” rainfall, a five day period (August 12, 2020 to August 17, 2020) over which 2.0 inches of rainfall occurred was evaluated. The  $\Delta H$  measured in response to this rainfall was 9.4 inches. Applying Eq. 1, and an  $S$  value of 0.1, the resultant value for  $I_w$  under the “moderate” rainfall condition is 0.47, which is in excellent agreement with the value of 0.49 estimated on the PET.



#### References:

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Gumuła-Kawęcka, A., Jaworska-Szulc, B., Szymkiewicz, A., Gorczewska-Langner, W., Pruszkowska-Caceres, M., Angulo-Jaramillo, R. and Šimůnek, J., 2022. Estimation of groundwater recharge in a shallow sandy aquifer using unsaturated zone modeling and water table fluctuation method. *J. Hydrology*, 605, 127283.

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## APPENDIX B: LIST OF SCIENTIFIC PUBLICATIONS

1. Schaefer, C.E., Nguyen, D., Christie, E., Shea, S., Higgins, C.P., Field, J.A., 2021. Desorption of Poly- and Perfluoroalkyl Substances from Soil Historically Impacted with Aqueous Film-Forming Foam. *J. Environ. Engin.* 147, 2021.
2. Schaefer, C.E., Nguyen, D., Christie, E., Shea, S., Higgins, C.P. and Field, J., 2022. Desorption Isotherms for Poly-and Perfluoroalkyl Substances in Soil Collected from an Aqueous Film-Forming Foam Source Area. *J. Environ. Engin.* 148, 04021074.
3. Schaefer, C.E., Lavorgna, G., Lippincott, D.R., Nguyen, D., Christie, E., Shea, S., O'Hare, S., Lemes, M., Higgins, C.P., Field, J. 2022. A Field Study to Assess the Role of Air-Water Interfacial Sorption on PFAS Leaching in an AFFF Source Area. *J. Contam. Hydrol.* 248, 104001.
4. Schaefer, C.E., Lavorgna, G.M., Lippincott, D.R., Nguyen, D., Schaum, A., Higgins, C.P. and Field, J., 2023. Leaching of Perfluoroalkyl Acids during Unsaturated Zone Flushing at a Field Site Impacted with Aqueous Film Forming Foam. *Environ. Sci. Technol.* 57, 1940-1948.
5. Shea, S.M., Schaefer, C.E., Illangasekare, T., Higgins, C.P. Release of Poly- and Perfluoroalkyl Substances (PFAS) from Aqueous Film Forming Foam (AFFF)-Impacted Soils: Impacts of Soil Saturation. *Under review in Environ. Sci. Technol.*