ESTCP

EXECUTIVE SUMMARY

PFAS Leaching at AFFF-Impacted Sites: Insights into Soil-to-Groundwater Ratios

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ACRONYMS AND ABBREVIATIONS

AFFF	aqueous film-forming foam
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
FTS	fluorotelomer sulfonate
PCSL	porous cup suction lysimeter
PFAS	per- and polyfluoroalkyl substances
PFBS	perfluorobutanesulfonate
PFHxS	perfluorohexanesulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
PFPeA	perfluoropentanoic acid

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1.0 INTRODUCTION

Use of aqueous film-forming foams (AFFF) at Department of Defense (DoD) facilities has resulted in persistent subsurface impact of per- and polyluoroalkyl substances (PFAS). At many of these locations, the retention and slow release of PFAS from the unsaturated zone to underlying groundwater is the suspected (or known) cause of PFAS groundwater impact. However, due to the unique complexities associated with PFAS phase behavior (e.g., sorption at air-water interfaces, retention of cationic species) and migration (e.g., rate-limited desorption), the relationship between PFAS levels measured in unsaturated soils and PFAS levels in percolating porewater (and, ultimately the underlying groundwater) is poorly understood. As a result, guidance is lacking regarding determination of soil screening criteria that are protective of underlying groundwater, as scientifically- or empirically-based data are generally lacking; this has proven to be a challenge with respect to site management. Thus, improved insights into the relationship between unsaturated zone PFAS composition and concentration, soil physical and chemical properties, and PFAS levels in percolating porewater/underlying groundwater are urgently needed.

As DoD efforts to characterize AFFF-impacted source areas and attain insights into the mechanisms controlling PFAS fate and transport in unsaturated soils are ongoing, ***field-based in situ characterization of PFAS leaching (via unsaturated zone pore-water measurements) coupled with soil characterization and underlying groundwater impacts represent a practical dataset that is largely absent***. Such practical information and field-based data, coupled with DoD's ongoing mechanistic studies, have potential to provide unique insights into developing/validating meaningful predictive models of PFAS soil-to-groundwater ratios (or mass discharge from AFFF-impacted soils in the vadose zone), and ultimately guidance for determining soil concentrations protective of groundwater. Furthermore, traditional approaches for soil screening to estimate impact-to-groundwater values may be inappropriate due to PFAS sorption at air-water interfaces and perfluoroalkyl acid precursor transformation.

2.0 OBJECTIVES

The overall goal of this project was to demonstrate improved insight into PFAS leaching through the unsaturated zone to serve as a basis for developing soil cleanup criteria and facilitating site management. Obtaining a field-based dataset relating PFAS soil levels, soil characteristics, and porewater leaching to underlying groundwater impacts would provide the DoD with much needed information to validate conceptual site models and develop soil management guidelines. Specific objectives were to:

- Assess the factors controlling PFAS leaching in the vadose zone.
- Determine how soil properties impact PFAS porewater migration and overall source longevity.
- Identify unsaturated zone characteristics that impact PFAS migration to groundwater.
- Attain insight into the role of PFAS air-water interfacial retention on vadose zone migration.
- Develop a screening-level basis for PFAS soil concentrations protective of underlying groundwater that can be used for improved site management.

3.0 TECHNOLOGY DESCRIPTION

Please note that portions of the Technology Description and Performance Assessment have been reprinted (adapted) with permission from the pre-print of {Schaefer, C.E., Nguyen, D., Fang, Y., Gonda, N., Zhang, C., Shea, S. and Higgins, C.P., 2024. PFAS Porewater concentrations in unsaturated soil: Field and laboratory comparisons inform on PFAS accumulation at air-water interfaces. Journal of Contaminant Hydrology, 264, p.104359.}. Copyright 2024. Elsevier.

A multi-phased approach was employed to attain insight into soil-to-groundwater PFAS leaching, and ultimately guidance for determining soil concentrations protective of groundwater. This approach was utilized at five primary sites selected for this technology demonstration. At each demonstration site, an initial high-resolution characterization was performed of site soil, equilibrium (i.e., static) porewater sampling of the collected soil cores, and, finally, in situ measurements of PFAS concentrations using porous cup suction lysimeters.

A 5.4-cm soil core was collected at each site (Sites A through E) using a gas-powered core sampling kit (AMS, Inc., American Falls, ID). PFAS in the collected soil core were analyzed every 0.1 to 0.2 m for a total depth (depending on the site) of up to 2.4 m. Soil samples were also collected for total organic carbon, cation exchange capacity, and moisture content. Three lysimeters were installed within a 0.8 m radius of the soil core for Sites A, B, C, and D; the borehole used for soil sampling was used for one of the installed lysimeters. For Site E, three lysimeters were initially installed to a depth of 1.7 m below ground surface, but failed to produce any water. Two lysimeters were then re-installed adjacent to the initial locations to depths of 0.76 m below ground surface. In addition to Sites A through E, an additional DoD sites (Sites F) was also used to supplement this demonstration. Site F was also historically exposed to AFFF.

Lysimeter installation and sampling were performed as described previously (Schaefer et al., 2022). Porous cup suction lysimeters (4.8 cm diameter), with 3.8 cm long ceramic heads and a 2 bar bubbling pressure, were purchased from Soil Moisture Equipment Corp. (Goleta, CA). A silica flour (200 mesh) slurry was poured into the lysimeter boreholes so that the slurry reached several centimeters above the porous cup; addition of this slurry was intended to maintain a saturated connection between the lysimeter and the native soil. Sand was layered above the silica flour, with bentonite chips used to fill the remaining annular space. A bromide tracer (500 mg/L bromide as NaBr) was included with the silica flour slurry to account for any potential dilution of the porewater by the slurry water.

A hand pump was used to apply vacuum (typically 65 centibar) and extract porewater, where several hours to overnight extraction was typically needed to collect water. When possible, the initial sample of porewater collected for each lysimeter (approximately 20 mL) was used for purging and then discarded; up to 3 subsequent rounds of porewater collected for PFAS analysis were performed within a 2 to 6 day period. The first round of samples from one of the 3 lysimeters at Site C was excluded from the dataset because PFAS porewater concentrations were approximately two standard deviations less than that observed in the other seven porewater samples collected.

An additional intact soil core, collected during installation of the lysimeters, was collected for bench-scale porewater testing. The purpose of the bench-scale porewater testing was to serve as a comparison to the field-measured PFAS porewater concentrations, where the bench-scale system represented a static (or equilibrated) sample compared to the dynamic (and potentially non-equilibrated) field sample. Bench-scale porewater samples were collected using micro-sampling lysimeters that had a 0.95 cm outside diameter, were 18 cm long, and had a porous ceramic head 3 cm in length (Soil Moisture Equipment Corp., Goleta, CA). Vacuum (approximately 55 centibar) was applied to collected soils using 10 mL disposable syringes, where the vacuum was typically applied overnight. Methanol used to rinse the micro-sampling lysimeters and syringes was collected and analyzed with the collected porewater to limit any PFAS sorptive losses to the porewater extraction system; prior testing showed that sorptive losses to the field lysimeters were negligible for perfluorooctanesulfonate (PFOS) (Schaefer et al. 2022). Ideally, porewater was extracted from an intact core at the same depth where the field lysimeter was placed, with 2 additional duplicates extracted within 15 cm of this depth (3 samples total). However, due to relatively dry soil conditions, only porewater from the Site D soil core could be collected in this manner. For the other sites, soil was homogenized in the 20-30 cm depth interval that overlapped the depth of the field lysimeter deployment; soil in this interval was visually homogeneous. This soil was then wetted using a 5 mM $CaCl_2$ solution, packed in polypropylene centrifuge tubes (approximately 80 g samples prepared in triplicate), and equilibrated for a minimum of three days before extracting the porewater with the micro-sampling lysimeters. Figure ES-1 shows the bench-scale porewater sampling set-up. Even after wetting, porewater could not be extracted in the laboratory from the homogenized soil for Site E; thus no bench-scale porewater samples were collected from Site E soil.

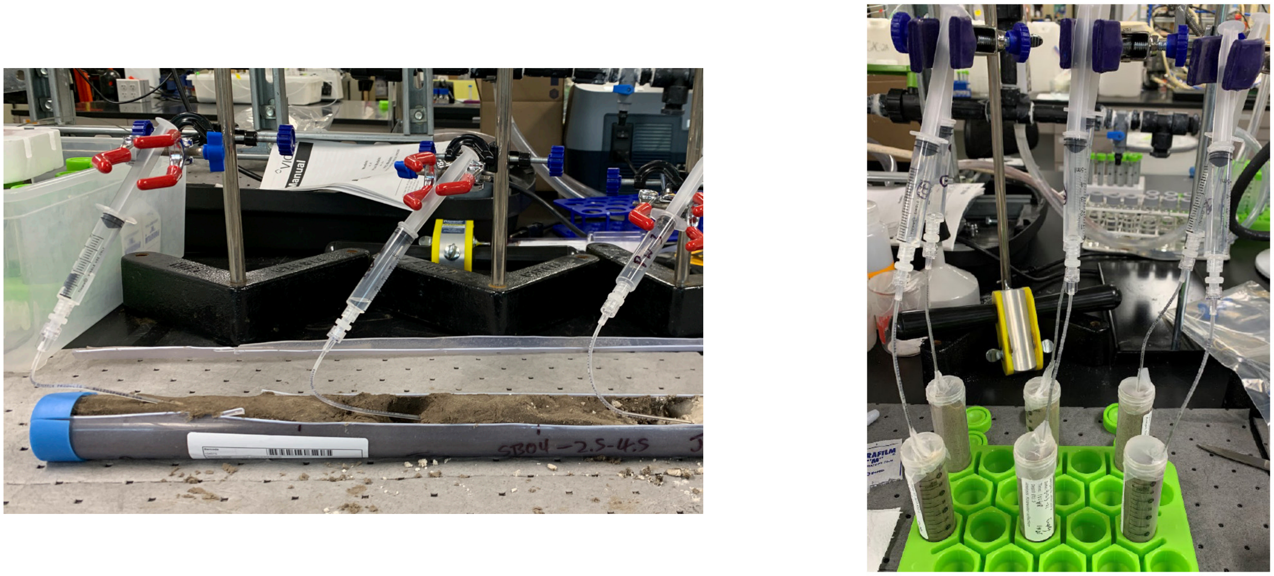

Figure ES-1. Bench-scale Porewater Sampling Using the Micro-sampling Lysimeters.

Sampling in an intact core is shown, and sampling from wetted and re-packed soil is shown.

4.0 PERFORMANCE ASSESSMENT

4.1 PFAS SOIL CONCENTRATIONS

In all cases, PFOS exhibited the most elevated PFAS concentration measured in the collected soil samples. The perfluorinated sulfonate relative concentration versus depth profiles for Sites A and B showed clear chromatographic separation (Figure ES-2). The least hydrophobic compound (perfluorobutanesulfonate (PFBS)) had the deepest concentration maximum, while the PFOS concentration maximum was near the soil surface. In contrast, for Sites C and E, the relative concentration profiles were similar for each perfluorinated sulfonate, and no chromatographic separation was observed (Figure ES-2). Site D is omitted from Figure ES-2 due to the large number of perfluorinated sulfonate results that were below the analytical detection limit. Similar results with respect to the vertical concentration profiles were observed for the perfluorinated carboxylates. The reason for the differences between Sites A and B, and Sites C and E, were unclear, as they could have been due to the nature of AFFF releases, rainfall, and/or other soil properties.

4.2 PFAS POREWATER CONCENTRATIONS

Figure ES-3 summarizes target (quantified) PFAS concentrations measured in the collected lysimeter porewater for each site, corrected for the appropriate bromide dilution factor (based on the bromide concentration in the sampled field lysimeter porewater relative to the bromide concentration used in the silica flour slurry). At Site A, porewater PFAAs were largely dominated by shorter-chained (≤6 perfluorinated carbons) compounds. These porewater results were consistent with the corresponding soil data collected at the lysimeter installation depth of 1.5 m below ground surface. For Site B, 4:2 fluorotelomer sulfonate (FTS) accounted for the majority of the identified PFAS mass in the porewater, although 4:2 FTS was only observed in one of the two water-producing lysimeters and was not observed in any soil samples. Besides this detection of 4:2 FTS, similar to Site A, porewater at Site B also was dominated by shorter-chained PFAS.

PFOS and/or perfluorohexanesulfonate (PFHxS) were the predominant PFAAs for Sites D and E. These results for Sites D and E were consistent with the soil data, and could reflect the greater migration of PFOS and PFHxS at these sites due to increased rainfall and shallower lysimeter placement compared to Sites A and B. In contrast to Sites D and E, the porewater data for Site C was not indicative of the soil concentrations, as perfluoropentanoic acid (PFPeA) and PFHxA were the predominant porewater PFAAs despite the fact that PFOS was by far the predominant PFAA in the soil. This apparent discrepancy was likely due to the elevated affinity of PFOS to the soil compared to PFPeA and PFHxA, and/or the relative affinity of PFOS to the air-water interface. It was also possible the predominance of PFPeA and PFHxA in Site C porewater was due to biotransformation of precursors present in Site C soil.

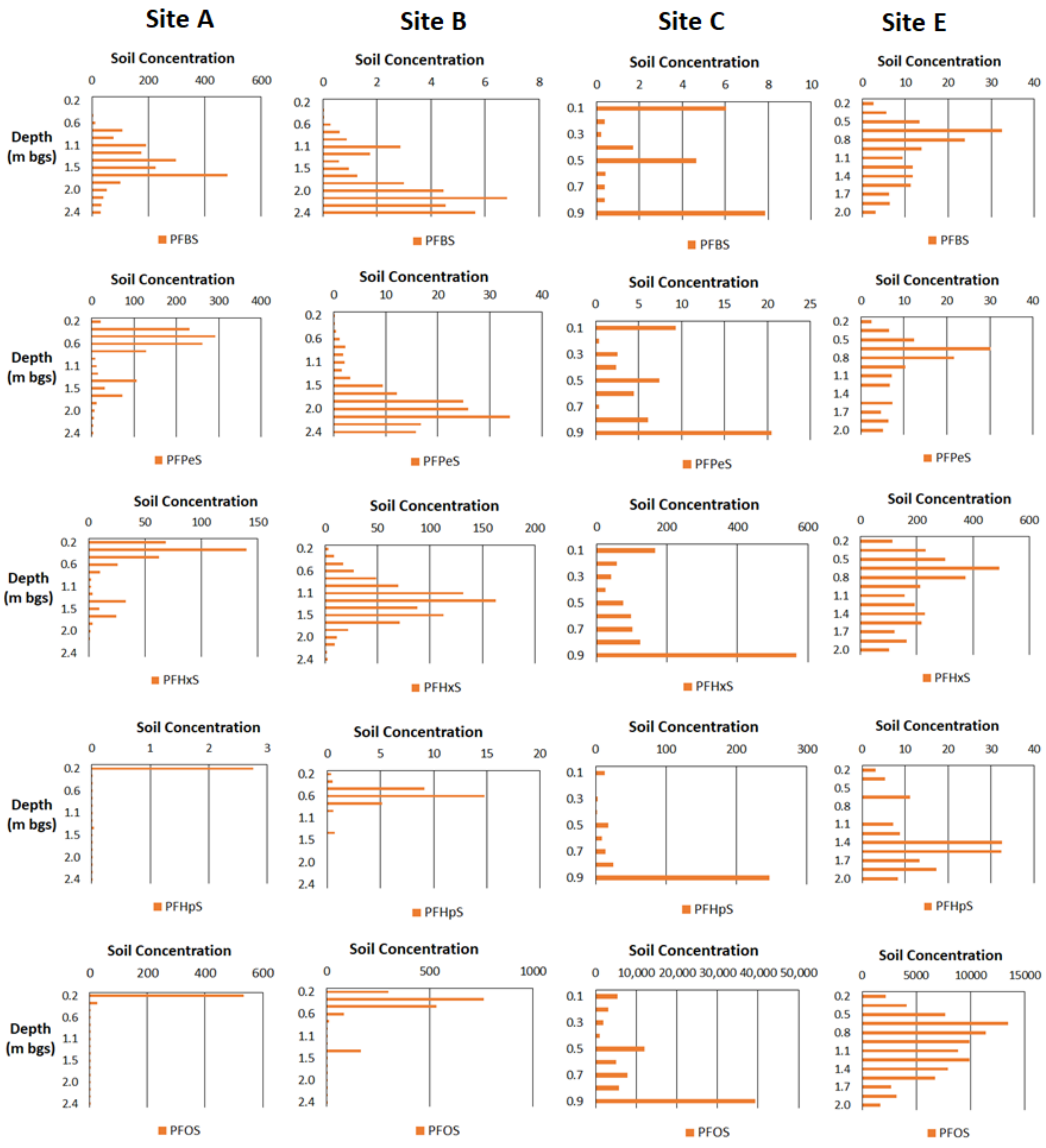

Figure ES-2. Perfluorinated Sulfonate Soil Concentrations (µg/kg) Measured as a Function of Depth in the Unsaturated Zone for Sites A. B, C, and E.

Non-detect results are plotted as 10% of the reporting limit. PFBS = perfluorobutanesulfonate, PFPeS = perfluoropentanesulfonate, PFHxS = perfluorohexanesulfonate, PFHpS = perfluoroheptanesulfonate, and PFOS = perfluorooctanesulfonate.

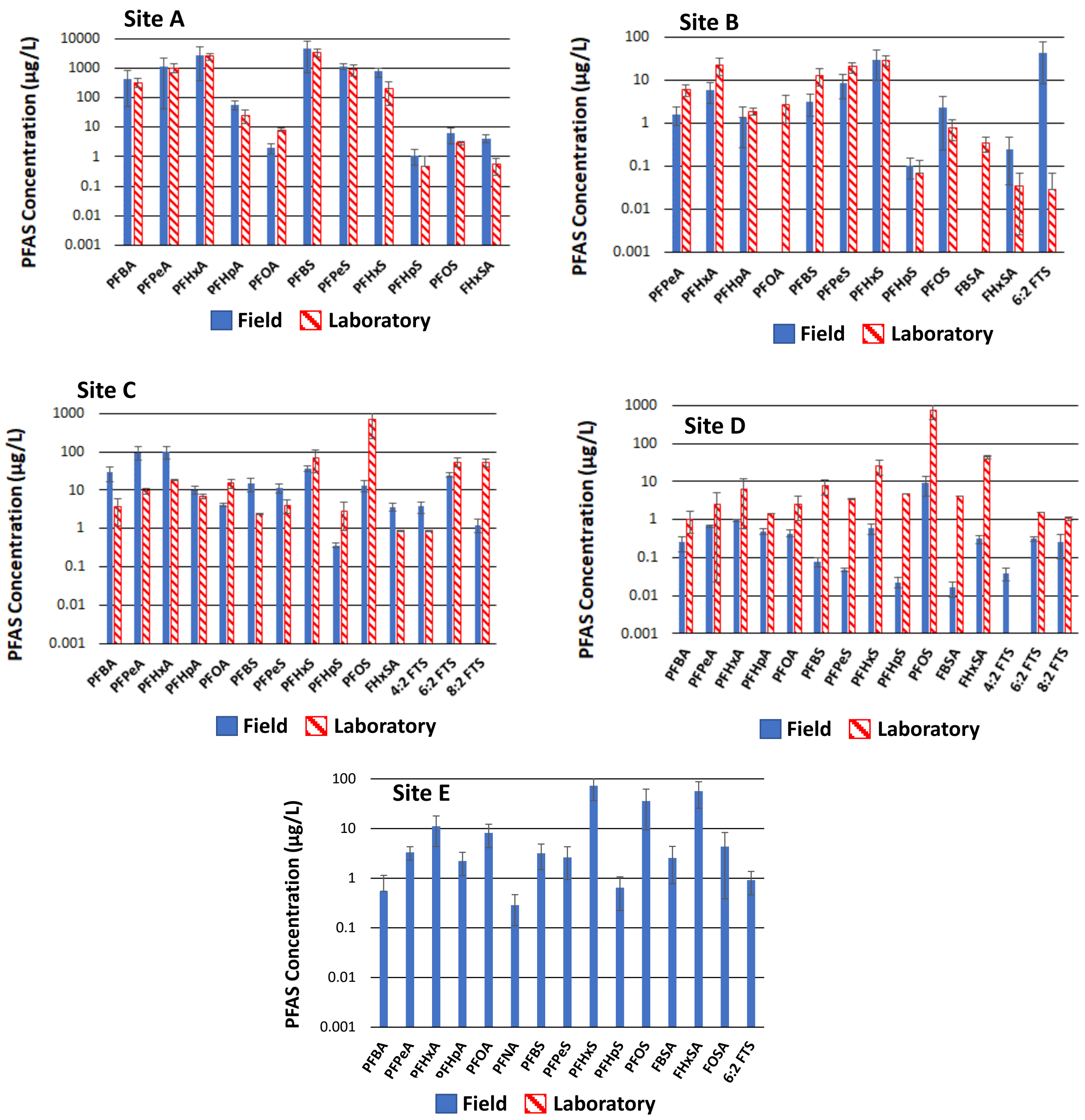

Figure ES-3. PFAS Porewater Concentrations for Quantifiable Analytes from Both the Field-deployed Lysimeters and in the Laboratory Using Porewater from the Collected Soil Cores.

Error bars represent 95% confidence intervals. For Site E, laboratory-based porewater samples could not be collected.

A comparison of the quantified PFAS porewater concentrations measured in the field lysimeters to those measured in the laboratory from the collected soil cores for each site, with the exception of Site E (field data only), is also provided in Figure ES-3. The small soil grain size for Site E precluded extraction of porewater in the laboratory from the collected soil core at the bench-scale.

For Sites A and B, PFAS concentrations measured in the field-collected porewater and in laboratory-collected porewater were typically within a factor of 2 to 5. Given the potential pore-scale variability among field-collected porewater and collected soil samples, such order of magnitude agreement was considered reasonable. Notable exceptions for Sites A and B were perfluorooctanoic acid (PFOA) and 6:2 FTS. For PFOA, the limit of quantification for the field-collected porewater sample was 0.57 µg/L, which was just over 4-times less than that PFOA concentration measured in the laboratory-collected porewater. The large (3 orders of magnitude) discrepancy for 6:2 FTS in Soil B was not readily explained but may have been due to the variability of 6:2 FTS measured between lysimeters in the field (greater than 50 µg/L in one lysimeter, but below the limit of quantification of 0.11 µg/L at the other lysimeter).

For Site C, comparison between the field-collected porewater and laboratory-collected porewater were similar to that observed for Sites A and B. However, the concentrations for the long-chained compounds PFOS and 8:2 FTS were nearly 100-times greater in the laboratory-collected porewater sample than in the field-collected porewater sample. PFOS and 8:2 FTS were the most surface-active PFAS evaluated in this comparison (Lyu et al., 2018; Brusseau et al., 2019), and the wetting needed for the laboratory-collected porewater sample likely caused a substantial decrease in air-water interfacial area and subsequent release of PFAS into the aqueous phase.

Using a PFAS mass balance model similar to that previously developed (Schaefer et al., 2022), which is based on equilibrium relationship between soil, aqueous, and air-water interfacial phases, the impact of wetting and air-water interfacial area collapse on PFAS distribution and ultimately PFAS porewater concentrations was determined. Table ES-1 compares the measured versus predicted PFAS porewater concentrations in the laboratory-measured (wetted soil core) samples. The generally reasonable (factor of 3) agreement between predicted and measured values suggests that the evaluation of PFAS concentrations in the collected soil cores could be used as a reasonable approximation for PFAS concentrations measured in situ using the porous cup suction lysimeters. These results also suggested that equilibrium relationship were generally appropriate for describing phase behavior. Site D PFAS concentrations measured in the field-collected porewater were generally 5- to 100-times less than those measured in the laboratory-collected porewater; Site D soils were not wetted prior to the laboratory-scale sampling (intact core was used). Thus, unlike Sites A, B, and C, the local equilibrium assumption did not appear to be valid for Site D. While a conclusive explanation for the discrepancy between the field-collected and laboratory-collected PFAS porewater concentrations for Site D was not resolved for this study, it was notable that the backfilled material in Site D was quite heterogeneous. Specifically, core logging noted what appeared to be polyethylene plastic sheeting and cm-sized pieces of concrete/rubble intermittently dispersed within the soil cores. In addition, ground penetrating radar surveying performed prior to lysimeter installation showed several anomalies throughout, indicating discontinuities throughout the interrogated zone and suggesting the presence of voids or other debris. Such discontinuities could result in preferential or non-uniform flow that could bias PFAS concentrations in the lysimeters. The applicability of porous cup suction lysimeters in this type of media warrants further study.

Table ES-1. For Sites A, B, and C, Comparisons of PFAS Porewater Concentrations measured in the field Lysimeters (C_1) and in the Wetted Soil Cores (C_2) to the Model-Predicted Wetted Soil Core Values.

± values indicate 95% confidence intervals. 8:2 FTS and PFHpS comparison for Sites A and B are not provided because these compounds were not detected in the porewater and/or in the soil (at the depth of the lysimeters) at these two sites.

	Measured Porewater Concentration In Situ (C_1) (µg/L)	Measured Porewater Concentration in Wetted Laboratory Cores (C_2) (µg/L)	Predicted Porewater Concentration (C_2) (µg/L)
Site A			
PFOS	6.2 ± 3.4	3.0 ± 0.37	6.6 ± 3.3
Site B			
PFOS	2.2 ± 2.0	0.78 ± 0.38	2.8 ± 2.0
Site C			
PFOS	13 ± 4.1	680 ± 460	164 ± 75
8:2 FTS	1.2 ± 0.46	52 ± 13	16 ± 6.0
PFHpS	0.36 ± 0.051	2.9 ± 2.0	5.9 ± 3.4

5.0 COST ASSESSMENT

A cost assessment was presented to estimate the resources needed to provide bench-scale validation/evaluation of PFAS concentrations measured in situ using porous cup suction lysimeters. Specifically, costs associated with the micro-lysimeter porewater sampling of collected soil sample (Fig. ES-1) was determined. For the micro-lysimeter sampling, the estimated cost (including PFAS analysis) for evaluation within a typical fire-training area was $7,750. This cost was largely driven by the PFAS analysis ($450/sample x 12 samples assumed).

6.0 IMPLEMENTATION ISSUES

The field-scale and bench-scale porewater sampling employed in this study were generally readily implementable. Specific challenges are noted as follows:

- Dry soil conditions. Sufficient soil moisture is needed to extract field porewater samples. Herein, porewater collection was challenging in the two driest soils (3.5% and 4.3% moisture content). Although a sufficient volume and number of porewater samples were collected for quantitative analyses, the targeted number of lysimeter samples was not obtained. Results of this study suggested that a soil moisture content of approximately 5% was needed for routine porewater collection use porous cup suction lysimeters (PCSL) (although this value also was dependent upon the soil grain size and texture). At many semi-arid or arid sites, this may necessitate timing lysimeter sampling events with rainfall events. Another option would be to apply vacuum for a longer period of time than what was used herein (typically 8 to 12 hours). Such extended vacuum application would require additional labor efforts, or the use of a vacuum manifold system.

For the microlysimeters, a soil moisture content of approximately 7% was needed to effectively extract porewater; this higher moisture content was due to the fact that the maximum vacuum that could be applied on the microlysimeters was less than that which could be applied to the field-deployed lysimeters.

- Low permeability soils. It is well-known that low permeability soils can prevent the effective collection of porewater when using PCSLs. Sites E and F had clay contents of 14% and 15%, respectively. Despite elevated moisture contents (9.6% and 13% for sites E and F, respectively), collecting porewater was challenging. For Site E, sufficient porewater was collected for quantitative analyses, but not all lysimeters produced water and no porewater was collected for some of the sampling rounds; site F yielded insufficient porewater to include in the study. Porewater collection results for site F, given the elevated moisture and average grain size of 0.2 mm, were particularly surprising. One possibility was that local heterogeneity in the clay distribution may have contributed to the difficulties in collecting porewater at site F. Overall, results of this study suggested that elevated clay levels could result in challenges when attempting to collect porewater using PCSLs.

- Applied vacuum. Another issue that occurred was that the lysimeters would occasionally not hold vacuum, and therefore porewater collection was limited. In most cases, this was due to improperly securing either the lysimeter cap or improperly securing/crimping the vacuum tubing. Thus, proper attention should be given to these details. Another challenge (observed herein and in other lysimeter studies in which the project investigators were involved) the lysimeter caps appeared to be tampered with by wildlife. Thus, proper securing of the lysimeter caps is recommended.

- Site heterogeneity. For this project, lysimeters were installed at a single depth, and within a single stratigraphic zone. For sites where the soil data suggest that the geology and PFAS distribution are likely not uniform throughout the unsaturated zone, installing lysimeters at multiple depths should be considered to better inform on overall PFAS leaching and mass discharge to underlying groundwater. While such evaluation was beyond the scope of this current study, it is important to recognize that the spatially limited lysimeter investigation performed herein would need to be expanded to provide appropriate site characterization.

- Comparison of lab vs field Collected porewater. While reasonable agreement (typically within a factor of 3 and/or within the 95% confidence interval of the field measurements) was observed between field-collected porewater and porewater extracted in the laboratory from soil cores, two findings were noteworthy. First, in most cases, the soil needed to be wetted and re-packed to collected porewater in the laboratory. Second, if wetting caused a significant decrease in the air-water interfacial area, the impact on PFAS porewater concentrations due to release of PFAS at the air-water interface had to be accounted for (via mass balance) to properly compare the laboratory PFAS porewater concentrations to the field data.

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