FACT SHEET

Assessing Per- and Polyfluoroalkyl Substances (PFAS) Leaching from Soil to Groundwater

MAR 2025

Why Consider the Assessment of PFAS Leaching?

Understanding the nature and strength of PFAS leaching from soil to groundwater is critical for effective site management. Soil can retain PFAS, potentially resulting in a long-term source of PFAS in groundwater. The unique physicochemical properties of PFAS result in complex fate and transport behavior in the vadose zone, and in some cases may require specialized evaluations to determine how soil to groundwater leaching fits into a particular conceptual site model (CSM).

This fact sheet will explain how different PFAS migrate through the vadose zone, how to estimate groundwater recharge rates, and how to estimate PFAS concentrations in porewater. In addition, awareness of new sensor-based methods for monitoring soil conditions may help in better understanding and managing PFAS leaching to groundwater.

Key PFAS Fate and Transport Processes in the Vadose Zone

There are potentially thousands of different PFAS in the vadose zone at impacted sites. PFAS are present in two main classes that can have different properties: PFAAs (perfluoroalkyl acids) and precursors that can produce PFAAs (polyfluoroalkyl acids). The Navy is authorized by the Department of Defense (DoD) to investigate specific PFAS (DoD 2024).

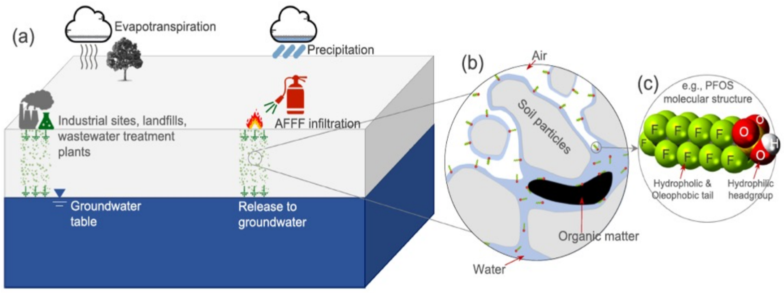

Figure 1. Schematic of a PFAS vadose zone source showing infiltration, recharge to groundwater, hydrophobic sorption, and air-water partitioning (Guo et al. 2020).

The fate and transport behavior of PFAAs partially depends on the chain length, and for PFAA's the head group (sulfonate or carboxylic acid head group), and the electrostatic charge (i.e., anionic, cationic, or zwitterionic). Key PFAS fate and transport processes are summarized in Table 1 and Figure 1. Table 1 also explains how key PFAS fate and transport processes for PFAAs compare to non-PFAS chemicals in groundwater.

Table 1. PFAAs Fate and Transport Processes in the Vadose Zone

Fate and Transport Process	Key Points for PFAAs	Different for PFAS Compared to Non-PFAS Chemicals?
Advection (Movement in Water)	PFAAs can travel in porewater that is moving through the vadose zone. This is why knowing the recharge rate (i.e., the rate that porewater is traveling to groundwater) is important.	**No,** also affects the fate and transport of many common non-PFAS chemicals.
Hydrophobic Sorption	PFAAs can attach to the natural organic carbon on soil particles. This effect is stronger for long-chain PFAS and for sulfonate PFAAs.	
Matrix Diffusion	PFAAs can diffuse into lower-permeability geologic media such as silts, clays, and limestones. While this process has been evaluated for groundwater, it occurs in the vadose zone as well.	
Electrostatic Sorption	Generally, this is an unimportant process for most PFAAs because they are anions (have a negative charge). However, precursors that are cations (positively charged) will tend to sorb strongly to soil particles (typically negatively charged).	**Yes,** different fate and transport processes than many non-PFAS chemicals.
Air-Water Partitioning	PFAAs and to a less extent PFAS precursors can attach to air-water interfaces, such as the thin film of water around soil particles in the vadose zone. This effect is strongest for perfluorooctanesulfonic acid (PFOS), with much less of an effect for shorter-chained PFAAs.	
Degradation	Some PFAS (PFAAs) are not known to degrade or transform in the natural environment.	
In Situ Production	Some PFAS precursors can potentially transform and produce PFAAs in the subsurface via biodegradation and chemical transformation processes. Transformation of precursors via aerobic biodegradation appears to be an important process.	

Assessing PFAS Leaching from Soil to Groundwater (Continued)

Using Mass Discharge to Understand PFAS Soil Leaching

One approach to account for the effect of some of the fate and transport processes in Table 1 is to quantify PFAS mass discharge from the vadose zone to groundwater (Anderson 2021; Newell et al. 2023). Three characteristics about a PFAS vadose zone source are used to calculate mass discharge:

1) The recharge rate at which porewater passes through the vadose zone and makes its way to groundwater (after accounting for near-surface evapotranspiration of porewater)
2) The concentration of PFAS in the porewater moving to groundwater
3) The size (area) of the source (the footprint of PFAS-impacted soils that contribute recharge to groundwater flow)

By multiplying these three metrics together (with appropriate conversions), the annual mass discharge of PFAS from soil to groundwater within suspected source areas can be estimated (in units of grams per year). This PFAS mass discharge from the vadose zone can then be compared to the mass discharge of PFAS flowing horizontally in groundwater. This knowledge can improve CSMs and Feasibility Studies. These three characteristics are further described below.

1) Recharge: Understanding Vadose Zone Moisture Dynamics

During wet weather conditions, porewater in the vadose zone migrates downward towards groundwater, starting out as infiltration (precipitation moving into the subsurface). The porewater flows downward as drainage, and then reaches groundwater as diffuse recharge as shown in Figure 2. Finally, focused recharge occurs at specific locations from perennial or ephemeral streams, lakes, or other water bodies (Healy 2010).

During dry weather conditions, shallow porewater can also travel upward toward the soil surface. This process occurs as evapotranspiration induces a negative pressure gradient, drawing water upward through capillary action, thereby retaining PFAS in near surface soils. The “zero-flux plane” divides where porewater travels upward versus where it travels downward. The zero-flux plane changes over time; it is closer to the surface or disappears during wet weather, and farther from the surface during dry weather.

The vertical upward porewater flow is one reason for the high concentrations of PFAS commonly observed in the shallowest 1–2 meters of soil at PFAS vadose zone sources (Figure 3).

Below the zero-flux plane, the movement of groundwater recharge is steady and less affected by large pulses of infiltration, except during very large rain events. Above the zero-flux plane, vadose zone soils experience dynamic moisture redistribution, which can impact PFAS transport.

Accurate estimation of recharge and characterization of vadose zone moisture dynamics are critical components in the assessment of PFAS leaching. Recharge can be estimated several ways, ranging from simple but less accurate desktop methods to complex field programs. Newell et al. (2023) have developed a tiered system highlighting 15 methods that are appropriate to estimate recharge at PFAS sites.

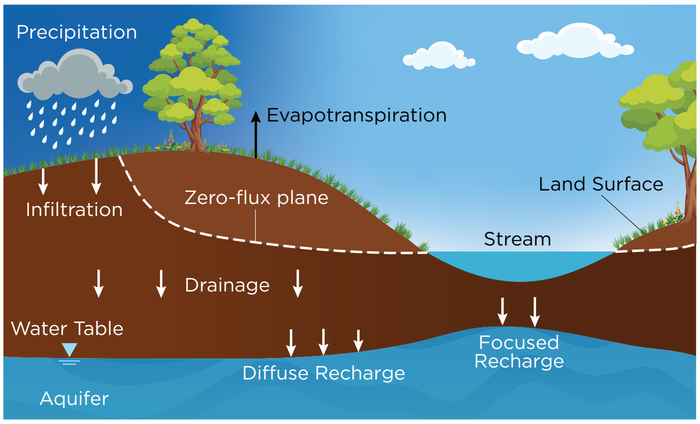

Figure 2. Conceptual vertical cross-section of key recharge processes in the vadose zone (Courtesy of NAVFAC)

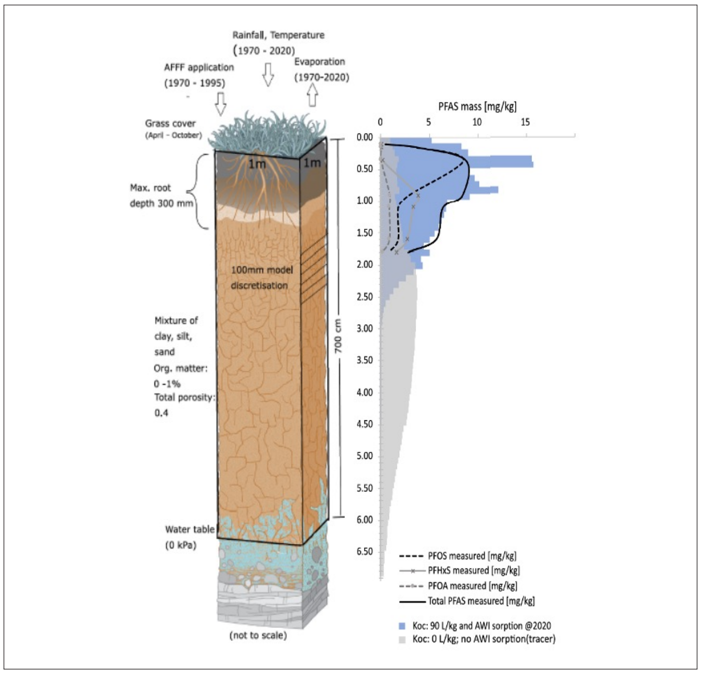

Figure 3. Cross-section of a PFAS vadose zone source illustrating a typical pattern for PFAS mass retention (Wallis et al. 2022)

Assessing PFAS Leaching from Soil to Groundwater (Continued)

2) Concentration: Three Methods to Estimate PFAS Porewater Concentrations

Three methods are available to estimate PFAS porewater concentrations during leaching from soil to groundwater: 1) soil sampling coupled with partitioning calculations, 2) laboratory leaching tests, and 3) field sampling of porewater.

Soil sampling coupled with partitioning calculations involves the collection and analysis of soil samples for PFAS and soil properties, followed by the application of partitioning equations in the form of PFAS leaching models to estimate PFAS porewater concentrations and mass discharge. While relatively straightforward to implement with existing soil data, this approach relies on assumptions about partitioning behavior and may not account for all retention mechanisms. The air-water partitioning that affects long-chained PFAS introduces a layer of complexity that can add uncertainty to the results from PFAS leaching models.

Because of the complexity of multiple retention and transport mechanisms for PFAS in the vadose zone (Anderson 2021) models should be used with caution and an understanding of uncertainties. There has been significant progress in the development of PFAS vadose zone models for practitioners, such as the PFAS Leach Modeling system (Guo et al. 2020, 2022; Environmental Security Technology Certification Program [ESTCP] Project ER23-7850) and a HYDRUS for modeling PFAS (Strategic Environmental Research and Development Program [SERDP] Project ER18-1389; Silva et al. 2020).

Laboratory leaching tests provide a standardized method for estimating potential PFAS releases to groundwater. These tests subject soil samples to controlled leaching conditions and analyze the resulting leachate for PFAS concentrations. While valuable for comparing leaching potential across sites and simulating various environmental conditions, laboratory tests might not accurately represent field conditions and could potentially overestimate leaching due to the disruption of the soil structure. In addition, the effects of PFAS air-water partitioning are not considered (due to the saturated nature of the leaching tests), which could cause PFAS retention to be underestimated. Use of this approach is not recommended at this time. Further research is needed before this approach can be utilized as demonstration studies are ongoing to validate this method across a range of geologic and hydrologic conditions (Rovero et al. 2023).

Field sampling of porewater utilizes suction lysimeters to directly collect porewater samples from the unsaturated zone and provides direct in situ measurements of mobile PFAS concentrations (Figure 4). There has been extensive research for this technology by the DoD (e.g., Schaefer et al. 2022; ESTCP Projects ER20-5088, ER23-7754). Anderson et al. (2022) reported, “Overall, these data validate the use of suction lysimeters for short-term site characterization deployments and emphasize the importance of in situ porewater samples for interrogating PFAS transport within source zones.” However, implementation challenges could arise in certain soil types, particularly in arid areas where it can be difficult to extract sufficient porewater for testing, and results can be subject to spatial variability. Variability can be reduced by focusing on collecting porewater samples below the root zone and, if possible, below the zero-flux plane. To optimize placement of lysimeters in the field, the nature and extent of PFAS within soil at a site should be well understood, including an understanding of the source zone and downgradient areas.

Figure 4. Porewater collection in field-deployed porous cup-suction lysimeters (ESTCP Project ER20-5088)

3) PFAS Source Zone Area: How to Calculate

Maps of PFAS soil concentrations can be used to estimate the area of impacted soil needed to calculate mass discharge (see Figure 5).

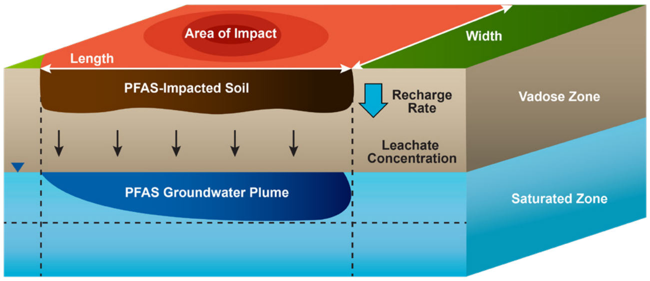

Figure 5. Use of PFAS soil concentrations to estimate the area of impact (Courtesy of NAVFAC)

Assessing PFAS Leaching from Soil to Groundwater (Continued)

Using Sensors to Better Understand Soil Characteristics

Field equipment used for real-time measurement of soil characteristics has greatly improved. Testing is currently underway to better understand soil characteristics that can affect soil-to-groundwater leaching at PFAS sites. Under ESTCP Project ER22-7381, the field equipment listed below have been used for real-time measurement in the vadose zone at two PFAS-impacted field sites:

- Soil moisture probes to continuously measure soil moisture profiles, which can be used to identify wet conditions when it may be easier to sample mobile porewater that is moving toward groundwater.
- Pressure transducers to provide continuous measurements of the water table elevation (at more humid sites they can be used to estimate recharge rates via the water table fluctuation method; Figure 6).
- Tensiometers to collect soil water tension data to understand the impact of precipitation events for use in leaching computer models.
- Temperature sensors distributed vertically to record vertical temperature gradients.
- Oxidation-reduction potential (ORP) sensors to measures how oxidized or reduced the soil is, as well as the availability of electrons in soil, which can be used to assess whether aerobic conditions are present that could allow PFAS precursors to transform to PFAAs.
- Drain gauge lysimeters to collect recharge passing through a column of undisturbed soil (useful for complex sites).
- Weather stations to continuously track precipitation, temperature, wind speed, and solar radiation at a site.
- Experimental capillary fringe sampling to evaluate whether continuous multichannel tubing (CMT) groundwater sampling devices installed around the water table can be used to collect samples that can serve as reliable proxies for porewater entering groundwater, potentially replacing suction lysimeters.

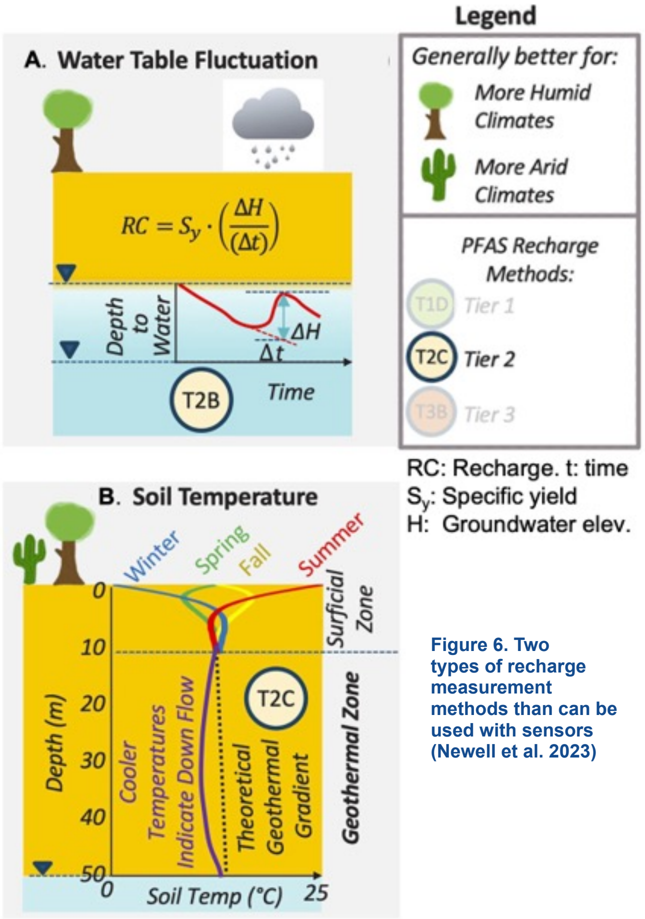

Figure 6. Two types of recharge measurement methods than can be used with sensors (Newell et al. 2023)

Remote data collection can be conducted to allow results to be viewed via internet dashboards. This helps Remedial Project Managers and their consultants to 1) estimate the recharge rate, which is needed to estimate the soil leaching mass discharge; 2) target sampling trips during rain events, for easier collection of porewater samples with suction lysimeters; and 3) provide high-quality vadose zone hydrologic data that then can be used in computer models to predict long-term PFAS leaching behavior. Standard operating procedures (SOPs) for specific sensors are typically provided by the sensor vendor. More general recommendations for installing and operating a wide variety of sensors to help manage PFAS sites will be developed by the completion of ESTCP Project ER-22-7381 (Using Real-Time Sensors to Reduce the Cost of Monitoring at PFAS Vadose Zone Sources).

Disclaimer

This publication is intended to be informational and does not indicate endorsement of any particular product or technology by the DoD. Neither should the contents be construed as reflecting the official policy or position of any of those agencies. Mention of specific product names, vendors, sources of information, trademarks, or manufacturers is for informational purposes only and does not constitute or imply an endorsement, recommendation, or favoring by the DoD. Note that some of the technologies and site management approaches are still being developed and may not have been widely used as of 2024.

Assessing PFAS Leaching from Soil to Groundwater (Continued)

References

Anderson, R. 2021. “The Case for Direct Measures of Soil-to-Groundwater Contaminant Mass Discharge at AFFF-Impacted Sites.” *Environmental Science & Technology* 55(10):6580–6583.

Anderson, R., J. Field, H. Dieffenbach-Carle, O. Elsharnouby, and R. Krebs. 2022. “Assessment of PFAS in Collocated Soil and Porewater Samples at an AFFF-Impacted Source Zone: Field-scale Validation of Suction Lysimeters.” *Chemosphere* 308:136247.

DoD. 2024. Assistant Secretary of Defense for Energy, Installations, and Environment [ASD(EI&E)] PFAS Web Site. https://www.acq.osd.mil/eie/eer/ecc/pfas/index.html. Accessed February 2025.

Guo, B., J. Zeng, and M. Brusseau. 2020. “A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances in the Vadose Zone.” *Water Resources Research* 56(2):e2019WR026667.

Guo, B., J. Zeng, M. Brusseau, and Y. Zhang. 2022. “A Screening Model for Quantifying PFAS Leaching in the Vadose Zone and Mass Discharge to Groundwater.” *Advances in Water Resources* 160:104102.

Healy, R. 2010. *Estimating Groundwater Recharge*. Cambridge: Cambridge University Press.

Newell, C., D. Adamson, P. Kulkarni, B. Nzeribe, J. Connor, J. Popovic, and H. Stroo. 2021. “Monitored Natural Attenuation to Manage PFAS Impacts to Groundwater: Scientific Basis.” *Groundwater Monitoring and Remediation* 41(4): 76–89.

Newell, C., E. Stockwell, J. Alanis, D. Adamson, K. Walker, and R. Anderson. 2023. “Determining Groundwater Recharge for Quantifying PFAS Mass Discharge from Unsaturated Source Zones.” *Vadose Zone Journal* 22(4):e20262.

Rovero, M., D. Cutt, F. Klanchar, E. Gleason, T. Lee, R. Griffiths, J. Costanza, and R. Wilkin. 2023. “Application of Modified Impact-to-Groundwater Tools for PFAS Assessment.” Fall 2023 Interstate Technology & Regulatory Council Conference. November. Available at: https://clu-in.org/conf/tio/FRTRFall23/slides/5Slide_Presentation_for_Wilkin_and_Rovero.pdf.

Schaefer, C., G. Lavorgna, D. Lippincott, D. Nguyen, E. Christie, S. Shea, S. O’Hare, M. Lemes, C. Higgins, and J. Field. 2022. “A Field Study to Assess the Role of Air-Water Interfacial Sorption on PFAS Leaching in an AFFF Source Area.” *Journal of Contaminant Hydrology* 248:104001.

Silva, J. A. K., J. Šimůnek, and J. McCray. 2020. “A Modified HYDRUS Model for Simulating PFAS Transport in the Vadose Zone.” *Water* 12(10)

Wallis, I., J. Hutson, G. Davis, R. Kookana, J. Rayner, and H. Prommer. 2022. “Model-based Identification of Vadose Zone Controls on PFAS Mobility under Semi-Arid Climate Conditions.” *Water Research* 225:119096.

DoD ESTCP and SERDP Projects Related to PFAS Soil Leaching in the Vadose Zone

DoD ESTCP Project Number ER-5041: Development and Demonstration of PFAS-LEACH—A Comprehensive Decision Support Platform for Predicting PFAS Leaching in Source Zones.
https://serdp-estcp.mil/projects/details/7b8e05de-6446-4992-adc2-c7e632972991

DoD ESTCP Project Number ER20-5088: PFAS Leaching at AFFF-Impacted Sites: Insight into Soil-to-Groundwater Ratios.
https://serdp-estcp.mil/projects/details/5497b019-2da3-4590-8f47-b3277c8847f0

DoD ESTCP Project Number ER22-7381: Using Real-Time Remote Sensors to Reduce the Cost of Long-Term Monitoring and Remediation Performance Monitoring at PFAS Vadose Source Zones.
https://serdp-estcp.mil/projects/details/d2ff9af0-237d-4239-a080-94383c8cf7b3

DoD ESTCP Project Number ESTCP Project ER23-7754: Assessing Mass Discharge from PFAS Vadose vs. Saturated Zone vs. Matrix Diffusion Sources to Improve Conceptual Models and DoD RI/FS.
https://serdp-estcp.mil/projects/details/5f8d4355-d416-452a-930a-c0b4a096c17c

DoD ESTCP Project Number ER23-7850: Integrated Toolkit for Measuring and Predicting Vadose Zone Mass Discharge of PFAS.
https://serdp-estcp.mil/projects/details/41a03eac-2c38-4e2b-979d-0a2b429ece0a/integrated-toolkit-for-measuring-and-predicting-vadose-zone-mass-discharge-of-pfas

DoD SERDP Project Number ER18-1389. Baseline Data Acquisition and Numerical Modeling to Evaluate the Fate and Transport of PFAS within the Vadose Zone.
https://serdp-estcp.mil/projects/details/f85916e1-6a39-4ccd-b21e-210c674e1b1d