

# NAVFAC OER2 Understanding PFAS Leaching: Key Processes, Decision Frameworks, and Management Strategies

7 May 2025

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#### • Why Attend?

- Obtain and hear about the latest DOD and DON's policies/guidance, tools, technologies and practices to improve the ERP's efficiency
- Promote innovation and share lessons learned
- FEEDBACK to the ERP Leadership

#### Who Should Attend?

- ERP Community Members: RPMs, RTMs, Contractors, and other remediation practitioners who support and execute the ERP
- Voluntary participation

#### Schedule and Registration:

- Offered quarterly
- Registration link for each topic (announced via ER T2 email)

#### Topics and Presenters:

- ERP community members to submit topics (non-marketing and DON ERP-relevant) to s (Nate Delong at <u>nathan.a.delong2.civ@us.navy.mil</u> or <u>EXWC\_T2@us.navy.mil</u>)
- Selected topic will be assigned Champion to work with presenter









## Charles Schaefer CDM Smith

### Charles Newell GSI Environmental Inc.

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- **1. Introduction: Lets Take a Quick Look at Three Graphics**
- 2. How Does PFAS Leaching Work: Key Processes
- 3. One Key Decision-Making Framework: PFAS Mass Discharge
- 4. How to Characterize PFAS Leaching Sources
- **5. PFAS Leaching Computer Models**
- 6. Key Decisions for Managing PFAS Leaching
- 7. Wrap Up
- 8. Q&A

**Three Graphics** 

## **PFAS Classes and Nomenclature**





# What Is, What Can We Do About PFAS Leaching to Groundwater?





Guo et al., 2023

### Another Visualization of PFAS Leaching to Groundwater



(a) The fire-training area (FTA)



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Zeng & Guo (2023)

## Key Questions That Need to be Answered



- How does PFAS go from soil down to groundwater?
- What parameters do I need to measure to understand PFAS leaching?
- How do I analyze the leaching data that I collect?
- Is PFAS leaching at my site causing a groundwater problem?
- If it is causing a problem, how do we forecast its future behavior?





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# **Key Decisions for Managing PFAS Leaching**



Key Decision	Details
Mass discharge (M <sub>d</sub> ) (g/yr)?	(Porewater conc) x (recharge) x (area)
How to determine PFAS porewater concentrations & leaching?	<ul><li>How to install/sample lysimeters?</li><li>Other measurements needed?</li></ul>
Recharge rate (inches/yr)?	Multiple methods to estimate or measure
Dilution Factor (-)	Is unsaturated zone leaching impacting the dissolved groundwater plume?
Construct Model of Site?	Is a numerical model always needed?
Key Models?	What models are available?

## **PFAS Leaching Processes**

### And Now for Something Completely Different: PFAS Air/Water Partitioning, Electrostatic Attraction



#### **Air/Water Partitioning**

- Long-chained PFAS have more accumulation at the air-water interface than short-chained PFAS than shortchained PFAS.
- It depends on the air/water interfacial area which can be modeled.
- This area depends on soil moisture, type of soil



#### **Electrostatic Partitioning**

PFAAs are anions (-) and don't stick to soils
Examples: PFOS, PFOA, PFHxS etc.
Some precursors are cations (+) and will stick
Example: TAmPr-N-MeFASA



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## **PFAS Retention at Air-Water Interfaces**



# **Measuring PFAS Mass Discharge**



### Why is this important?

- "Soil-to-groundwater contaminant mass discharge (M<sub>d</sub>) is the authoritative metric defining source strength at sites impacted by per- and polyfluoroalkyl substances (PFAS) and is increasingly being reported."
- Mass Discharge integrates three things:
  - 1. Concentration
  - 2. Amount of water flowing through the source
  - 3. The size of the source





## Calculating Mass Discharge (grams per year) From Vadose Zone PFAS Sources



#### Recharge x PFAS Leachate Concentration = PFAS Mass Flux

#### PFAS Mass Flux x Area = PFAS Mass Discharge (mass/time)



# The Concentration Side:Option 1Take a Soil Sample andApply a Soil:Water Partitioning Equation to Get Porewater Conc.



#### Key idea: Convert ng/Kg data to ng/L data for vadose zone. But we have issues:

- **Simplistic Assumptions:** Linear isotherm partitioning assumes instantaneous, reversible sorption based solely on hydrophobic interactions, which does not capture the complex behavior of PFAS.
- Difficulty Account for Air/Water Partitioning : Standard Koc and foc values do not reflect this process.
- **Conclusion:** Despite advances in modeling, the uncertainty remains high, so relying solely on these models for PFAS site management decisions may not be best course of action?



ITRC, 2023

$$R_{d}^{comp} = \left(1 + K_{d*}\frac{\rho_{b}}{\theta_{w}} + H\frac{\theta_{a}}{\theta_{w}} + K_{n}\frac{\theta_{n}}{\theta_{w}} + K_{aw*}\frac{a_{aw}}{\theta_{w}} + K_{nw*}\frac{a_{nw}}{\theta_{w}} + K_{an*}\frac{a_{an}}{\theta_{w}} + K_{c*}X_{c}\right)$$
(2)

where  $a_{an}$  is the specific air-NAPL interfacial area  $(L^2/L^3)$ ,  $a_{aw}$  is the specific air-water interfacial area  $(L^2/L^3)$ ,  $a_{nw}$  is the specific NAPL-water interfacial area  $(L^2/L^3)$ ,  $K_{an^*}$  is the nonlinear air-NAPL interfacial adsorption coefficient  $(L^3/L^2)$ ,  $K_{aw^*}$  is the nonlinear air-water interfacial adsorption coefficient  $(L^3/L^2)$ ,  $K_{c^*}$  is the nonlinear distribution coefficient for sorption by colloids  $(L^3/M)$ ,  $K_{d^*}$  is the nonlinear solid-phase adsorption coefficient  $(L^3/M)$ ,  $K_n$  is the NAPL-water partition coefficient (-),  $K_{nw^*}$  is the nonlinear NAPL-water interfacial adsorption coefficient  $(L^3/M)$ ,  $K_n$  is the NAPL-water partition coefficient  $(L^3/L^2)$ ,  $X_c$  is the concentration of colloidal material in porewater  $(M/L^3)$  and  $\theta_n$  is volumetric NAPL content  $(L^3/L^3)$ .

Brusseau and Guo, 2023

# The Concentration Side: Developing Unsaturated Zone Soil Clean-Up Criteria







## The Concentration Side: Complexities and Challenges with PFAS Leaching in Unsaturated Soils





Assumes equilibrium K<sub>d</sub> model for soil

### Learning from PFAS Leaching Lab Studies: Air Water Partitioning is A Big Deal for Leaching





Field Slurry

# PFOS & 8:2 FTS are greater in the slurry than in porewater



Leaching tests under saturated conditions may not be appropriate for estimating leaching and ultimately developing appropriate soil clean-up criteria

## **PFAS Desorption from Soil**





A simple K<sub>d</sub> model is typically not appropriate for developing soil clean-up criteria, as much of the PFAS mass in the soil may not readily desorb



#### **Desorption Isotherm**





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## Why air-water interfacial sorption and soilwater desorption are important



			PFOS		Revised
		Parameter	Standard Model	Revised Model	Desorption Model
		Dilution Factor (DF)	20	20	
		Attenuation Factor (AF)	1	1	
	Contents lists available at ScienceDirect Journal of Hazardous Materials Letters	Dilution-Attenuation Factor (DAF)	20	20	
ELSEVIER	journal homepage: www.sciencedirect.com/journal/journal-of-hazardous-materials-letters	Bulk density (ρ <sub>b</sub> , g/ cm <sup>3</sup> )	1.5	1.5	
		Water content ( $\theta_w$ , -)	0.2	0.2	
Revising the	e EPA dilution-attenuation soil screening model for PFAS	Air content ( $\theta_a$ , -)	0.2	0.2	
Mark L. Brusseau <sup>a, b, *</sup> , Bo Guo <sup>b</sup>		Porosity (n, -)	0.4	0.4	
	Sorption coefficient (K <sub>d</sub> , cm <sup>3</sup> /g) <sup>a</sup>	2	2		
	Henry's Law constant (H, -)	0	0		
	Air-water interfacial adsorption coefficient (K <sub>aw</sub> , cm) <sup>b</sup>	NA	0.12		
	Air-water interfacial area (a <sub>aw</sub> , cm <sup>-1</sup> ) <sup>c</sup>	NA	446		
	Distribution term (R <sub>d</sub> , -)	16	283.6		
	Target groundwater concentration (C <sub>gw</sub> ,	0.1	0.1		
		Soil Screening Level	4.3	75.6	290

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(SSL, µg/kg)

## The Concentration Side: <u>Option 2</u>: Can we use Synthetic Precipitation Leaching Test (SPLP) to Evaluate Leaching?



#### **Research perspective 1:**

- Potentially, but needs validation at additional sites
  - With few modifications, SPLP provides an excellent framework for impactto-groundwater evaluation at PFAS-contaminated sites
  - Application provides flexibility to address the needs of particular projects
  - Validation at additional sites is ongoing to determine whether results hold across varied geologic and hydrologic conditions, different PFAS compositions

#### Rovero et all, 2023 Battelle



DOE, 2016

#### **Research perspective 2:**

- But Potential Unrealistic Testing Conditions: The SPLP employs liquid-tosolid ratios that exceeding natural pore volumes, eliminating key retention mechanisms.
- *Disruption of Soil Integrity*: Aggressive agitation disperses water-stable aggregates and colloids, artificially boosting contaminant desorption. Anderson et al., 2022

#### **Research perspective 3:**

- DoD SERDP/ESTCP is harmonizing PFAS-leach testing by applying SPLP and EPA LEAF (Leaching Environmental Assessment Framework) Methods 1313-1316 to soils, concrete, and asphalt
- Key projects using these protocols: ER20-1126, ER20-5088, ER23-3761 (plus related ER23-3835 and ER-5041)

#### The Concentration Side Option 3: A Review of Using Porous Cup

#### Suction Lysimeters (PCSLs) for PFAS Leaching (Constanza et al., 2025)



#### **Application of Suction Lysimeters**

- Widely used for evaluating the mobility of PFAS from vadose zone soils to groundwater.
- Collect porewater samples by applying vacuum, suitable for fine to medium sandy soils.

#### Key Advantages

- Provides direct measurements of porewater concentrations.
- Easier and less intrusive installation compared to drainage lysimeters.

#### **Preliminary Limitations**

- May not be representative of all PFAS due to interactions with lysimeter materials, air-water interfaces, and vacuum application.
- Spatial and temporal variability requires numerous lysimeters for accurate site representation.



# The Concentration Side: Porous Cup Suction Lysimeters (PCSLs)





- Pre-rinsing (PFAS-free water and methanol)
- Limit annular space (6.4 cm borehole / 4.8 cm diameter PCSL)
- *PFOS* sorption:
  - Sorption tests to silica flour showed negligible uptake
  - Negligible PFOS sorption
- Bromide tracer added to the silica flour slurry
- First collected round of porewater samples not used for PFAS testing

# The Concentration Side: Porewater Extraction from Collected Soil Cores





- 0.95 cm dia. "microlysimeter"
- Equilibrated ≥3 days
- 55 cb applied vacuum

#### Wetted and Re-Packed Soil



 Validity of effective equilibrium assumptions? **Intact Soil Core** 





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### **The Concentration Side:** PCSL Porewater Sampling Results Compared to Effectively Equilibrated Bench-Scale Testing





# **The Concentration Side:** But Agreement Between Field PCSLs vs. Porewater Samples from Soil Cores is Not Always Observed





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## **The Concentration Side:** Impacts of Changing Moisture Content (Soil Texture at JBCA)



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## Calculating Mass Discharge (grams per year) From Vadose Zone PFAS Sources



#### Recharge x PFAS Leachate Concentration = PFAS Mass Flux

#### PFAS Mass Flux x Area = PFAS Mass Discharge (mass/time)



#### The Hydrology Side: What is Recharge? How Do I Measure it at My Site?





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# The Hydrology Side: Tiered Approach To PFAS Recharge



Tier	Objective	Target PFAS Sites	Need Field Data?	Level of Effort
<b>Tier 1</b> (4 types)	Simple source zone recharge estimate	Smaller, low risk	No	Little or no field time. A few hours for analysis.
<b>Tier 2</b> (6 types)	Moderate level of effort	Moderate risk	Limited	A few days in the field and a few days for analysis.
<b>Tier 3</b> (5 types)	Detailed recharge estimates	Most complex, important sites (e.g., exposure, litigation)	Extensive	More extensive field and analysis time than Tier 2 methods.

Newell et al., 2022 Search: PFAS vadose recharge Open access paper.

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The Hydrology Side: Example of Tier 1 Recharge Method Groundwater Recharge Map by Reitz et al. (2017)



#### The Hydrology Side: Tier 2 and Tier 3 **Recharge Methods For PFAS Sites**



Newell et al., 2022

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## Mass Discharge (M<sub>d</sub>) Estimates From Five Sites



Site	PFAS	Vertical M <sub>d</sub> Unsaturated Zone (g/year)	Horizontal M <sub>d</sub> Saturated Zone (g/year)	Unsat ÷ Sat Zone (%)
JBCA, SC	Total PFAS	1,300	7,200	18%
FE Warren AFB, Wyoming	Total PFAS	64	4800	1%
Arnold AFB, Tennessee	Total PFAS	22	pending	-
South Dakota Site (Anderson et al,. 2022 (Carey et al,. 2022)	PFOA	17	270	6%
Camp Grayling, MI (Quinnan et al., 2021)	PFOS + PFOA	0.4	22	2%

Leaching Investigation: Obtaining the Right Information



- Geologic Investigation
  - Grain size
  - OC
- Example Soil Investigation
  - Homogenized 1 foot intervals through first 5 feet
  - Larger intervals beyond 5 foot if needed
  - Must consider geology
  - Initial work might focus on trying to understand higher concentrations at sites...
  - Then additional borings at more interrogative intervals can be a separate effort in just primary soil source zones.





#### Lysimeter Installation

- Guided by PFAS soil data
  - Soil locations >> lysimeter locations
  - PFAS concentration
  - PFAS composition
- Guided by geology
- Collect soil sample within interval of lysimeter porous cup
- Placement 1 to 2 ft above seasonal high water table, but:
  - Consider PFAS soil profile
  - Consider soil moisture/recharge
  - Geology
  - Surface/root impacts vs. groundwater
  - Consider multi-depth lysimeters?
- Background? (compare mass discharges)





#### Lysimeter Sampling

- Corresponding soil moisture content
- Monitor water table elevation
- Example Sampling Program:
  - 4 rounds of sampling (after purge round) to assess temporal and site-specific climatic ranges of leaching rates.
- Coordinate with rainfall events (esp. in arid climates)
  - Consider low vs high infiltration events
- Minimum sample volume?





- Desorption behavior (kinetic and isotherm)
  - Batch soil slurry testing
- K<sub>i</sub>
  - Empirical correlations
  - PFAS concentrations
  - Porewater ionic strength
- Air-water interfacial area
  - Grain size and moisture content
- Soil moisture content
- Recharge estimate
- Porewater extractions (e.g., microlysimeters)
  - Can be used at depth when soil is too dry for lysimeters
  - Verification of field data

Enables estimate of PFAS porewater concentrations



## Predicting PFOS Porewater Concentrations With Mass Balance Model

- Desorption isotherms
- K<sub>i</sub> estimates
- a<sub>a-w</sub> estimates





# PFAS background assessments will be a component of remedial decision-making at DoD facilities

#### MCL: maximum contaminant level



ASSISTANT SECRETARY OF DEFENSE 3400 DEFENSE PENTAGON WASHINGTON, DC 20301 3400

September 3, 2024

MEMORANDUM FOR ASSISTANT SECRETARY OF THE ARMY (INSTALLATIONS, ENERGY AND ENVIRONMENT) ASSISTANT SECRETARY OF THE NAVY (ENERGY, INSTALLATIONS AND ENVIRONMENT) ASSISTANT SECRETARY OF THE AIR FORCE (INSTALLATIONS, ENVIRONMENT AND ENERGY) DIRECTOR, NATIONAL GUARD BURKAU (JOINT STAFF, J3/4/7) DIRECTOR, DEFENSE LOGISTICS AGENCY (INSTALLATION MANAGEMENT)

SUBJECT: Prioritization of Department of Defense Cleanup Actions to Implement the Federal Drinking Water Standards for Per- and Polyfluoroalkyl Substances Under the Defense Environmental Restoration Program

On April 26, 2024, the Environmental Protection Agency (EPA) published a final National Primacy Drinking Water Regulation (NPDWR) sciabilishing nationsvide drinking water standards for certain per- and polyflacorably l substances (PFAS) under the Safe Drinking Water Act (SDWA). This rule applies to public drinking water systems. DoD remains committed to fulfilling our PFAS-related cleanup responsibilities and will take necessary actions to incorporate SDWA levels into our cleanup program. In accordance with the Comprehensive Environmental Response, Compensation, and Lishily Act (CBRCLA) and the National Contingency Plan (40 C.F.R. Part 300). The CERCLA process can take time to complete, but also provides a consistent, science-based approach across the Nation for cleanup and includes federal and state environmental regulator review and public participation. This memorandum describes DoD's plans to incorporate the drinking water rule into DO's ongoing PFAS cleanups and prioritize actions to address private drinking water wells with the highest levels of PFAS from DoD activitites.

EPA's drinking water rule includes enforceable maximum contaminant levels<sup>1</sup> (MCL) for five PFA's, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluoroomanoic acid (PFAA), hexafluoropropylene oxide dimer acid (HFO-DA, commonly known as GenX), and perfluorohexane sulfonic acid (PFIAS). It also includes a Hazard Index (HI) MCL, for aniture of at least two or more of PFIAS, PFAA, perfluorobatune sulfonic acid (PFBAS), and HPO-DA (GenX) chemicals. The rule provides five years for regulated public water systems to comply with hexe MCLs as specified below.

- Individual MCLs in parts per trillion (ppt):
  - PFOS = 4 ppt
     PFOA = 4 ppt
  - PFOA = 4 p

<sup>1</sup> SDWA defines a "maximum contaminant level" or MCL to be "the maximum permissible level of a contaminant in water which is delivered to any user of a public water system." 42 U.S.C. § 300f(3). September 3, 2024, memo on prioritization of DoD Cleanup Actions to implement PFAS MCLs

#### Long-Term Remedial Actions

CERCLA requires a site-specific risk assessment during the remedial investigation to establish risk-based cleanup levels. This includes considerations of "background" levels of chemicals present at a site, which can be highly variable across the country. Throughout the CERCLA process DoD coordinates with both EPA and state regulators and EPA and DoD jointly select remedies at National Priorities List sites. Accordingly, DoD will work with EPA and state regulators, as appropriate, to evaluate background levels of PFAS on a site-specific basis to determine a final cleanup level.

For remedial actions, the DoD Components will address drinking water down to the MCLs or background, in accordance with CERCLA, once the DoD Component has established levels of PFAS are below the MCLs, then DoD Components will take remedial actions to address PFAS that will meet the MCLs as the final cleanup levels.<sup>6</sup> If background levels of PFAS are found above an MCL at a site, DoD Components will work collaboratively with regulators and transparently with the public to determine the appropriate remedial goals (i.e., final cleanup levels) at that site.

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## **Background PFAS – Assessment Objectives**





#### Groundwater



releases

# **PFAS Leaching Models**

# **Simplified Models for Screening**





- Spreadsheet-based
- Average recharge rate (steady flow)
- Desorption, K<sub>i</sub>, A<sub>aw</sub> estimated based on lab data and empirical models
- A<sub>aw</sub> constant
- Estimate of mass discharge and source longevity

## Screening Model: Long-Term PFAS Rebound in Porewater





predicted rebound level [based on measured mass removal and desorption isotherm]

Bench-scale testing informs on field-scale behavior

## ESTCP's PFAS Leach Platform (Guo et al.)



## Detailed PFAS Modeling of Vadose Zone Zeng & Guo (2023): Heterogeneities Matter



#### **Simulated PFOS**



# Modeling porewater concentrations of PFAS within the upper soil profile





# Wrap Up

# **Key Decisions for Managing PFAS Leaching**



Key Decision	Details
Mass discharge (M <sub>d</sub> ) (g/yr)?	(Porewater conc) x (recharge) x (area)
How to determine PFAS porewater concentrations & leaching?	<ul><li>How to install/sample lysimeters?</li><li>Other measurements needed?</li></ul>
Recharge rate (inches/yr)?	Desktop methods: T1-A, T1-B, T1-C. Field methods? T2-B (humid), T2-E (arid)
Dilution Factor (-)	Compare vertical leaching flow to horizontal groundwater flow
Construct Model of Site?	Yes if you want to forecast $M_d$ vs. time No if you just want to know current $M_d$
Key Models?	Screening Model, ESTCP's PFAS- LEACH, REMFluor-MD





### **Questions? Email to** EXWC.T2@us.navy.mil

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- Thank you for participating!

SPARE SLIDES

## The Concentration Side: Pros and Cons of

**Different Porewater Conc. Methods (Navarro et al., 2024)** 



Method	Pros	Cons
Batch Leaching Methods	Quick, simple, cost-effective; conservative estimates	May not represent realistic field conditions; disrupts soil structure and neglects air-water interfaces
Column Methods	Realistic conditions; simulates leaching kinetics; assesses transport processes	Complex, time-consuming, costly; typically conducted under saturated conditions
Static Leaching	Simpler than column; moderate realism; useful for point-in-time assessments	Less rigorous; may underestimate leaching in dynamic conditions
Rainfall Simulation and Ponding Experiments	Incorporates wet/dry cycles and runoff; realistic for surface leaching	Large-scale setup; requires substantial resources
Lysimeters (Pan and Suction)	Direct in-situ measurement; captures real field conditions; detailed temporal data	High cost; complex installation; potential variability

#### **Overall Recommendations**

•Align method choice with assessment objectives and scenarios.

•Combine multiple methods for comprehensive evaluation.

#### METHODS TO ESTIMATE METRIC 1 (M<sub>d-vad</sub>) – PFAS MASS DISCHARGE FROM VADOSE ZONE





Images from CDM Smith-led SERDP Project ER18-204 "Insights into the Long-Term Mass Discharge & Transformation of AFFF in the Unsaturated Zone" field site. CDM Smith's porous cup suction lysimeter (PCSL) is shown to the right.

# Two ESTCP PFAS Leaching Demonstration Sites

## Matric Potential (Suction Required to Remove Water from Soil) Over Time and Depth (Arid Site)



#### Key Point: Deep Matric Potential Does Not Change Much Over Time





## Performance Assessment: Spatial Profiles of Water Content (3 ft bgs)



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## Performance Assessment: TEROS 32 Sensors at Arnold AFB



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FE Warren – 31 July 2024: Total PFAS (ng/L)



## Arnold – 13-14 August 2024: Total PFAS (ng/L)



## **PFAS Mass Discharge: JBCA**

#### Is PFAS leaching from the unsaturated zone sustaining the PFAS groundwater plume?



