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Updated Best Practices for PFAS Soil-to-Groundwater Leaching Evaluations at USAF Installations

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Acknowledgements

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Agenda

- Objectives
- Roadmap of Updated Approach
- Site-Specific Screening, Recharge & Mass Discharge Evaluations
- Guidelines for Lysimeter Investigations
- Guidelines for Data Modeling
- Data Collection Summary
- Soil Screening Level (SSL) Selection
- Data Gaps and Continued Research
- Next Steps

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Objectives

- Updated guidance is needed to incorporate best practices that minimize uncertainties in data collection and interpretation.
- Should consider range of site conditions based on soil types and climate, and a more standardized set of best practices and tools.
- The new tiered approach provides an updated framework for determining SSLs that will address an immediate need for technical direction in scoping and conducting the next phase of PFAS RIs.

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Roadmap of the Updated Approach

- Step 1 – Site-Specific Screening, Recharge & Mass Discharge Evaluations
  - 1a – If amenable to lysimeters and porewater available, estimate recharge, conduct mass discharge evaluation
  - 1b – If amenable to lysimeter and porewater not available, install minimum # of lysimeters, estimate recharge, conduct mass discharge evaluation
- Step 2 – Pre-Installation Monitoring, Lysimeter Installation & Sampling
- Step 3 – Site-Specific DAF Estimation
- Step 4 – SSL Determination
  - <u>Option 1</u> – Linear Regression Using Paired Soil and Lysimeter Porewater Sampling Results
  - <u>Option 2</u> – PFAS-LEACH Modeling Tool
  - <u>Option 3</u> – Hybrid Approach

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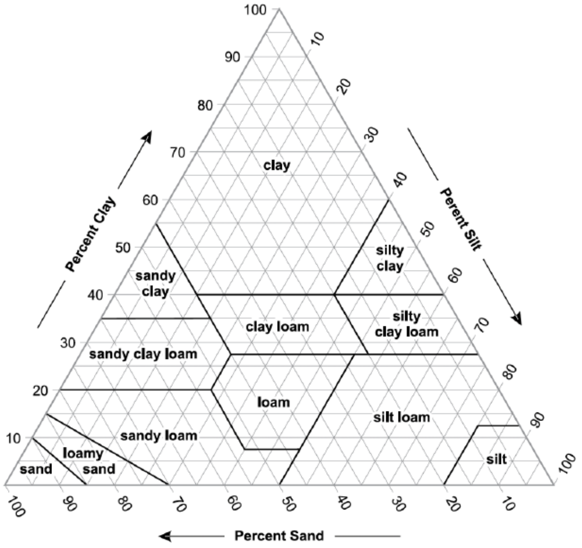
Site-Specific Screening

- Site setting and climate
  - Evaluate viability for lysimeter investigations based on climate category and depth to groundwater
  - Support recharge and mass discharge evaluations
- Geology and soil type
  - Focus on dominant soil type
  - Supports estimates of K_{sat} and van Genuchten parameters (pedotransfer functions, Web Soil Survey)
  - Supports lysimeter data evaluation and modeling phases
- Groundwater table
  - Significant influence on viability of lysimeter investigations



12 Basic Soil Classes (USDA)

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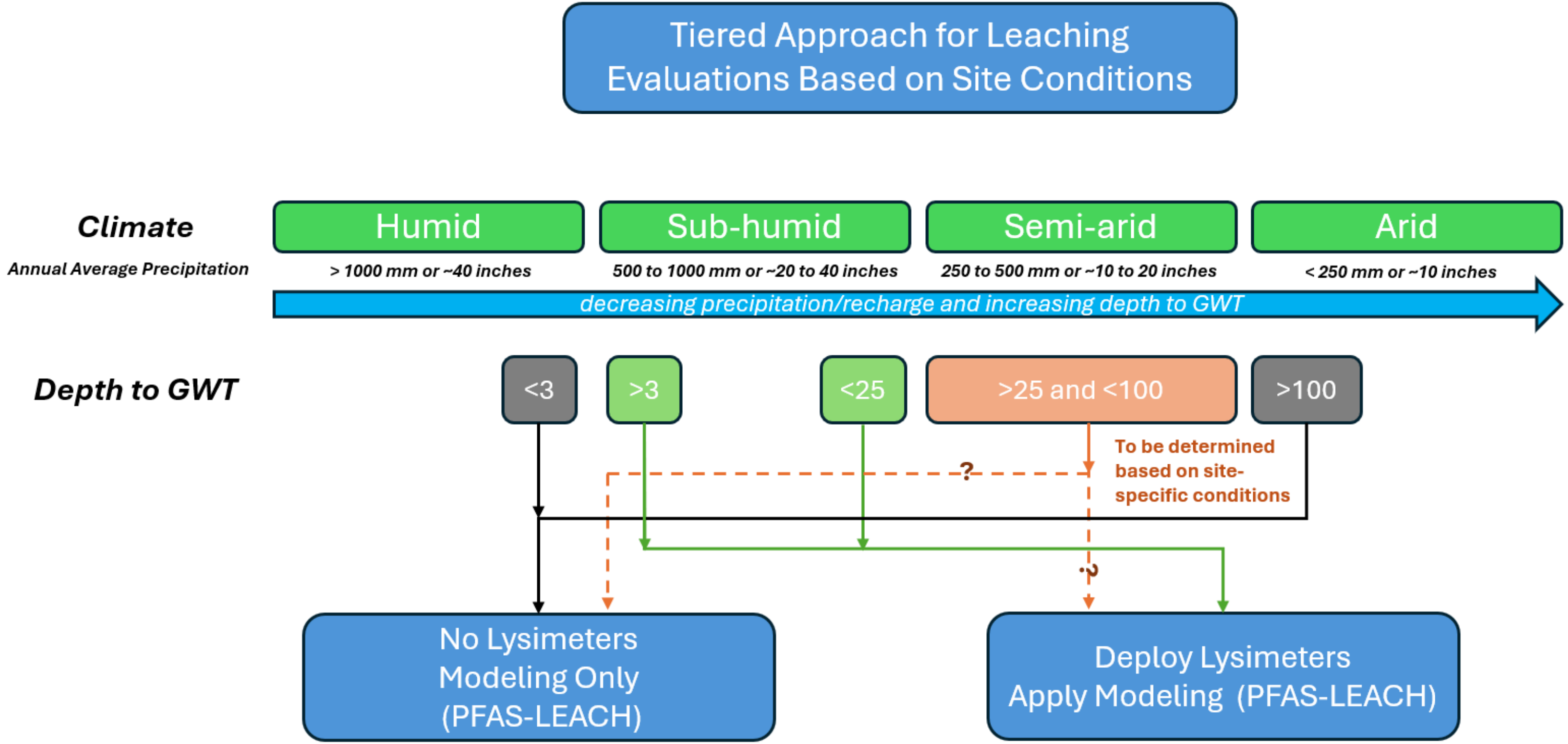
Site-Specific Screening (cont'd)



GWT = groundwater table

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Recharge Evaluation

- Recharge is a significant component of downward PFAS mass flux from the vadose zone to groundwater
- 40 methods summarized in Newell et al. (2023)
  - Tier 1 – Low complexity, low cost
  - Tier 2 – Advanced tools, moderate cost
  - Tier 3 – Complex assessments, high cost

Determining groundwater recharge for quantifying PFAS mass discharge from unsaturated source zones

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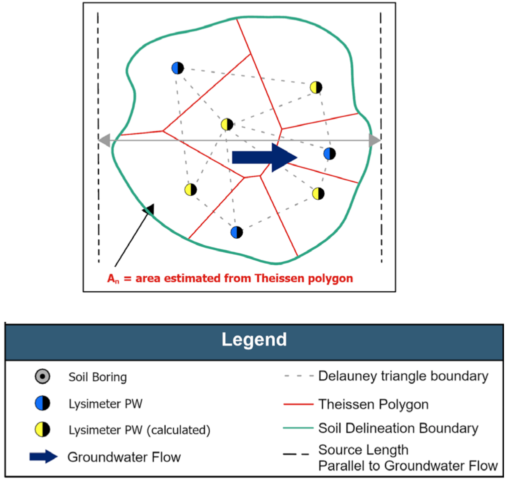
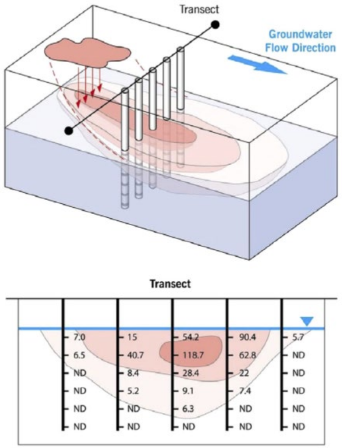
Mass Discharge

- Required as part of 7-Step DQO process for UFP-QAPP Worksheet #11
- Vadose zone mass discharge
  - Annual precipitation, infiltration, porewater concentrations from source area, soil delineation boundary
  - Thiessen polygon or PFAS-LEACH data modeling approaches
- Groundwater mass discharge
  - Groundwater concentrations, hydraulic conductivity (K), horizontal hydraulic gradient (*i*), impacted cross-sectional area (A)

Vadose Zone Mass Discharge



Groundwater Mass Discharge



Source: Newell et al. (2023)

DQO = data quality objective

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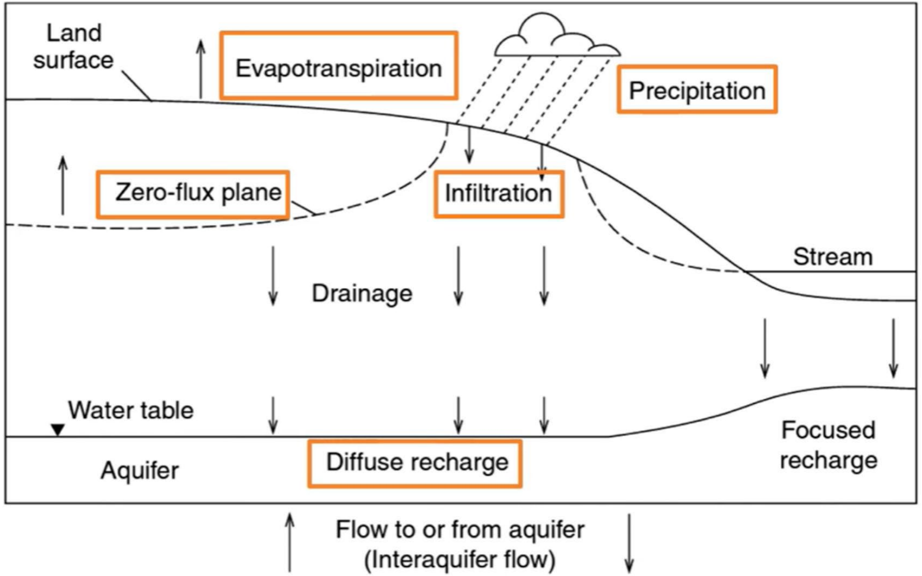
Guidelines for Lysimeter Investigations

- Planning and design
- Capillary fringe estimation
- Pre-installation monitoring
  - Soil sampling and analysis
  - Groundwater table monitoring
  - Paired tensiometers
  - Soil moisture probe
- Lysimeter installation and sampling
  - Co-located soil and porewater
  - Minimum of 10 lysimeters per installation
- Additional lysimeter siting

Key Recharge Processes (Healy, 2010)



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Guidelines for Lysimeter Investigations, cont’d

- Focused additional data evaluation based on lessons learned

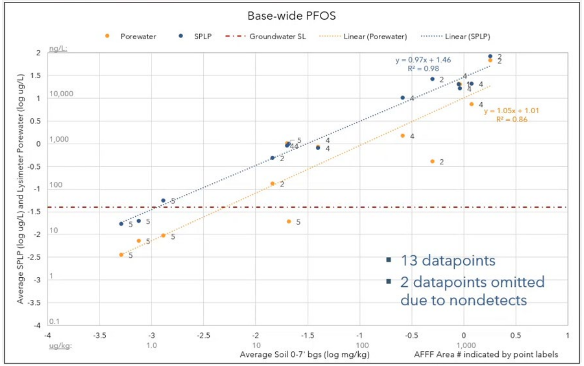
Correction of porewater sampling results using bromide tracer

$$CF = \frac{Br_{batch\ conc}}{Br_{batch\ conc} - Br_{PW\ conc}}$$

$$C_{PFAScorrected} = C_{PFASmeasured} \times CF$$

Statistical modeling with linear regression

- Exploratory data analysis (EDA)
- Evaluation of linear regression models and assumptions
- Sample size and high-leverage points



$$[\log C] = \frac{[\log C_W] - b}{m}$$

$$C_w = MCL\ (or\ TSL\ or\ RSL) * DAF$$

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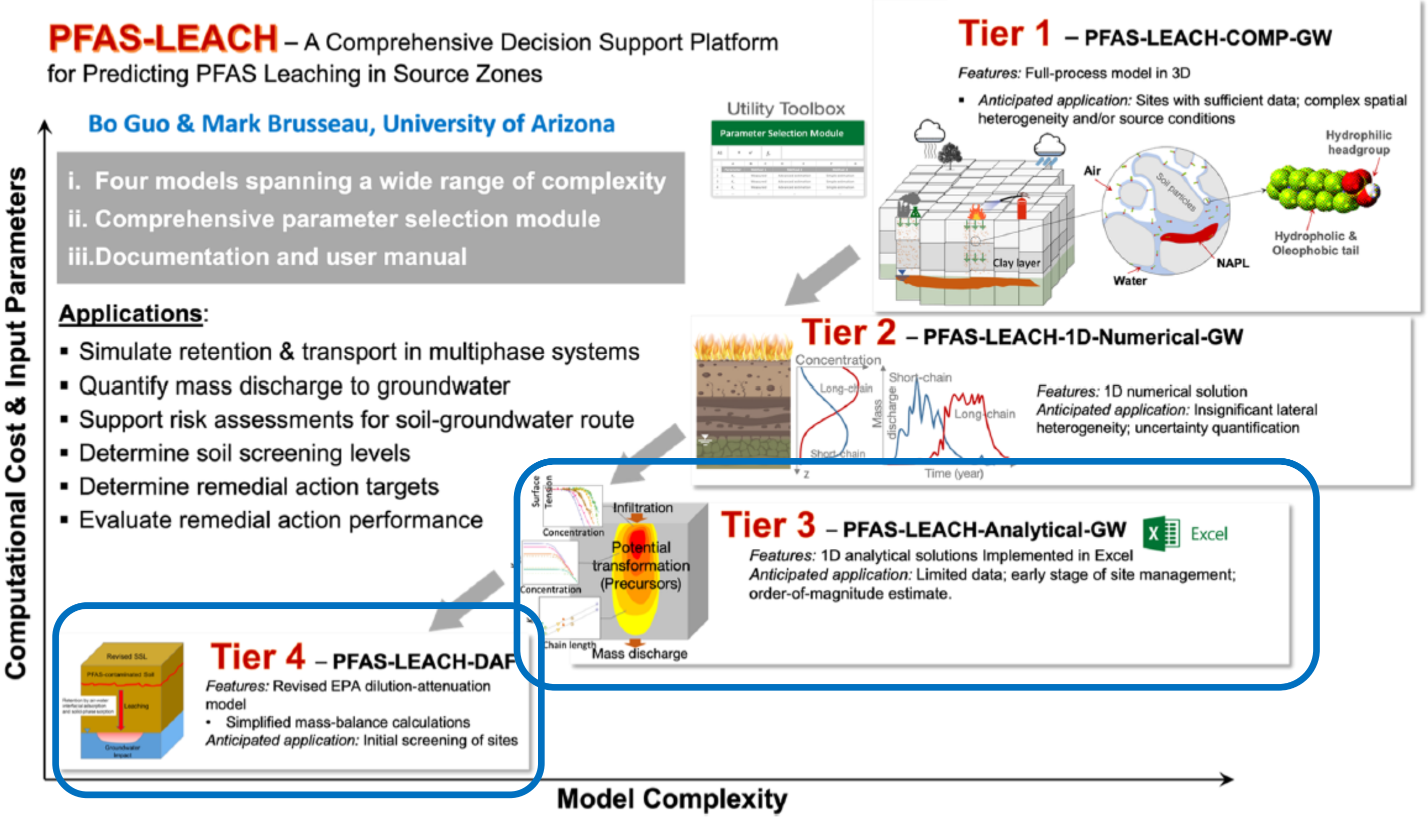
Guidelines for Data Modeling



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Guidelines for Data Modeling, cont'd

① Soil Properties and Site Conditions

Set Default Values

Parameter	Symbol	Unit	Parameter Values
Depth to groundwater*	Z_w	cm	300
Contaminated site area (or unit area)	A	m^2	2500
Temperature	T	°C	20.00
Net infiltration*	I_f	cm/yr	25.92
Soil bulk density*	ρ_b	g/cm^3	1.53
Saturated hydraulic conductivity	K_s	cm/day	44.87
Residual water content	θ_r	cm^3/cm^3	0.064
Saturated water content*	θ_s	cm^3/cm^3	0.370
Median grain size	d_{50}	cm	0.005
Organic carbon fraction	f_{oc}	%	0.41
van Genuchten parameter	α	cm^{-1}	0.018
van Genuchten parameter	n	(-)	1.51
Longitudinal dispersivity*	α_L	cm	13.42
Water content*	θ	cm^3/cm^3	0.219
Air–water interfacial area scaling factor	SF	(-)	4.7
Air–water interfacial area*	A_{aw}	cm^2/cm^3	753.9

Soil Type: User defined

Estimate α_L | Estimate θ | Estimate SF | Estimate A_{aw}

② PFAS Properties

Parameter	Symbol	Unit	Parameter Values
Surface tension parameter	a	mg/L	62.1
Surface tension parameter	b	(-)	0.19
Surface tension parameter	σ_0	dyn/cm	71.0
Molar mass*	M	g/mol	414.07
Molecular diffusion coefficient*	D_0	cm^2/s	4.90E-06
Molar volume	V_m	cm^3/mol	237.20
Organic carbon-water partition coefficient	K_{oc}	cm^3/g	136.2
Solid–phase adsorption coefficient*	K_d	cm^3/g	0.56
Air–water interfacial adsorption coefficient*	K_{aw}	cm^3/cm^2	3.69E-03

NOTE: Fs and α_s are only needed for using the advanced solver.

Parameter	Symbol	Unit	Parameter Values
Instantaneous solid-phase sorption fraction*	F_s	(-)	0.50
Kinetic solid-phase sorption rate constant*	α_s	1/hour	1.00E-04

PFAS Type: PFNA

Estimate K_d | Estimate K_{aw}

③ Groundwater Dilution

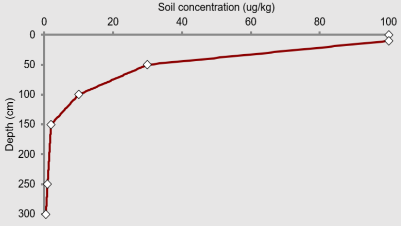
Parameter	Symbol	Unit	Parameter Values
Groundwater darcy flux	U_{gw}	m/yr	365.00
Lateral site width	L	m	3.00
Saturated zone thickness	b_{sat}	m	0.35
Vertical dispersivity	α_v	m	0.02
Mixing zone thickness	δ_{gw}	m	0.32
Dilution Factor*	DF	(-)	151.0

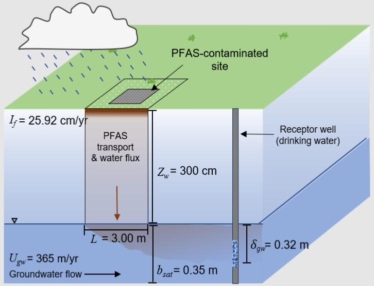
Estimate α_v, δ_{gw}, DF

④ Initial PFAS Soil Conc. & Lysimeter Porewater Conc.

Interpolation Method: Piecewise Linear Interpolation

Re-apply interpolation whenever datapoints are updated.





Depth (cm bgs)	PFAS soil conc. (ug/kg)	Depth (cm bgs)	PFAS soil conc. (ug/kg)
0	100		
10	100		
50	30		
100	10		
150	2		
250	1		
300	0.5		

Lysimeter Data
(for estimating A_{aw} scaling factor in Box ①)

Estimate Local SF

Depth (cm bgs)	Porewater conc. (ug/L)	Water content (cm^3/cm^3)	A_{aw} scaling factor (-)
20	50	0.2	1.83
60	20		1.55
100	5	0.25	5.70

⑤ Simulation Information

Parameter	Symbol	Unit	Parameter Values
Simulation time (time series)*	t	yr	100
Output time interval (time series)*	dt	yr	1
Output time points (profiles)*	t_p	yrs	5,10,30,50
able groundwater concentration*	$C_{gw,a}$	ug/L	0.004

Basic Solver (Equilibrium solid-phase sorption)

Advanced Solver (Kinetic solid-phase sorption)

Introduction | Module0_Input | Module0_Output | Module1_Input | Module1_Output | Module2_Input | Module2_Output | Module2_ParaToolkit

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Guidelines for Data Modeling, cont’d

- Model inputs
  - Site soil properties, site conditions, PFAS properties, groundwater dilution, and PFAS soil concentrations
    - Module0 – base model for quantifying PFAS leaching and deriving SSLs
    - Module1 – adds the capability of parameter sensitivity analysis with left/right bound deviation from a median value
    - Module2 – adds the additional capacity for conducting Monte-Carlo-type uncertainty analysis on input parameters

- Model outputs:

	Abbreviation	SSL Equation	Source
	$SSL_{EPA\ Standard}$	$SSL_{EPA\ Standard}=C_{gw,a}\times DF\times\left[K_d+(\theta_w)\frac{1}{\rho_b}\right]$	USEPA, 1996a; USEPA, 1996b
Algebraic solution	$SSL_{PFAS\text{-}LEACH\ Tier\ 4}$	$SSL_{PFAS\text{-}LEACH\ Tier\ 3}=C_{gw,a}\times DF\times\left[K_d+(K_{aw}A_{aw}+\theta_w)\frac{1}{\rho_b}\right]$	Brusseau and Guo 2023
Analytical solution	$SSL_{PFAS\text{-}LEACH\ Tier\ 3}$	$SSL_{PFAS\text{-}LEACH\ Tier\ 4}=C_{gw,a}\times AF_{vz}\times DF\times\left[K_d+(K_{aw}A_{aw}+\theta_w)\frac{1}{\rho_b}\right]$	Brusseau and Guo 2023

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Data Collection Summary

Data Parameter	Method	Analysis	Requirement
Soil			
Soil Texture	NA	Vadose zone observed texture.	LI, DM
Grain Size Analysis	Laboratory	Sieve and hydrometer ASTM D6913/D7928/D422 AASHTO T88	DM
Bulk Density/Total Porosity	Laboratory	ASTM D7263	DM
Saturated Hydraulic Conductivity (K_{sat})	Laboratory	ASTM D5084/D5856/D2434	DM
TOC/Foc	Laboratory	Walkley-Black method as modified in Want et al. (2012)	DM
PFAS Concentration	Laboratory	USEPA Method 1633	LI
Matric Potential	Tensiometer	Time-series evaluation for assessment of recharge wave reachng the lysimeter depth location at applicable installations.	LI
Soil Moisture	Probe	Time-series evaluation with soil moiture conditions estimated to coincide with porewater lysimeter sample events.	DM
Water Retention Parameters	NA	Estimated from dominant vadose zone soil type.	DM
Porewater			
PFAS Concentration	Lysimeter	USEP Method 1633	LI
PFAS Concentration	SPLP	USEPA SW846, Test Method 1312 and Leachate by USEPA Method 1633	LI
Groundwater			
PFAS Concentration	Laboratory	USEPA Method 1633	LI, DM
Groundwater Levels	Water level meter and pressure transducer	Synoptic and time-series evaluation for assessment of groundwater table flow/fluctuation and hydraulic gradient analysis.	LI, DM
Hydraulic Conductivity (K)	Pressure transducer	Hydraulic conductivity estimates calculated from testing results using method(s) that align with test type and response data evaluation.	DM
Climate			
Precipitation and Barometric Pressure	Weather Station or Equivalent	Time-series evaluation for seasonanility and applicable data compensation or corrections for pressure transducers.	LI

TOC = total organic carbon
Foc = fraction or organic carbon

LI = lysimeter investigation
DM = data modeling

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Soil Screening Level (SSL) Selection

- Prioritized list of SSL selection:
  - Option 1 – Linear Regression Using Paired Soil and Lysimeter Porewater Sampling Results
  - Option 3 – Hybrid Approach
  - Option 2 – PFAS-LEACH Modeling Tool

- A PFAS anthropogenic background soil concentration for each PFAS compound with an MCL, TSL or RSL should be estimated based on available information.
  - If background > site-specific SSL, use background concentration to define response action for soil.

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Data Gaps and Continued Research

- Poorly understood complexities related to multi-phase retention of PFAS
  - Rate-limiting desorption-adsorption kinetics (non-equilibrium processes)
  - Precursor transformation effects on desorption-adsorption kinetics
  - Standardized batch desorption laboratory procedures
  - Metal oxide and oxyhydroxide retention
  - Efficacy of PFAS leaching evaluations in fractured bedrock
  - PFAS sorptive losses to silica flour and/or ceramic suction lysimeter cups
  - Impact of a fluctuating groundwater table
  - Specific effects of heterogeneities on accelerated downward PFAS migration
  - Appropriate sample volume for evaluation of bromide tracer dilution
  - Use of multi-level lysimeters, microlysimeters and multichannel tubing (CMT) for porewater collection

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Next Steps

- Additional refinements are expected based on feedback from targeted external reviewers
- For additional information, please contact Noblis:
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