PFAS Migration to Groundwater: Measuring Soil Leaching & Partitioning

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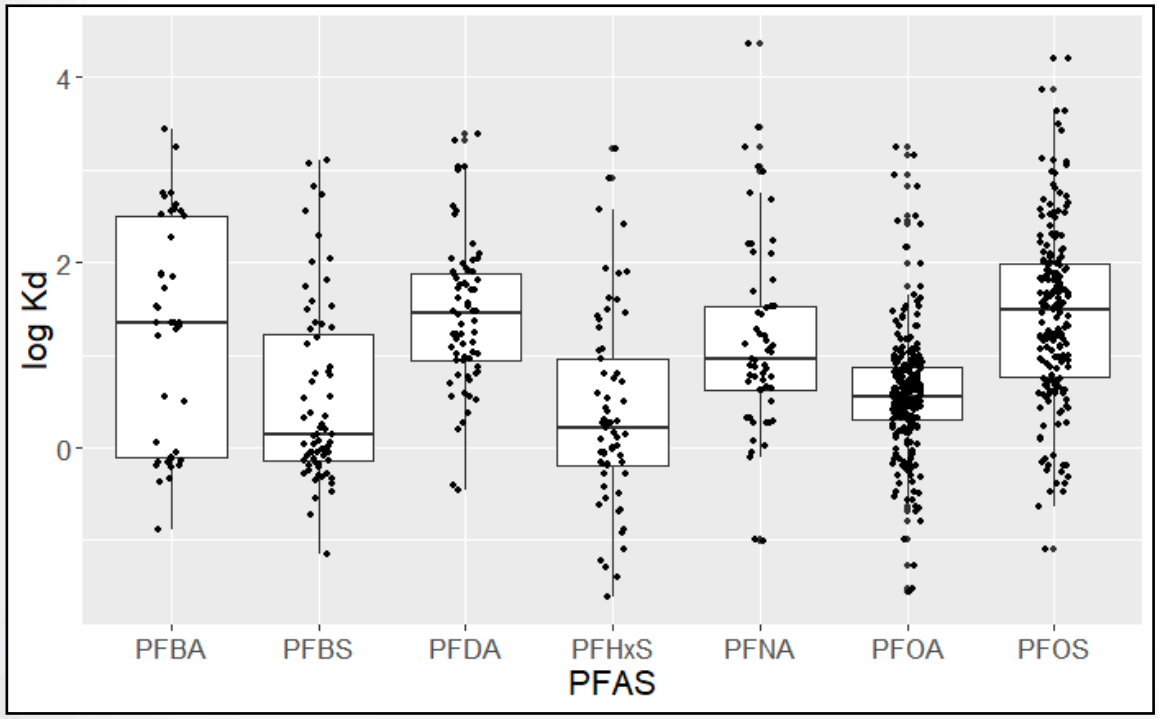
Background

Soil-water partition (Freundlich) equations may be suitable for PFAS, but no consensus on appropriate K_d or K_{OC} values limit usefulness.

It is unclear which factors contribute to variation in measured bulk partitioning.



Simple methods for determining site-specific partition coefficients or PFAS leachability will benefit remedial investigations.

Modeling and leaching methods were considered.

Distribution of log K_d values reported in literature for seven anionic PFAS. Data from Rovero et al. (2021)

Modeling PFAS Migration

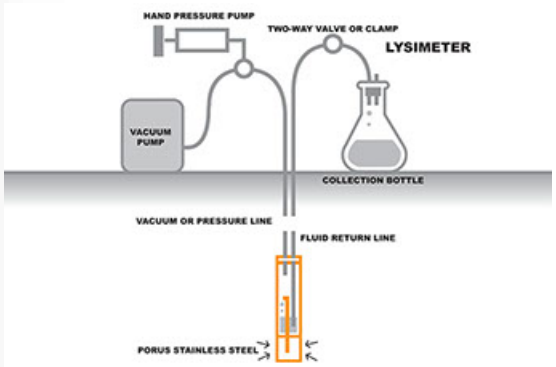
- Models of PFAS migration in the unsaturated zone often require measurement of unusual parameters with specialized equipment.
- Limited laboratory availability can increase cost and time required
- Some factors (e.g., air-water interfacial area) may change with precipitation, seasons, site activity, etc., and require multiple measurements.

Standard commercial lab	**Specialized commercial lab**	**Highly specialized lab**
Bulk density	Clay mineralogy	Air-water interfacial area
Porosity	Solid surface area	Soil-water partition measurement (K_d)
Soil texture (gravel, sand, silt, clay)	Saturated hydraulic conductivity (Ksat)	Air-water interfacial adsorption coefficient (K_{aw})
Particle size distribution	Soil water characteristic curve	Ionic composition
Soil pH		
Cation exchange capacity (CEC)		
Anion exchange capacity (AEC)		
Soil electrical conductivity		
Soil organic carbon content (OC)		
Soil total carbon (TOC)		
Metal oxides		

Table of parameter measurements suggested for adsorption modeling

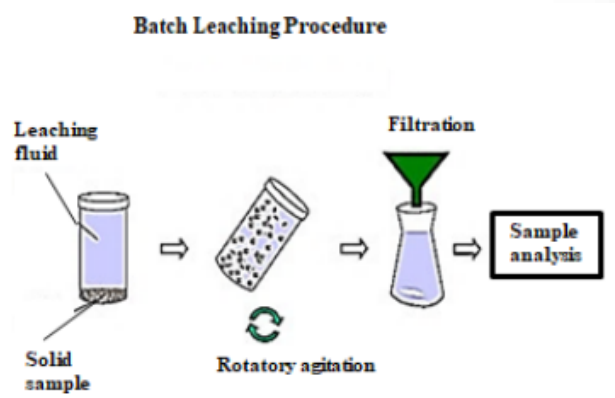
Site-specific Leaching

Lysimetry



- Directly sample porewater
- "Snapshot" of leaching behavior
- Captures seasonal variation
- Longer sampling timeline required
- Unpredictable sample volume
- Not suitable for volatile compounds

Laboratory Leaching



- Generate leachate from soil in lab
- Long-term leaching potential
- Can capture leaching by depth
- Simpler fieldwork, single visit

Other leaching methods may be appropriate

Our research approach

Modified SPLP

SW-846 Test Method 1312: Synthetic Precipitation Leaching Procedure

The following document explains the method designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

- 20:1 liquid to solid ratio
- Mix 18 hours to generate leachate
- Extraction fluid: deionized water adjusted to pH 4.2 or 5.0

Modified

- Use only PFAS-free materials (e.g., methanol-rinsed HDPE containers)
- Reduced sample mass
- Remove filtration step
- Centrifuge to separate solids

PFAS Sites Selected

Valmont Superfund Site
West Hazleton, PA

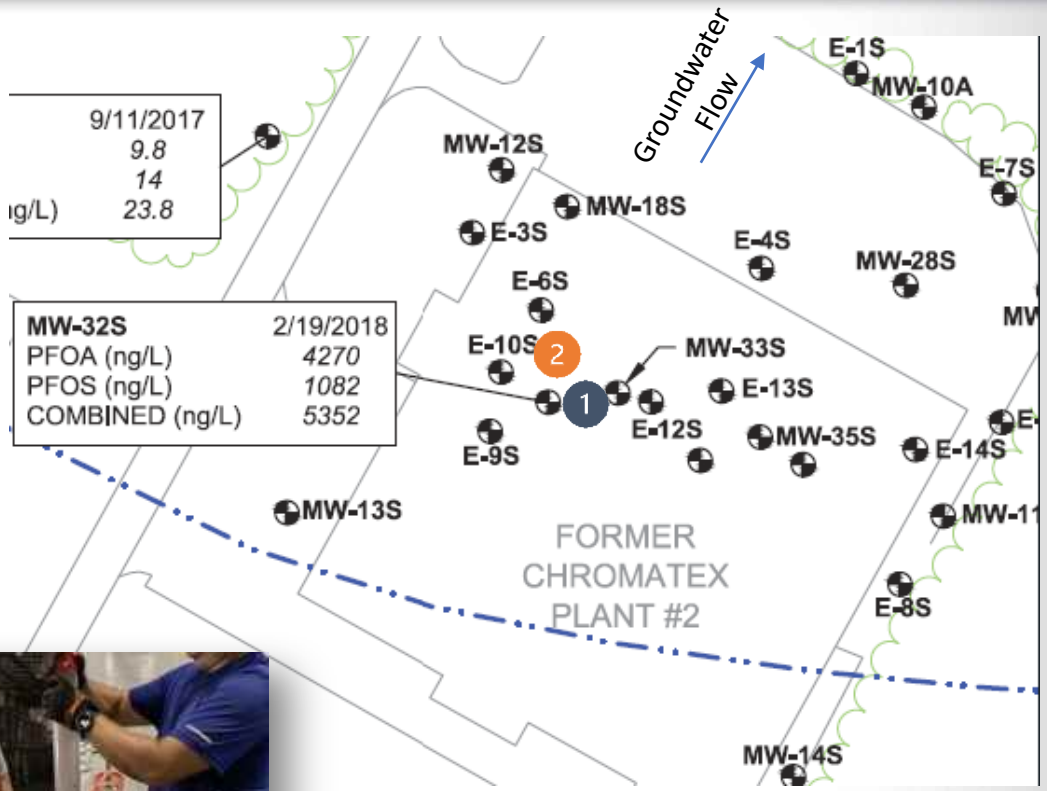
- Former manufacturer that applied PFAS-based stain repellent to fabric.
- Site is co-contaminated with trichloroethylene (TCE), but no known use of AFFF.
- Suspected PFAS sources under the site building – this area targeted for sampling
- Clayey soils, depth to groundwater 11’

Eielson Airforce Base
Moose Creek, Alaska

- PFAS detected in groundwater in 2014, AFFF used on site.
- Legacy contamination from BTEX, chlorinated solvents, lead, and PCBs
- Construction projects also resulted in 130,000 cubic yards of contaminated soil, stockpiled until remediation.
- Multiple source zones in large area
- Sandy loam, layers of gravel, peat, silt, depth to groundwater 5-11’

Valmont Sampling

- Two soil cores were collected from beneath the building's concrete slab in August 2021 from near the suspected source zone, along with groundwater samples from monitoring wells.
- Cores were subsampled in the laboratory to capture ~1ft depth intervals and sieved to <2mm.

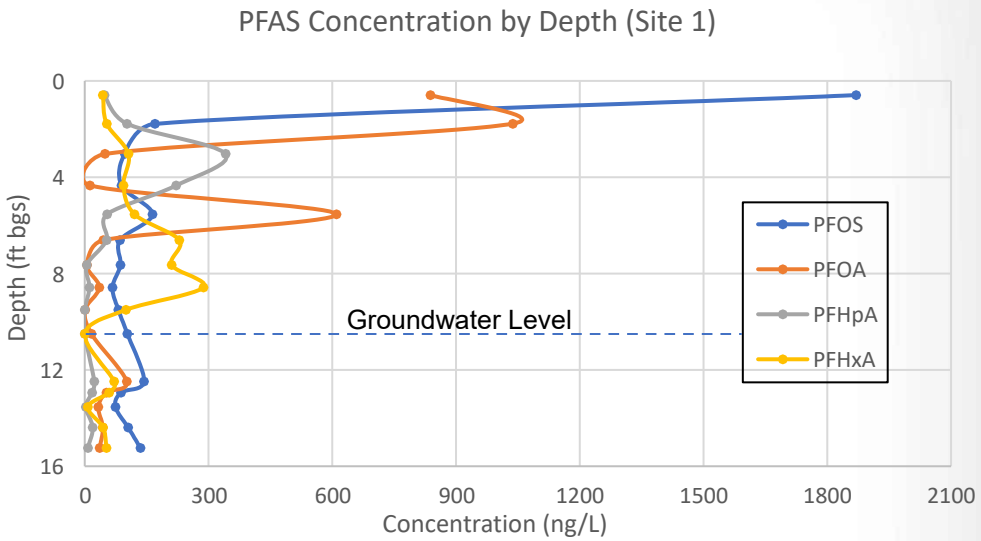


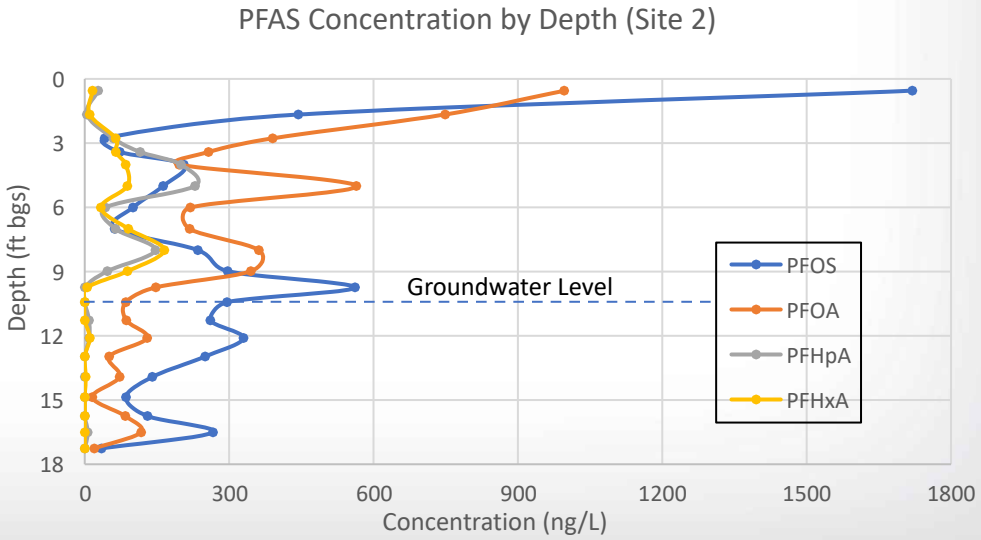
Valmont Subsamples

Subsampling allows for detailed understanding of PFAS migration through the soil column.

At this site:

- PFOA and PFOS remain concentrated near surface
- Accumulation of PFAS just above water level
- Decreasing concentrations below water table suggests movement into groundwater
- Future groundwater contamination is expected from the vadose zone
- Useful for targeting site remedies



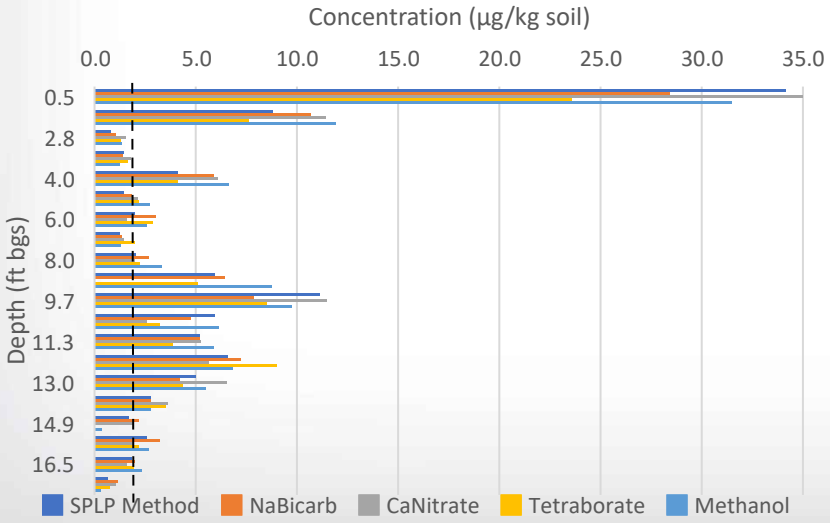


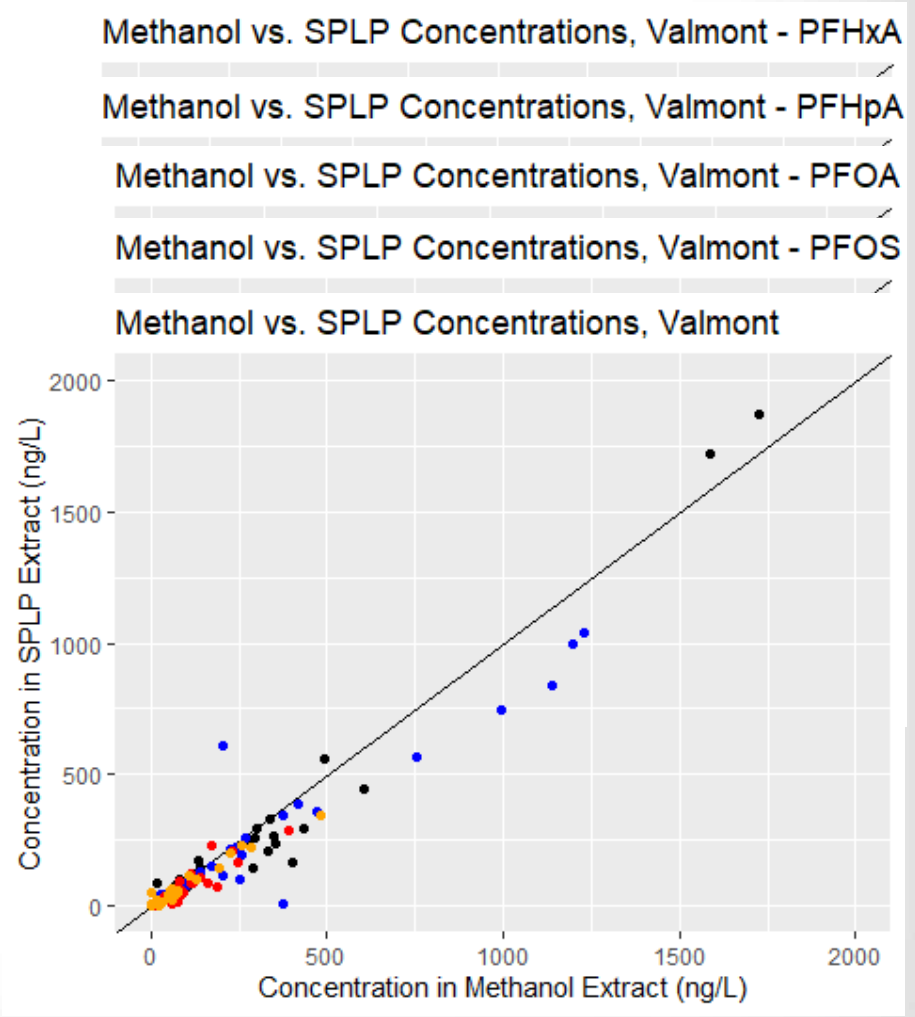
Extraction Fluids

Five extraction fluids were evaluated:

- Standard SPLP (pH 4.2 or 5.0 DI water)
- Sodium bicarbonate solution (1mM)
- Calcium nitrate solution (1mM)
- Basic methanol (1% ammonium hydroxide)
- Sodium tetraborate buffer

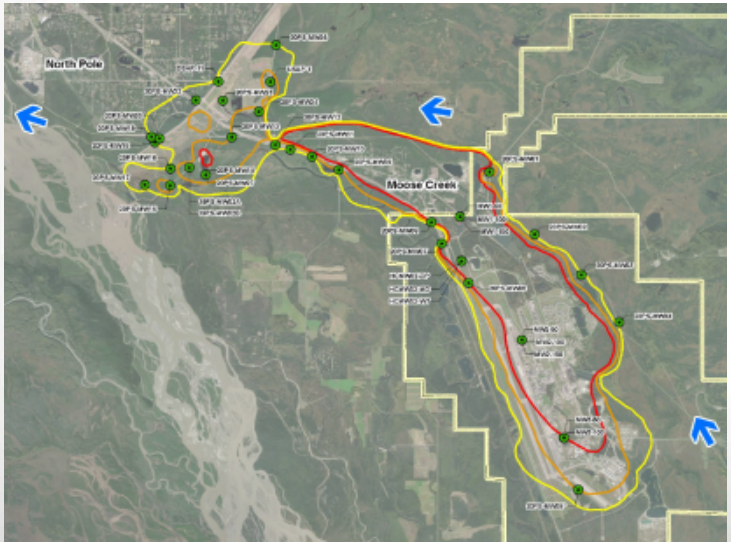
Results from Valmont showed all five solutions performed similarly - water extracts about as well as methanol at 20:1 liquid to solid ratio.

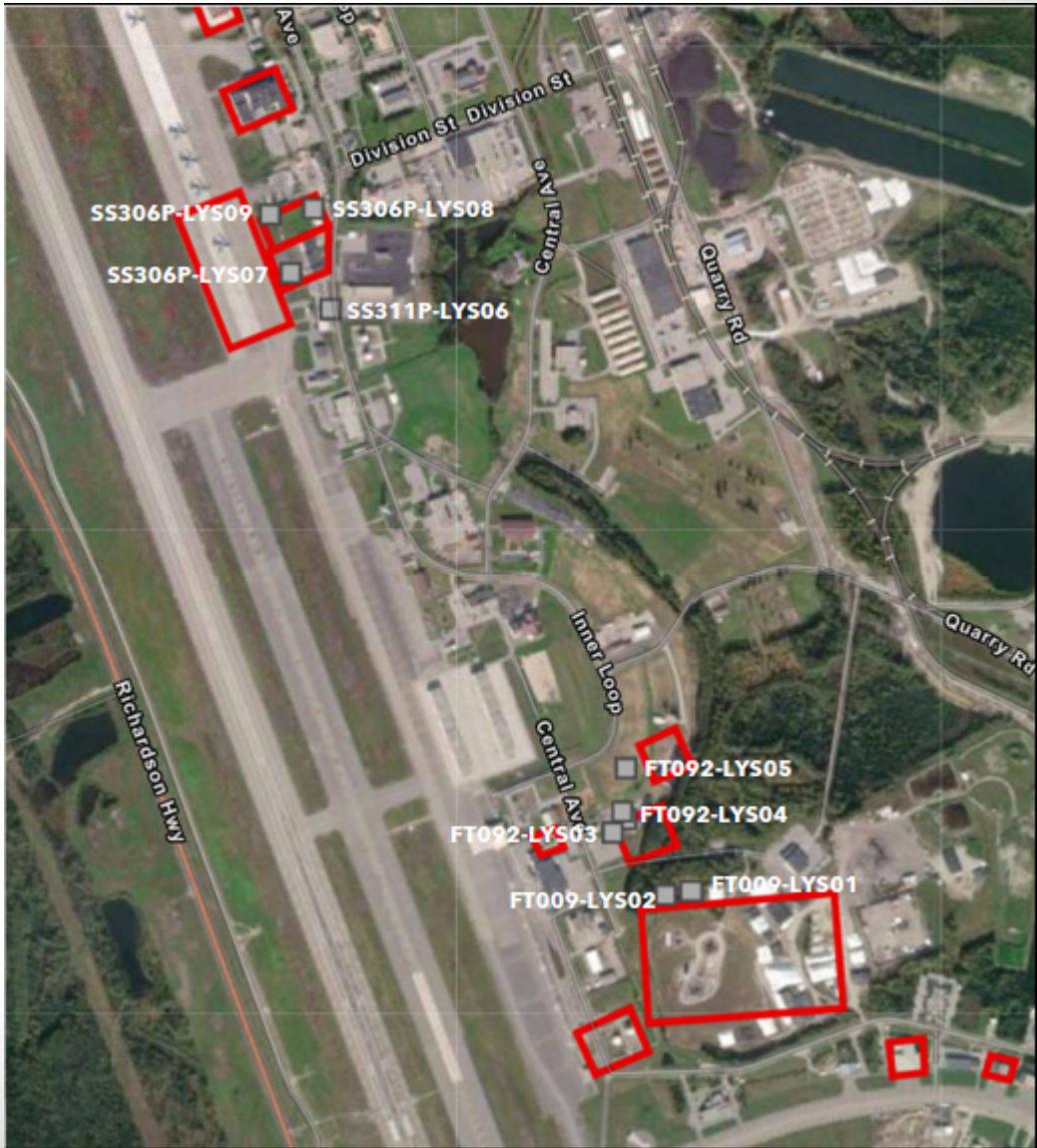




Eielson AFB Sampling

- Air Force Civil Engineer Center (AFCEC) conducted lysimeter study to evaluate PFAS migration through unsaturated zone
- Sampling locations selected in source zones and adjacent areas
- Depths selected based on soil core inspection, targeting zones likely to yield porewater (sandy soils, minimal clay and silt, free from gravel)





Eielson AFB Parallel Study

Lysimeters installed by AFCEC May 2023

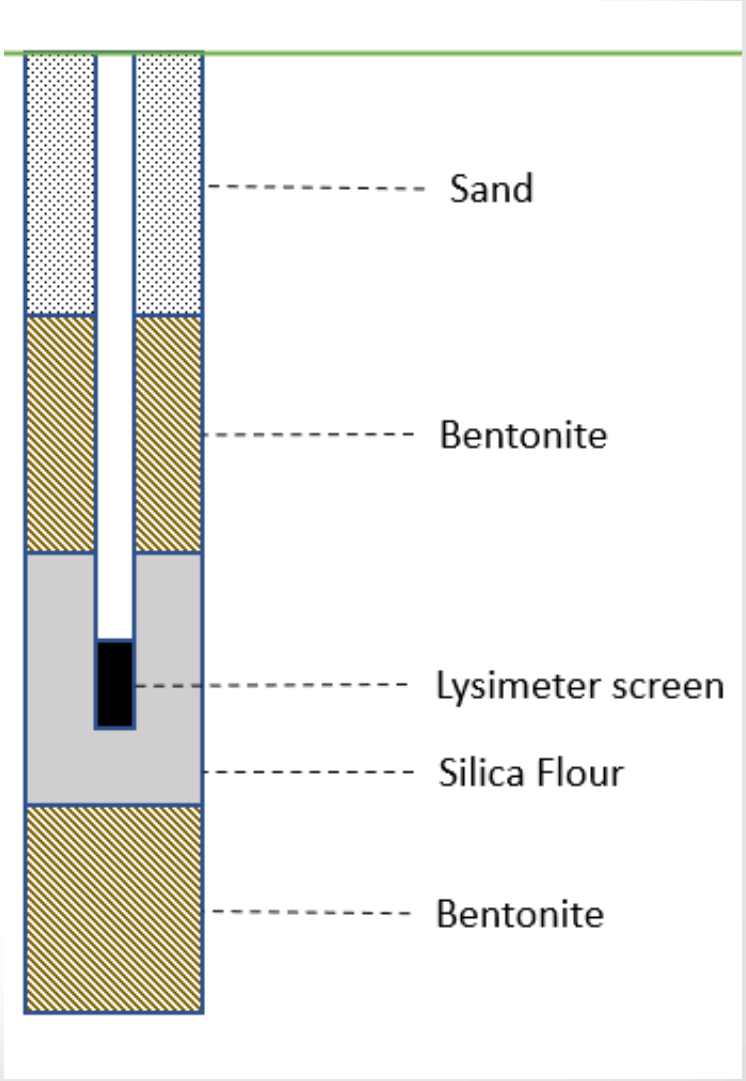
- 9 locations, 1-3 lysimeters at different depths per site, 22 total
- Four rounds of sampling over 4 months before winter freeze

EPA collected soil samples from lysimeter installation boreholes to conduct modified SPLP

- Samples 6-10” above lysimeter screen
- Are results consistent with data from Valmont?
- Are SPLP and lysimeter data comparable?

EPA collecting additional lysimeter samples in 2024

- Effect of snowmelt on PFAS migration
- Reliability & reproducibility



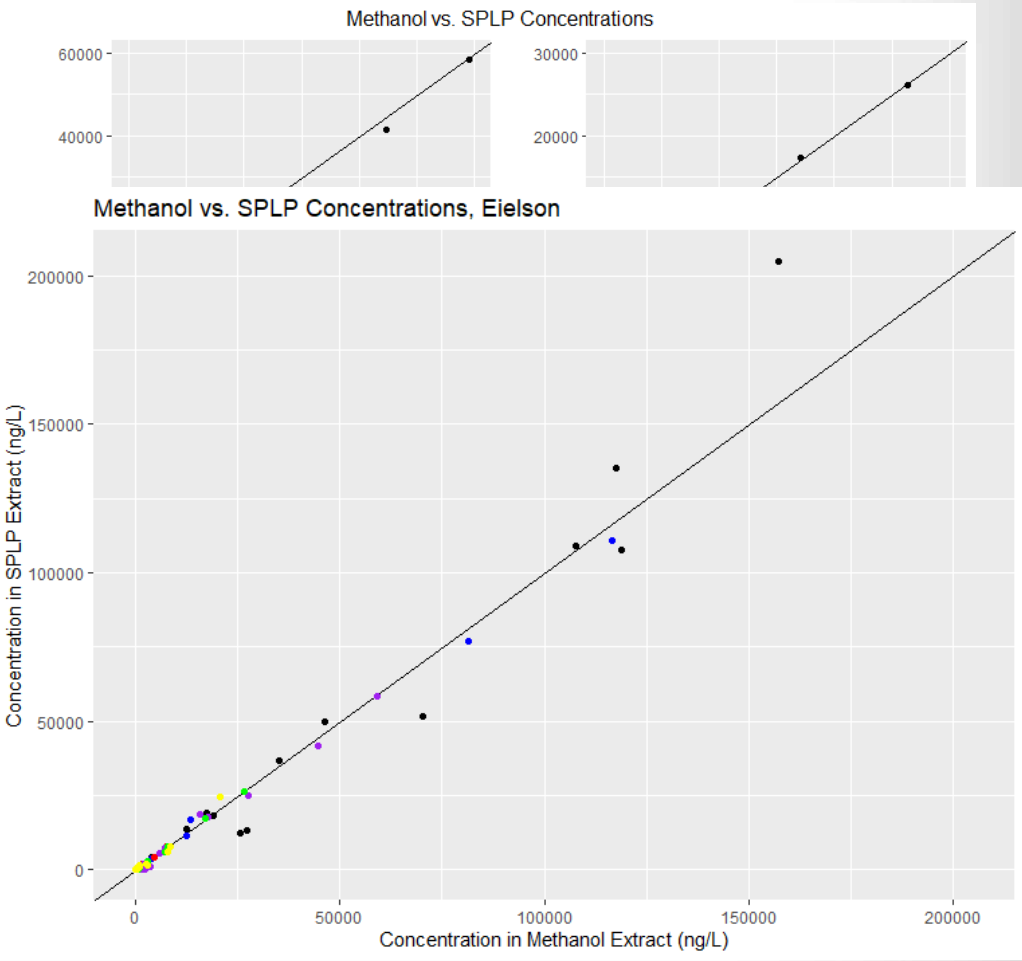
Eielson Initial SPLP Results

Different PFAS mixtures than Valmont

- PFHxA, PFOA, PFOS
- PFHpA in some locations
- PFHxS, 6:2 FTS, 8:2 FTS

SPLP and methanol extractions continue to perform very similarly across wide concentration ranges for all compounds detected

Different soil environment between the two sites does not appear to influence extraction performance

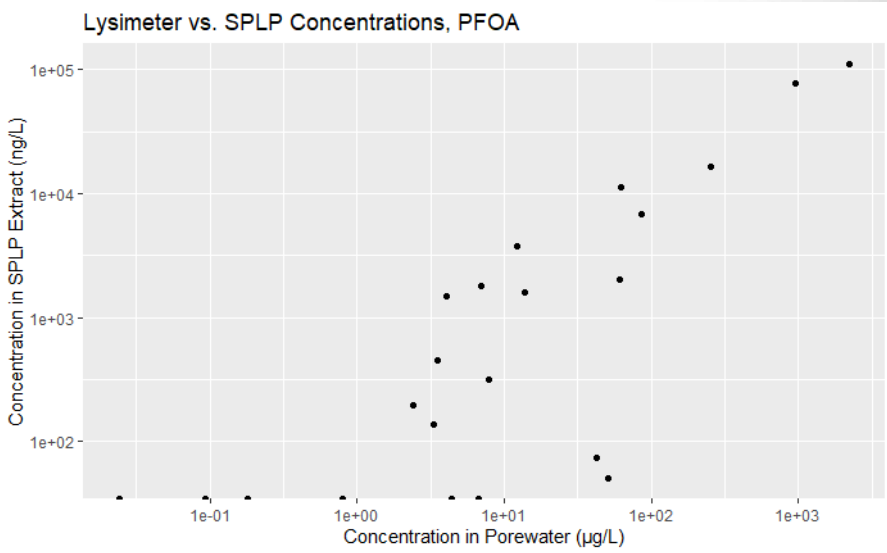


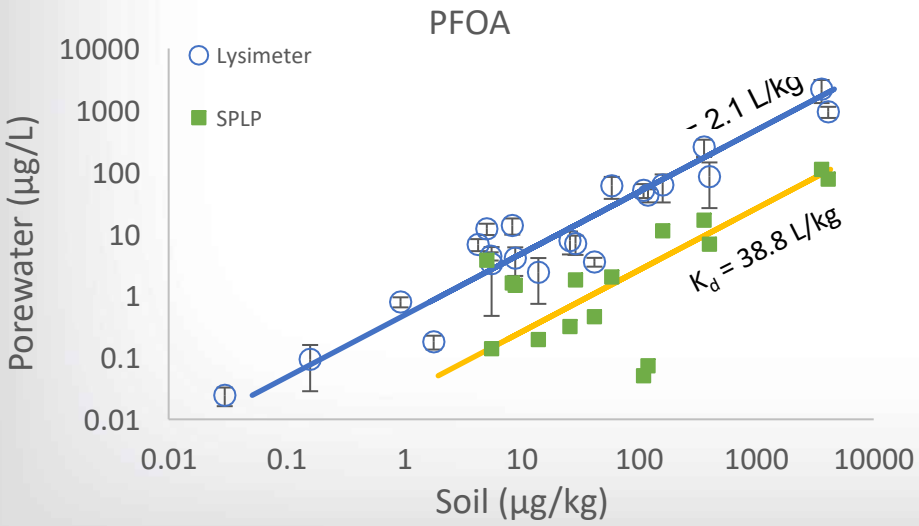
Eielson Lysimeter Comparison

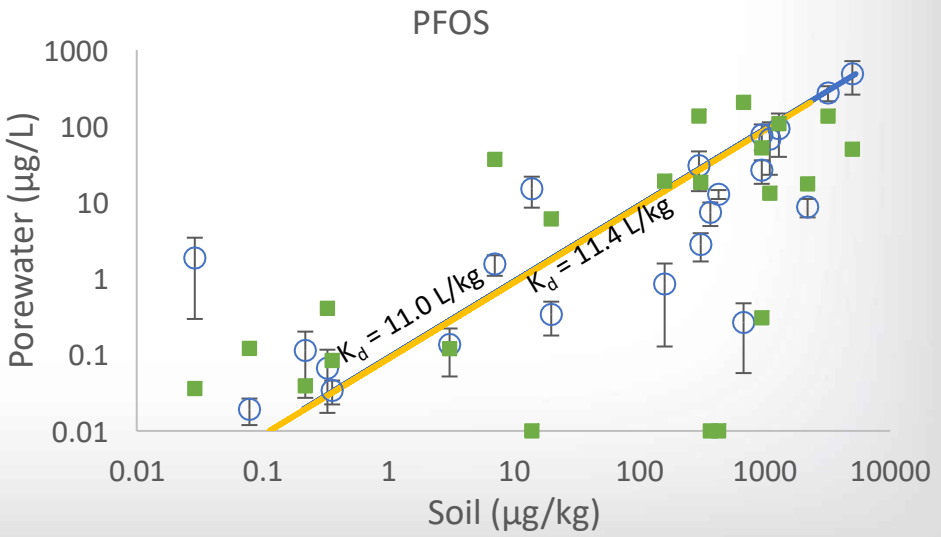
Lysimeter porewater concentrations and SPLP concentrations are well correlated for two of three common detections:

R^2: PFOA=0.95, PFHxA=0.92, PFOS=0.01

Discrepancy in PFOS driven by a few samples with high concentration in porewater and low in SPLP extract – similar response seen in some PFOA samples.



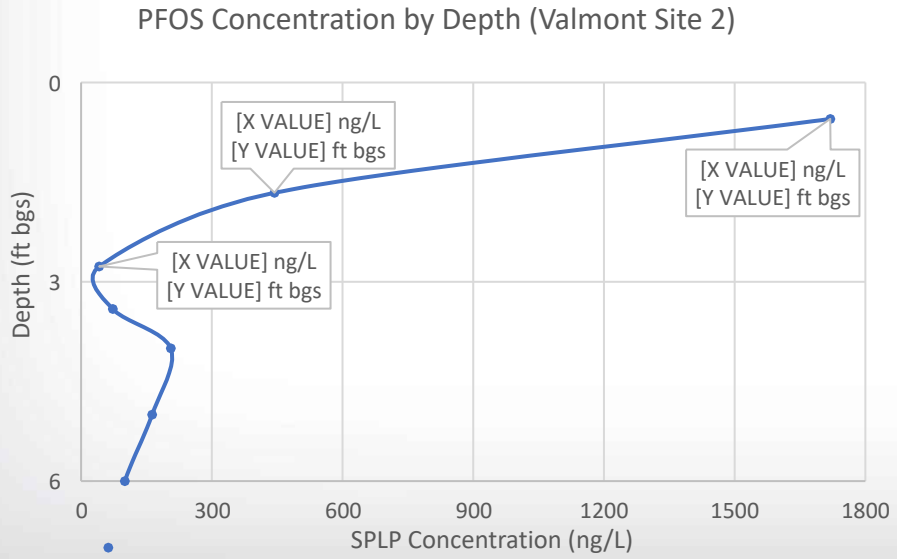




Eielson Lysimeter Comparison

Soil samples used for SPLP were offset from lysimeter depths, differences may reflect actual soil concentrations from distinct samples.

Soil concentration determined by heated methanol/acetonitrile extraction. Different extraction methods may not be suitable for all compounds – short chain, volatile, precursors, etc.



Soil Leachate – Risk to Groundwater

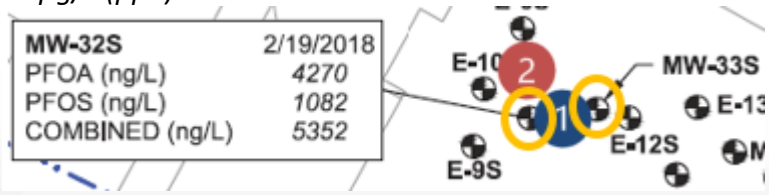
The methodology for calculating soil screening levels for the migration to groundwater pathway using PFAS SPLP results requires additional research.

Standard Approach: $C_{GW} = C_w \div DAF$ Conservative default DAF = 20

Using maximum SPLP leachate values directly (DAF = 1) provides reasonable estimates at Valmont.

PFAS	Core 1	Core 2	MW-32	MW-33
PFOS	1.09	1.72	1.89	0.67
PFOA	1.02	1.00	3.05	1.03
PFHpA	0.34	0.20	1.24	0.49
PFHxA	0.28	0.17	2.5	1.02

All units in µg/L (ppb)



- Results are within roughly a factor of 10 for the four most common contaminants
- Depth of max. contamination may not be obvious
- Make considerations for mobility of each compound
- May not hold across all PFAS, concentration ranges, soils

Soil Leachate – Risk to Groundwater

- SPLP results represent potential PFAS contribution to groundwater from tested soil.
- Valmont is ideal: single, localized source zone.
- Eielson has multiple source zones, spread across wide area, from multiple types of applications. Contaminated materials have been moved, removed, or covered over.

Conclusion

The goal of our research is the development of a robust, usable tool for assessing PFAS risk to groundwater. SPLP appears suitable for this use with only minor modifications, enabling the procedure to be carried out in standard laboratory settings without specialized equipment.

This method keeps field work to a minimum, does not require large numbers of samples to be collected, and can produce results quickly at (relatively) low cost. Sample collection can easily be expanded to meet project needs or further characterize PFAS migration in soil.

Additional research is being performed to better understand how to use SPLP data in determining groundwater risk and determining comparability with other methods.

Questions?