



Application of Modified Impact-to-Groundwater Tools for PFAS Assessment

Matt Rovero

D. Cutt, F. Klanchar, E. Gleason, T. Lee, R. Griffiths, J. Costanza, R. Wilkin

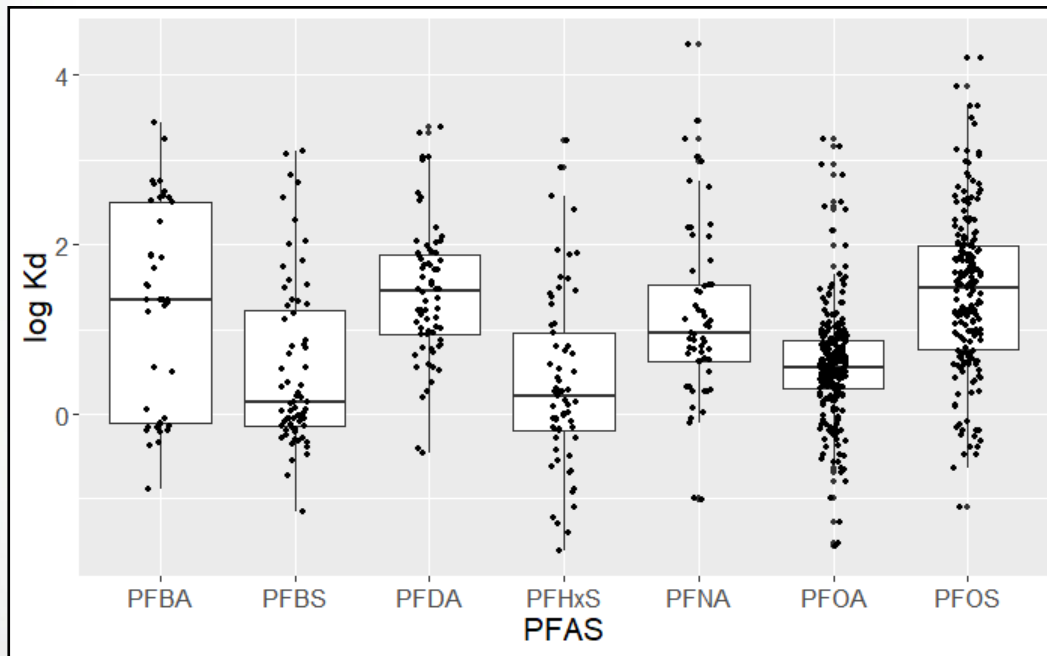
EPA Office of Research and Development
Center for Environmental Solutions and Emergency Response
Subsurface Remediation Branch



Background

Regional staff need a method to estimate or predict PFAS migration to groundwater without extensive site characterization.

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



Unclear which factors contribute to variation in measured bulk partitioning

Determining site-specific partition coefficients reduces uncertainty using partition equations



Modeling PFAS Migration

Models of PFAS migration in the unsaturated zone often require measurement of unusual parameters with specialized equipment.

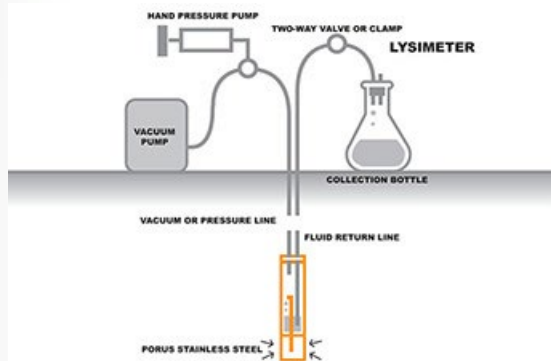
Limited laboratory availability can increase cost and time required for risk-to-groundwater assessment.

Some factors (e.g., air-water interfacial area) may change with precipitation, seasons, site activity, etc., and require multiple measurements.

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

Table of parameter measurements suggested for adsorption modeling

Lysimetry

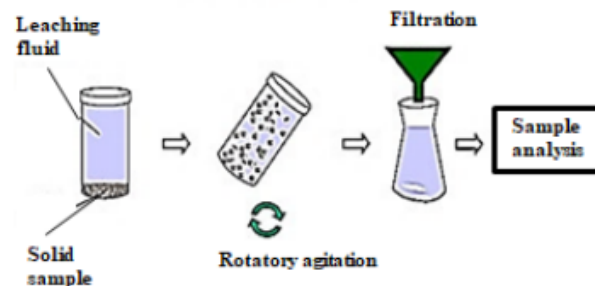


- Directly sample porewater
- “Snapshot” of leaching behavior
- Captures seasonal variation
- Longer sampling timeline required
- Unpredictable sample volume
- Not suitable for volatile compounds

Other methods may be appropriate

Laboratory Leaching

Batch Leaching Procedure



- Generate leachate from soil in lab
- “Worst case” leaching potential
- Can capture leaching by depth
- Simpler fieldwork, single visit

Our research approach

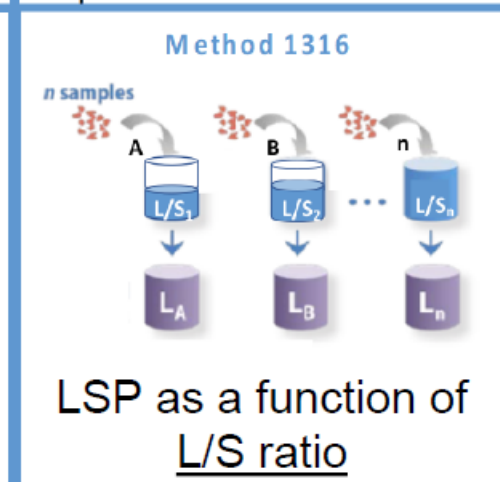
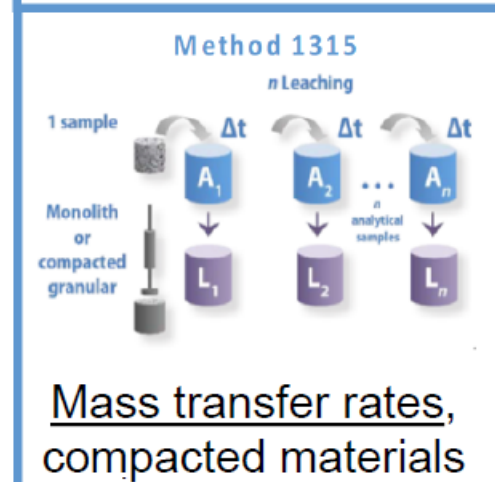
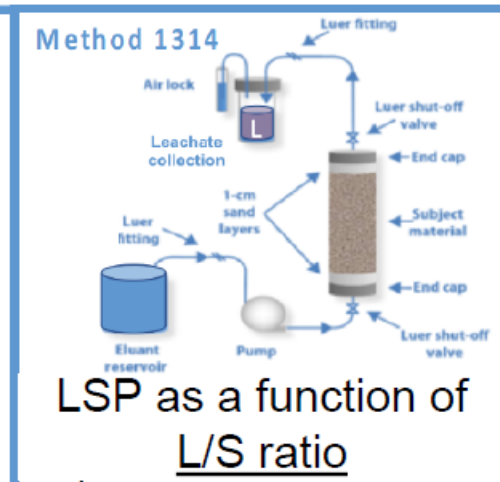
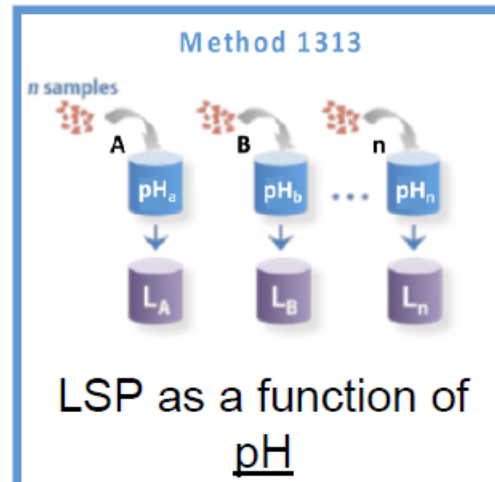
Two Approaches to Leaching

Synthetic Precipitation Leachate Procedure (SPLP)

- Simple single extraction
- Uses rain simulant (unbuffered pH 4.2 or 5.0 DI water) as extractant
- 20:1 liquid-to-solid ratio
- Already in regulatory use

Leaching Evaluation Assessment Framework (LEAF)

- Up to four independent leaching assessments
- Multiple extractions required per sample for batch methods (1313, 1316)
- Column methods more complex to set up (1314, 1315)



Notes: LSP = liquid-solid partitioning; L/S = Liquid to solid



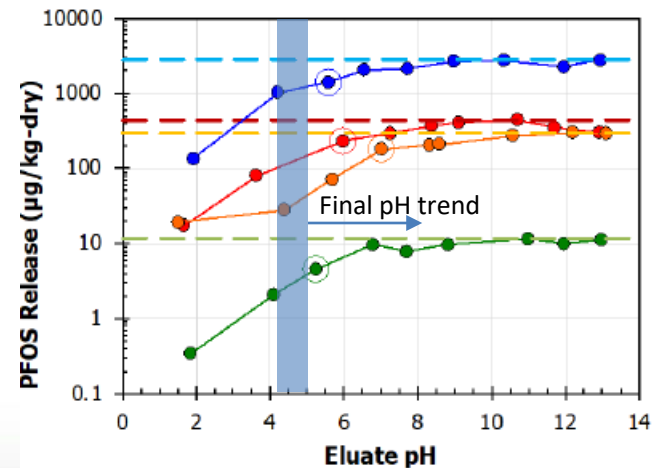
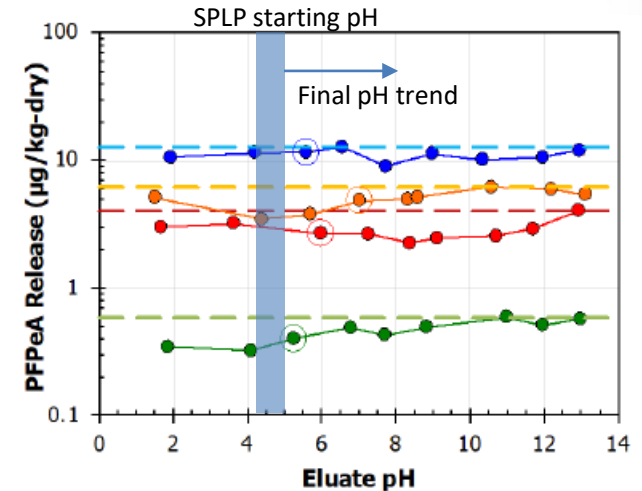
Two Approaches to Leaching

Lessons from LEAF (data from Guelfo et al.)

- Extractant pH has little effect on leaching potential for PFAS shorter than C8
- Reducing L/S ratio from 20 used in SPLP provides less-conservative estimates of leaching potential

SPLP remains simplest method to estimate leaching potential, requiring analysis of the fewest samples, with environmentally-relevant parameters.

Further investigation into SPLP L/S ratio ongoing.





Is SPLP Too Aggressive?

“SPLP leachate testing provides an estimate of vadose zone leaching through an *aggressive* soil extraction process”
Quinan et al., 2021

“Considering most of these methods are performed under *aggressive conditions*, i.e., tumbling under saturated conditions for 18 h or more, the results from these tests can provide a conservative estimate of leaching potential”
Navarro et al., 2023

SPLP is not intended to replicate typical conditions within the vadose zone:

- Physical agitation (end-over-end tumbling) will cause particle size reduction
- Saturated conditions increase PFAS leaching by eliminating air-water interfaces
- High liquid-to-solid ratio favors partitioning into extraction fluid

- Estimates *long-term* leaching potential
- Likely to be conservative, but not *worst case* due to mild extraction fluid
- Interpretation of results critical to application



Modified SPLP

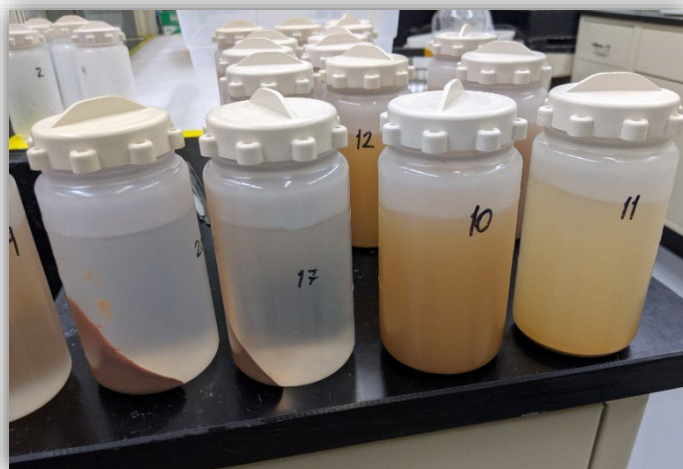
SW-846 Test Method 1312: Synthetic Precipitation Leaching Procedure

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
- Four alternate extraction fluids



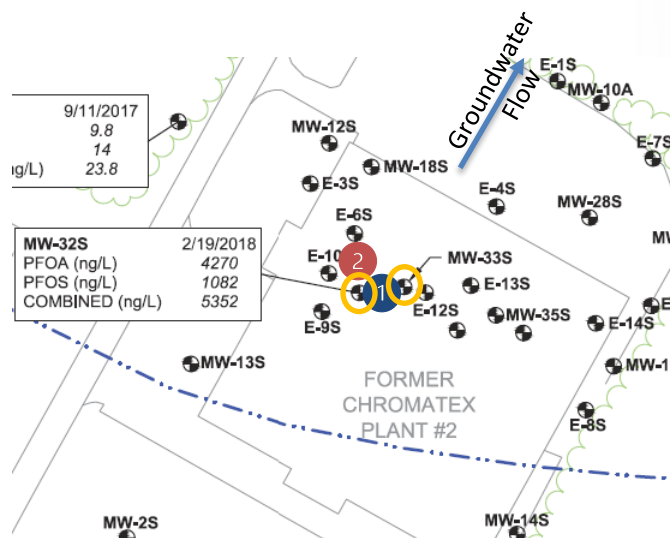


Valmont Site Description

The Valmont Superfund Site in West Hazleton, PA, is the former location of a manufacturer that applied PFAS-based stain repellent to fabric. Site is co-contaminated with trichloroethylene (TCE), but no known use of AFFF.

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.





Target Analytes

Analysis of target compounds performed using coupled LC-MS-MS.

- Quantitation Limit (QL): 0.1 µg/L (except PFBA)
- Detection: ~0.02 µg/L (except PFBA)

Due to SPLP extraction ratio, soil detection and quantitation limits are elevated:

- QL: 2 µg/kg
- DL: ~0.4 µg/kg

Chain Length	PFCA	PFSA
C4	PFBA	PFBS
C5	PFPeA	PFPeS
C6	PFHxA	PFHxS
C7	PFHpA	PFHpS
C8	PFOA	PFOS
C9	PFNA	PFNS
C10	PFDA	PFDS
C11	PFUnDA	
C12	PFDoDA	PFDoDS
C13	PFTTrDA	
C14	PFTeDA	
C16	PFHxDA	
C18	PFODA	

Other Compounds

4:2 FTS

6:2 FTS

8:2 FTS

HFPO-DA



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Many compounds not detected in any samples.

Highlighted compounds discussed further.

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C5	PFPeA	PFPeS
C6	PFHxA	PFHxS
C7	PFHpA	PFHpS
C8	PFOA	PFOS
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C10	PFDA	PFDS
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C12	PFDoDA	PFDoDS
C13	PFTrDA	
C14	PFTeDA	
C16	PFHxDA	
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Other Compounds

~~4:2-FTS~~

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~~HFPO-DA~~

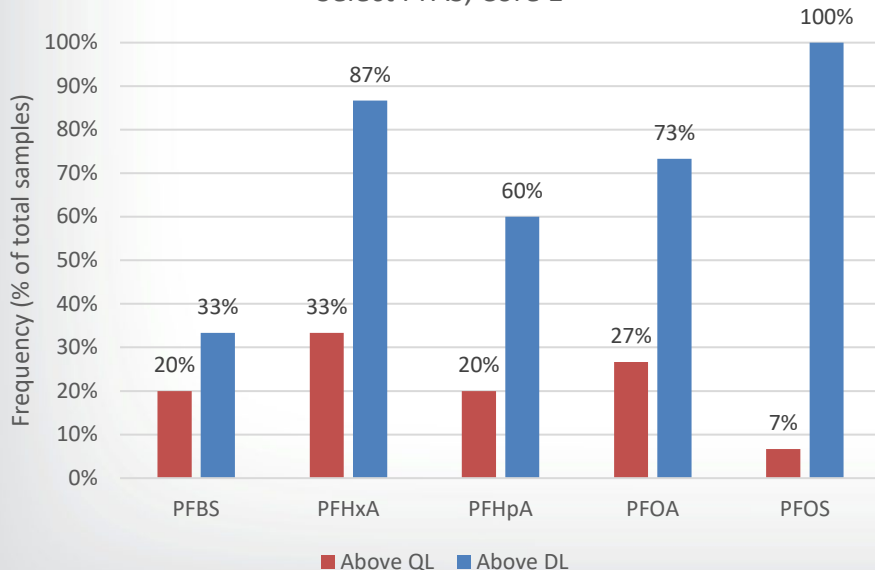


PFAS SPLP:Valmont

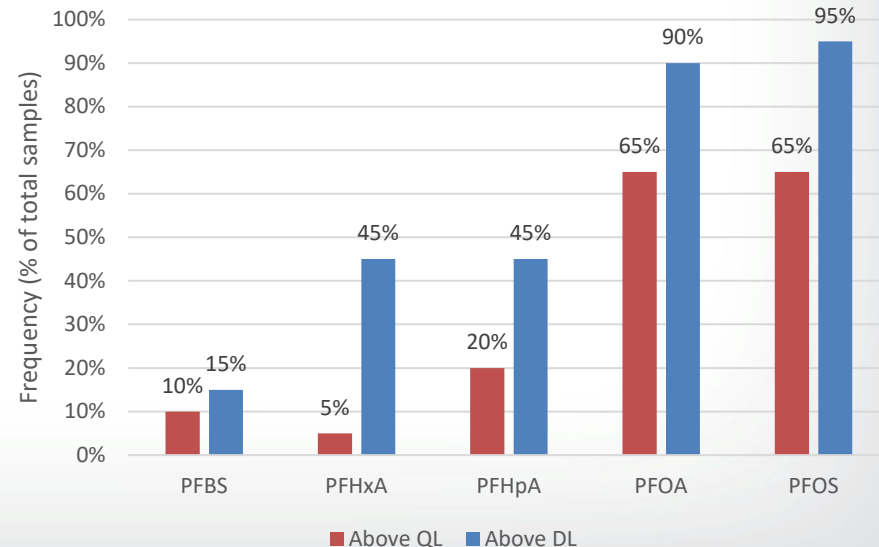
- Same compounds identified from both soil cores
- Higher concentrations in Core 2
- Similar compounds to GW data

Groundwater Samples				
Rank	MW32	MW33	Core1	Core2
1	PFOA	PFOA	PFHxA	PFOA
2	PFHxA	PFHxA	PFPeA	PFHxA
3	PFOS	PFOS	PFHpA	PFHpA
4	PFHpA	PFBS	PFOA	PFOS
5	PFBS	PFHpA	PFBA	PFHxS

Frequency of Detection
Select PFAS, Core 1



Frequency of Detection
Select PFAS, Core 2



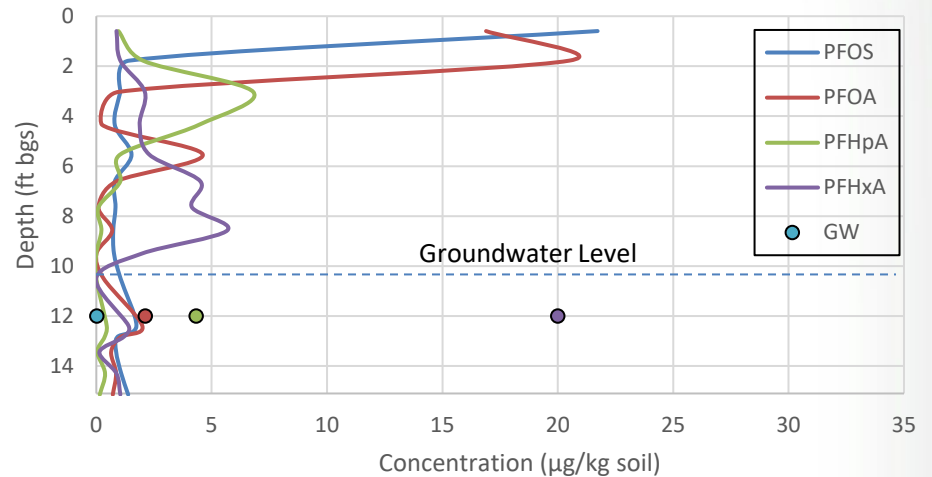


PFAS SPLP: Valmont

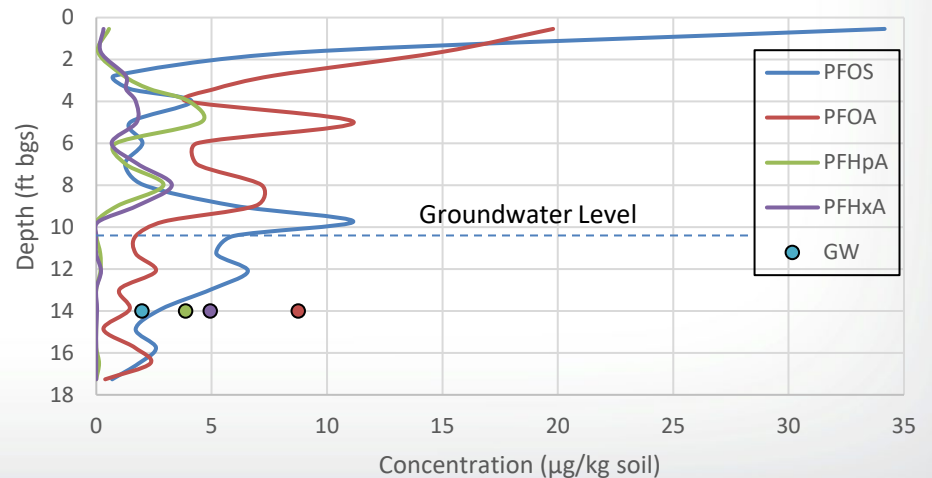
Subsampling allows for understanding PFAS migration profile through the soil column

- PFOA and PFOS concentrated near surface
- Concentration spike above groundwater level
- “Washing away” below water table suggests movement into groundwater
- Future groundwater contamination is expected from the vadose zone
- Research needed on effects of age, precipitation, application method, etc.

PFAS Concentration by Depth: Core 1



PFAS Concentration by Depth: Core 2





Translation to Groundwater

Translating SPLP results into groundwater risk requires additional research.

Standard Model:

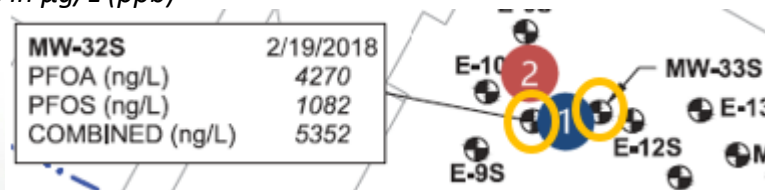
1. Determine [PFAS] in appropriate leachate
2. Apply dilution-attenuation factor (DAF)

Using maximum SPLP leachate values directly with no DAF provides reasonable estimates.

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

- 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

All units in $\mu\text{g/L}$ (ppb)





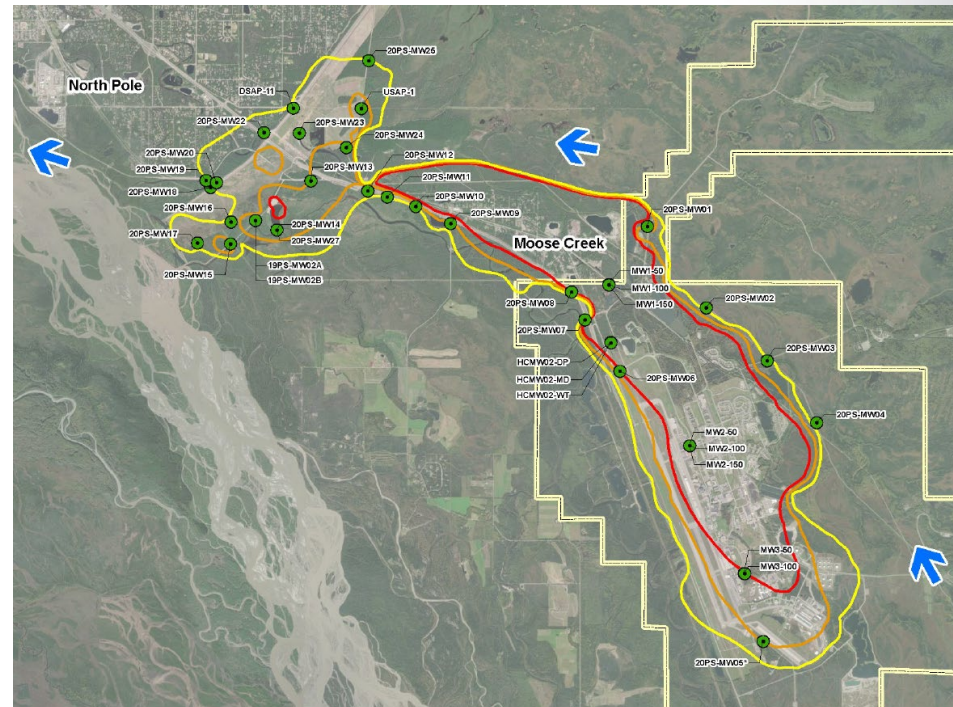
Additional Research Sites



Eielson AFB Site Description

Eielson Airforce Base in central Alaska has been a listed NPL site since 1989 due to surface water, soil, and groundwater contamination from BTEX, chlorinated solvents, lead, and PCBs.

PFAS contamination of drinking water was detected in 2015. Construction projects also generated approximately 130,000 cubic yards of contaminated soil, currently stockpiled until remediated via soil washing.





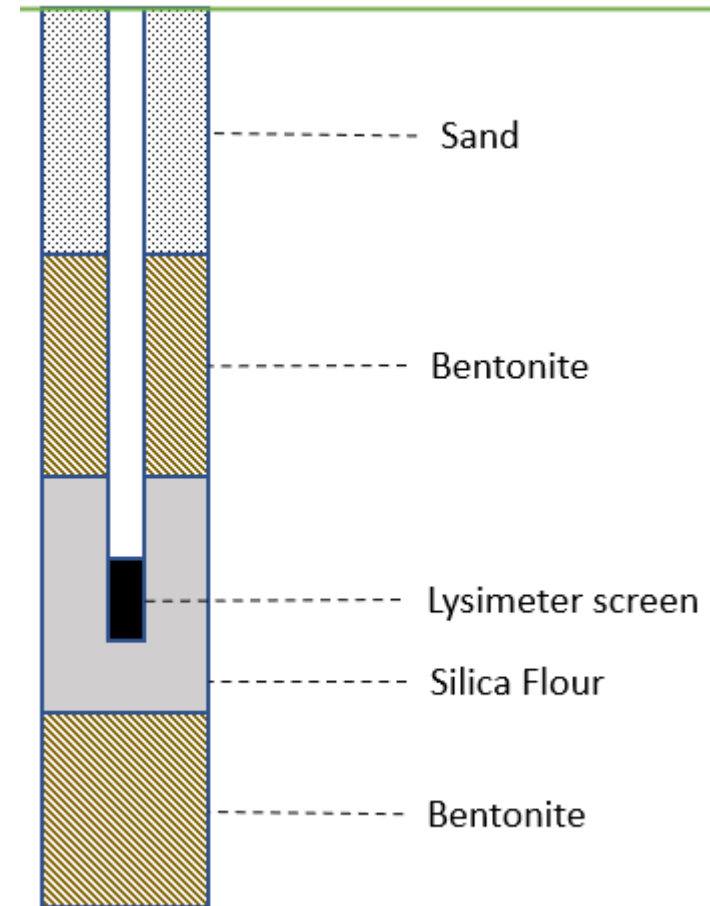
Eielson AFB Parallel Study

Air Force Civil Engineer Center (AFCEC) conducting lysimeter study to determine the threat of PFAS migration through the unsaturated zone.

- Lysimeters installed May 2023
 - 9 locations, 1-3 lysimeters at different depths per site, 22 total
- Four rounds of sampling before winter freeze

GCRD collected soil samples from installation boreholes at lysimeter depths to conduct modified SPLP

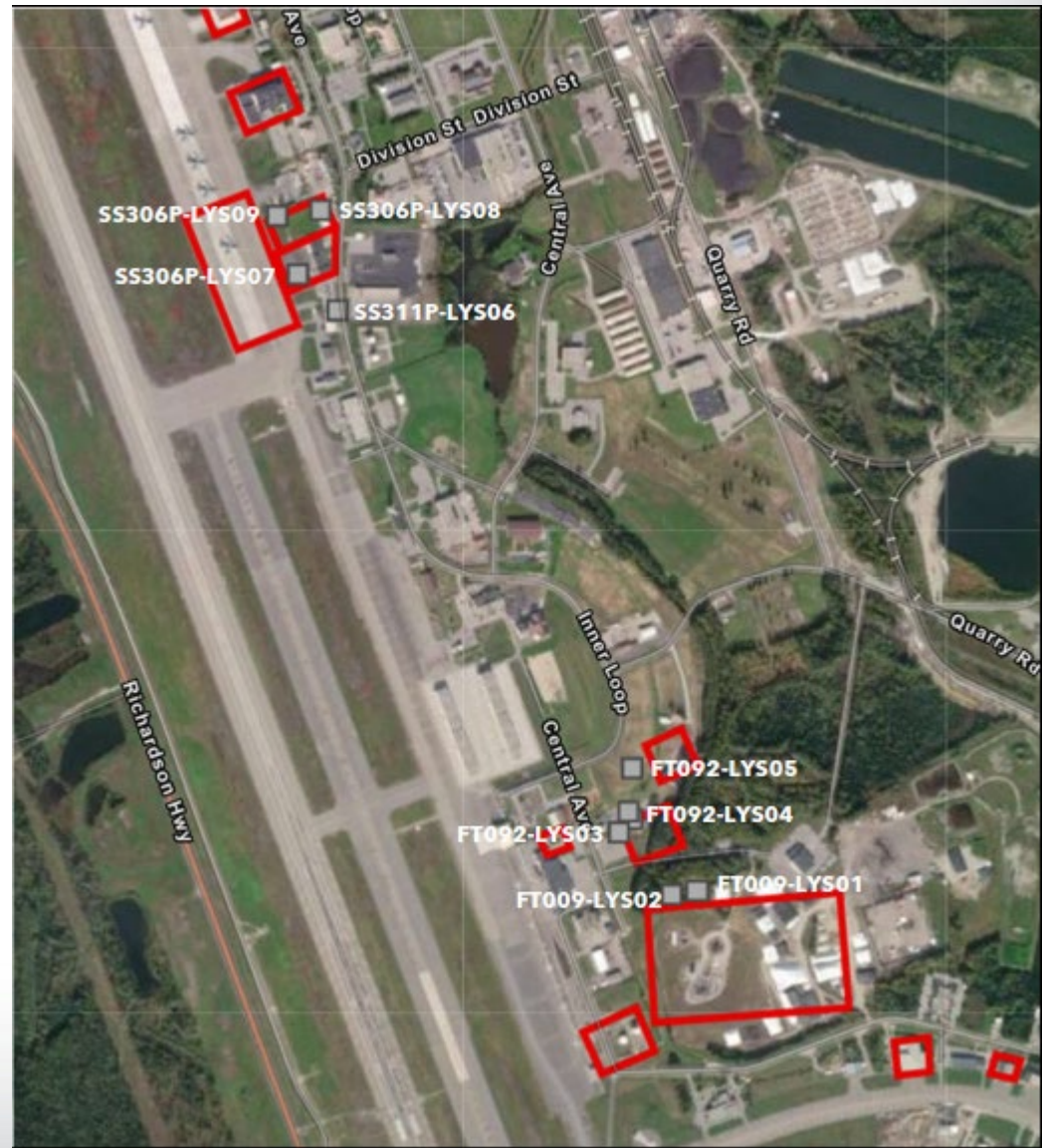
- Are results consistent with data from Valmont?
- Are SPLP and lysimeter data comparable?





Eielson AFB SPLP Study

- Sampling locations selected in both contaminated zones and unimpacted areas
- Depths selected based on soil core inspection, targeting zones likely to yield porewater (sandy soils, minimal clay and silt, free from gravel)
- Very distinct from Valmont
 - Valmont soil mostly clay
 - Higher infiltration - unpaved vs. under building
 - Higher pH
 - Contamination from AFFF

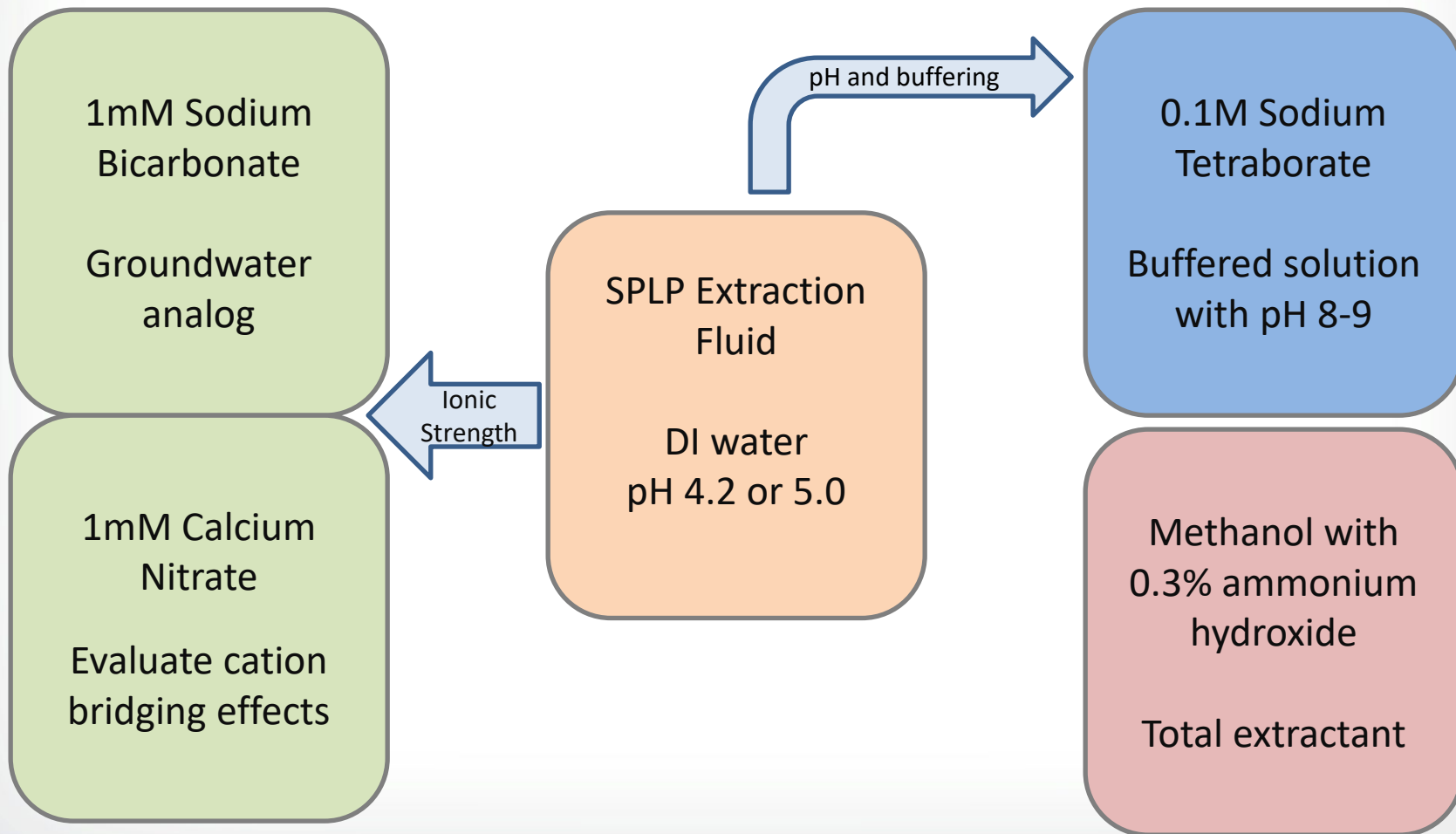




Additional SPLP Modifications



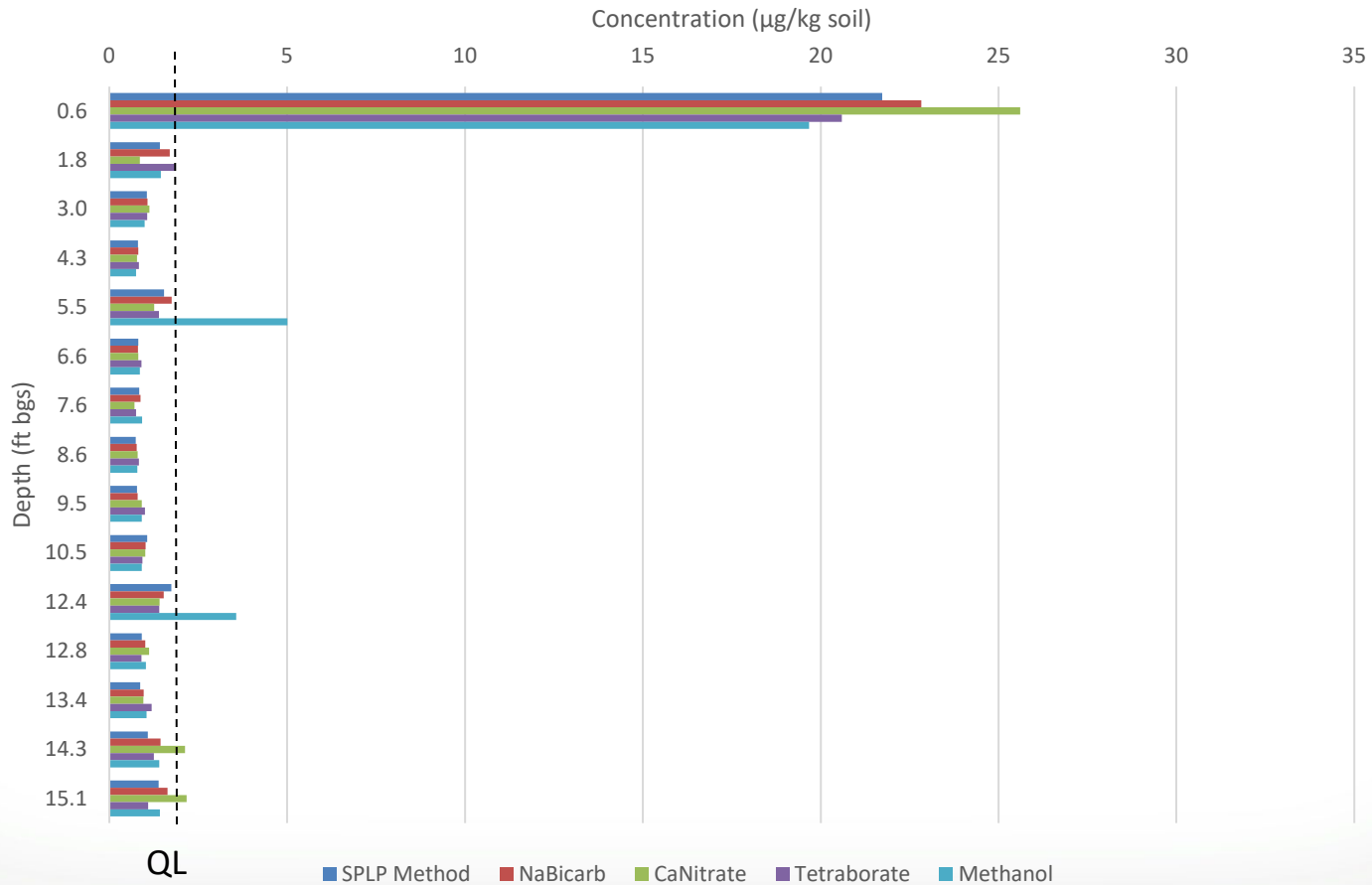
PFAS SPLP: Extraction Fluids





PFAS SPLP: Extraction Fluids

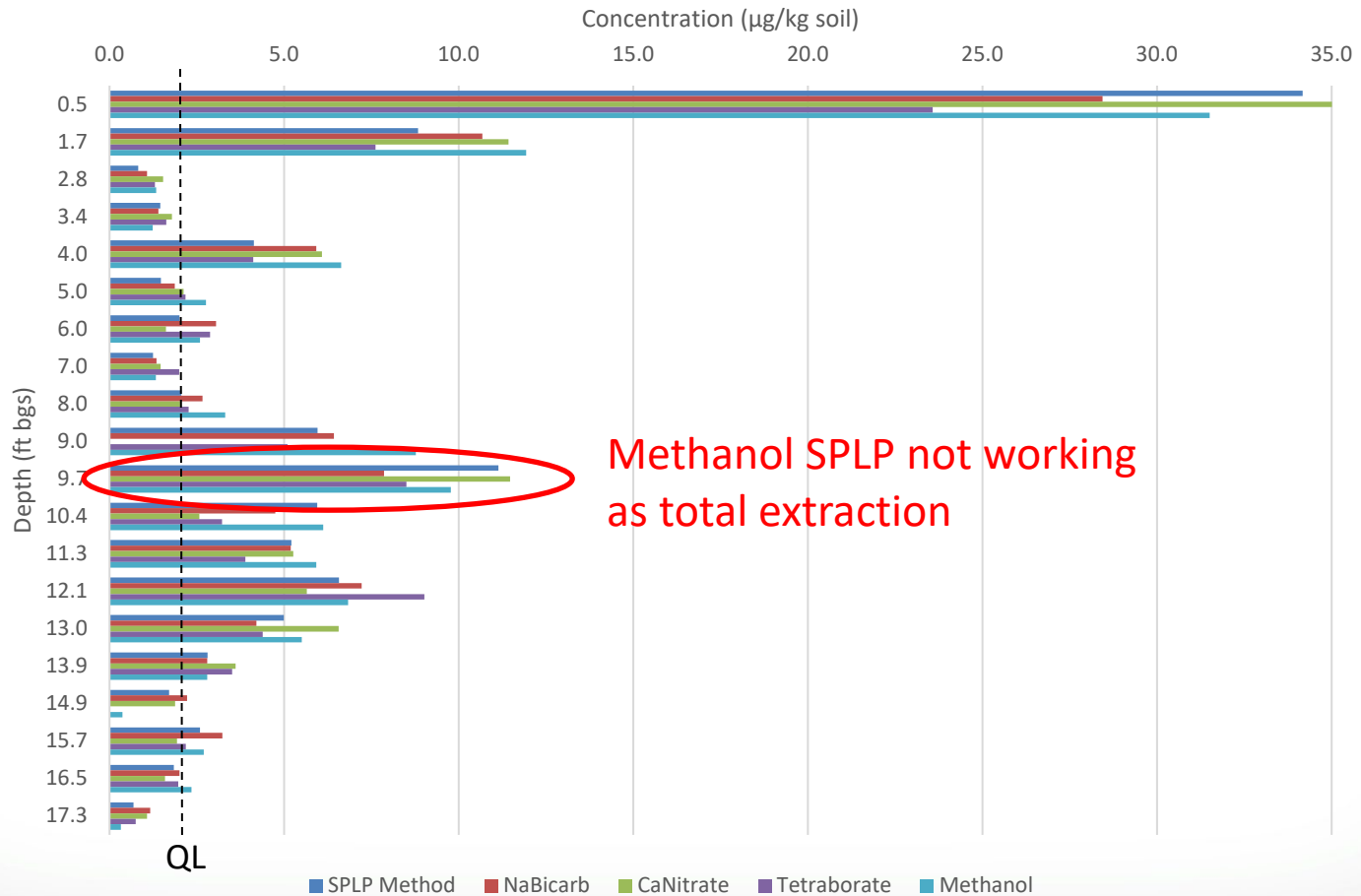
PFOS Concentration by Depth
Core 1





PFAS SPLP: Extraction Fluids

PFOS Concentration by Depth
Core 2

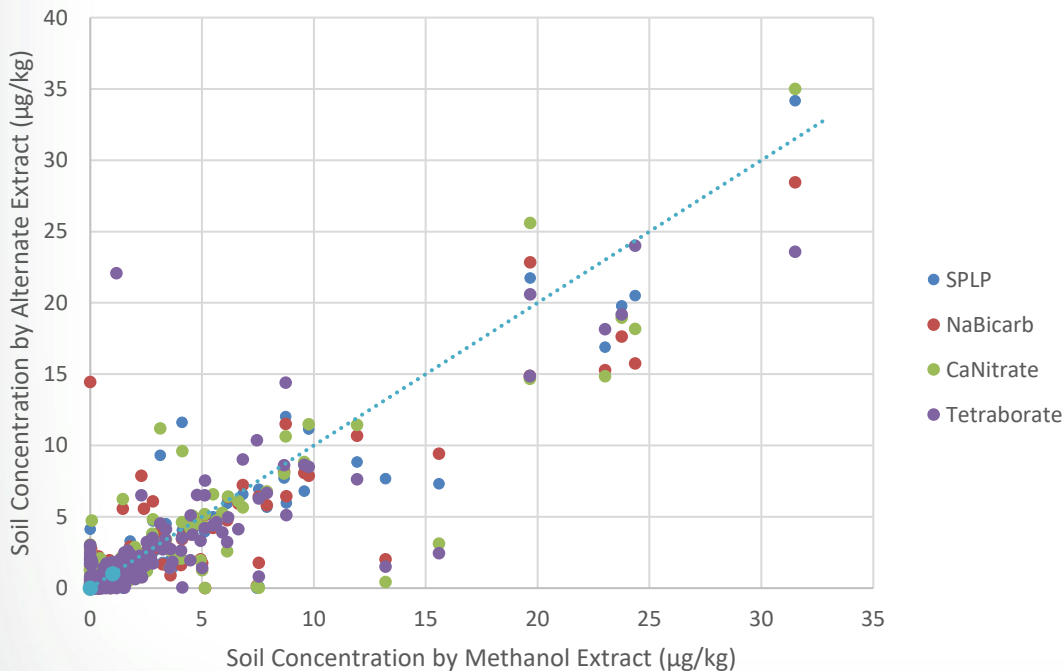




PFAS SPLP: Methanol Extraction

Methanol extracts had similar PFAS concentrations to standard SPLP extraction fluid and alternate extraction fluids.

Evaluation of Methanol as Total Extractant



Either methanol is not performing a total extraction OR other extraction fluids also readily extract majority of PFAS.

Results suitable for groundwater impact assessment, but not for calculating site-specific K_d if “total” concentration (C_t) is the same as leachable fraction (C_w)

$$K_d = \frac{C_s}{C_w} \text{ or } \frac{C_T - C_w}{C_w}$$



PFAS SPLP: Extraction Ratio

By reducing the volume of extraction fluid, the relative extraction efficiencies of SPLP and methanol should pull apart. Find breaking point where methanol extraction leaches the same mass of PFAS, but SPLP extraction fluid does not.

- Similar idea to LEAF - EPA Method 1316
- Liquid/solid ratios of 20 (SPLP), 10, 5, 2, 1 by mass

PFOA	Ext. Concentration (ng/L)		
Ratio	SPLP	Methanol	Ext. Eff.
20	297.4	293.3	101%
10	598.9	623.5	96%
5	1154.7	1236.8	93%
2	2380.0	2860.0	83%
1	4380.0	5500.0	80%

When does [SPLP]/[Methanol] split?

PFOA	Soil Concentration (ng/kg)			
Ratio	SPLP	Normal	Methanol	Normal
20	5947.9	100%	5865.9	100%
10	5988.9	101%	6235.0	106%
5	5773.6	97%	6183.8	105%
2	4760.0	80%	5720.0	98%
1	4380.0	74%	5500.0	94%

Does methanol still capture full concentration?



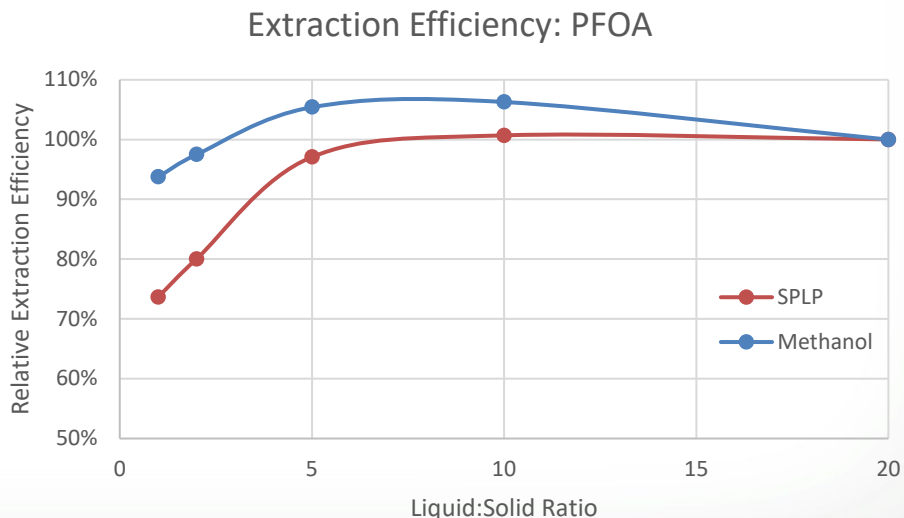
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Summary and Future Work

- With few modifications, SPLP provides an excellent framework for impact-to-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
- Use of more complex extraction fluids may not be necessary for PFAS
- Method may be optimized depending on intended use (e.g., calculating K_d) but further research is needed before specific recommendations

Questions?



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This project would not have been possible without support from the rest of our team.

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