Are Regulatory PFAS Screening Levels Good Enough to Assess the Soil to Groundwater Pathway?

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Prepared by:

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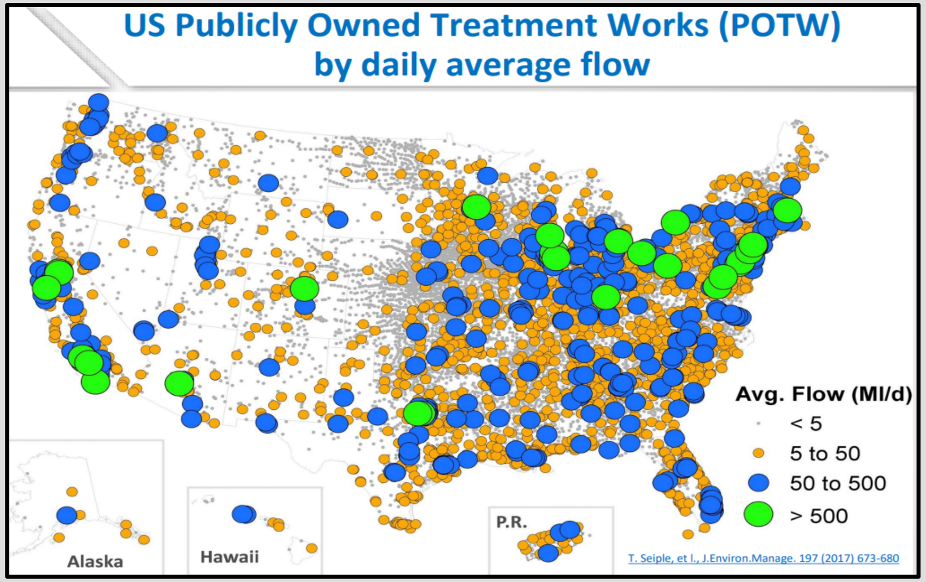
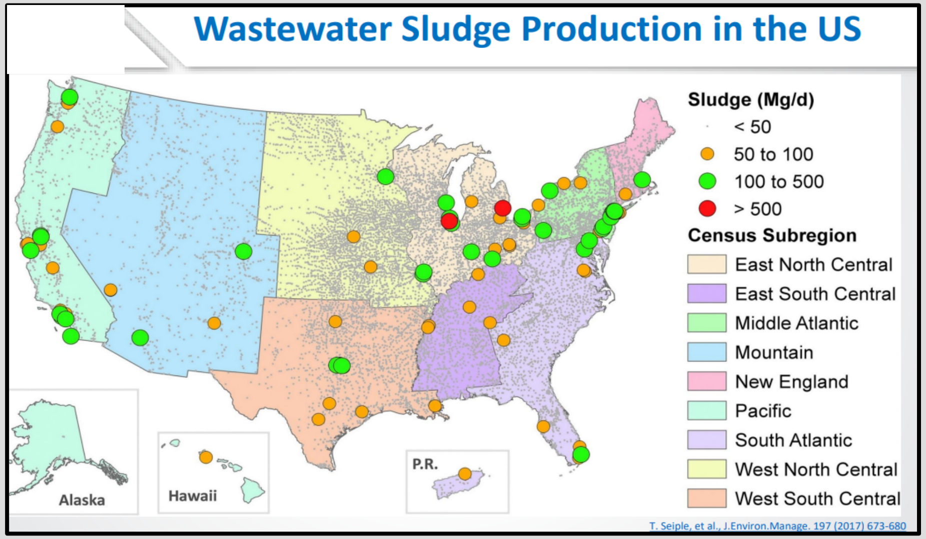
Agenda

- Challenge and Introduction – What's the big deal about soil to groundwater?
- Project Description and Results – What did we do?
- Results Analyses – What did we make of all this sampling?
- Comparisons – How did our results compare to generic and site-specific screening criteria?
- Conclusions - What does all this mean?

Challenge

- **What to do with soil?**
  - Current in practice treatment is landfilling (Subtitle C or similar)
  - Stockpiles of soil are forming for those who know
  - Current disposal pricing $250 – 350 per ton
- **Where are there PFAS impacted solids outside of known release areas?**
  - Construction sites (commercial airports and MILCON)
  - Biosolids land application sites
    - CT recommends biosolid fertilizer <1.4 ug/kg (combined for 5 PFAS)
  - Biosolids generation facilities





Introduction

- Remediation goal development for PFAS sites are underway
  - Risk assessments for direct contact from soil impacts for human health and ecological receptors are more developed
  - Soil to groundwater RGs need development/refinement as well
- Soil to Groundwater RG development has been performed for years
  - USEPA Soil Screening Level (SSL) Equation generic values
  - Site-specific SSL calculations
  - Site-specific modeling
  - Soil leachate analysis
- PFAS has unique properties that affect contaminant flux from soil to groundwater versus other organic compounds
- How do SSL calculations compare to soil leachate analyses?

Introduction - Typical PFAS Release Profile

Source (AFFF in soil, biosolid land applications, etc.)
- Complex chemistry
- Interaction with soil geochemistry and other contaminants
- Source strength function of soil type, infiltration, and PFAS concentration

Transitional (vadose zone)
- Sorption and retardation
- Precursor transformation
- Differential mobility

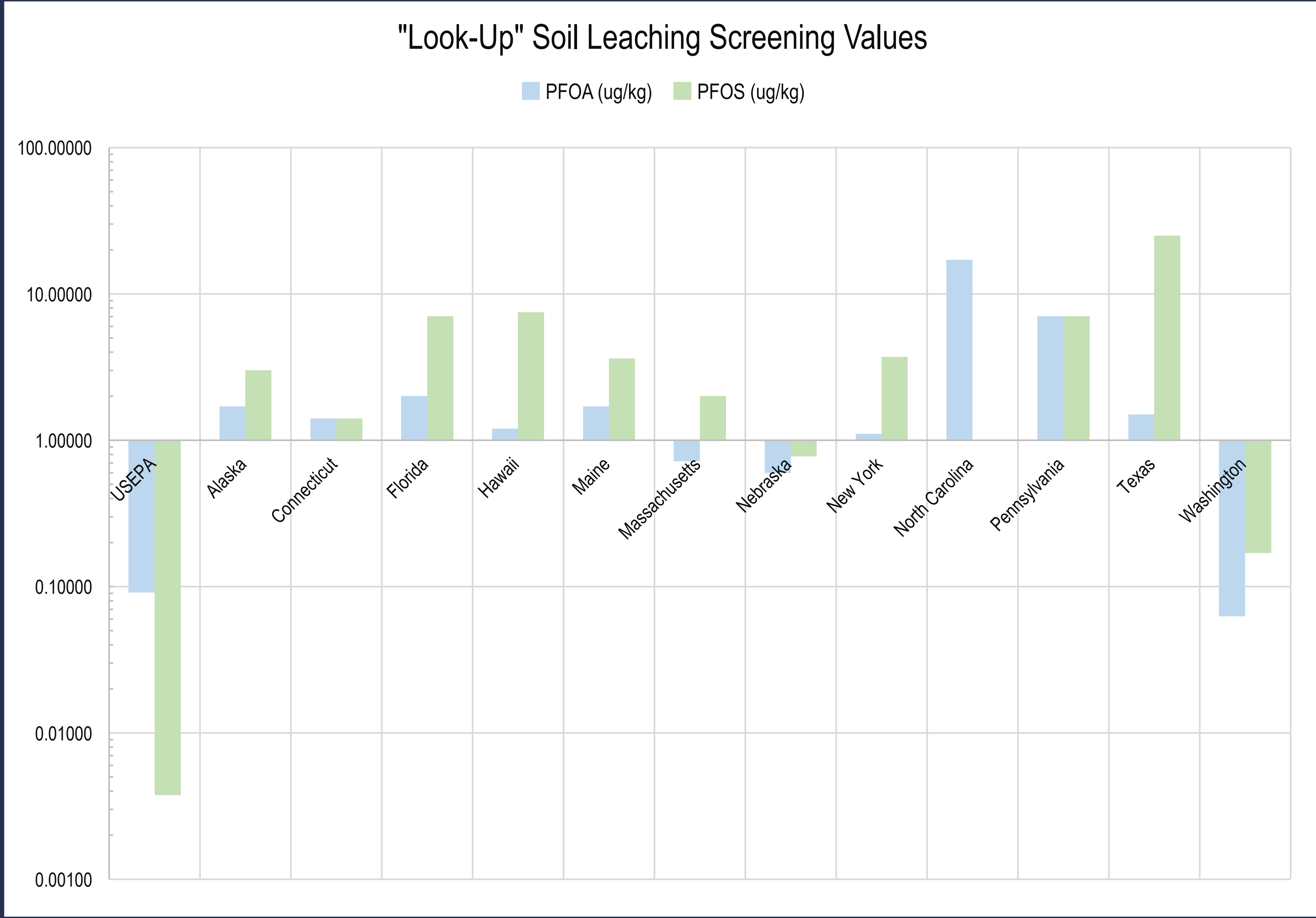
Groundwater or Groundwater interaction with Surface water
- Differential mobility more apparent
- Transformation of precursors can alter chemistry
- Stable terminal end products

Nature of release
- Duration
- Extent
- Type

Soil Type
- permeability
- Clay content
- Organic content
- Moisture profile
- pH

Hydrogeology
- Advective transport
- Geochemistry

Introduction - Comparison of Soil Leaching Values



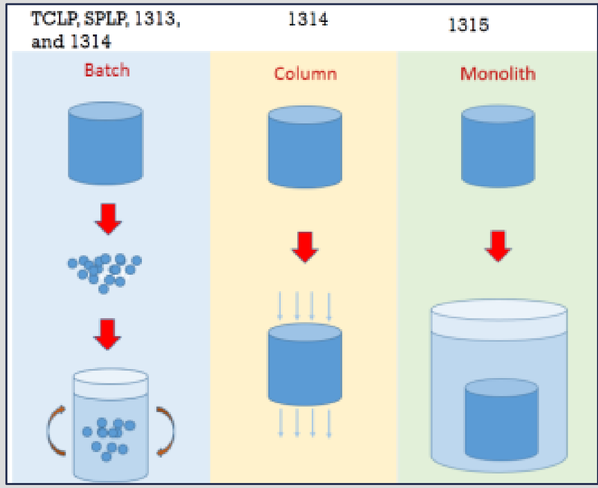
Why are there differences in criteria developed by Agencies?

- **GW criteria utilized**
- **Partitioning coefficients**
- **Selection of target risk-based GW endpoint (HI of 1 or 0.1)**
- **Choice of uncertainty factors**
- **Selection of model or equations**
- **Choice of DAF**
- **Soil type**
- **Climate/hydrogeologic considerations**

***EPA SSLs shown are based on HI of 0.1 and GW RSLs of 4 and 6 ng/L**

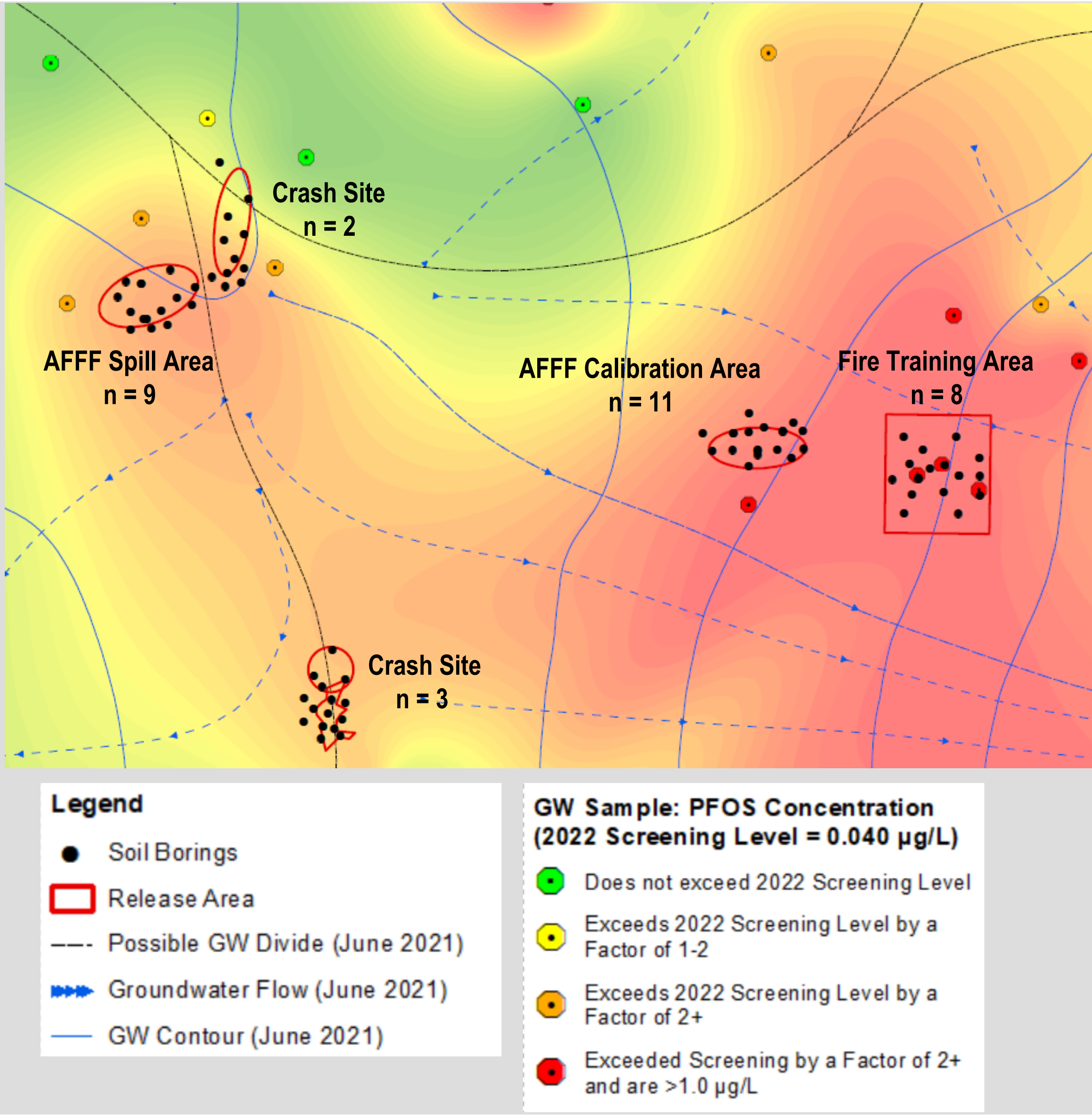
Introduction – Soil Leaching Potential Methods

- Due to uncertainty associated with PFAS in modeling programs (K_{oc} and air-water partitioning), soil-to-groundwater equations and modeling may not be best for evaluating of site conditions.
- Currently, lysimeters and SPLP analysis are used to evaluated site-specific PFAS leaching potential
  - SPLP is cost-effective (ex. NYSDEC requires SPLP for soil to groundwater assessment and can be reasonable worst case)
  - Lysimeters likely to provide better site-specific leachate concentrations but can be problematic in arid environments
- USEPA's Leaching Environmental Assessment Framework (LEAF) is under evaluation as another alternative
  - Widely used for inorganics
  - Two concurrent studies including Dr. Guelfo (Texas Tech University) under SERDP and Dr. Townsend (University of Florida) under Hinkley Center are evaluating LEAF for PFAS



Project/Site Description

- Project consists of a DoD facility with documented AFFF releases to the environment
- Semi-arid environment (rainfall of 16 in./year)
- Five release areas identified for SPLP sampling
  - Previous soil sampling for PFAS confirmed releases
  - 33 SPLP samples (3 dups) collected across release areas
- Concurrent groundwater sampling determined there are likely other release points
  - Groundwater beneath some release sites is affected by known release sites and by unknown source areas

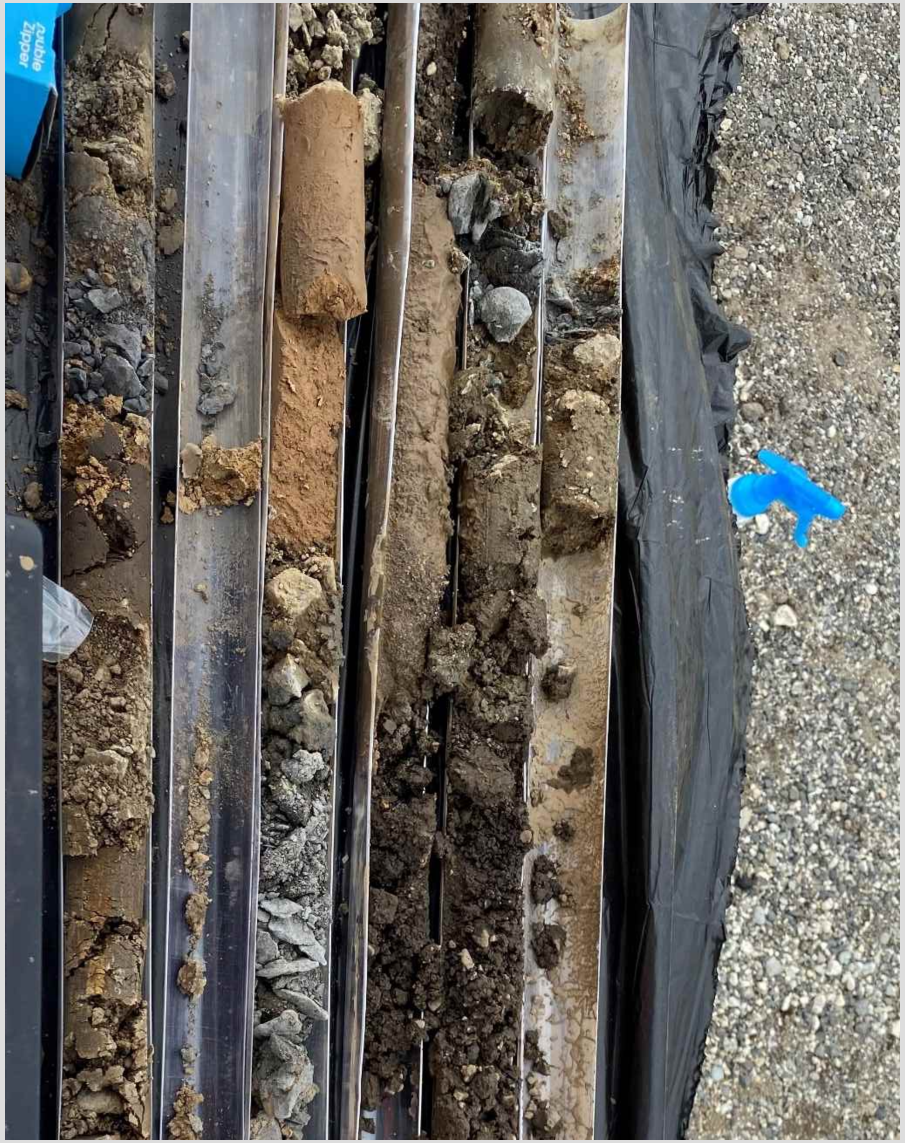


Project/Site Description

- Goal to correlate leachate concentrations from SPLP analysis to soil concentrations that would impact groundwater above 40 ug/L
    - Updated our analyses considering Draft MCLs (4 ppt)
- Soil and groundwater data collected contemporaneously with the SPLP samples

Project/Site Description

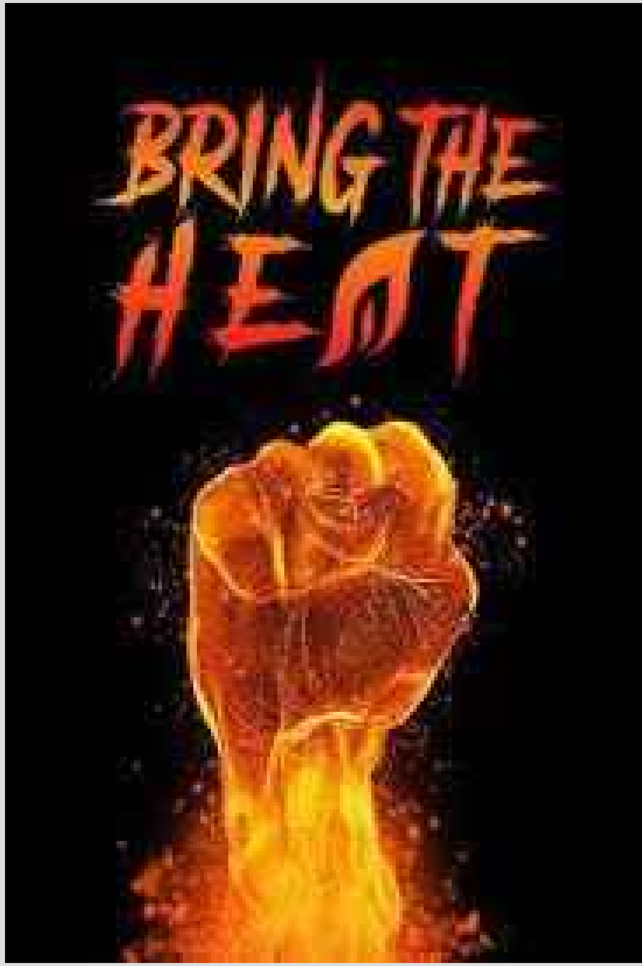
- Previous soil sampling identified 0 – 1 ft bgs as the most impacted at the release areas
  - SPLP sampling from 0 – 1 ft bgs
  - Co-located soil samples for PFAS collected
  - Co-located groundwater grab water table sample for PFAS (21 of 30 locations)
  - One SPLP boring performed from surface to water table
    - 0-1, 2-3, 4-5, 9-10, and 14-15 ft bgs
- Samples analyzed via Modified 537
  - Analyses focuses PFOA, PFOS, PFBS, PFHxS, and PFNA (no Gen-X)
  - Focused on PFAS with screening criteria



Sampling Results

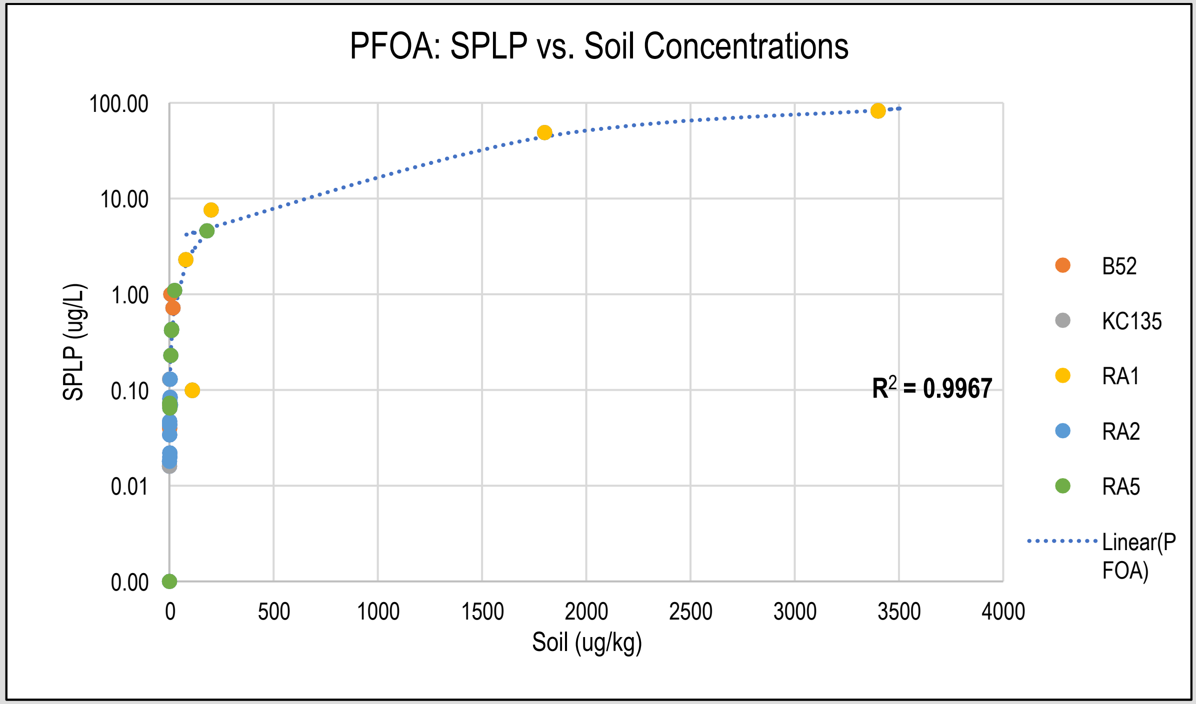
- Sampling focused on source areas soils and groundwater
  - Concentrations in the ppb level - not ppt levels!
  - Limited data variability

	PFOS			PFOA		
	GW (µg/L)	Soil (µg/kg)	SPLP (µg/L)	GW (µg/L)	Soil (µg/kg)	SPLP (µg/L)
Average	27.2	3,837	74.5	4.02	239.6	6.08
Median	13.0	580	14.6	0.96	2.1	0.080
Maximum	73	28,000	350	23	3,400	83



Analyses – SPLP vs Soil

- Surprisingly linear relationship for all 5 PFAS evaluated
  - R^2 range: 0.87 (PFOS) to 0.99 (PFHxS)
- Slope of regression used as indicator of relative leachability rates
- Comparison of leachability to log K_{oc}[1]
  - PFOA relatively leaches the fastest of the five PFAS evaluated
  - Generally correlated (higher $\log_{Koc}$ = less leaching), with the exception of PFBS



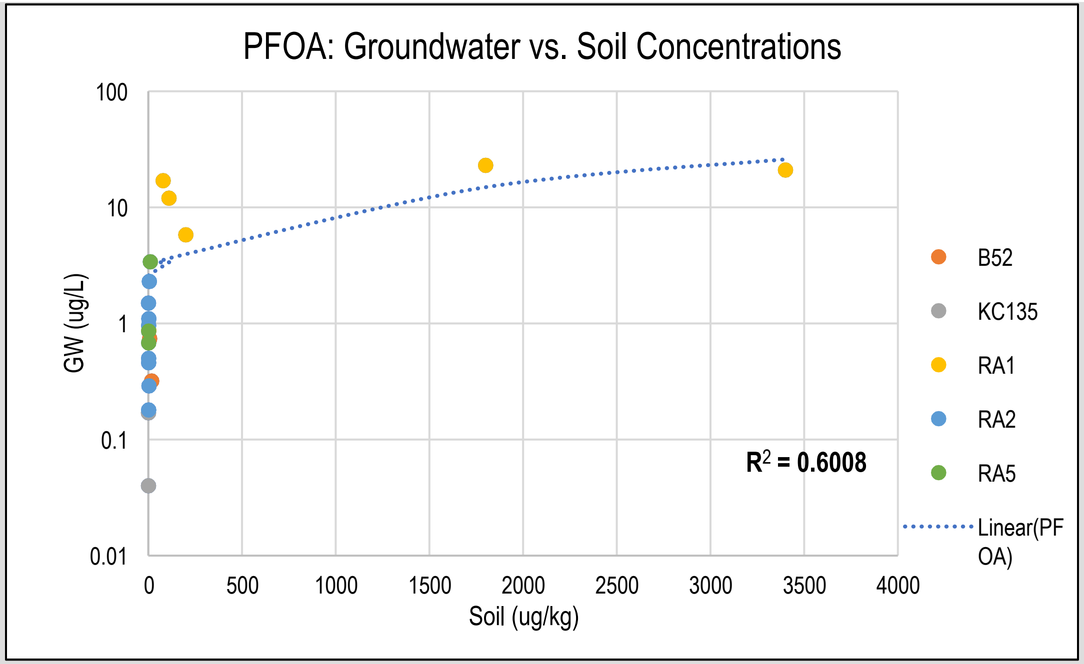
	Slope	$\log_{KOC}$	conversion factor (soil concentration/SPLP)
PFOA	2.46E-02	2.92	40.65
PFHxS	2.24E-02	2.66	44.64
PFNA	1.89E-02	3.6	52.91
PFOS	1.54E-02	3.58	64.94
PFBS	9.70E-03	2.55	103.09

Sorted by slope (greatest to smallest)
Greater slope = more leaching
Lesser slope = less leaching

1 – Log K_{oc} values from ITRC Physical and Chemical Properties Table 4-1 for select PFAS Excel file (updated October 2021)

Analyses – Groundwater versus Soil

- Correlation for all 5 PFAS evaluated was moderate
  - R^2 range: 0.41 (PFOS) to 0.60 (PFOA)
- Likely groundwater impacts from upgradient sources affect groundwater results for source area assessed
  - Attempted to tease out PFAS groundwater flux did not improve correlation
- Relative leachability correlates well to the $\log_{Koc}$
- Calculated conversion factor could be used to estimate soil concentrations that yield groundwater regulatory exceedance

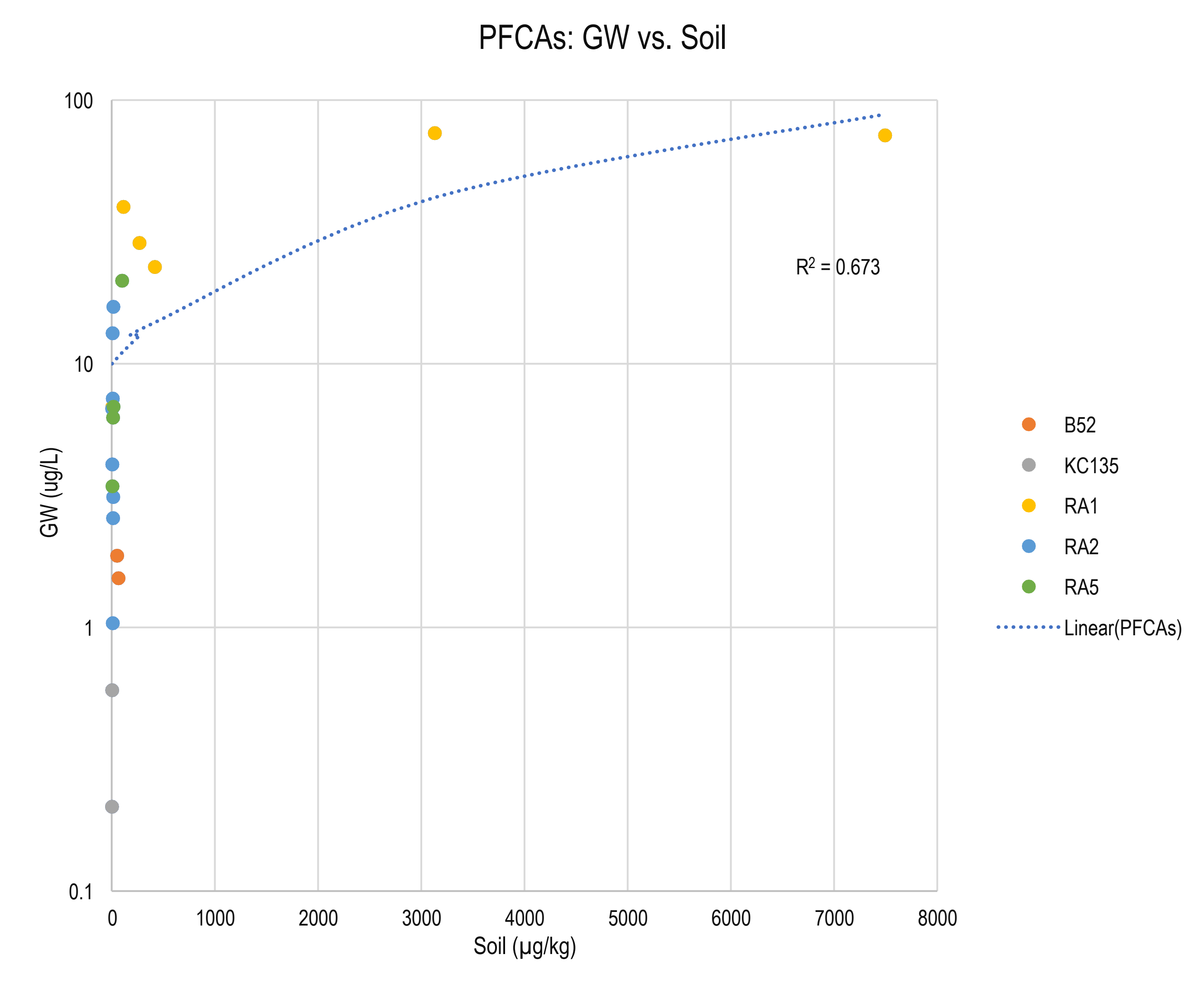


	Slope	$\log_{KOC}$	Conversion factor (soil concentration/GW) (L/kg))
PFOA	6.90E-03	2.92	144.93
PFBS	6.20E-03	2.55	161.29
PFHxS	4.30E-03	2.66	232.56
PFNA	3.50E-03	3.6	285.71
PFOS	2.10E-03	3.58	476.19

Sorted by slope (greatest to smallest)
Greater slope = more leaching
Lesser slope = less leaching

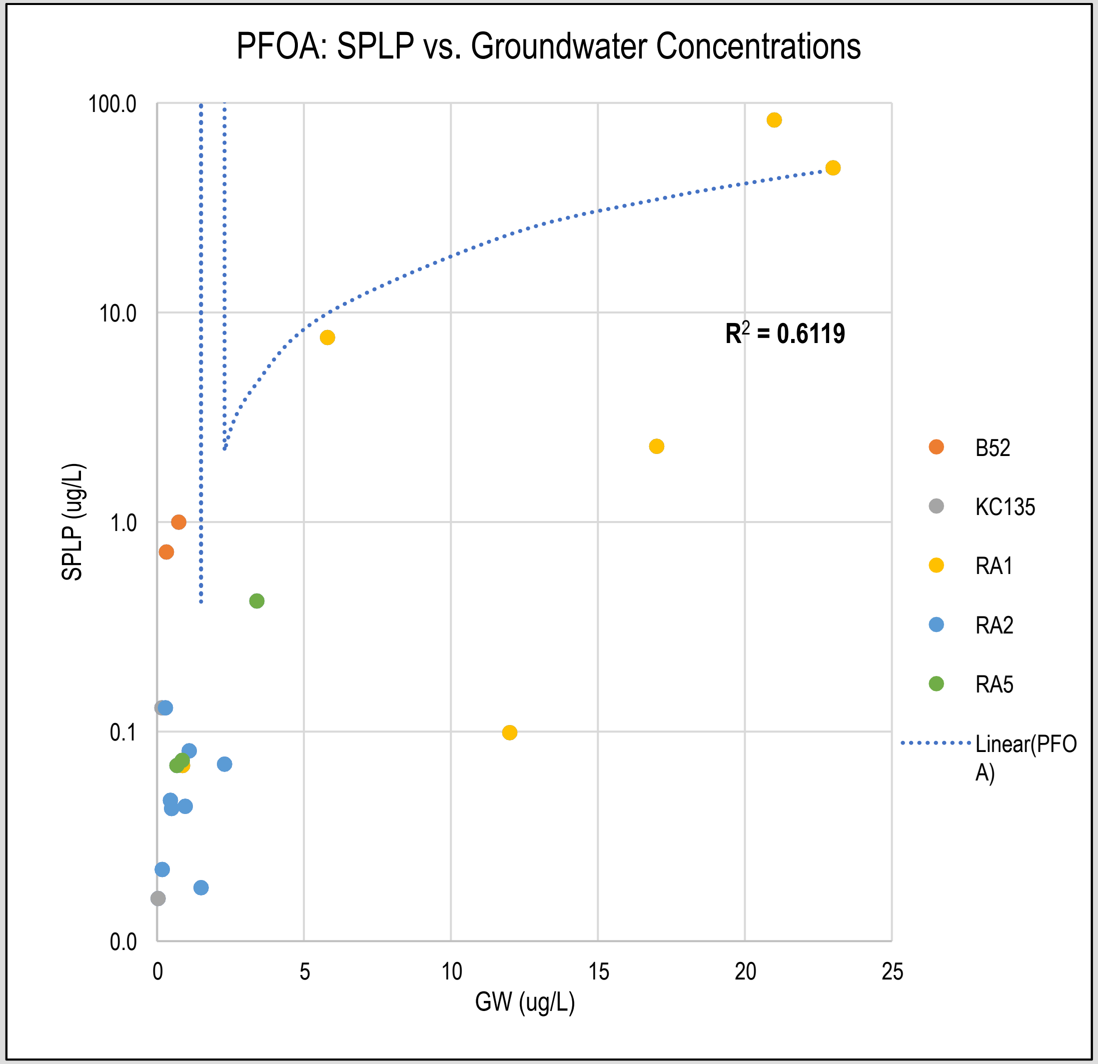
Analyses – Groundwater versus Soil

- Limiting regression to PFCAs improves correlation ($r^2 = 0.67$)
- Weaker correlation in regression of individual analytes ($r^2 = 0.41$ to 0.60) may be partially attributed to biotransformation
  - Available data does not include precursors or intermediates
  - Limiting to PFCAs reduces influence of biotransformation



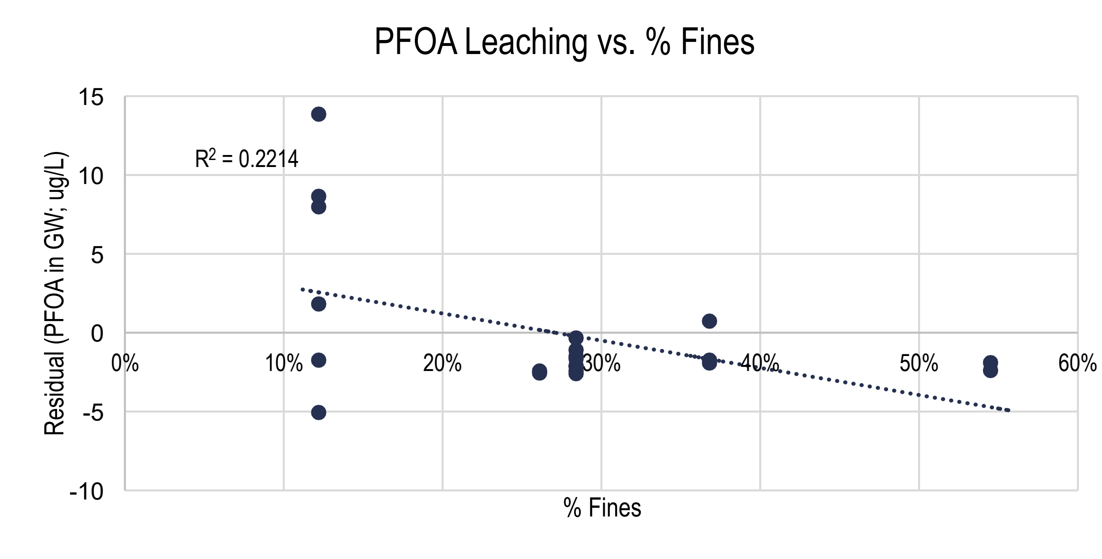
Analyses – SPLP versus Groundwater

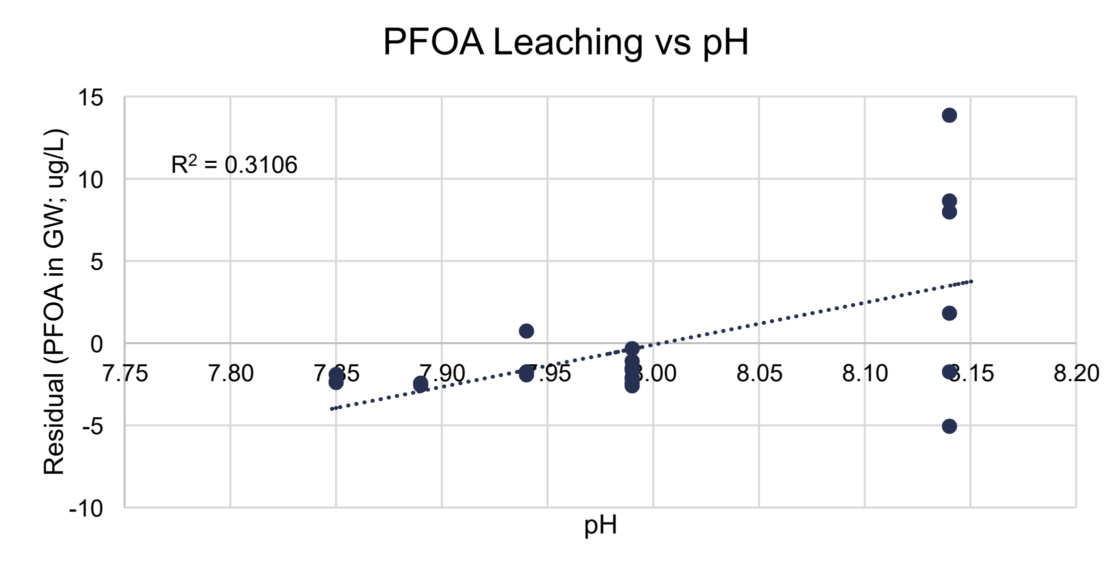
- Correlation for all 5 PFAS evaluated was moderate
  - R^2 range: 0.47 (PFOS) to 0.66 (PFBS)
- Likely groundwater impacts from upgradient sources affect groundwater results for source area assessed
  - Attempted to tease out PFAS groundwater flux, did not improve correlation
- Average Dilution Attenuation Factor (SPLP/GW concentration) = 0.8 to 2.6 (PFOA/PFOS) indicating little dilution of SPLP leachate to groundwater



Analysis – Assessment of Soil Variables on Leachability

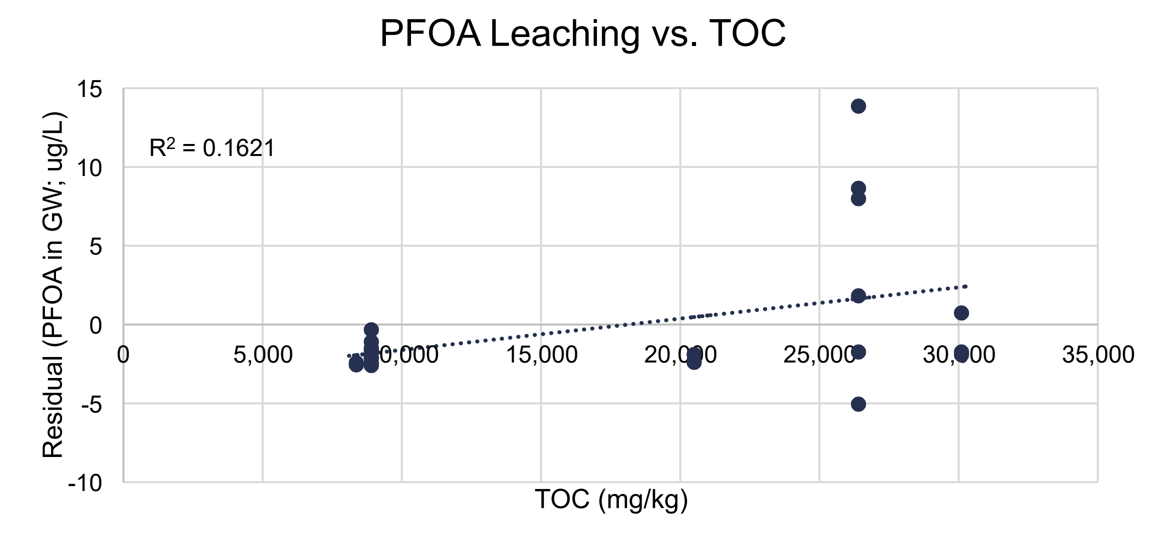
- Leachability compared to TOC, moisture content, pH, and clay content (% fines) using residuals from GW vs. Soil regression
  - Strongest correlation associated %fines
    - Higher clay content associated with lower leaching potential (negative residual)
  - Limited variation for pH – no trend assessment viable

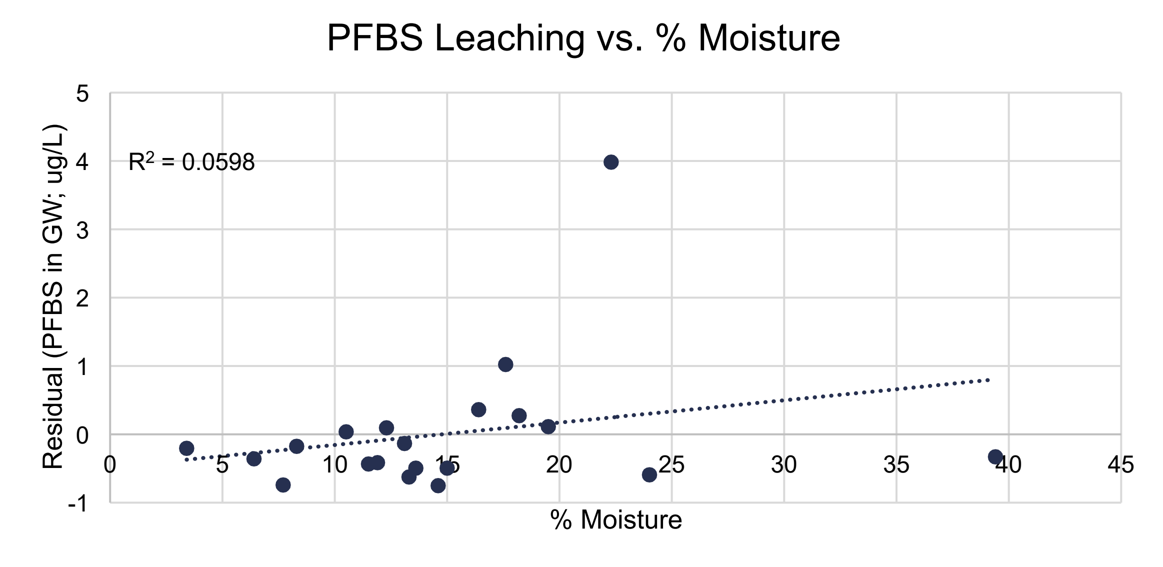




Analysis – Assessment of Soil Variables on Leachability

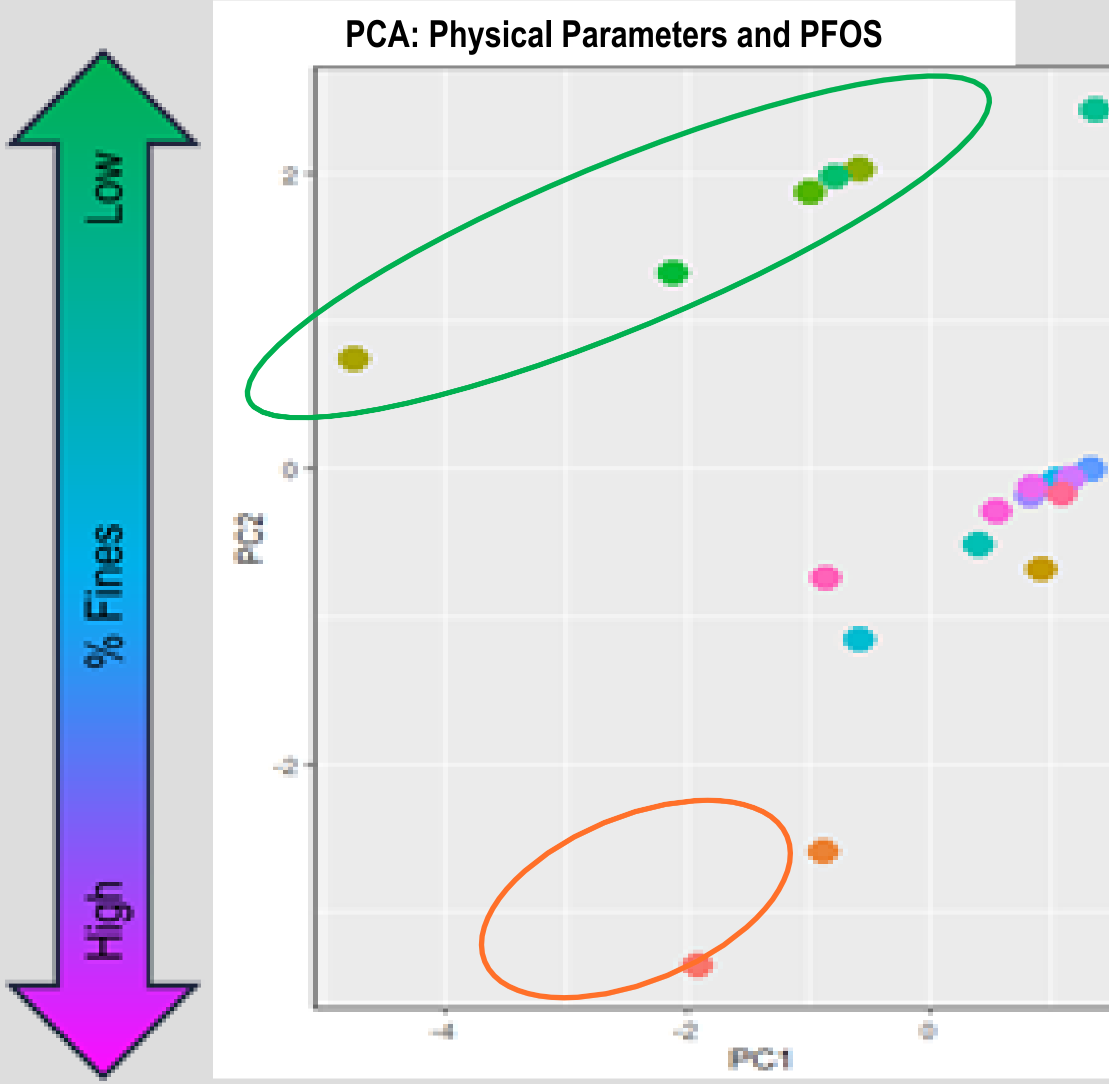
- **Weak correlation associated with TOC and moisture content**
- **Clay content, pH, TOC, and moisture likely impact leachability; however, data limitations include:**
  - **Only one historical measurement of TOC, pH, and clay content available per source area**
  - **Impact of upgradient sources on GW concentrations is not clear**
- **Higher variance associated with Release Area 1 appears to bias regressions**
  - **Standardized residuals did not improve regressions**





Principle Component Analysis: Physical Parameters

- Principle Component Analysis (PCA) performed on physical parameters and PFOS
  - TOC, moisture content, pH, and clay content (% fines)
  - PFOS analyzed as ratio of soil to water concentration
- PCA indicates three groupings, two of which are distinct release areas
  - PC2 driven primarily by %fines
  - Suggests variations in physical properties may contribute to variations in leachability between source areas



$$d = (0.0112L^2)^{0.5} + d_a\{1 - \exp[(-LI)/(Kid_a)]\}$$

Analyses – EPA SSL Calculations

- EPA SSL model used to develop risk-based, source-area-specific SSL
- Calculated mixing zone depth and dilution factor for each source area using:
  - Source length (L)– based on exceedances of HHRA SL for PFOS
  - Infiltration rate (I) – literature value
  - Aquifer hydraulic conductivity (K) – interpreted from slug tests
  - Hydraulic gradient (i) – calculated using static water levels
  - Aquifer Thickness (d_a) – from CSM based on historical well logs
- Source-area-specific SSLs developed using mixing zone depth as well as:
  - Target leachate concentration (remediation goal * calculated dilution factor)
  - Depth of source (d_s) – based on exceedances of HHRA SL for PFOS
  - Infiltration rate (I) and soil bulk density (ρ_b) – literature values
  - Exposure duration (ED) – assumed 70 years based on EPA guidance

Analyses – EPA SSL Calculations

- Calculated dilution attenuation factors for five source areas range from 1.2 to 3.2
- SSL for PFOS/PFOA first calculated using target leachate concentration of Draft MCL x Dilution Factor
  - SSLs range from 0.07 to 0.1 ug/kg
- SSL model used to back calculate soil concentration associated with SPLP concentration
  - SPLP concentration input as target leachate value
  - Predicted soil concentrations of PFOS ranged from 10-28% of measured soil concentrations

	Area 1	Area 2	Area 3	Area 4	Area 5
Mixing Zone Depth (m)	9.60	13.26	24.47	5.50	13.25
Dilution Factor (unitless)	1.12	1.58	1.38	3.15	1.08
SSL (PFOS/PFOA for Draft MCL) (ug/kg)	0.02	0.02	0.07	0.1	0.01
Calculated/Measured Soil Conc. - PFOA	10.42%	14.45%	47.42%	27.20%	12.31%
Calculated/Measured Soil Conc. - PFOS	10.61%	10.40%	28.17%	21.97%	10.32%

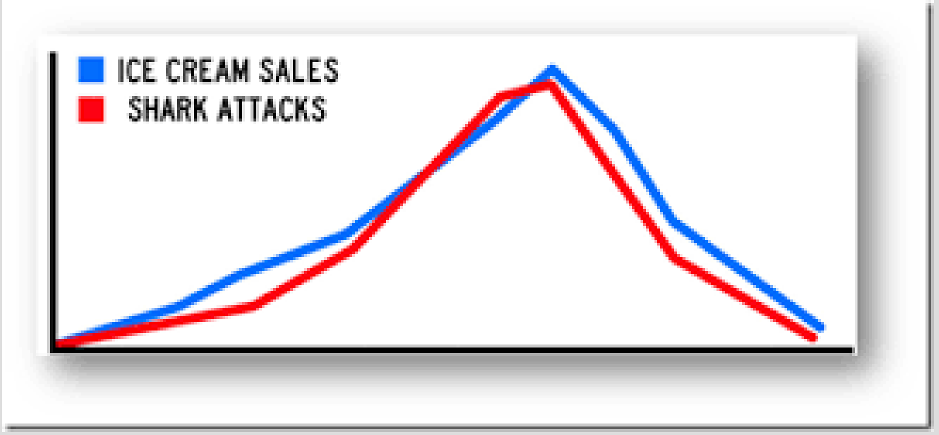
Conclusions – SPLP and SSL Comparisons

- SPLP data reasonable assessment of PFAS leachate to groundwater
  - Limited correlation of soil to groundwater and SPLP to groundwater suggests other PFAS-soil interactions are not well accounted and reduce leaching to groundwater.
  - SPLP results are likely biased high versus actual leaching – dilution attenuation factor results comparisons support (20 – 30%?)
- Site-specific use of the EPA SSL equation consistently overestimates PFAS leaching from soil concentrations by 3.5-10x
- Extrapolation of soil/groundwater ratios from site-specific
  - PFOS SSL = 18.5 ug/kg (EPA Look-up Value = 0.004 ug/kg)
  - PFOA SSL = 3.2 ug/kg (EPA Look-up Value = 0.092 ug/kg)

Conclusions – SPLP and SSL Comparison

- State generic soil leaching criteria closer to site-specific estimated results; however; state criteria generally based on higher groundwater standards
- Comparison of West Coast versus East Coast sites
  - West coast (arid and fine-grained materials) – 3 to 18.5 ug/kg
  - East coast (temperate climate with coarse grained sands) - 1 – 10 ug/kg
- Nice to Have!
  - Find upgradient soil for SPLP sampling to confirm estimated SSLs (i.e., less than 100 ug/kg PFOA/PFOS)
  - Collect lysimeter samples for comparison – quantify degree of bias

Correlation or Coincidence?



Thank You!

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