UF Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

Hinkley Center for Solid and Hazardous Waste Management

Characterization and Management of Per- and Polyfluorinated Alkyl Substances (PFAS) Remediation Residuals

Technical Advisory Group Meeting

May 26th, 2022

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE

Meeting Overview and Agenda

- Introduction
- PFAS background
- State of management and regulation
- Results of contaminated soil leaching
- Results of bulked PFAS-containing liquids leaching
- Open for discussion from technical advisors
- Conclude meeting

Key West firefighters applying AFFF during a training class

Previous Hinkley Center Work

TITLE: "PFAS Releases from Landfills in Florida"

FUNDING SESSION - 2019

PRINCIPAL INVESTIGATOR - "Helena Solo-Gabriele"

Per- and poly-fluorinated alkyl substances (PFASs) are found in consumer products that are stick and stain resistant such as Teflon, sealants, textiles, and paper products. PFASs are also known to affect human health. They are linked to thyroid and liver diseases, diseases of the immune system, and cancer. Given their wide ranging usage in consumer products and their long-term environmental persistence, landfills represent a logical end-of-service-life reservoir where PFASs can be ultimately removed from the environment to minimize subsequent human health impacts. Recent prior research supported through the Hinkley Center with in-kind support through the U.S. EPA has shown that PFASs are released in the leachates from landfills in Florida. However, no work has yet been done to quantify the amount of PFAS found in landfill storm water and groundwater. In addition, a mass balance analysis is lacking to quantify how much PFAS (kilograms per unit time) is released at landfills, through leachate, storm water, and groundwater. The objectives of this proposal are to: a) expand the sampling program for PFAS to include additional PFAS species in leachates plus the inclusion of storm water and groundwater at landfills, and b) conduct a mass balance analysis of PFAS at landfills using a readily-available landfill modeling software combined with PFAS measurement data. The results will be used to focus efforts in terms of treatment of potential water sources at landfills that carry PFAS.

PFAS Background

- PFAS are a group of over 4,000 compounds that are ubiquitous in industrial and consumer products
- PFAS are toxic, mobile in the environment, and extremely resistant biodegradation
- This combination has sparked regulatory agencies to develop standards to limit exposure to PFAS
- Focus was originally on drinking water, but recently more soil-based limits have been developed

Regulation

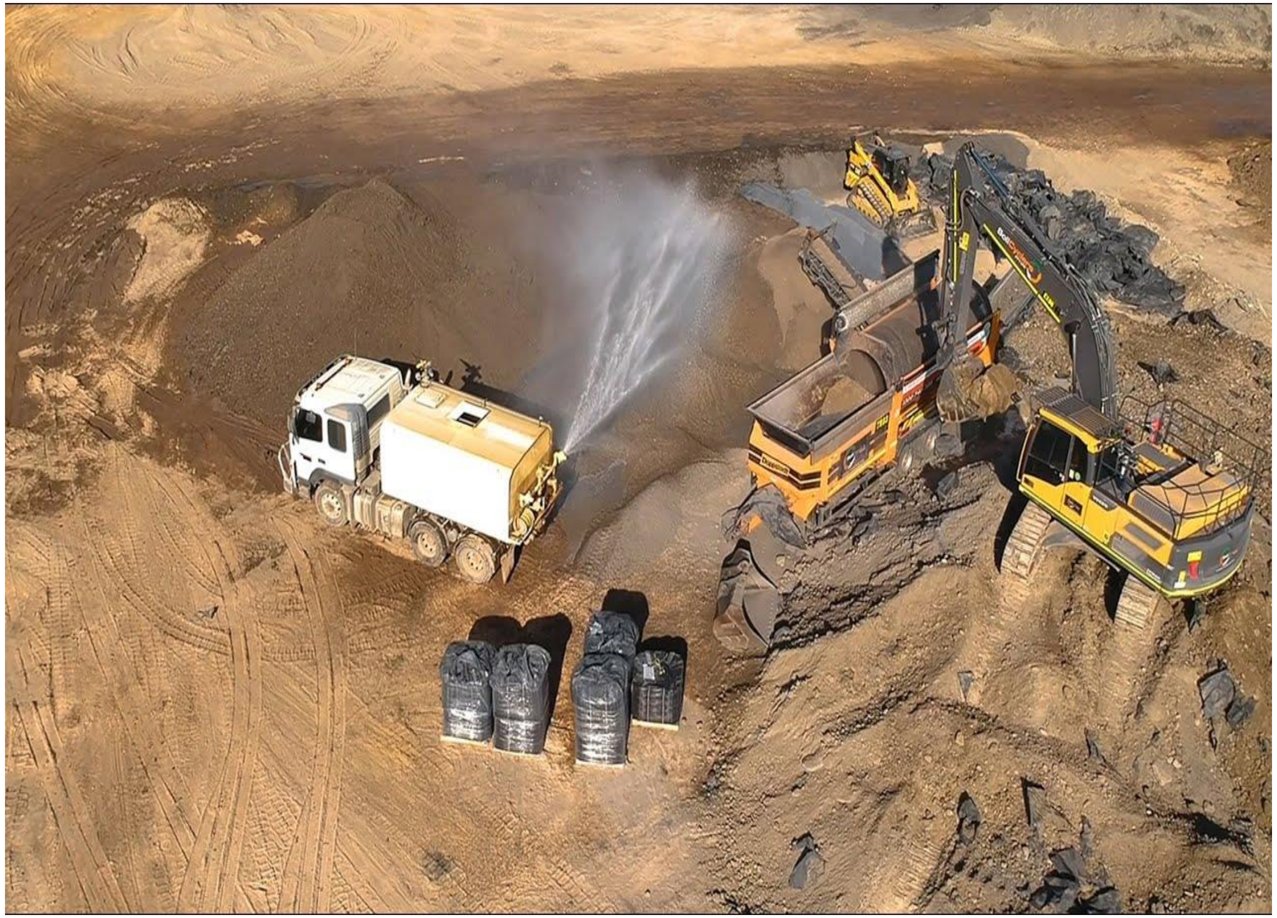
- In the last five years, regulations or advisories have been developed for PFAS impacted soils (EPA, Florida, Texas, Maine, Michigan, and New York)
- EPA Reginal Screening levels (RSLs) for PFOS,PFOA, PFBS, PFHxS, PFNA, and GenX
- FDEP Provisional Soil Cleanup Target Levels (PSCTLs) for PFOS and PFOA
- New regulations push remediation efforts

Compound	RSL Residential (mg/kg)	RSL Industrial (mg/kg)	FDEP Provisional SCTL Residential (mg/kg)	FDEP Provisional SCTL Industrial (mg/kg)
HFPO-DA (Gen-X)	0.23	3.5		
PFBS	19	250		
PFHxS	1.3	16		
PFNA	0.19	2.5		
PFOS	0.13	1.6	1.3	25
PFOA	0.19	2.5	1.3	25

Remediation and Waste Management

- EPA's interim guidance report on the management of PFAS-containing wastes suggests landfilling or thermal treatment of remediation residuals

- Management options
  - Landfilling (containment)
    - PFAS shown to migrate to landfill leachate (Solo-Gabriele, 2019)
  - Thermal treatment (destruction)
    - Not currently done on a commercial scale- research is still needed on the creation of PICs



Remediation of AFFF-impacted site (Rembind, 2019)

Questions That Need Answers

1. How do risk-based leachability thresholds compare to laboratory leaching data on contaminated soils?

2. How do you best manage PFAS-containing wastes?

   - Originally planned to investigate thermal destruction conditions of AFFF-impacted soils
   - Pivoted to exploring the management of PFAS-containing liquid wastes

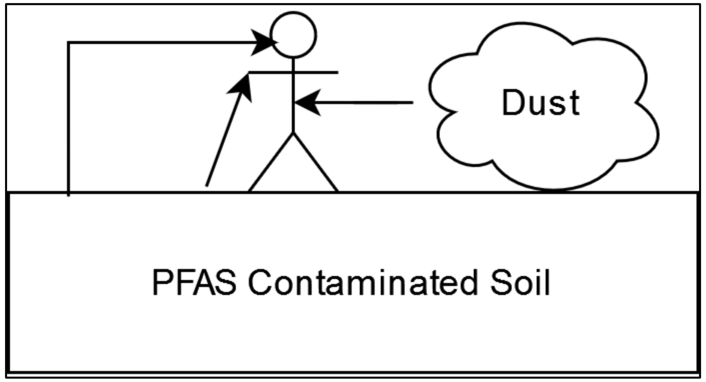
How do risk-based leachability thresholds compare to laboratory leaching data on contaminated soils?

Risk-Based Thresholds

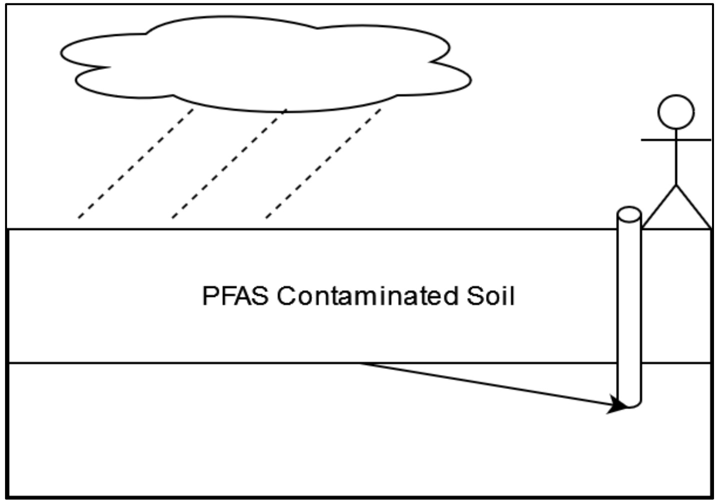
- In recent years, soil screening levels have been developed for certain PFAS to evaluate the risk of both direct exposure and contamination of groundwater through leaching (EPA, 2022; FDEP, 2019)

- Leachability-based cleanup levels are typically orders of magnitudes lower than direct exposure
  - E.g., 1.3 mg/kg direct exposure vs .002 mg/kg PFOA leachability (FDEP)
  - E.g., 0.13 mg/kg direct exposure vs 0.000038 mg/kg PFOS leachability (EPA)

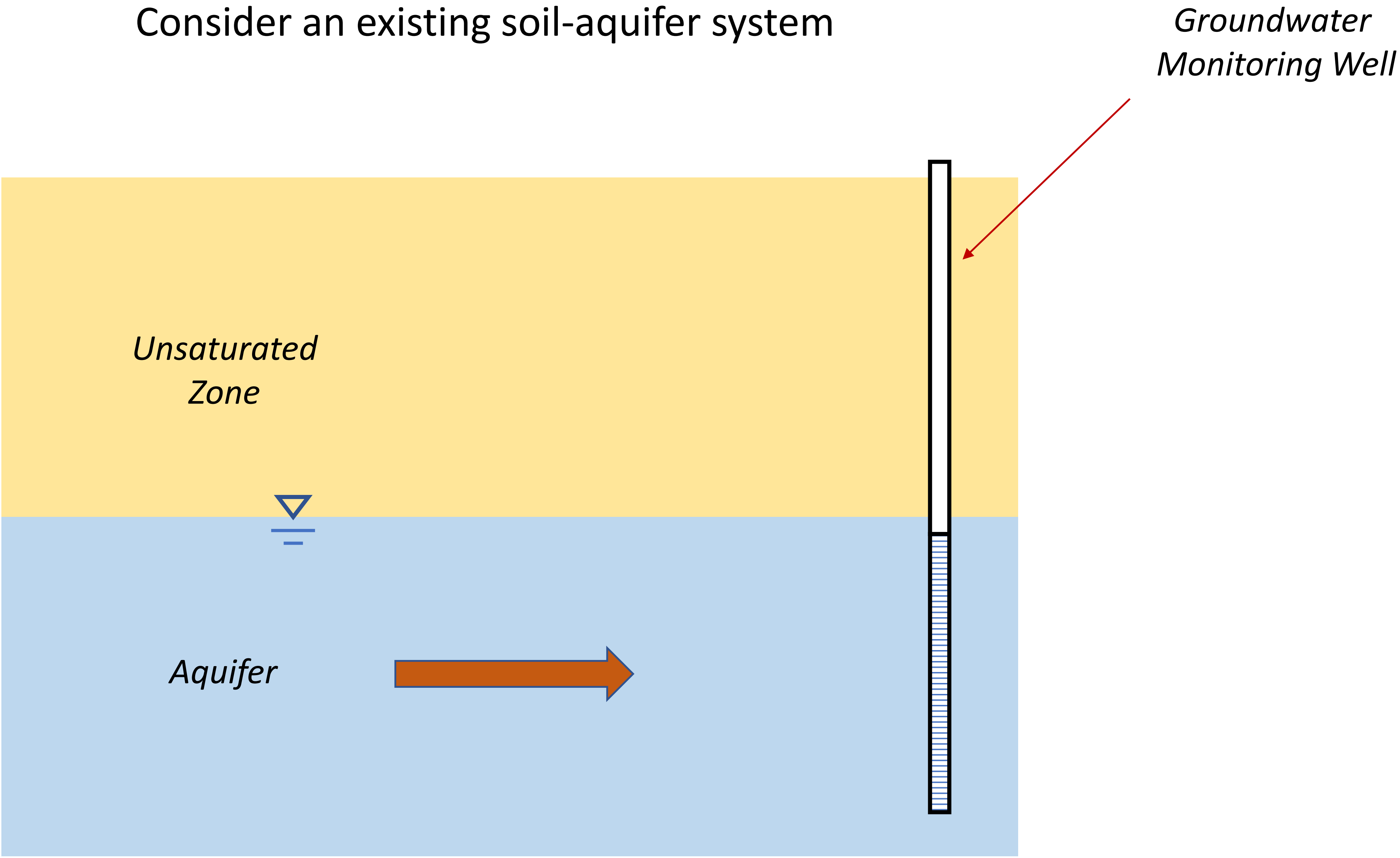
Direct Exposure

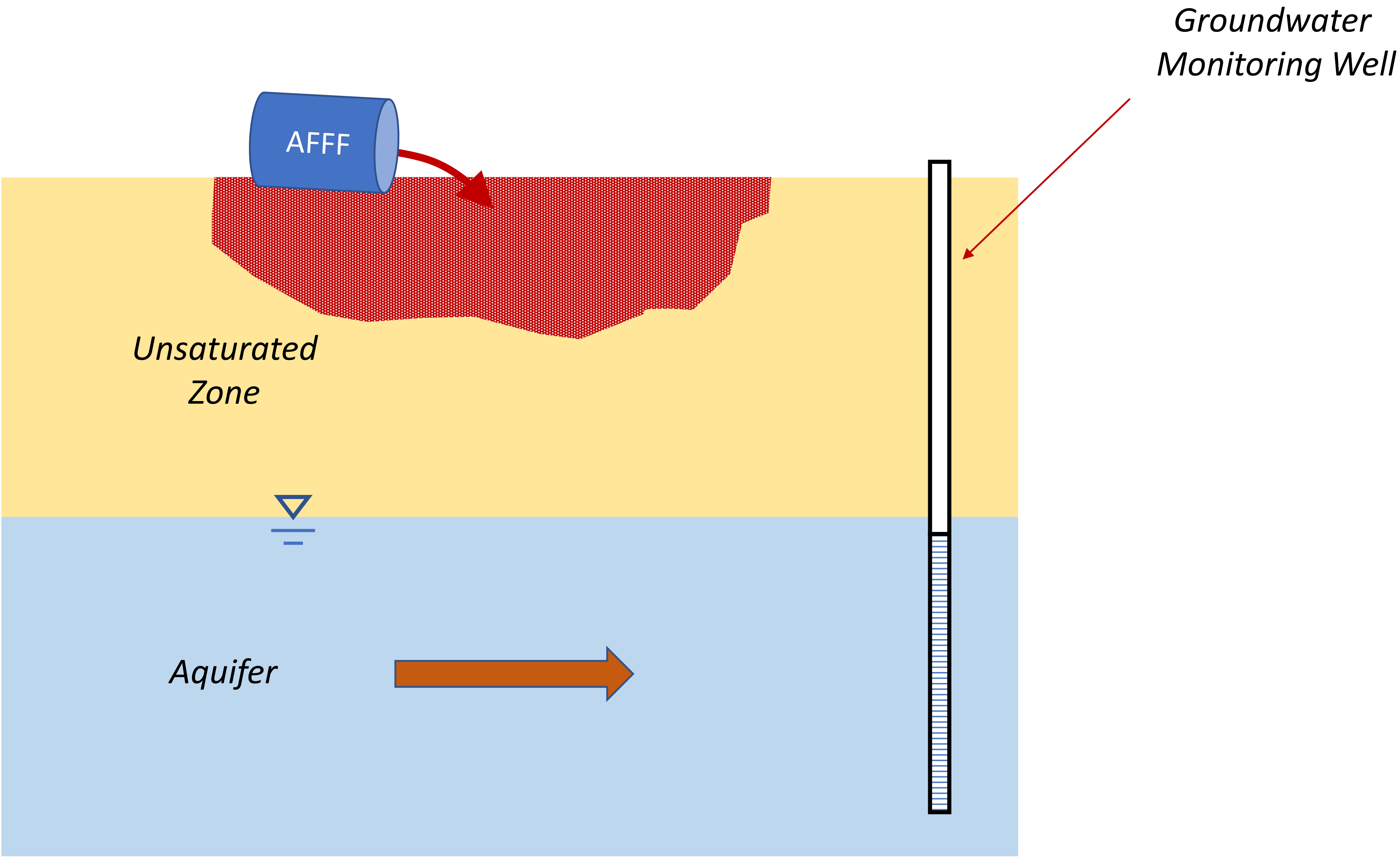


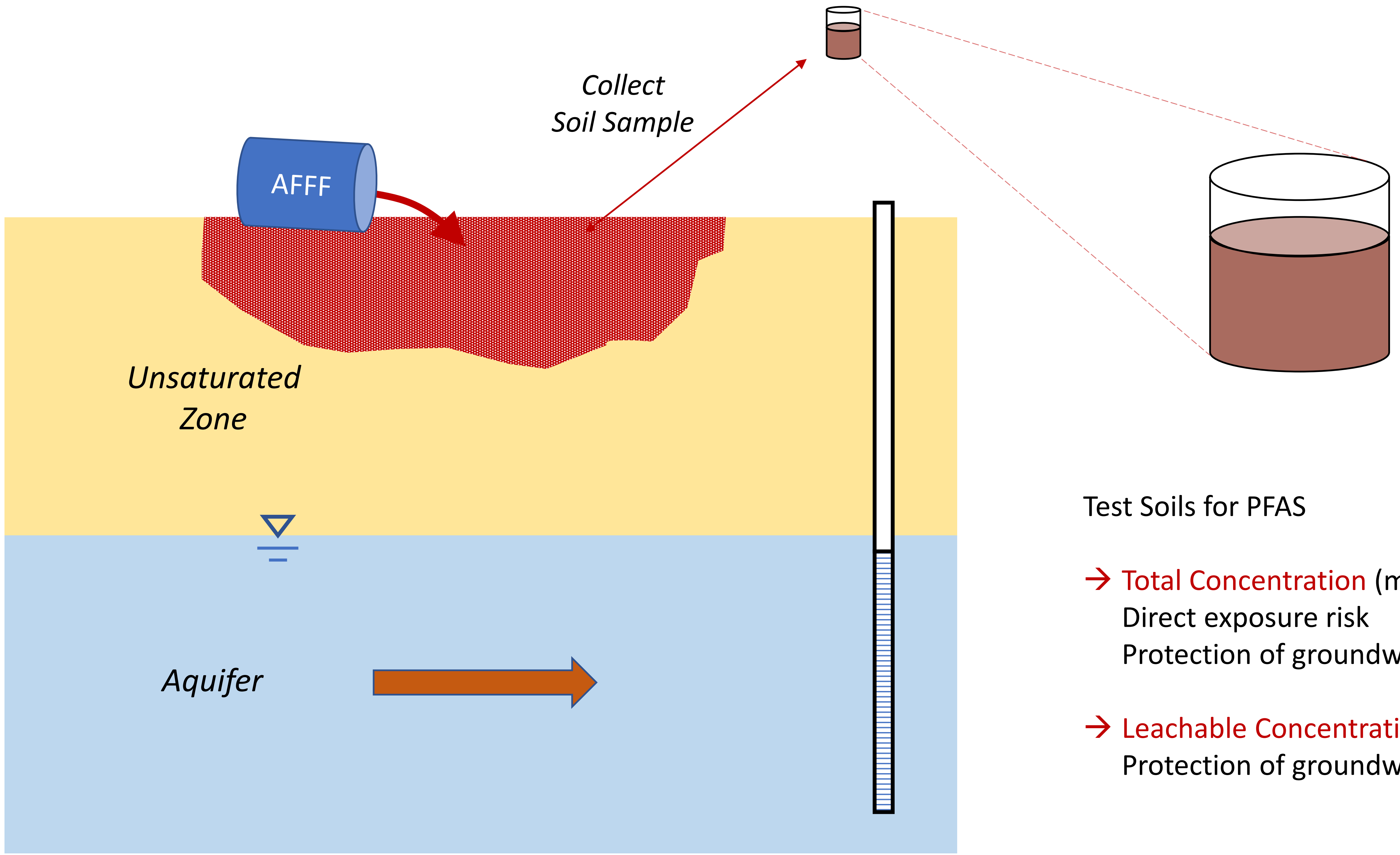
Leachability



Consider an existing soil-aquifer system




Groundwater
Monitoring Well
AFFF
Unsaturated
Zone
Aquifer

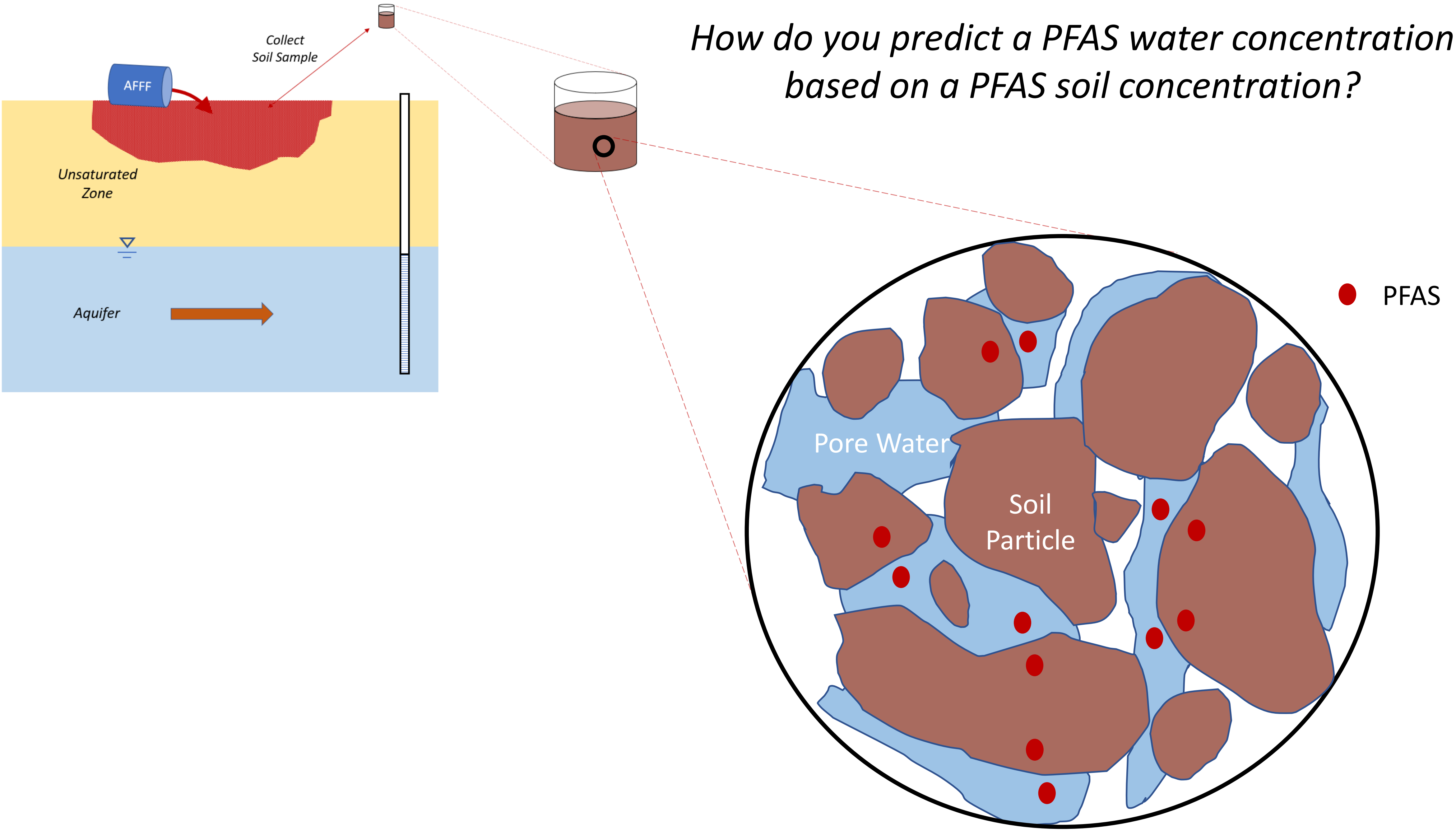


Test Soils for PFAS

→ Total Concentration (mg/kg)
Direct exposure risk
Protection of groundwater

→ Leachable Concentration (mg/L)
Protection of groundwater

How do you predict a PFAS water concentration based on a PFAS soil concentration?



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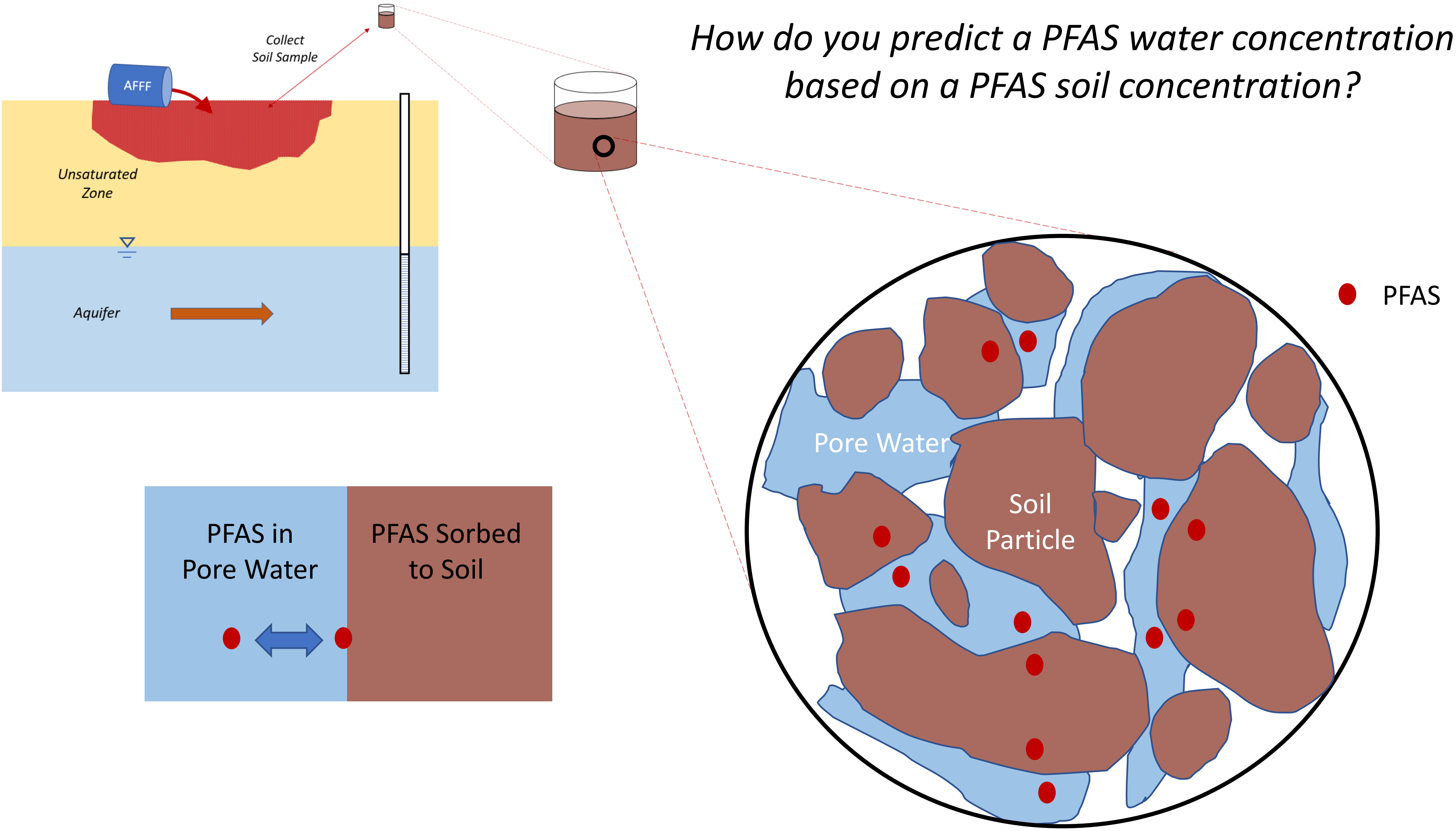

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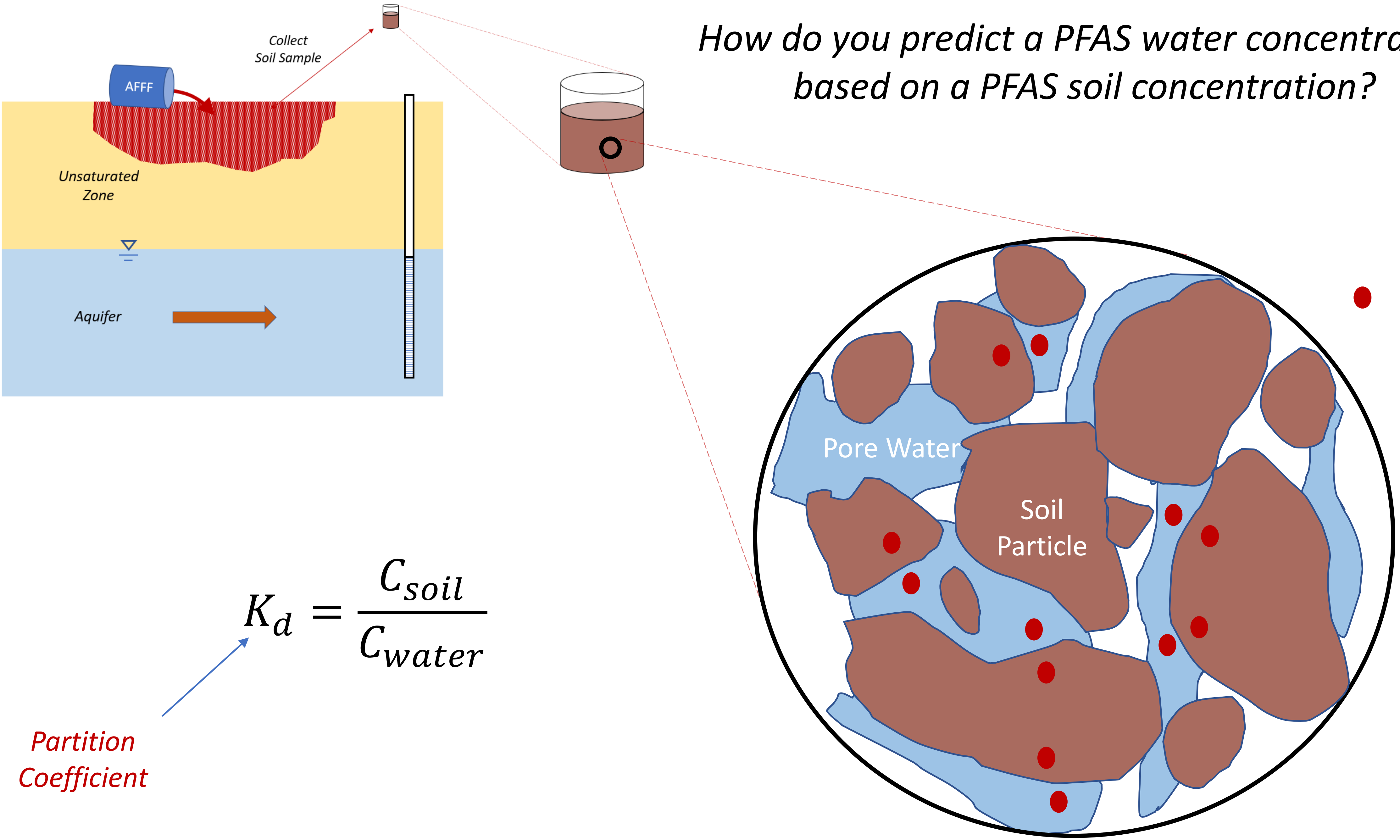


$$K_d = \frac{C_{soil}}{C_{water}}$$

Partition Coefficient

*Equation for the Soil Cleanup Target Level for Protection of Groundwater**

Note: Same approach used for US EPA Regional Screening Level

$$SCTL = GCTL \; x \; DF \; x \left[K_d + \frac{\theta_w}{\rho_b} \right]$$

Soil Cleanup Target Level for Protection of Groundwater (mg/kg)

Groundwater Cleanup Target Level (mg/L)

Dilution Factor

Partition Coefficient (L/kg)

Ratio of Water to Soil (L/kg)

** Note, this is simplified to neglect gas phase pollutant*

Simplify Equation

$$C_{Water} = \frac{C_{Soil}}{K_d + LS}$$

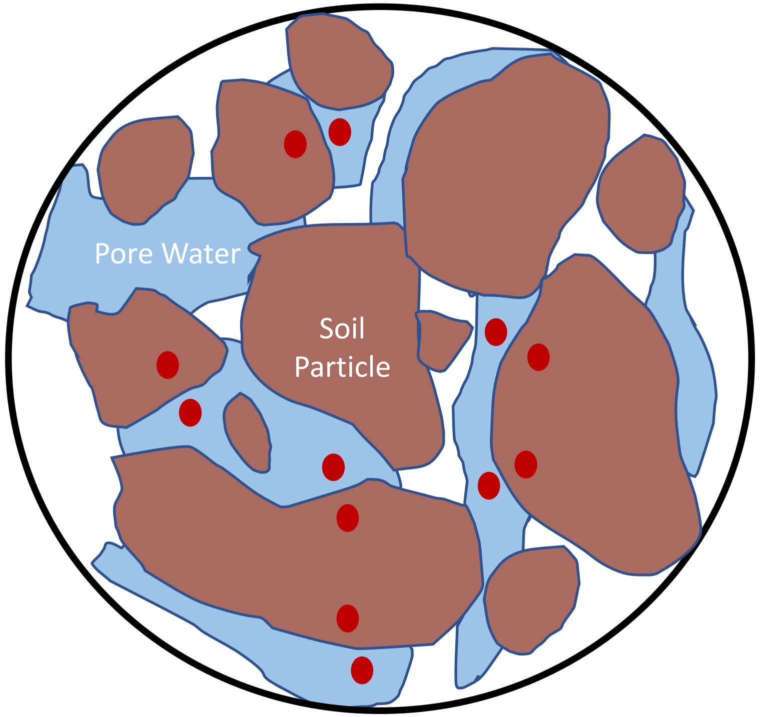
PFAS Concentration in Soil (mg/kg)

PFAS Concentration in Water (mg/L)

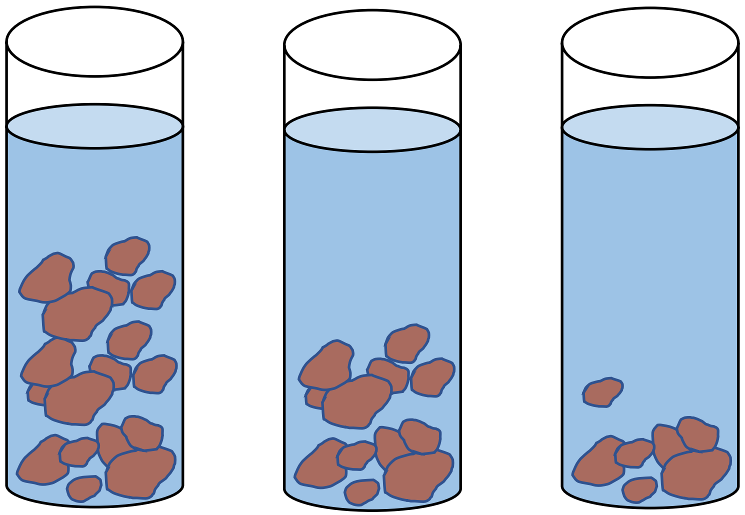
Partition Coefficient (L/kg)

Liquid to Solid Ratio (L/kg)

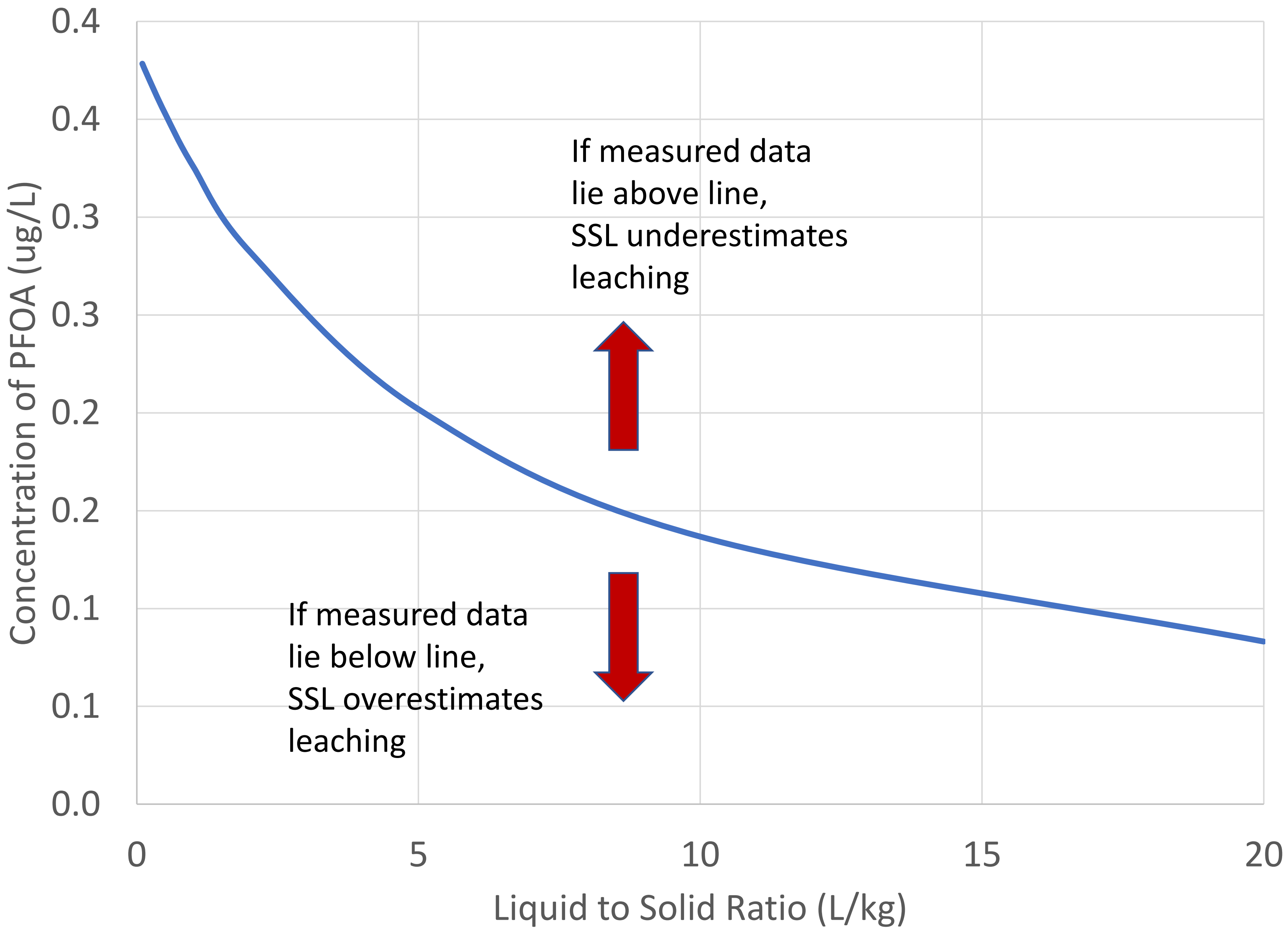
Opportunity for Comparison



Measure concentration of PFAS
in AFFF-contaminated soil and compare
to SCTL/SSL for protection of groundwater

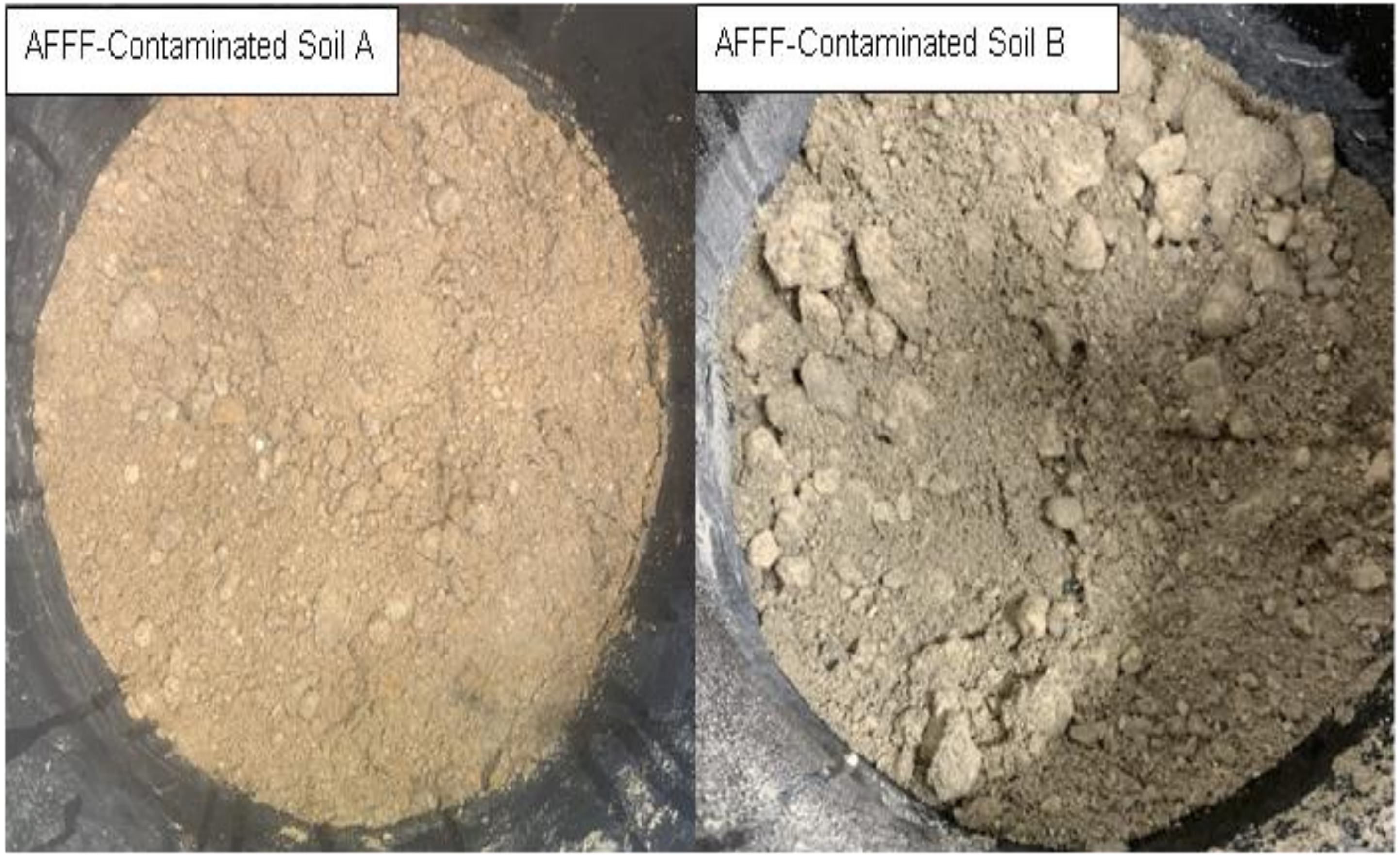


Perform leach tests on the same soil,
measure PFAS concentrations in the leachate,
and compare to GCTL

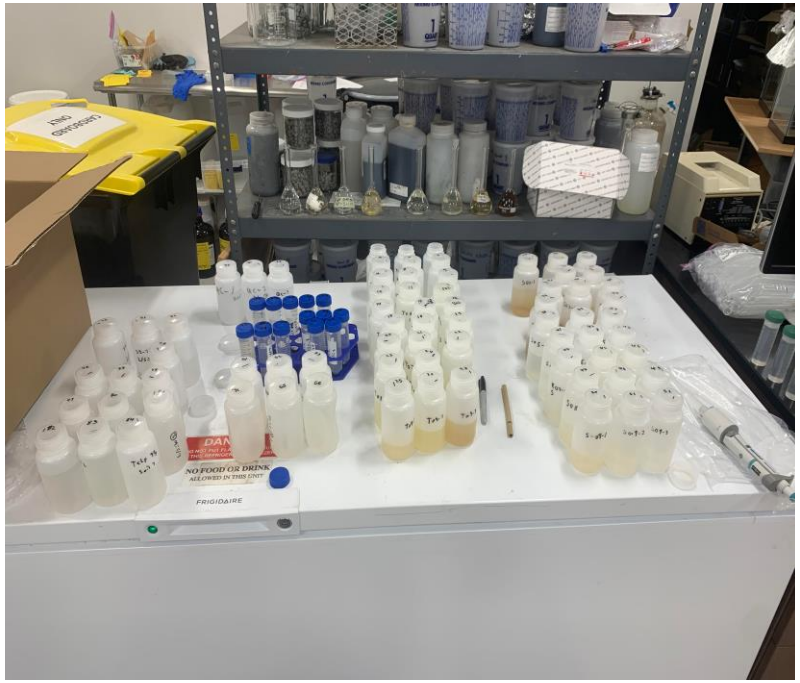

0.4
0.4
0.3
0.3
0.2
0.2
0.1
0.1
0.0
Concentration of PFOA (ug/L)
0
5
10
15
20
Liquid to Solid Ratio (L/kg)
If measured data
lie above line,
SSL underestimates
leaching
If measured data
lie below line,
SSL overestimates
leaching

Methods and Materials

- Two AFFF-impacted soils
- Soil characterization
  - Organic mater content
  - Moisture content
  - pH
  - Total PFAS
- Conducted three leaching tests
  - Method 1313 – Leaching as a function of pH
  - Method 1316- Leaching as a function of liquid to solid ratio
  - Method 1311 (TCLP) – Simulated release in a MSW landfill setting

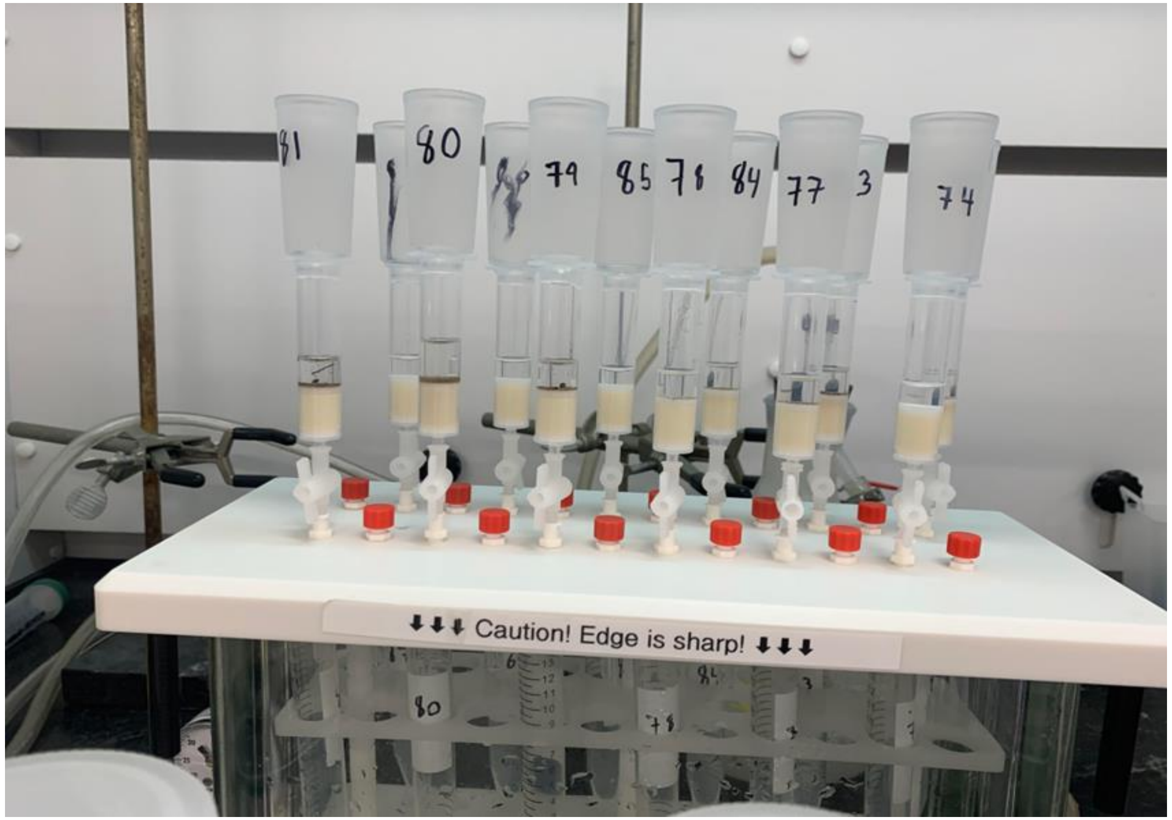


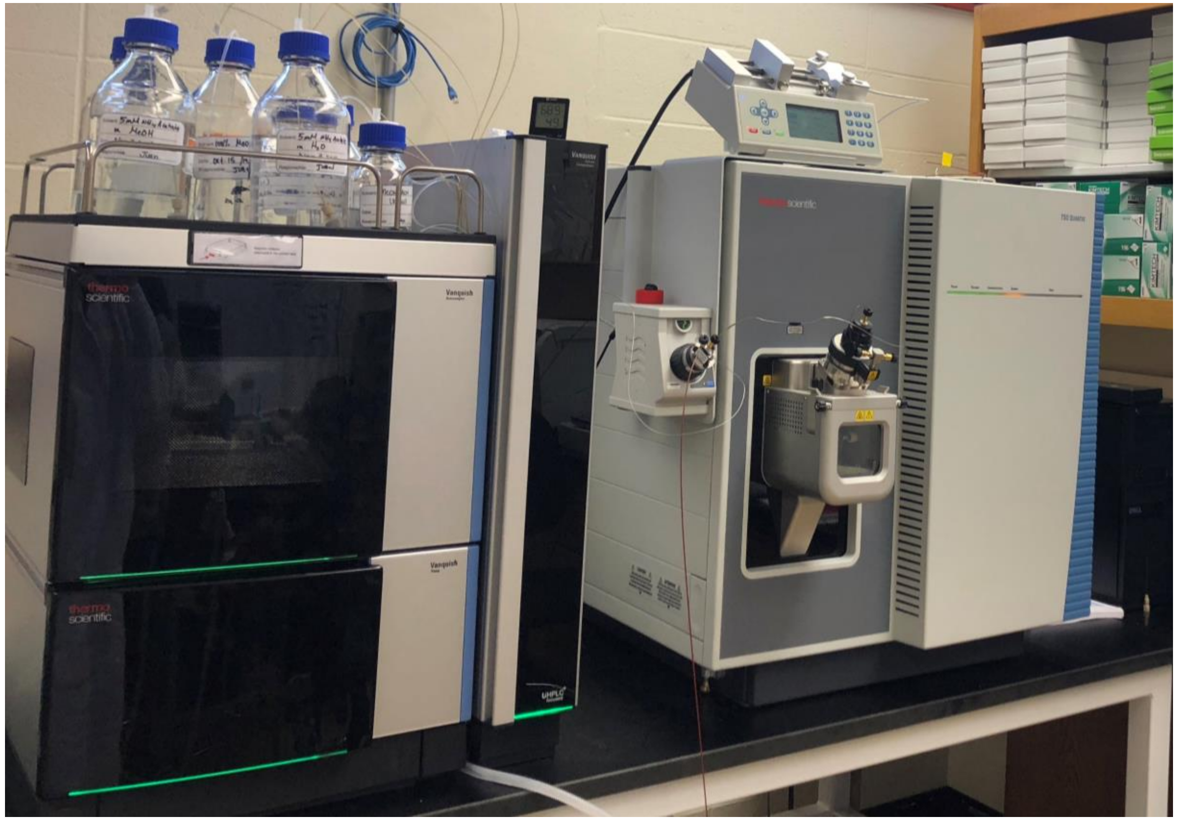
Batch Leaching Tests



Sample Preparation → Rotation → Leachate Collection + Addition of Internal Standard

Extraction and Analysis



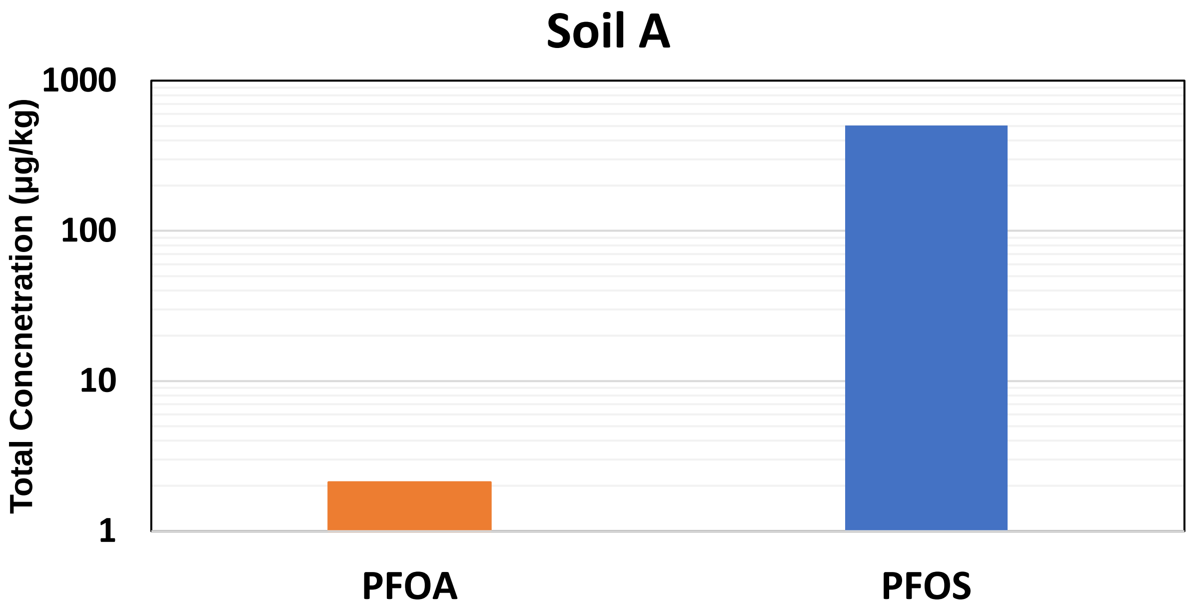


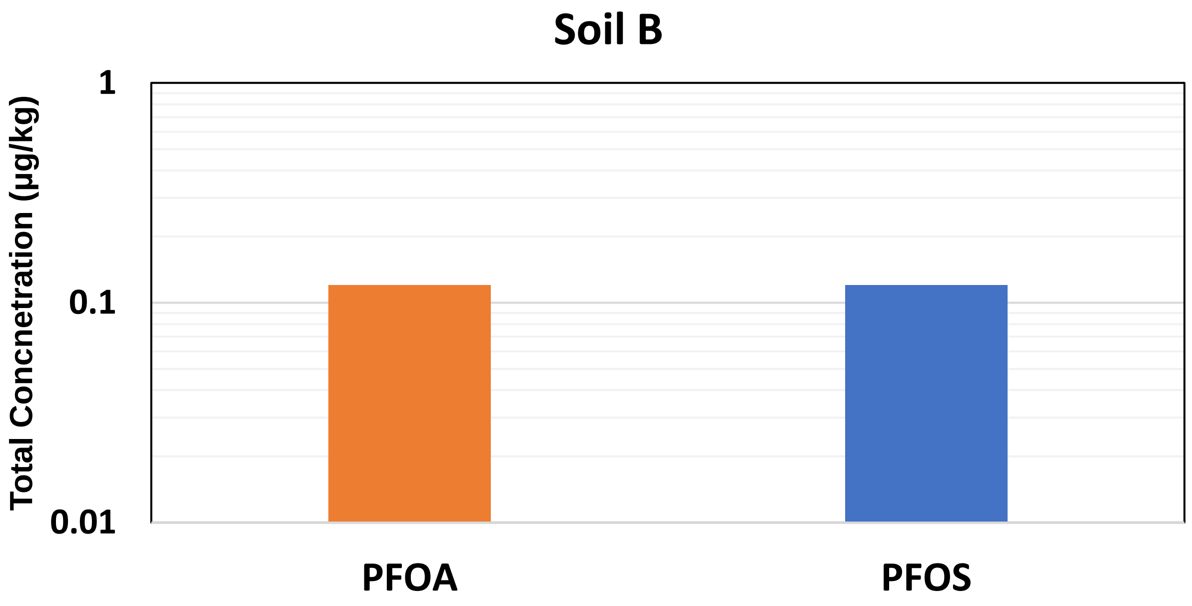
Total PFAS

- Soil A (high concentration)
  - PFOA – 2.12 (ug/kg)
  - PFOS – 502 (ug/kg)
  - Above RSLs for PFOA and PFOS
  - Above PSCTL for PFOA and PFOS
- Soil B (low concentration)
  - PFOA – 0.12 (ug/kg)
  - PFOS – 0.12(ug/kg)
  - Above RSL for PFOS

- FDEP's provisional SCTLs (leachability)
  - PFOA – 2.0 (ug/kg)
  - PFOS – 7.0 (ug/kg)

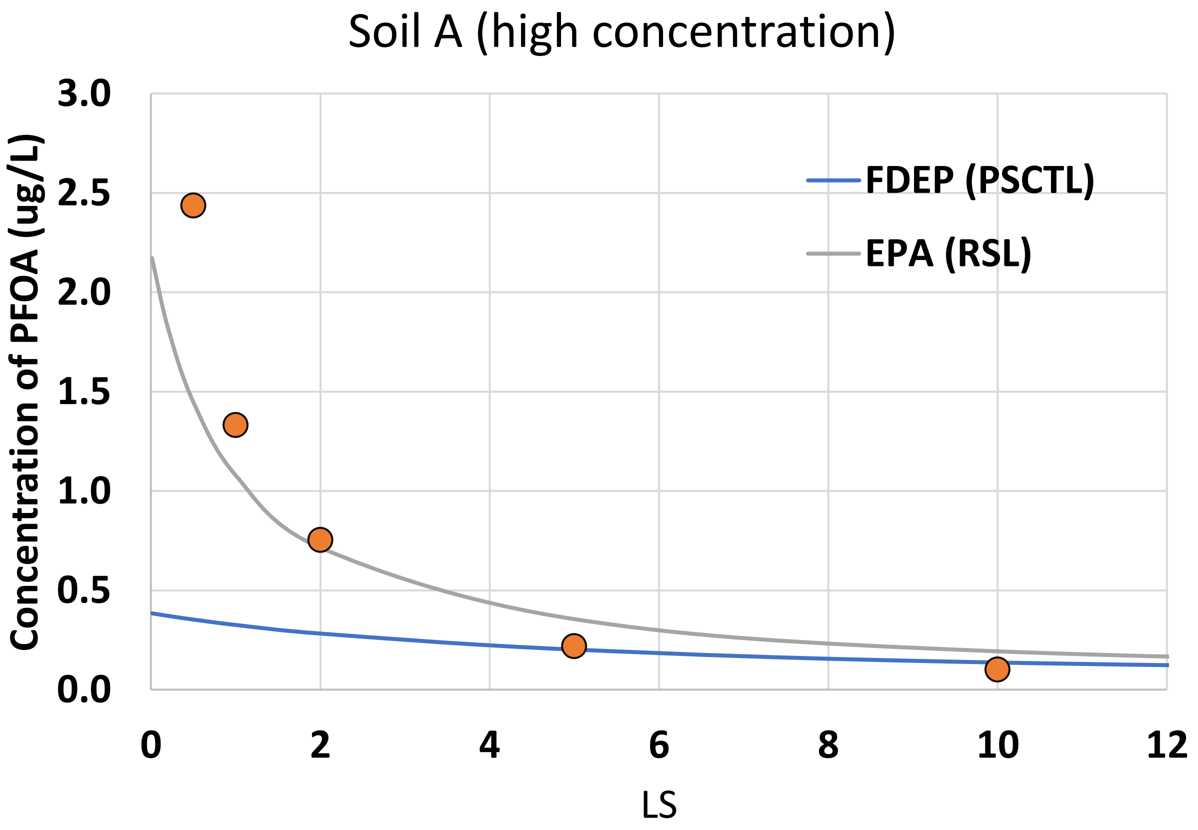
- EPA's RSLs (leachability)
  - PFOA – 0.92 (ug/kg)
  - PFOS – 0.038 (ug/kg)

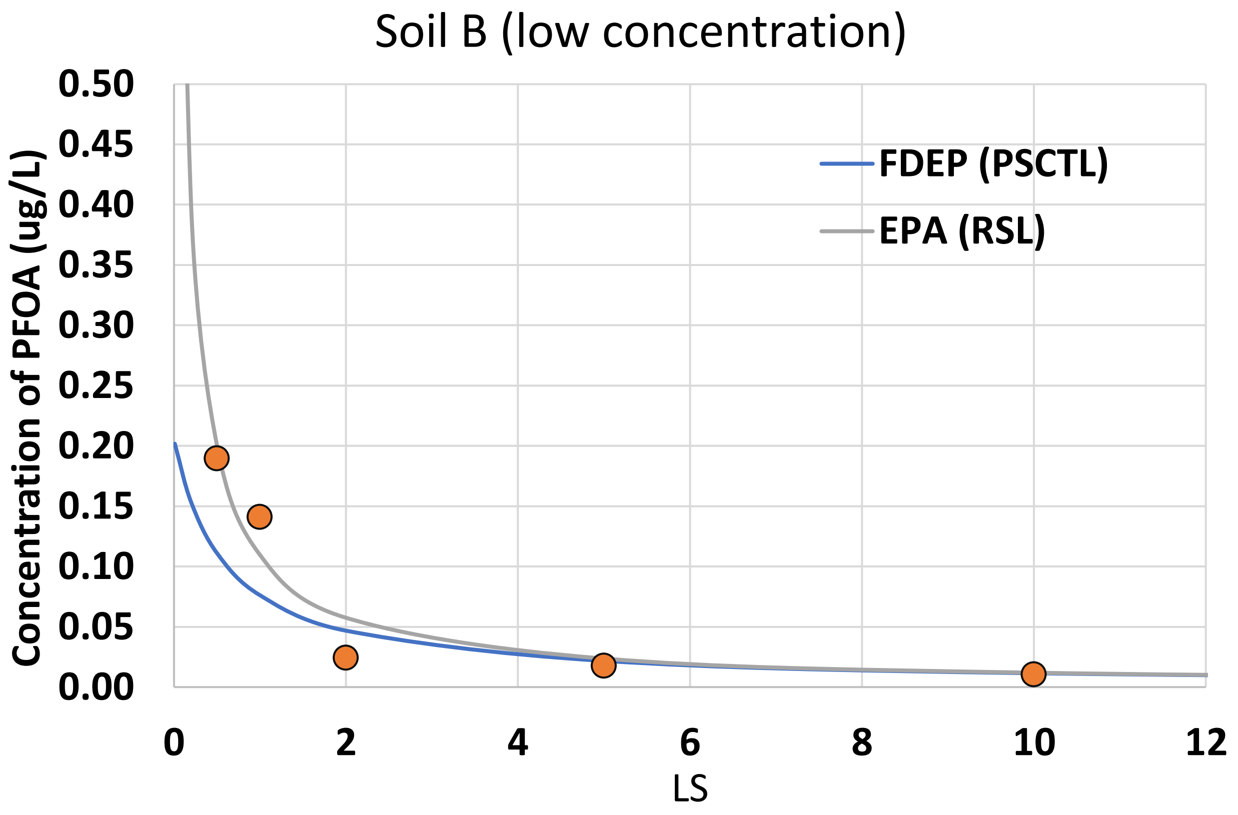




Comparing Leaching Data to Cleanup/Screening Levels

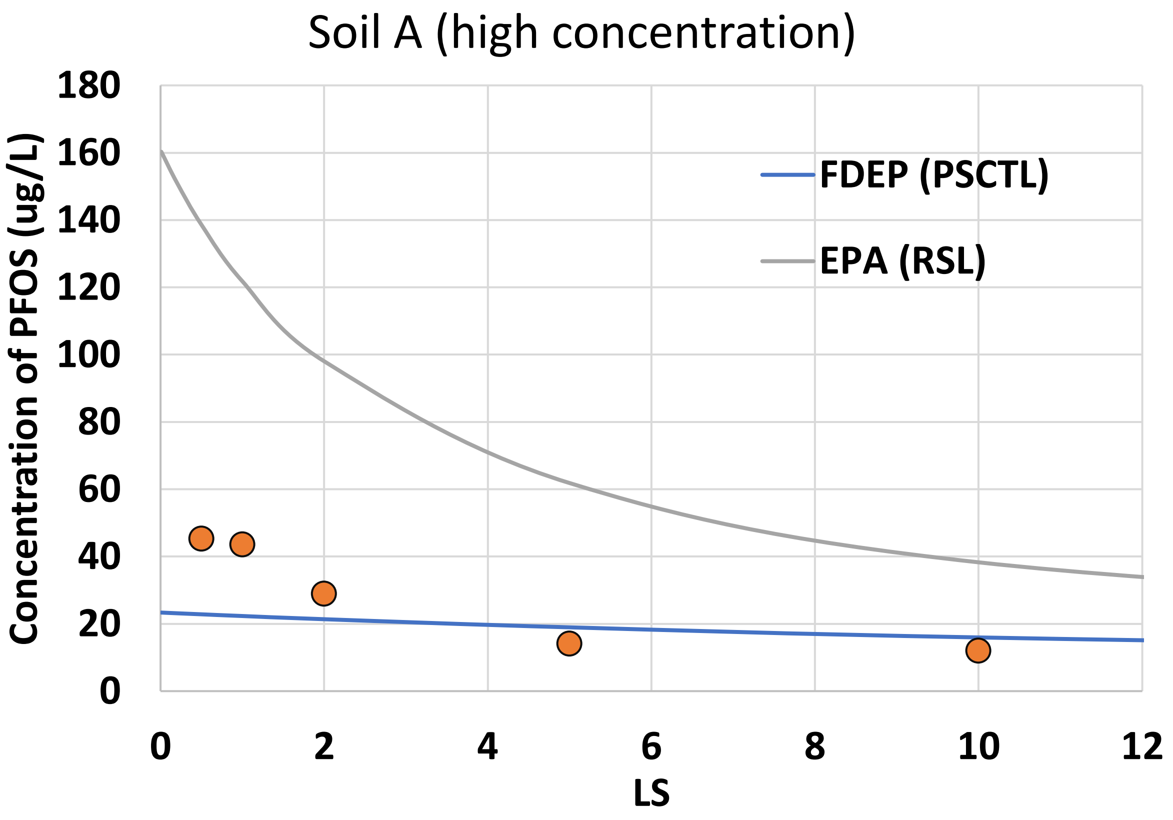
PFOA

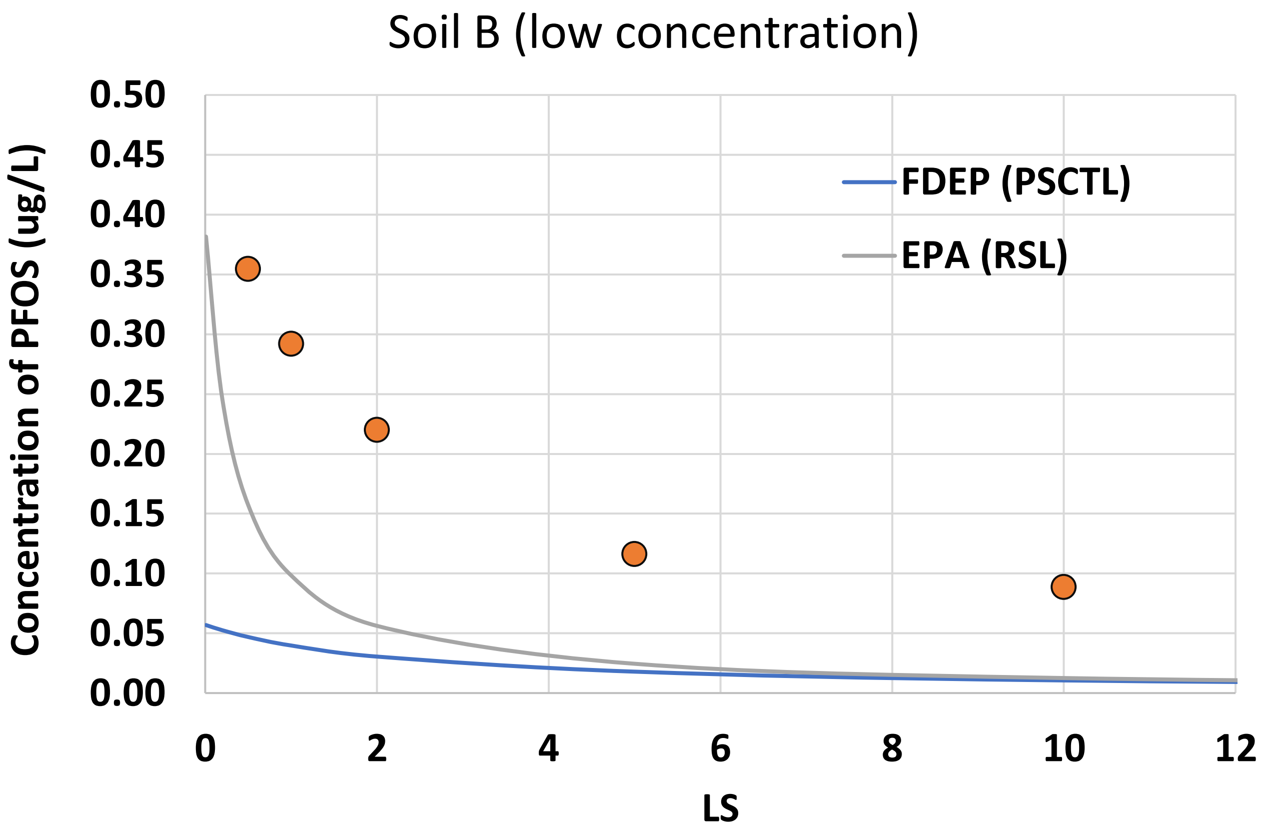




Comparing Leaching Data to Cleanup/Screening Levels

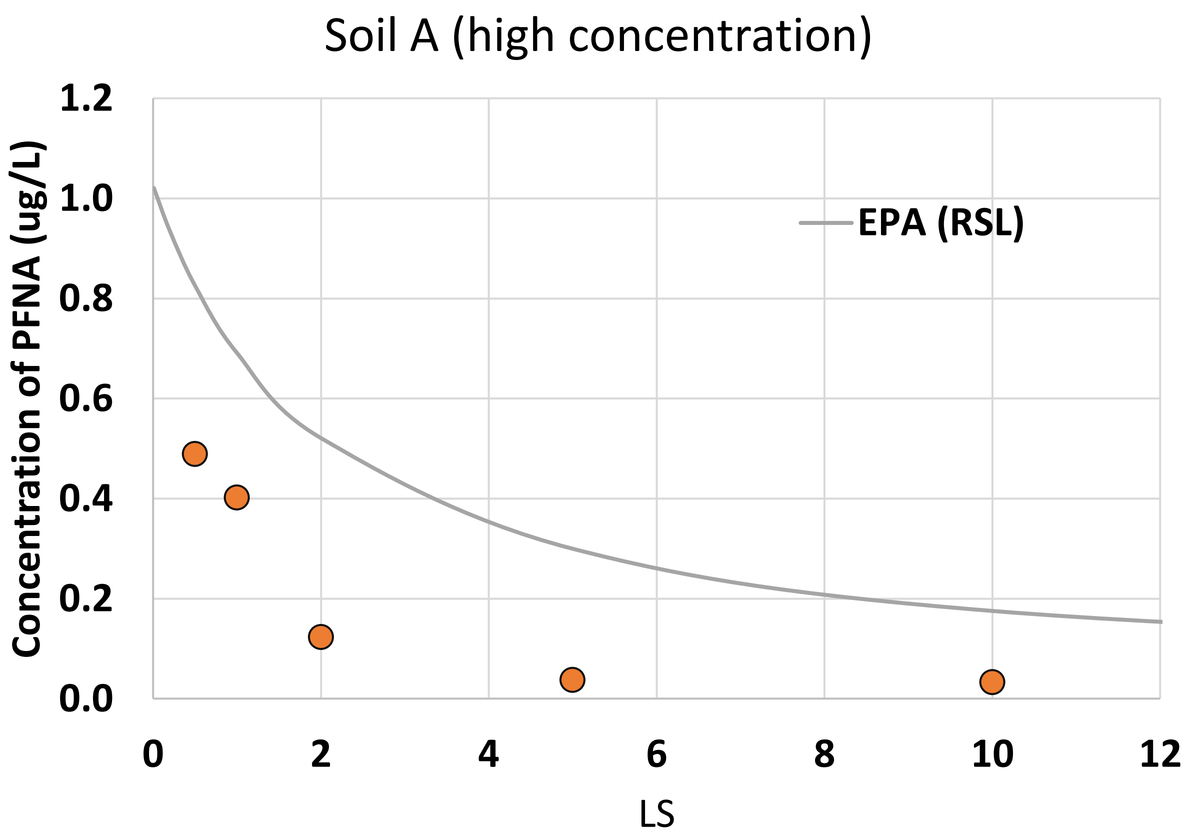
PFOS

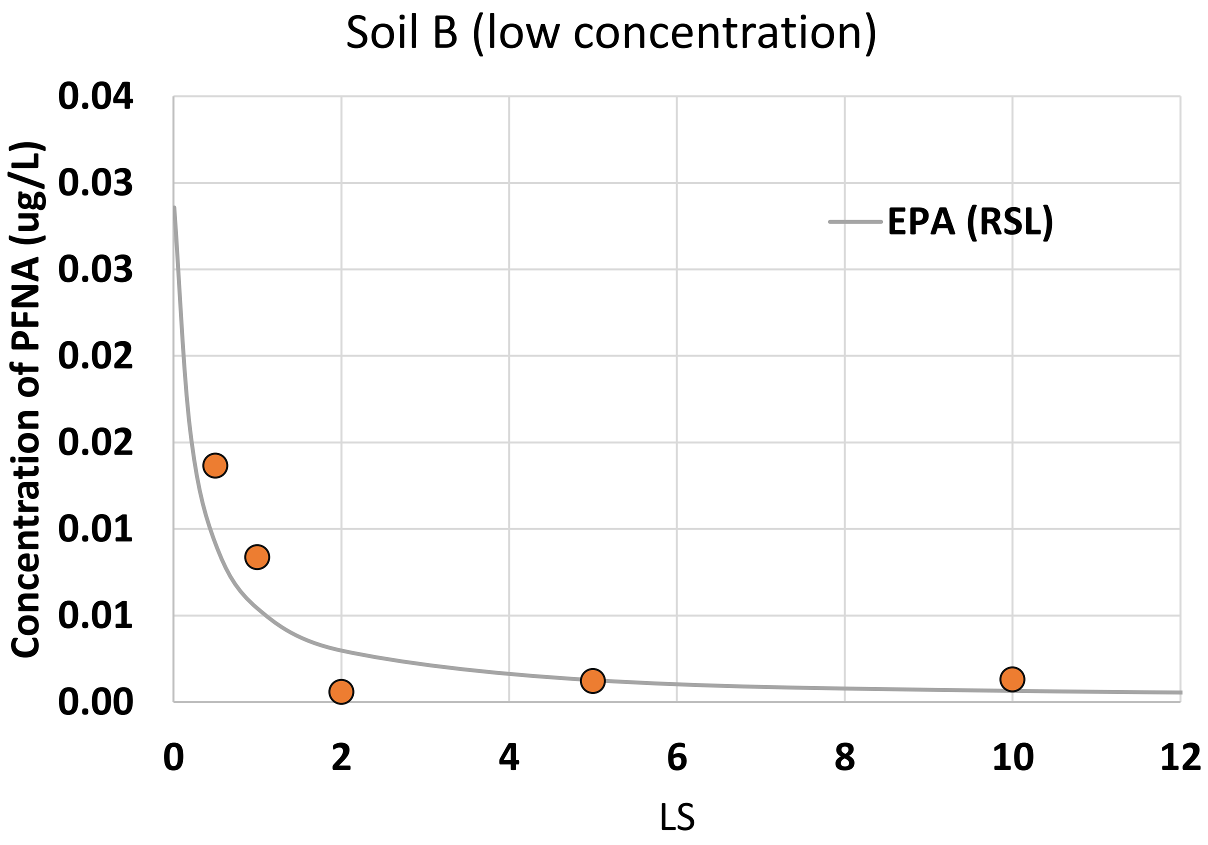




Comparing Leaching Data to Screening Levels

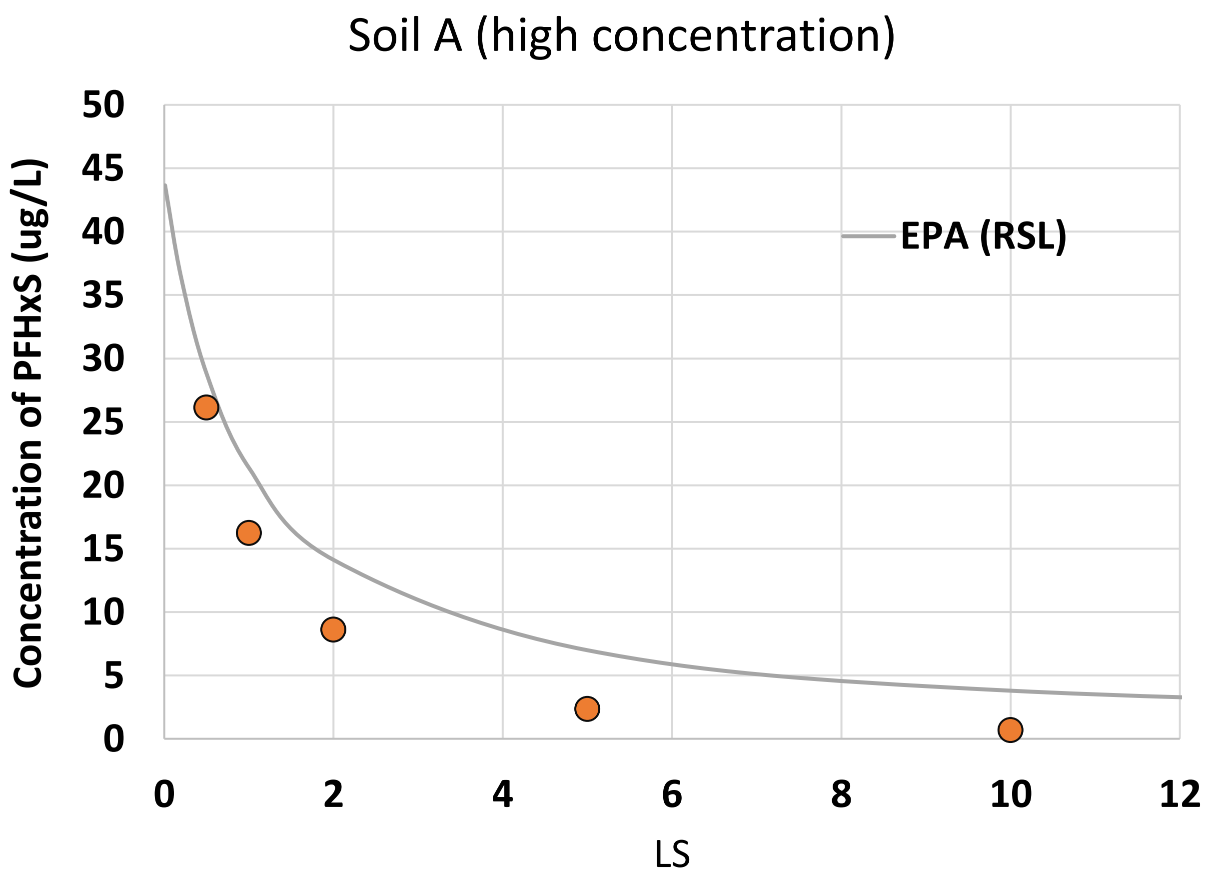
PFNA

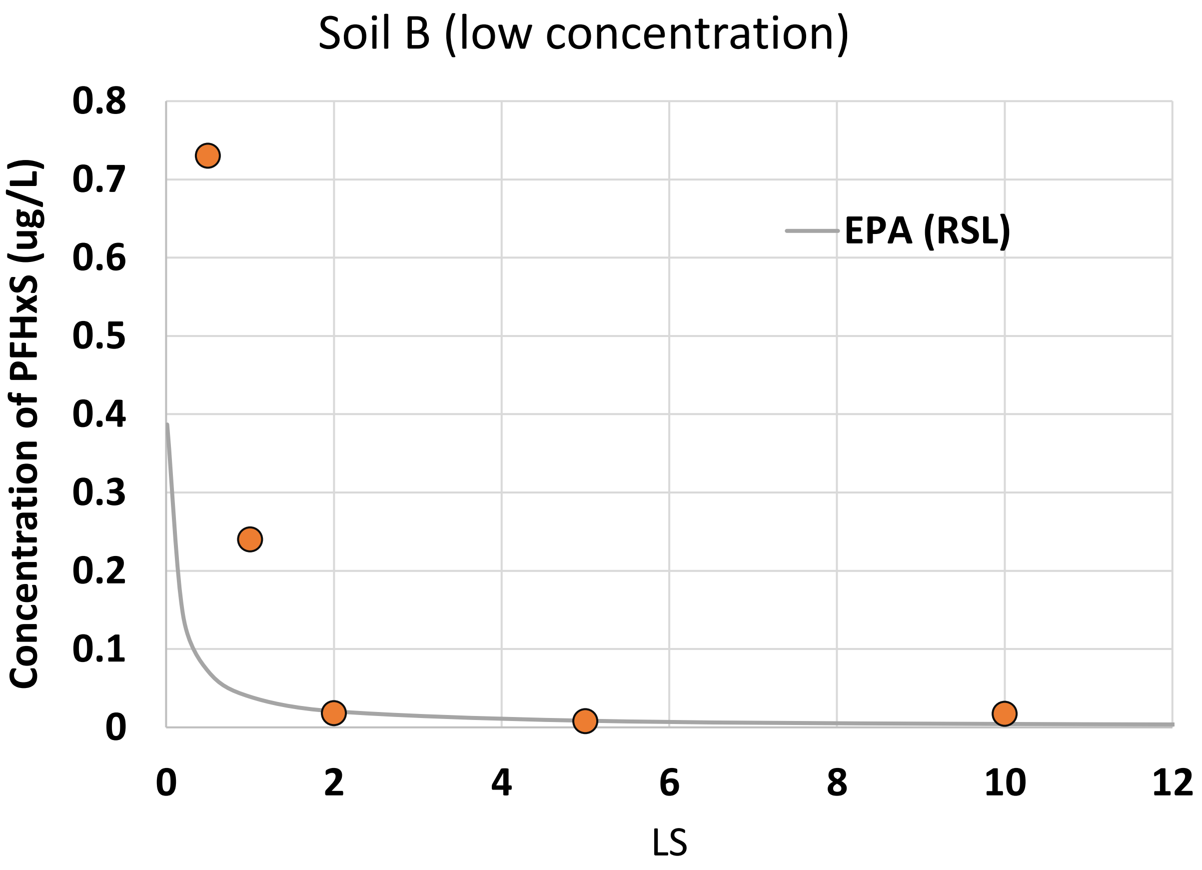




Comparing Leaching Data to Screening Levels

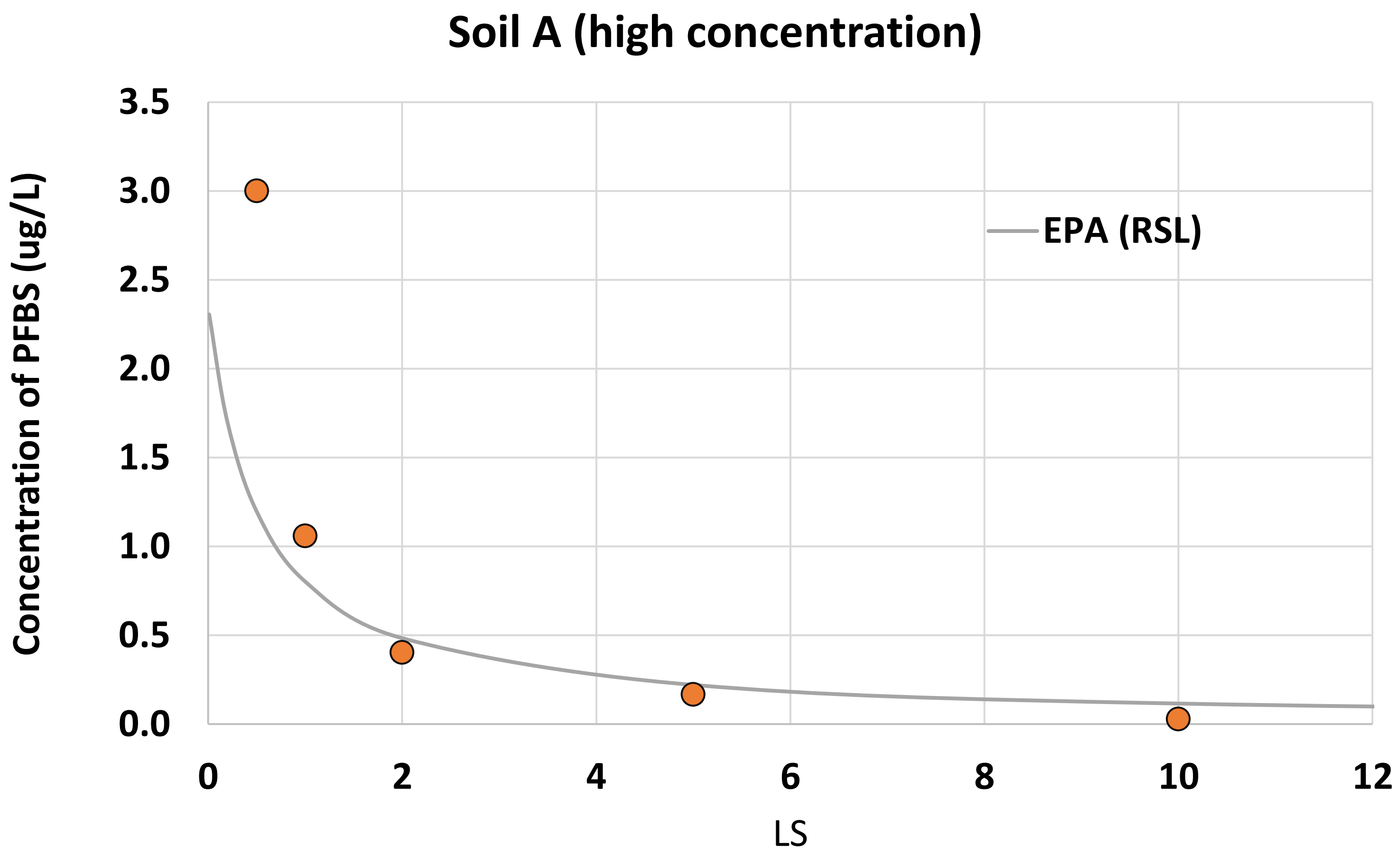
PFHxS





Comparing Leaching Data to Screening Levels

PFBS



Conclusions

- The (EPA) RSLs are more conservative than (FDEP) PSCTLs
- There are more factors controlling leachability then what governs leachability equations
- Measured leaching of PFOA, PFNA, PFHxS, and PFBS followed the predicted leachability of the RSLs accurately

K_{oc}
Soil-organic carbon partition coefficient (L/Kg)

	EPA (RSL)	FDEP (PSCTL)
PFOS	**373**	**2562**
PFOA	**115**	**655**
PFNA	**246**	
PFHxS	**112**	
PFBS	**61.7**	

How do you best manage PFAS-containing wastes?

Stabilization of PFAS-Containing Liquid Wastes

Project Background

- PFAS are not listed as a hazardous waste meaning they can be disposed of in a Subtitle D Landfill
- Many PFAS containing wastes are liquids (e.g., AFFF, remediation wastewaters, and industrial wastewaters)
- But liquids can not be disposed of directly in a landfill under 40 CFR § 265.314
- A common strategy is to add liquids to an absorbent material (stabilization/bulking agent) until they do not contain free liquids

Solidification Facility

Waste Stabilization/Bulking

- The presence of free liquids is determined by the paint filter test (wastes must pass PTF to be disposed of in a landfill)

- Different bulking agents can be used to stabilize liquid wastes

- Do different bulking agents have any effect on the retention of PFAS?

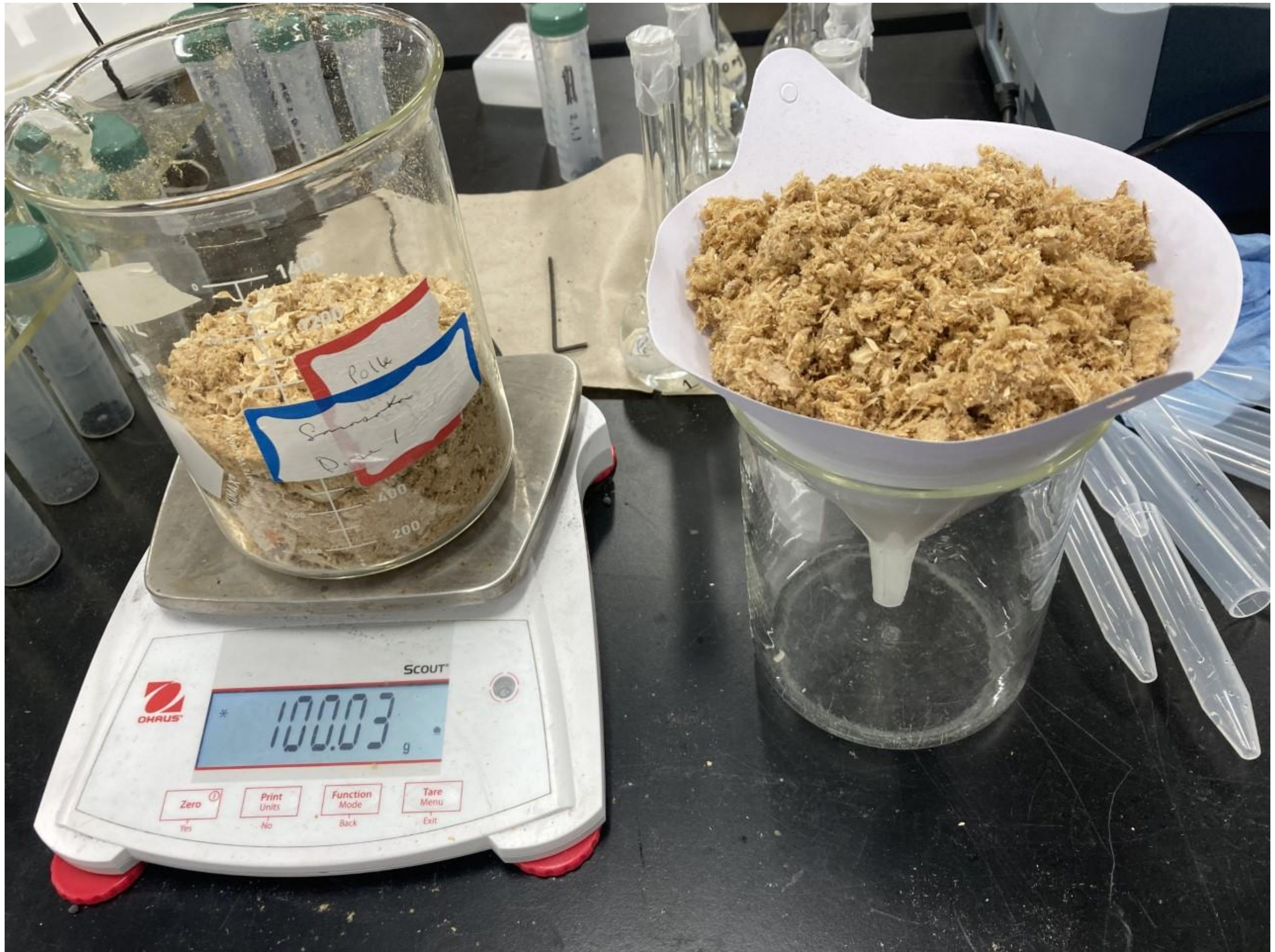
Methods and Materials

- Two PFAS containing liquids
  1. AFFF solution
  2. PFAS-contaminated wastewater

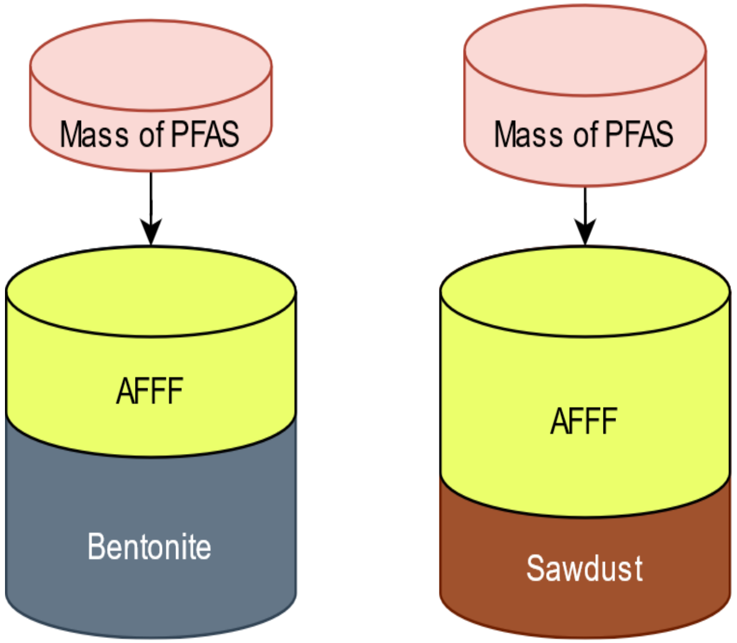
- Four bulking agents
  1. Bentonite clay
  2. Biochar
  3. Sawdust
  4. Cement

Leaching test

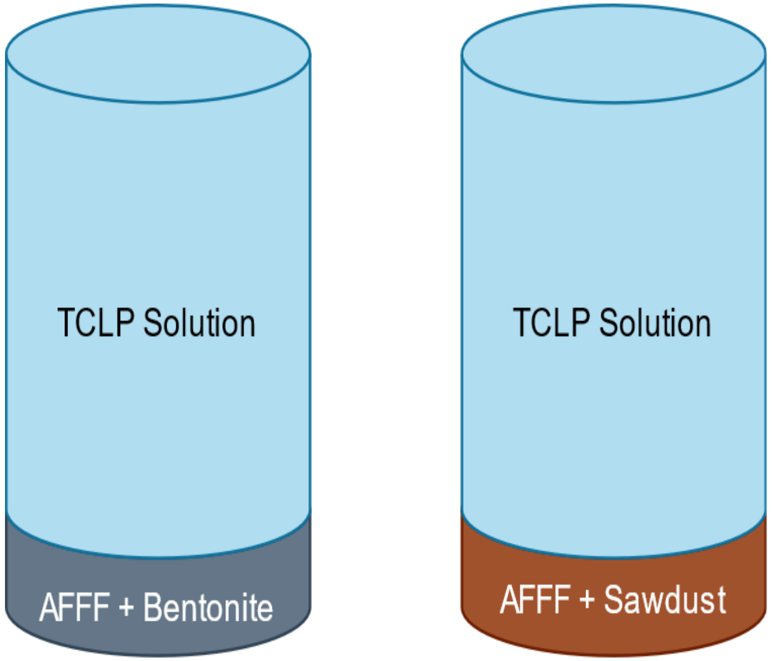
- Method 1311 – TCLP



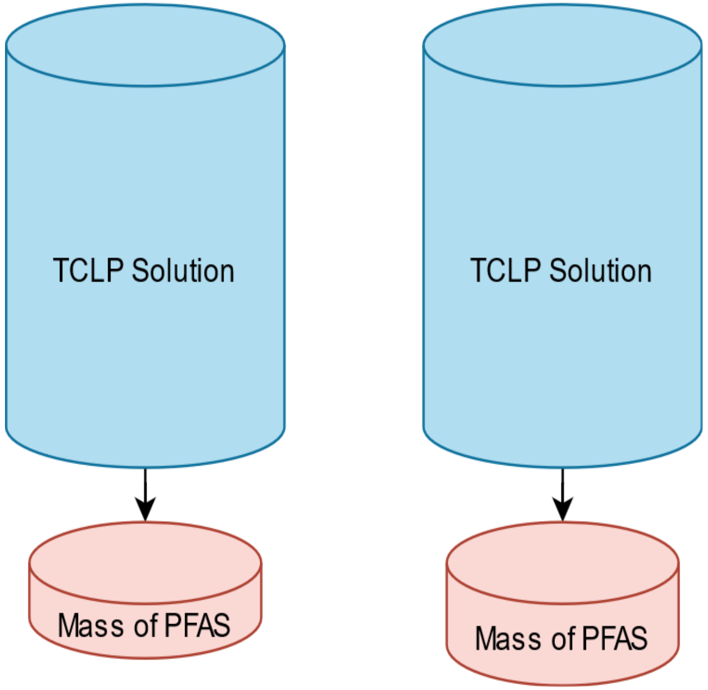
Addition of PFAS Liquids



Batch leaching



Mass Release



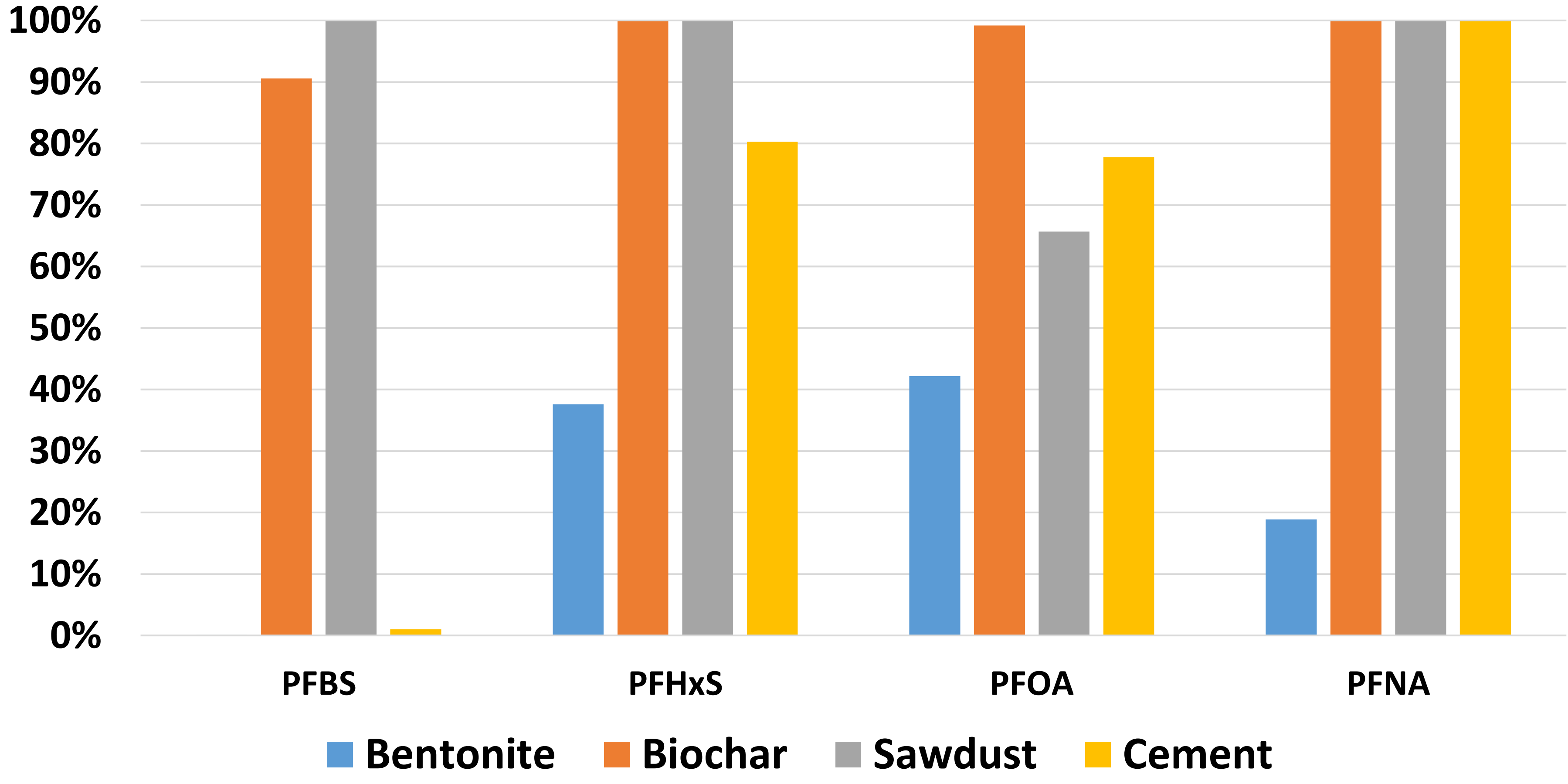
Experiment Workflow

Bulking of Liquids → **Leaching Test** → **Extraction**

AFFF Characterization

Compound	ug/L	% of total Concentration
PFBA	0.859	0.22%
PFPeA	1.25	0.32%
PFBS	0.092	0.02%
4:2 FTS	0.069	0.02%
PFHxA	4.44	1.12%
PFHpA	0.096	0.02%
PFHxS	0.395	0.10%
6:2 FTS	25.4	6.41%
PFOA	2.10	0.53%
PFNA	0.041	0.01%
PFHxPA	0.56	0.14%
FHEA	0.987	0.25%
N-CMAmP-6:2FOSA	359	90.66%
Totals	396	100.00%

% Retention of EPA Roadmap Compounds



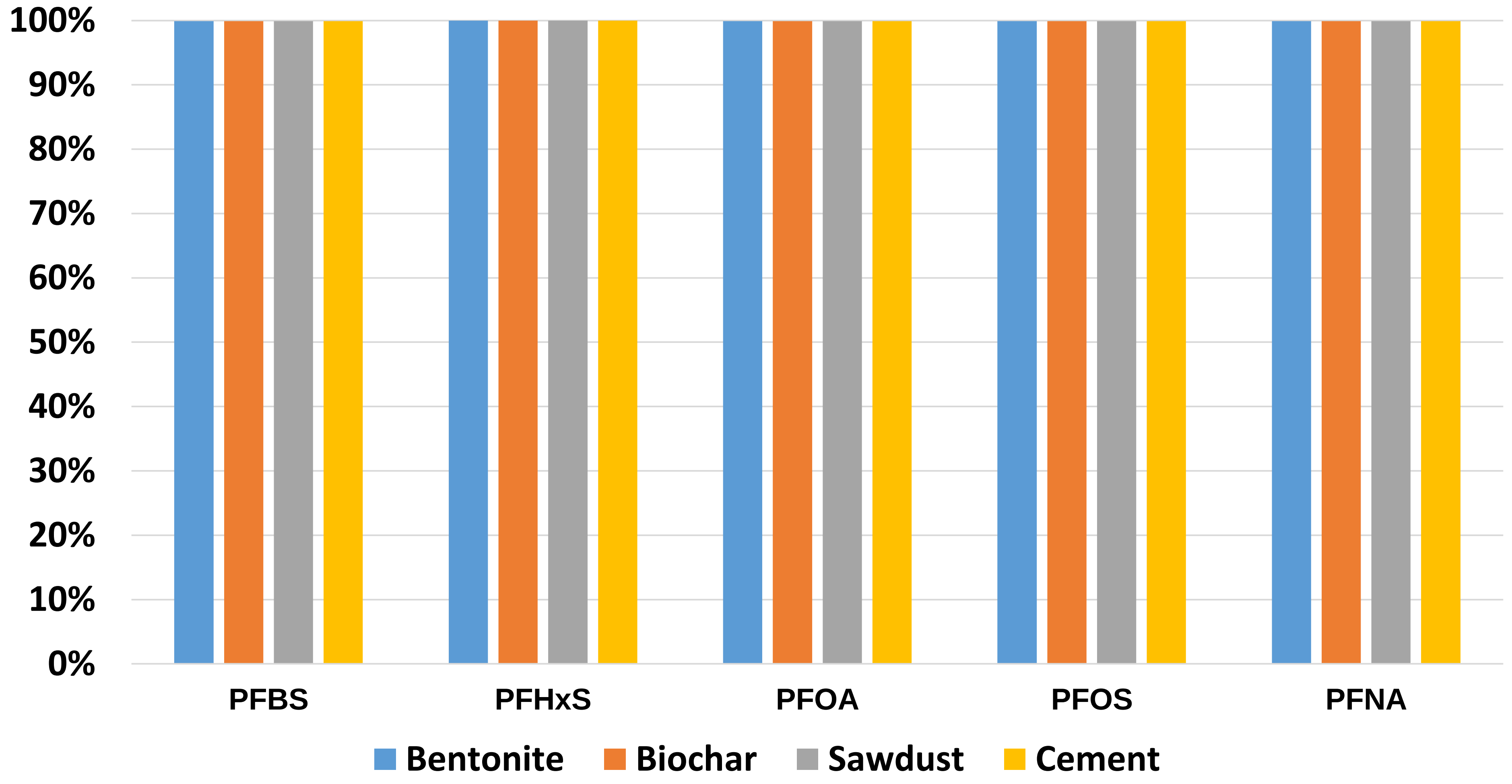
Compound	Bentonite	Biochar	Sawdust	Cement
PFBA	10%	14%	-88%	-248%
PFPeA	26%	34%	100%	-270%
PFBS	-6%	91%	100%	66%
4:2 FTS	-41%	88%	100%	-125%
PFHxA	-8%	53%	47%	-231%
PFHpA	-1%	91%	100%	-5%
PFHxS	38%	100%	100%	80%
6:2 FTS	69%	99%	94%	84%
PFOA	42%	99%	66%	78%
PFNA	19%	100%	100%	100%
PFHxpA	66%	100%	100%	100%
FHEA	-82%	100%	100%	87%
N-CMAmP-6:2	100%	100%	100%	46%
Totals	95%	99%	98%	43%

% Retention of PFAS by bulking agent

PFAS-impacted wastewater Characterization

Compound	ug/L	% of total Concentration
PFBA	0.082	4%
PFPeA	0.429	20%
PFBS	0.062	3%
PFHxA	0.448	21%
PFHpA	0.117	6%
PFHxS	0.050	2%
6:2 FTS	0.251	12%
PFOA	0.21	10%
PFOS	0.392	19%
PFNA	0.027	1%
Total PFAS	2.1	100%

% Retention of EPA Roadmap Compounds



Compound	Bentonite	Biochar	Sawdust	Cement
PFBA	68%	-26%	89%	15%
PFPeA	100%	-21%	100%	86%
PFBS	100%	100%	100%	100%
PFHxA	100%	-58%	71%	-86%
PFHpA	100%	100%	100%	100%
PFHxS	100%	100%	100%	100%
6:2 FTS	85%	76%	60%	-33%
PFOA	100%	100%	100%	100%
PFOS	100%	100%	100%	100%
PFNA	100%	100%	100%	100%
Totals	97%	30%	84%	38%

% Retention of PFAS by bulking agent

Conclusions

- Certain bulking agents are better at retaining specific PFAS species
- For the low concentration wastewater 99.9% of EPA roadmap PFAS were retained
- In general, the higher organic matter bulking agents retained more PFAS (i.e., biochar and sawdust)