Investigation of the Effect of Prior Remedial Treatment on the Fate and Transport of PFAS Present at AFFF-Impacted Sites

Kavitha Dasu, Ph.D. Battelle, Columbus, OH
and
John Kornuc, Ph.D. NAVFAC EXWC, Port Hueneme, CA

International Symposium on Bioremediation and Sustainable Environmental Technologies, Baltimore, MD.
April 15-18, 2019

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Background

- High water solubility and persistence
- Fate and transport data limited to anionic species
- Understanding the distribution of PFAS at AFFF-impacted sites and conditions under which precursors are degraded to PFSAs (incl. PFOS) and PFCAs (incl. PFOA) are critical
- Unintended increase in the PFAS levels resulting from remedial actions targeted towards other co-contaminants such as chlorinated solvents and petroleum hydrocarbons
- Significant knowledge gaps in understanding the distribution, fate and transport of PFAS at contaminated sites

McGuire et al. 2014; McKenzi et al 2015

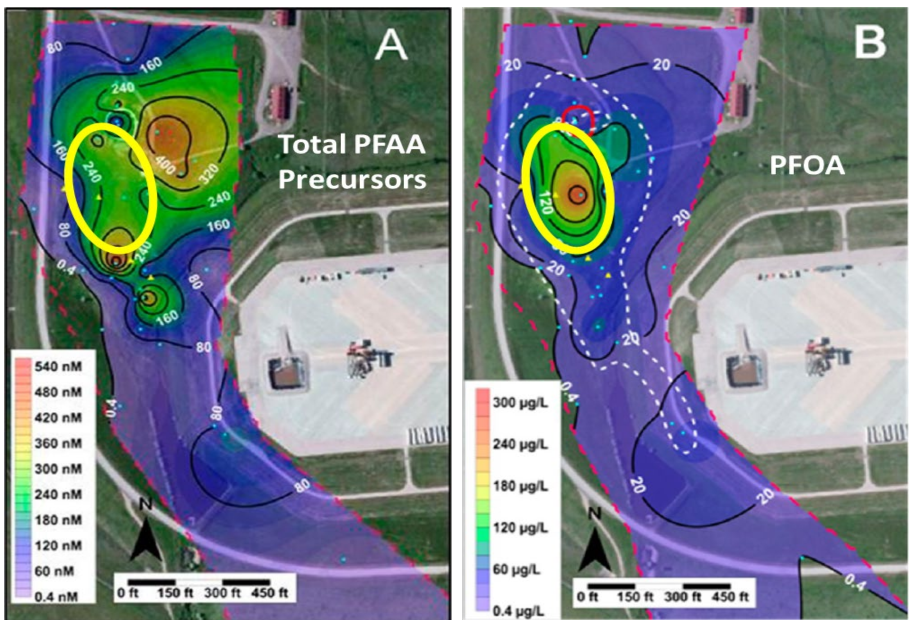
Common Remediation Techniques to Treat Other Contaminants

Common Co-contaminants: Petroleum hydrocarbons, chlorinated solvents, etc.

- Chemical
  - Oxidative and aeration methods
    Ex: Activated persulfate, permanganate, peroxide, air sparging, etc
  - Reductive methods
    Ex: Hydrogen releasing compounds, etc
- Biological
- Sorption
  - Thermal desorption
  - In-situ stabilization

Effect of Prior Remediation Practices on PFAS Distribution and Transport

- Evidence of remediation-induced alteration on PFAS distribution at a former firefighter training area.



- Effect of oxidation method
  - Precursor oxidation
  - Redistribution of PFAAs due to changes in mobility
- Aerobic biotransformation of PFAS precursors

McGuire, M. E., et al. 2014

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Study Objectives

- To evaluate the effects of various remediation technologies on distribution, fate and transport of PFAS and their precursors at AFFF impacted sites using AFFF impacted soil column studies

  - Hydrogen Releasing Compound (HRC) Treatment – conducted under anaerobic conditions - targeted to treat chlorinated solvents. Using NAS Warminster soil

  - Activated Persulfate Treatment – conducted under aerobic conditions - targeted to treat petroleum hydrocarbons. Using NAS JAX soil

PFAS Background Levels in Two AFFF impacted Soils

Analytes	JAX Soil	NAS WAR Soil
	ng/g Dry wt.	
PFBA	<5.35	<5.75
PFPeA	<5.35	<5.75
PFHxA	**8.97**	<5.75
PFHpA	<5.35	<5.75
PFOA	**35.03**	**7.58**
PFNA	<5.35	<5.75
PFDA	<5.35	<5.75
PFUnA	<5.35	<5.75
PFOSA	<5.35	<5.75
PFBS	<5.35	<5.75
PFPeS	<5.35	<5.75
PFHxS	**60.63**	**7.27**
PFHpS	**6.92**	<5.75
PFOS	**318.97**	**159.18**
PFNS	<5.35	<5.75
PFDS	<5.35	<5.75
4:2FTS	<5.35	<5.75
6:2FTS	**17.68**	**7.84**
8:2FTS	**7.24**	**19.88**

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HRC – Reduction Condition (using NAS WAR Soil)

Ground Water and Soil Characteristics

Parameters	GW Influent mg/L
Alkalinity as $CaCO_3$, Total	43
Chloride	92.3
Fluoride	0.8
Sulfate	163
Total organic carbon %	<0.5
Calcium	33
Iron	3.33
Magnesium	33.7
ORP (mV) Initial	-31.6

Soil
Soil Textural Class: Sandy Loam
pH: 7.7
CEC, meq/100g: 8.4

PFAS levels are below the limits of quantitation in the natural ground water used for the study

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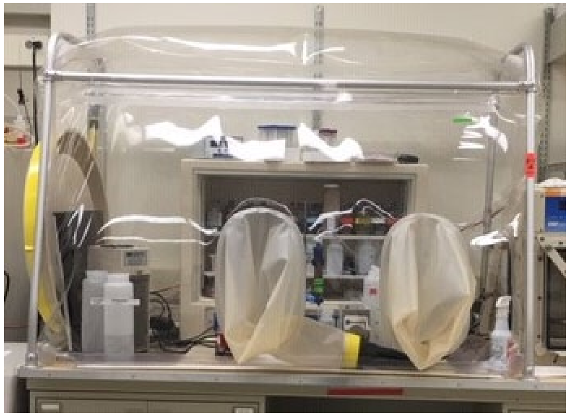
HRC Column Study



Place setup in anaerobic chamber

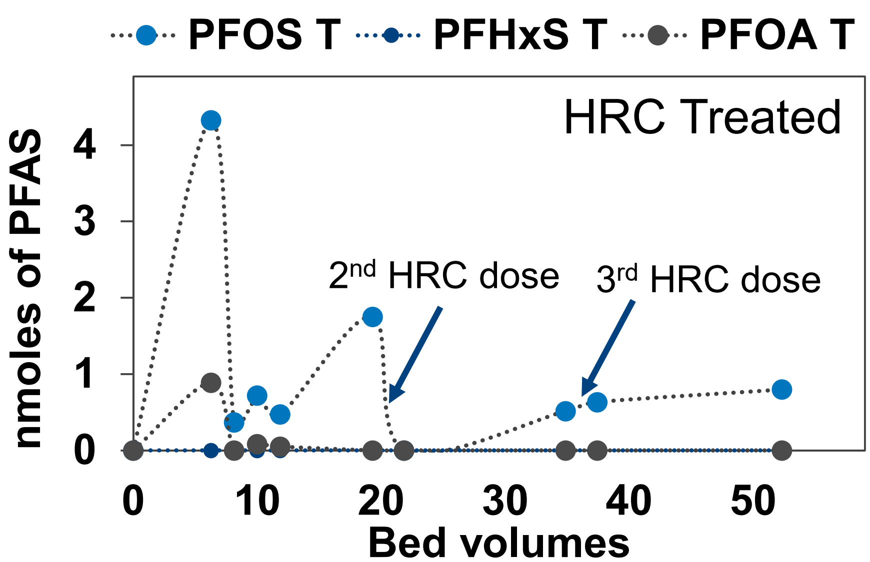
Pack 2 columns and load treatment column with sodium lactate

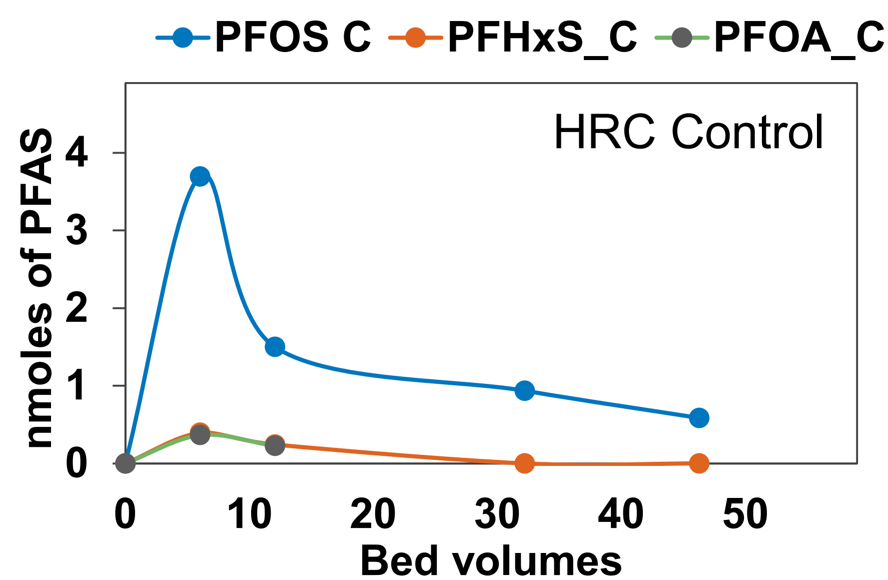
Run columns using PFAS-free natural ground water as influent

Aqueous influent, effluent and soil (Pre and post study) sample collection for following analyses:

1. PFAS using LC-MS/MS
2. Analysis of shorter chain organic acids
3. Volatile organic compounds
4. High resolution PFAS analysis –LC-ToF/MS
5. Water quality parameters

Breakthrough curves for HRC study





- Initial breakthrough of PFAS within 10 bed volumes in both the treated and control columns
- HRC-treated soil column showed retardation of PFOS for the first two applications

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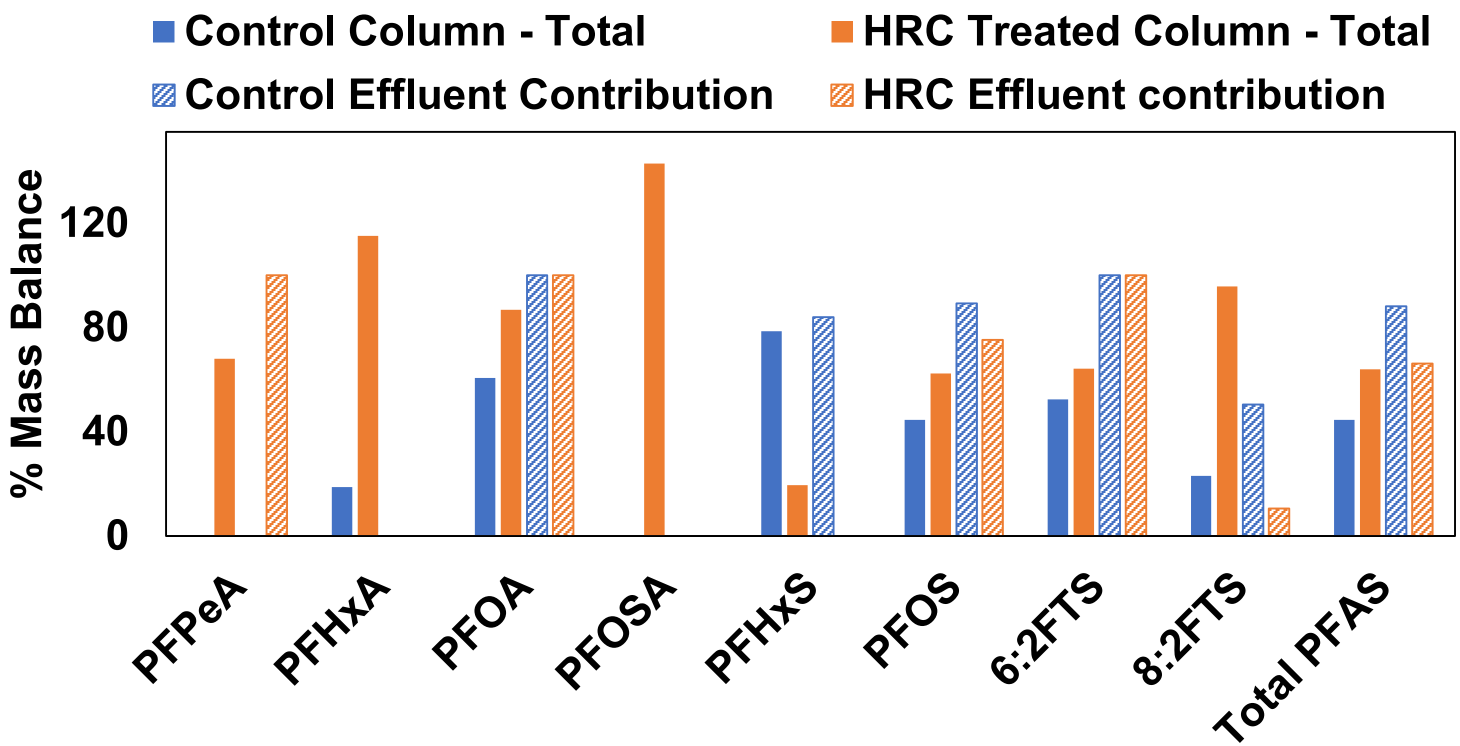
Monitoring Fatty Acids

Formation of shorter chain fatty acids from the lactic acid biotransformation is indicative of anaerobic conditions in the system

Fatty Acids	GW Inf	Effluent Day 0	Effluent Day 7	Effluent Day21
DL-Lactic acid, mg/L	<1	9100	550	<1
Acetic acid, mg/L	<1	45	52	27
Formic acid, mg/L	<1	2.3	0.53	36
Propionic acid, mg/L	<1		98	<1
Pyruvic acid, mg/L	<0.1	0.52	<0.1	<0.1

Mass Balance - HRC

- Overall mass balance in treated and control column was ~66 and 88% respectively
- Around 100% of the total mass balance for most analytes was recovered from effluent, except for longer chain sulfonates



Persulfate - Oxidation Condition using NAS JAX Soil

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Ground Water and Soil Characteristics

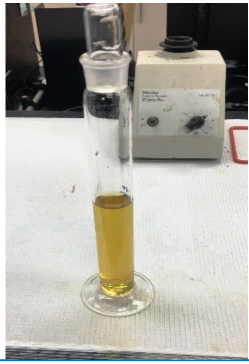
Parameters	GW Influent mg/L	Jax Soil, mg/Kg
Alkalinity as $CaCO_3$, Total	86	
Chloride	98.95	<4.2
Fluoride	0.97	<6.2
Sulfate	217	53.3
Total organic carbon	1.02	0.34 (%)
Calcium	61.6	67600
Iron	1.35	
Magnesium	49.15	496
ORP (mV) Initial	-31.6	
ORP (mV) Day 12	142.9	
Conductivity (mS/cm)	0.829	
Residual Persulfate (g/L)	0.0	

Soil
Collected from 5' – 35'
Textural Class: Sand
pH: 8.1
CEC, meq/100g: 23.8

PFAS levels are below the limits of quantitation in the natural ground water used for the study

Total petroleum hydrocarbons (C6 –C35 range): Non-detects in both GW and soil.

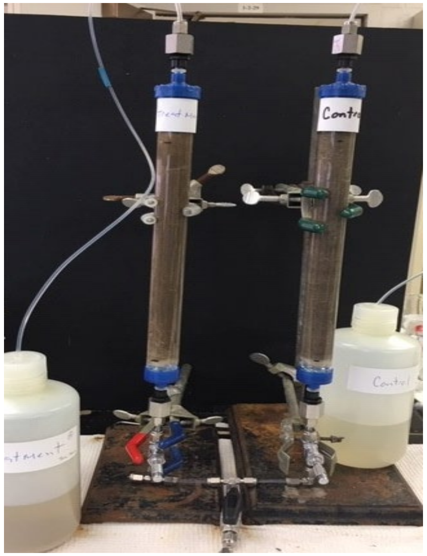
Persulfate Oxidation Column Study



Prepare oxidant solution

Tumble soil and oxidant solution for 72 hours

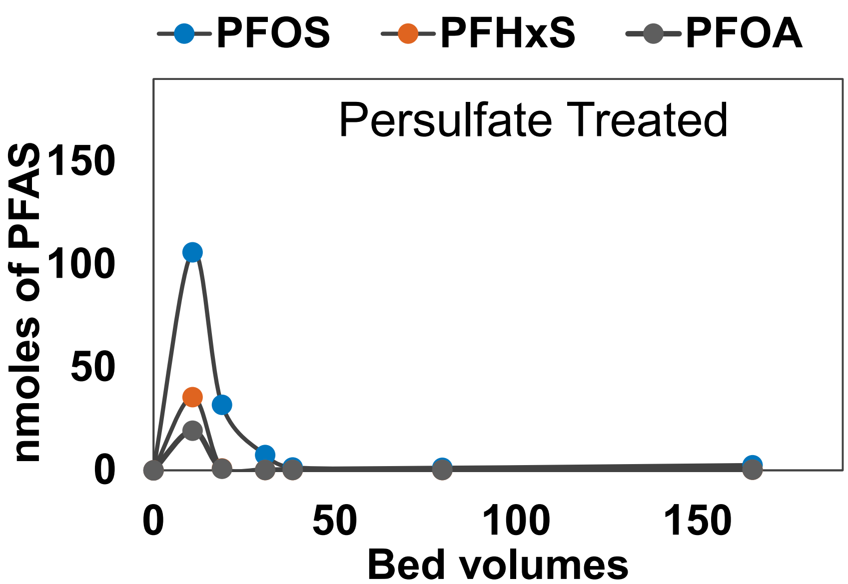
Pack treatment and control columns and run columns using PFAS-free natural ground water as influent

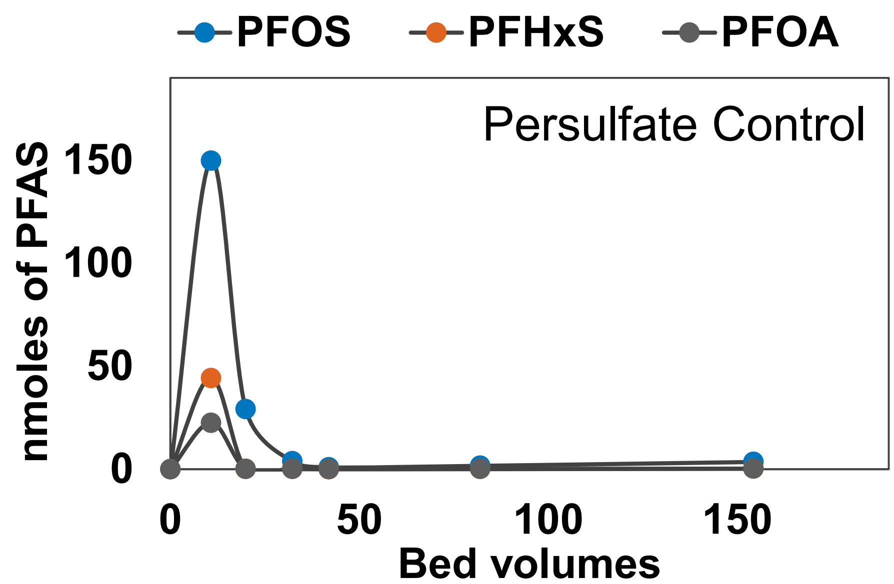


Aqueous influent, effluent and soil(end of the study) sample collection for following analyses:

1. PFAS using LC-MS/MS
2. Residual oxidant
3. Total petroleum hydrocarbons
4. High resolution PFAS analysis using LC-ToF/MS
5. Water quality parameters

Breakthrough Curves for Persulfate study





- Initial breakthrough happened within 10 bed volumes in both the treated and control columns

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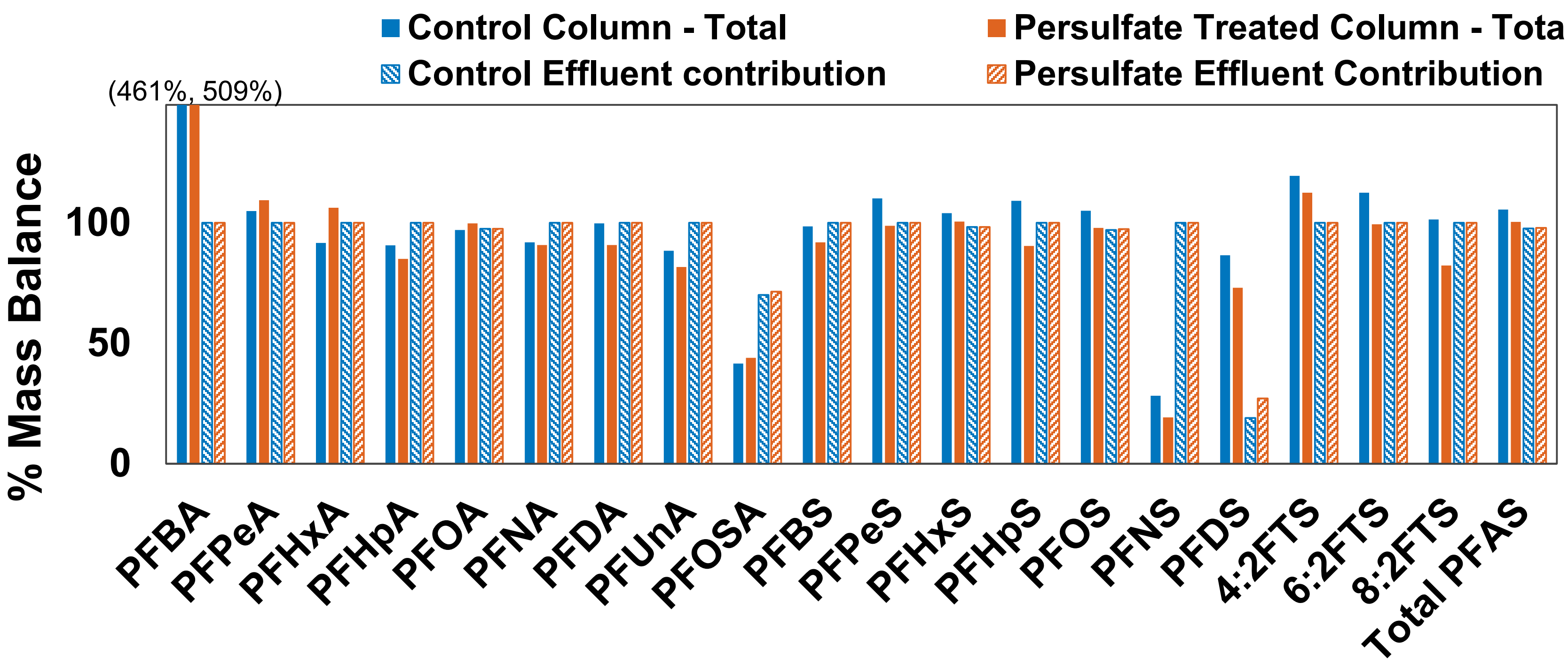
Mass Balance - Persulfate

- Overall mass balance of the persulfate study in both treated and control column was ~100 %
- Around 100% of the total mass balance for most of the analytes was from effluent except for longer chain sulfonates
- 100% mass balance of precursors (FTS) under oxidizing conditions



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Natural Water Infiltration Calculations

- Assumptions:

  Rainfall: 35” infiltrates out of 50” rainfall per year

  Depth: 5’ (surface to water table)

  Pore volume: 30%

  Bed volume: 18”

  Therefore, per year 2 bed volumes of water infiltrates

  150 bed volumes in our study = 75 years of water infiltration

  100 % PFAS leached in less than 10 bed volumes

Column infiltration was continuous in a relatively short time period compared to the intermittent infiltration under field conditions

Comparison of Literature Reported Studies

Study	Specifications	Conclusions	Reference
Flow through Column Study - >100 weeks	PFAS spiked into soil; 35 ml water added per week	80 - 90% PFAA leached in <5 weeks	Gellrich et al. 2012
Batch Desorption Study – 24 Hour	AFFF impacted Soil	77% – 130% PFAA leached	Braunig et al. 2019
PFAS measurement in GW and soil cores impacted by AFFF	AFFF impacted Soil	Deep seepage (>20 m) of many PFAS, including fluorotelomers, FTAB through soil, despite zwitterionic nature and clay layers	Dauchy et al. 2019
Column studies	AFFF applied to pristine soil	The presence of PFOS in the column leachate is indicative of reduced sorption and increased vertical transport.	Hoisaeter et al. 2019

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Conclusions

- Two column studies were conducted under both oxidizing and reducing conditions using AFFF- impacted soil
- HRC treatment showed slight retardation of PFOS when the concentrations of HRC are high – real world application of HRC is a slow release compound with continuous supply
- Overall, there was no apparent effect of treatment on the PFAS distribution in both the studies
- High leachability of PFAS in column experiments compared to those of field conditions at the AFFF impacted sites

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Conclusions (Cont'd)

- Column infiltration was continuous in a relatively short time period compared to the intermittent infiltration under field conditions
- Soil collection process disturbed the soil (including O_2 levels)
- Annual changes in saturation level of the soil pores can have an effect on the attenuation processes for PFOS in the unsaturated soil under field conditions
- Significant knowledge gaps in understanding the distribution, and fate and transport of PFAS during treatment at contaminated-sites, and these could result in uninformed decisions on strategies for site remediation

Questions ?

Thank You!

Kavitha Dasu

PFAS Lead Chemist

Battelle

Columbus, OH

dasu@battelle.org

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