In-Situ Treatment of the Air-Water Interface within a PFAS Source Zone Using Colloidal Activated Carbon

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InSitu Remediation Services

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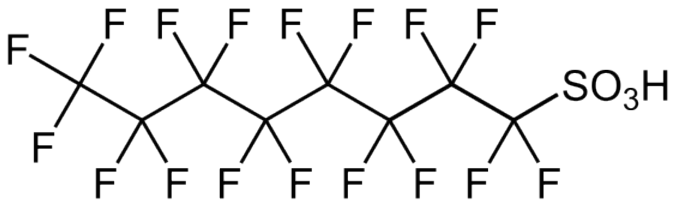
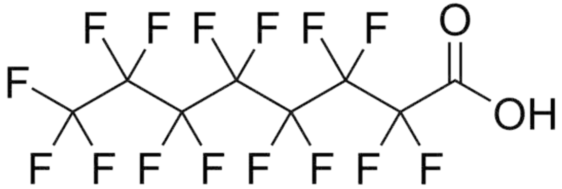
Aquífero Serviços de Remediação

June 2024

Agenda

- Overview of PFAS Insitu Remediation
- Review of Air-Water Source Zone Study
- Update of Ongoing Studies

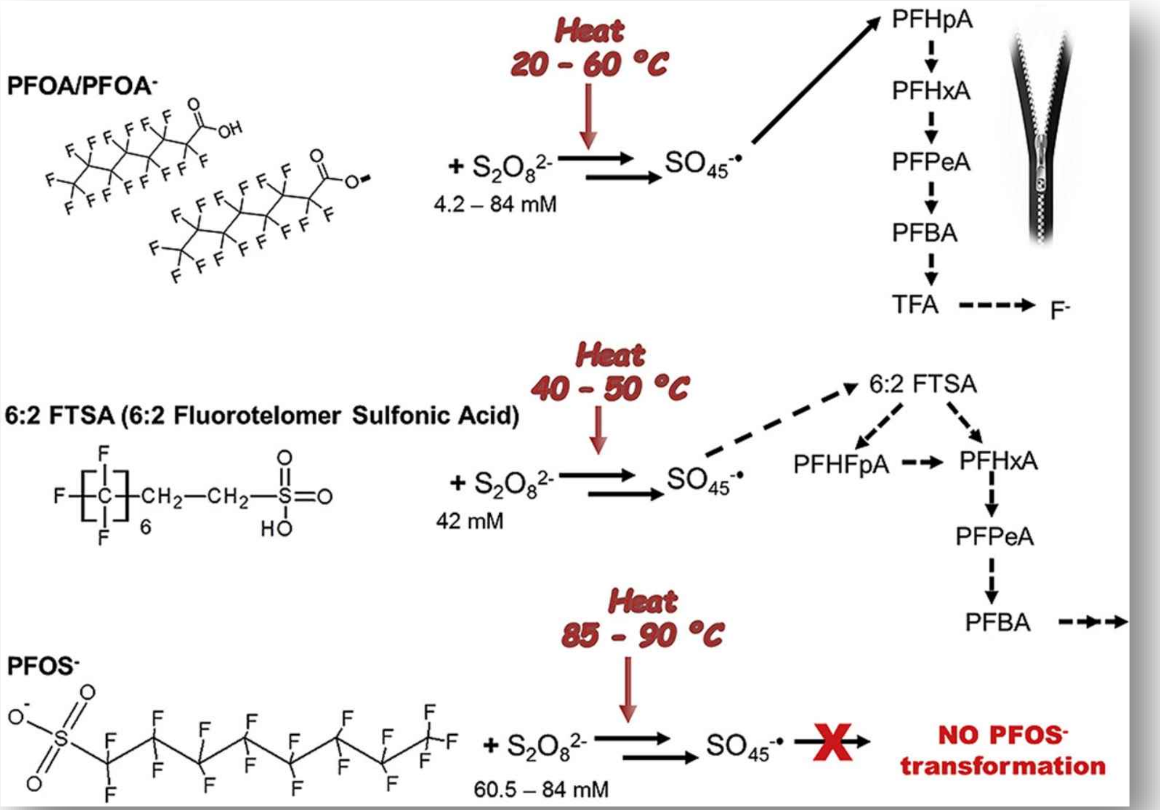




PFAS Remediation

Challenges:

- Limited demonstrated options
- Resistant to degradation due to carbon-fluoride bond
- Vast number of compounds/structures
- Evolving toxicity & analytical
- Low remedial concentrations required
- Sensitive to back & matrix diffusion
- Large diffuse plumes



Park et al., 2015

PFAS InSitu Remediation

Current Approaches

- Ex Situ based
- Pump & Treat
  - Sorptive based
    - Granular activated carbon
    - Ion exchange resin
- Foam Fraction
  - Concentrated waste generated
  - Expensive and never ending

PFAS InSitu Remediation

In Situ Treatment

– Limited demonstrated options
  - –Sorptive based
    - Colloidal activated carbon (PlumeStop™)
    - Dozens of applications
    - ESTCP (ER20-5182)

- Powder activated carbon
  - –Distribution and injection challenges
- Ion exchange resin
  - –Promising laboratory results
  - –Field test forthcoming (ESTCP, ER21-7554)

Air-Water Source Zone Site

- Current approaches focus on plume treatment, excavation & stabilization
- **Studies have shown PFAS**
  - Accumulate and attenuate at air-water interface (Anderson et al; Brusseau et al.)
    - Physical and chemical properties of PFAS
    - Surfactant-like qualities
    - **Factors:** aquifer properties, ionic strength, LNAPL presence, etc
    - Mass at interface can be orders of magnitude greater than in plume
  - **Potential Importance**
    - Long term source
  - Can we limit mass flux from the interface (Carey et al, 2024)

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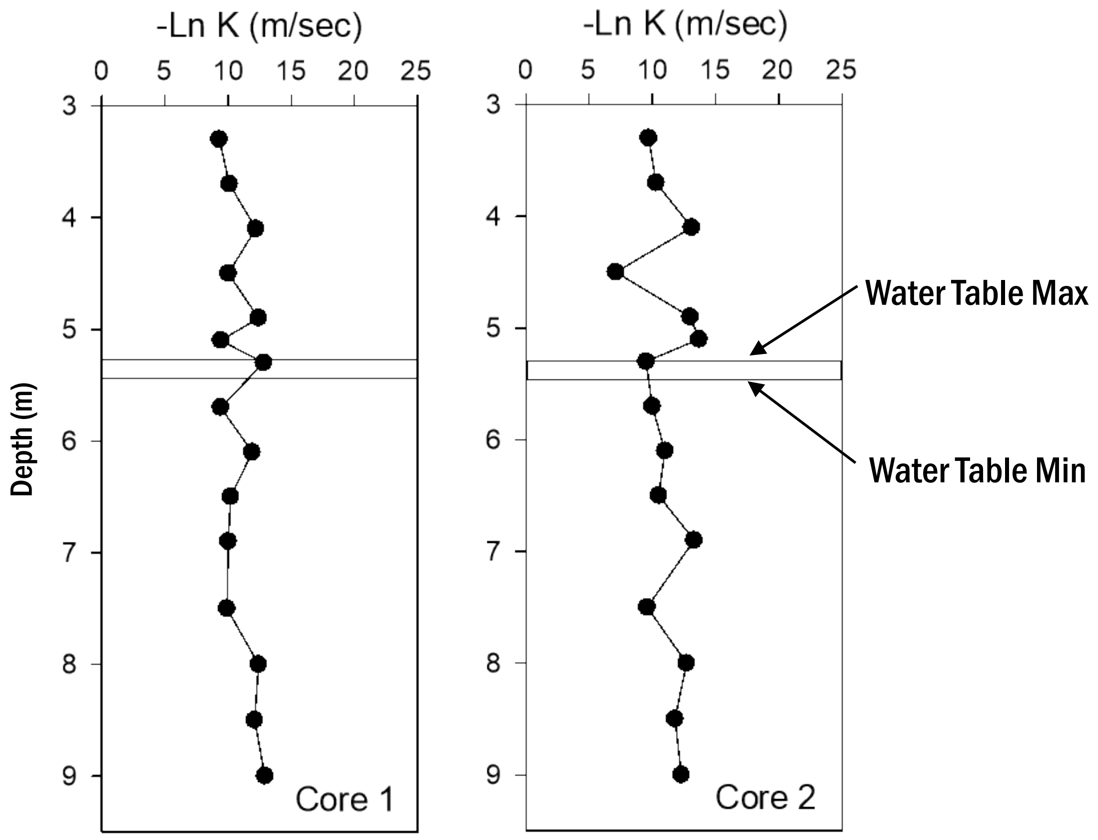
Study Site

- Former fire-fighting training area
- Geology
  - Silty sand
- Hydrogeology
  - Unconfined aquifer
  - Water table ~18 ft below surface
  - K: $1x10^{-6}$ to $9x10^{-4}$ m/sec
  - Groundwater velocity ~ 50 ft/year
- Geochemistry
  - Iron & sulfate reducing



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Study Site

- Shallow groundwater source zone
  - PHC & VOC plume with PFAS present
    - CVOC up to 459 ug/L
    - PHC F1/F2 up to 2,680 ug/L
  - 23 PFAS analyzed, 6 detected
    - C5 to C9 carbon chain
    - PFBA up to 6,720 ng/L
    - PFHxA up to 16,890 ng/L
    - PFHpA up to 5,890 ng/L
    - PFNA up to 2,140 ng/L
    - PFOA up to 3,560 ng/L
    - PFPeA up to 31,240 ng/L

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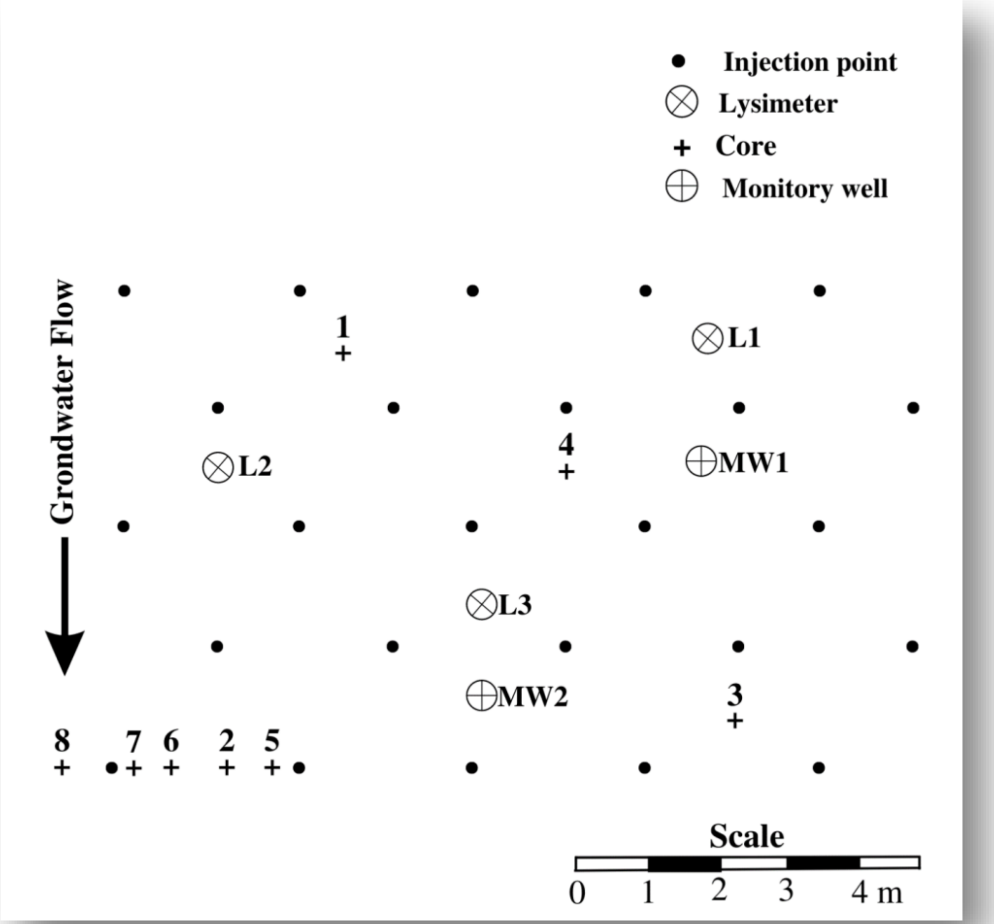
Study Site

Porewater collected from lysimeters

- 23 PFAS analyzed, 6 detected
- C5 to C9 carbon chain
    - PFBA up to 63,340 ng/L
    - PFHxA up to 164,350 ng/L
    - PFHpA up to 164,350 ng/L
    - PFNA up to 3,145 ng/L
    - PFOA up to 6,340 ng/L
    - PFPeA up to 307,450 ng/L

Study Site

- Test Area:
  - 100 m^2 area
  - Targeted air-water interface
- Reagents
  - Colloidal activated carbon (PlumeStop™)
  - 1,760 lbs injected in 30,400 gallons
- Injection
  - Grid – 6 foot spacing
  - 23 injection points
  - Direct push technology
  - Multiple vertical intervals
    - 20.3 ftbgs & 18.4 ftbgs



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Study Site

- Groundwater Monitoring
  - Combination of 2” wells (2) and lysimeters (9)
  - cVOCs, PHCs F1+F2, inorganics, general chemistry and PFAS
  - Groundwater
    - Pre-injection (2 events), Days 107, 293, 564 & 930
  - Porewater
    - Pre-injection (2 events), Days 107, 199, 293, 381, 564 & 930

- Aquifer Solids
  - Continuous cores for TOC, pre- & post injection
  - Distribution and “radius” of detection
- Aquifer Testing
  - Moisture content
  - Cores for flexible wall permeameter tests

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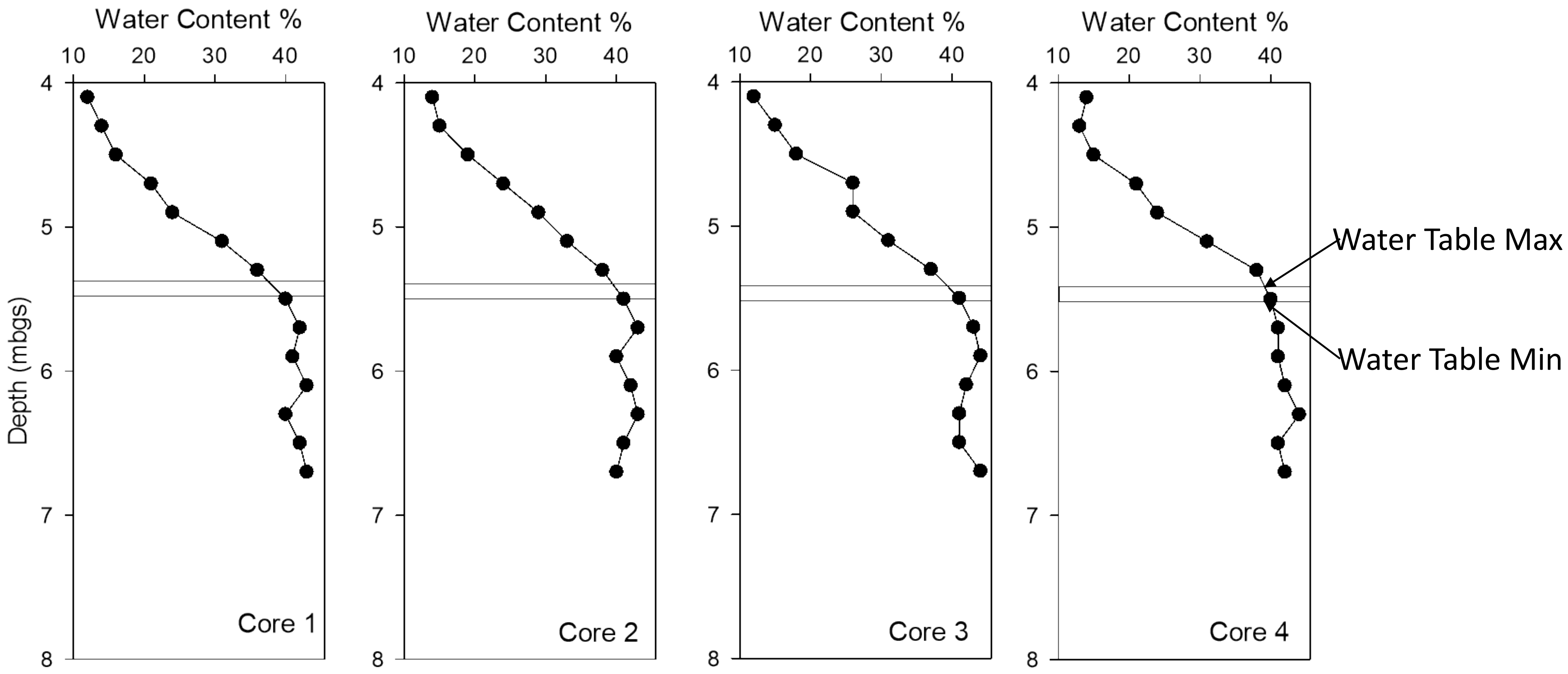
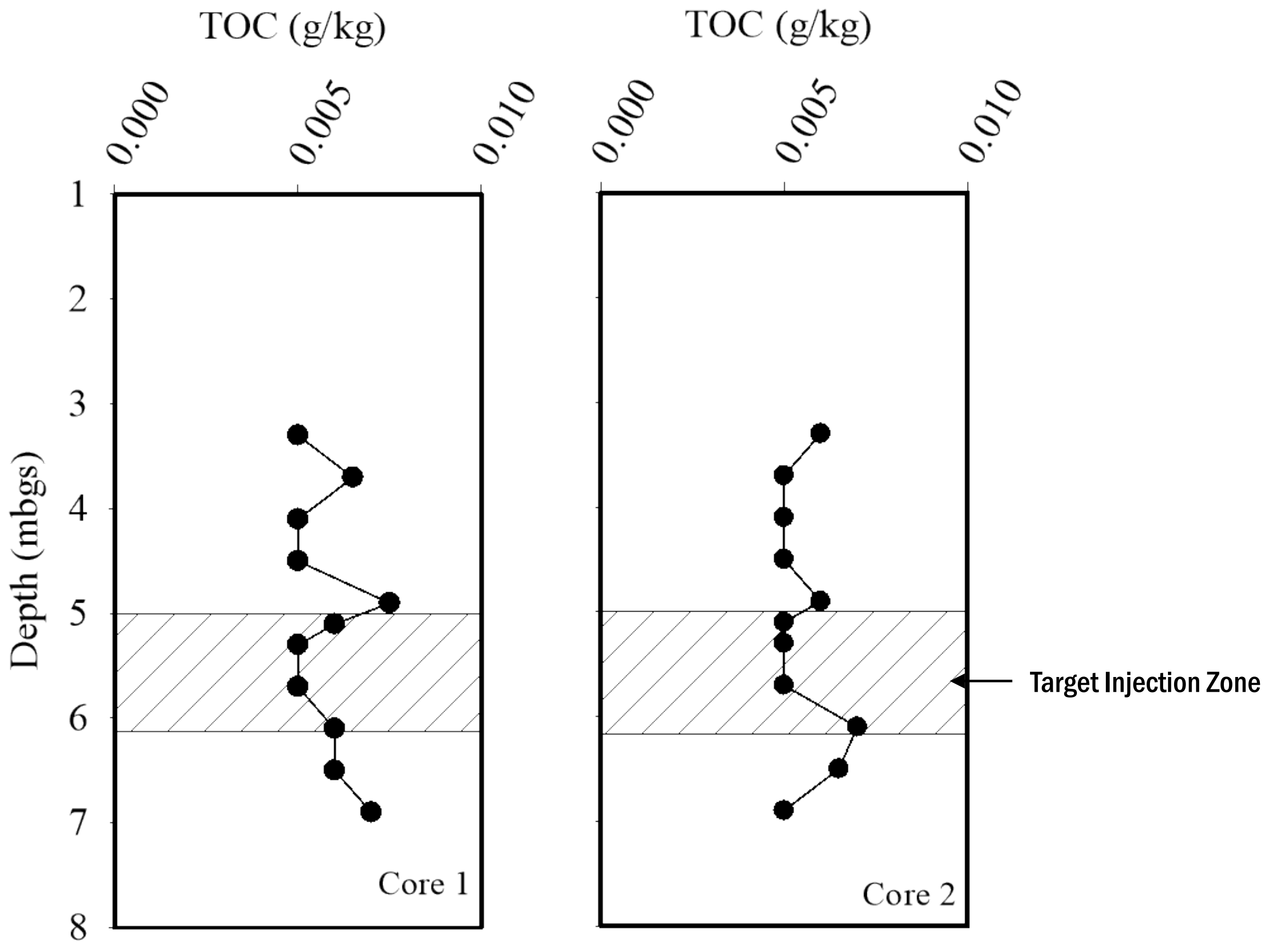
Study Site



Water Content %
10
20
30
40
Depth (mbgs)
4
5
6
7
8
Core 1
Core 2
Core 3
Core 4
Water Table Max
Water Table Min

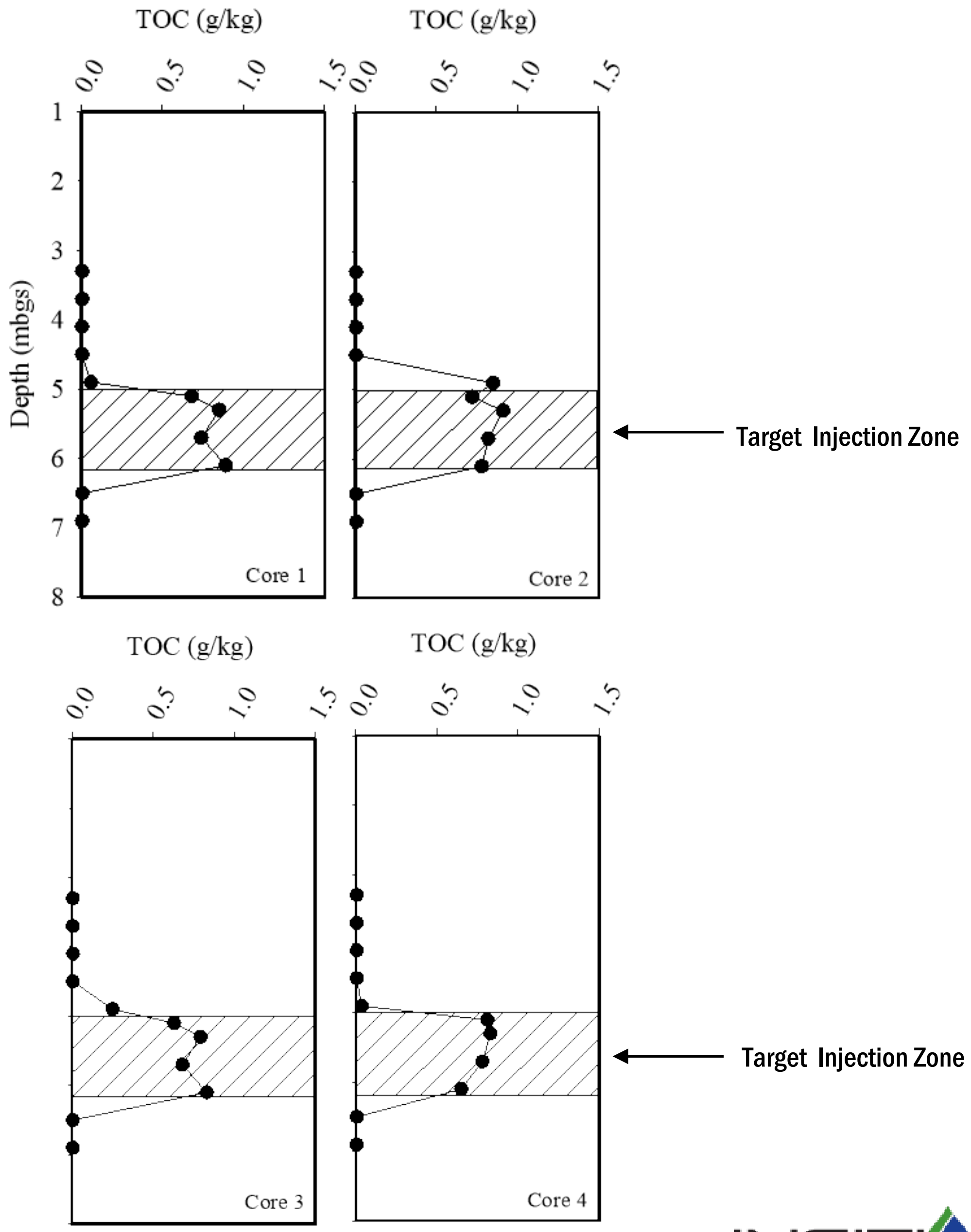
Study Site

- Pre-Injection TOC
  - Measurement of TOC
  - Corrected for inorganic C
- Results
  - Detection limit: 0.005 g/kg
  - Number: 22 samples
  - Maximum: 0.0075 g/kg
  - Minimum: 0.005 g/kg
  - Mean: 0.0057 g/kg

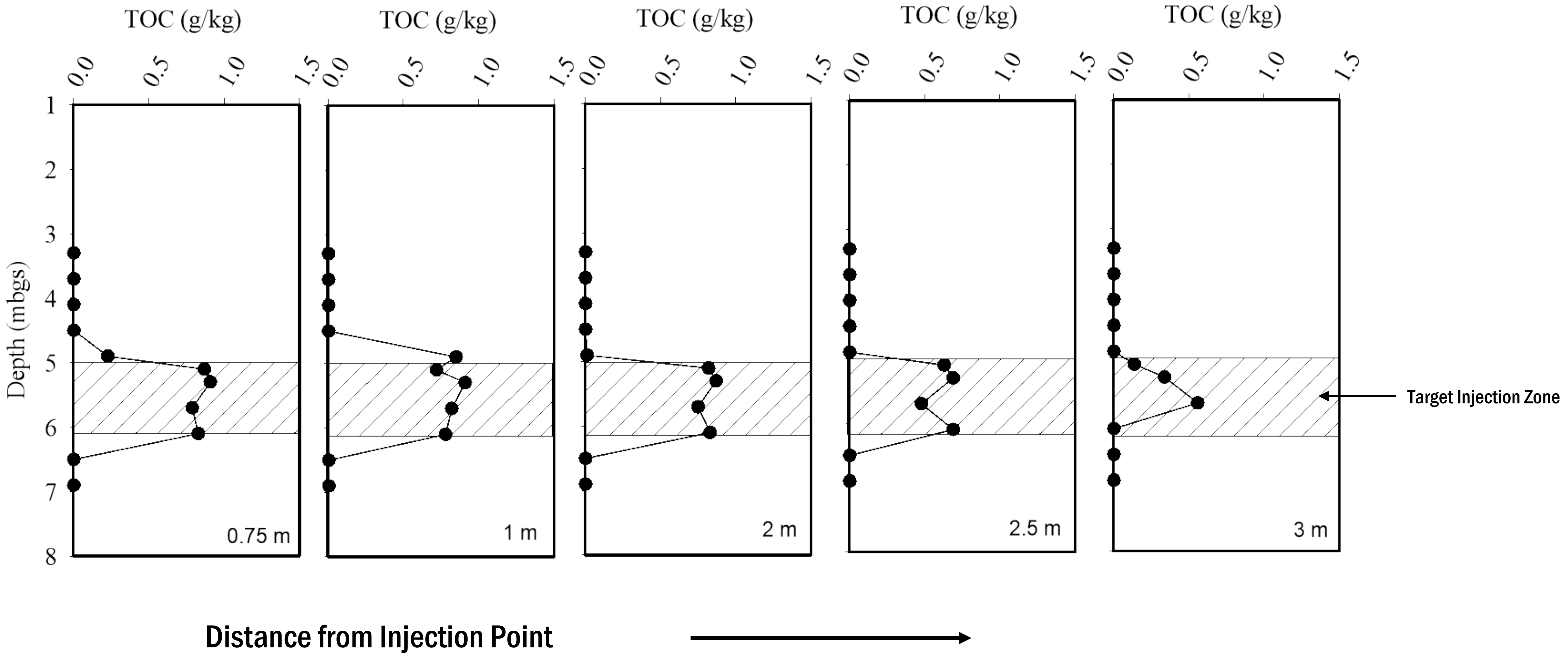


Study Site

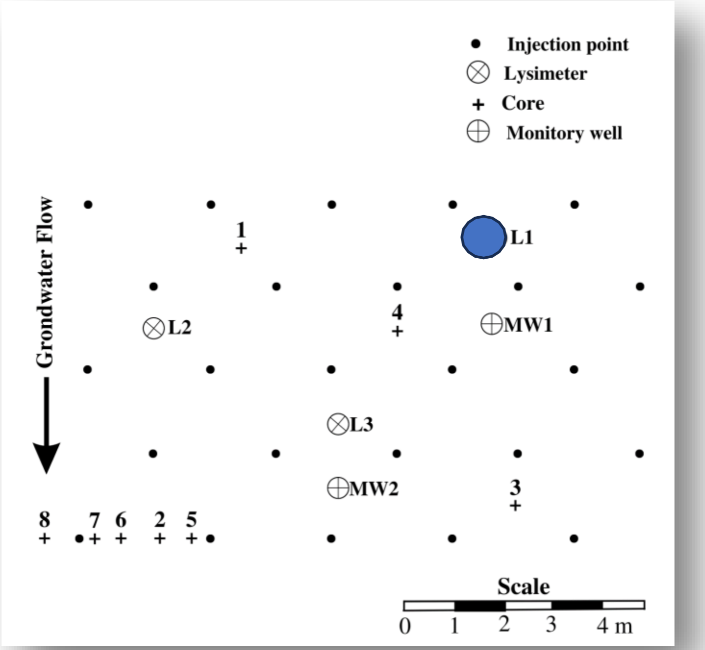
- Post-Injection TOC
  - Measurement of TOC
  - Corrected for inorganic C
- Results
  - Detection limit: 0.005 g/kg
  - Number: 88 samples
  - Maximum: 0.91 g/kg
  - Minimum: 0.005 g/kg
  - Mean: 0.276 g/kg
  - Mean TIZ: 0.706 g/kg
  - 100 % of samples within TIZ detected elevated TOC
  - 8.9 % of samples outside TIZ detected elevated TOC



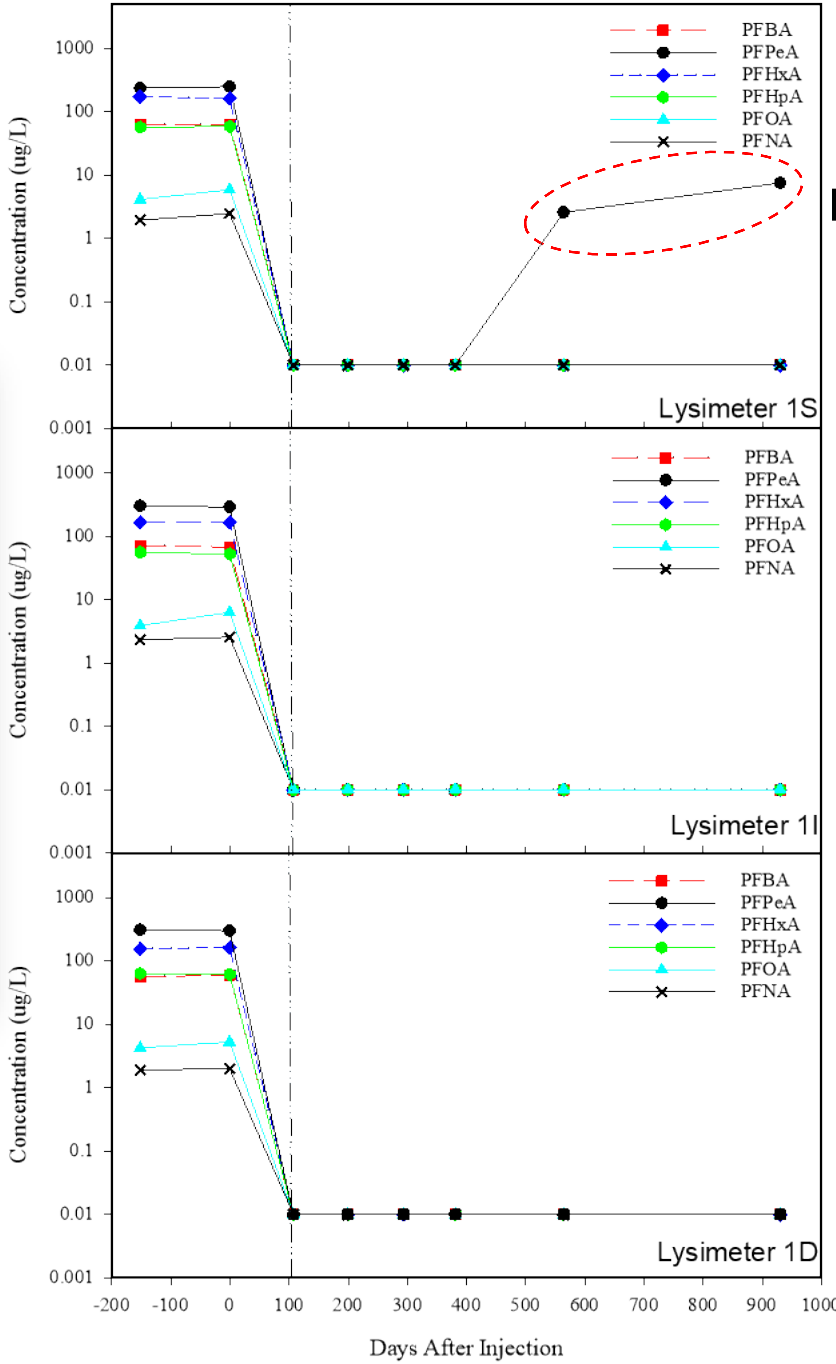
Study Site


TOC (g/kg)
0.0
0.5
1.0
1.5
Depth (mbgs)
1
2
3
4
5
6
7
8
0.75 m
1 m
2 m
2.5 m
3 m
Target Injection Zone
Distance from Injection Point

Study Site



Lysimeter 1



PFPeA – short C chain PFAS (5)

Detection Limit

Detection Limit

Detection Limit

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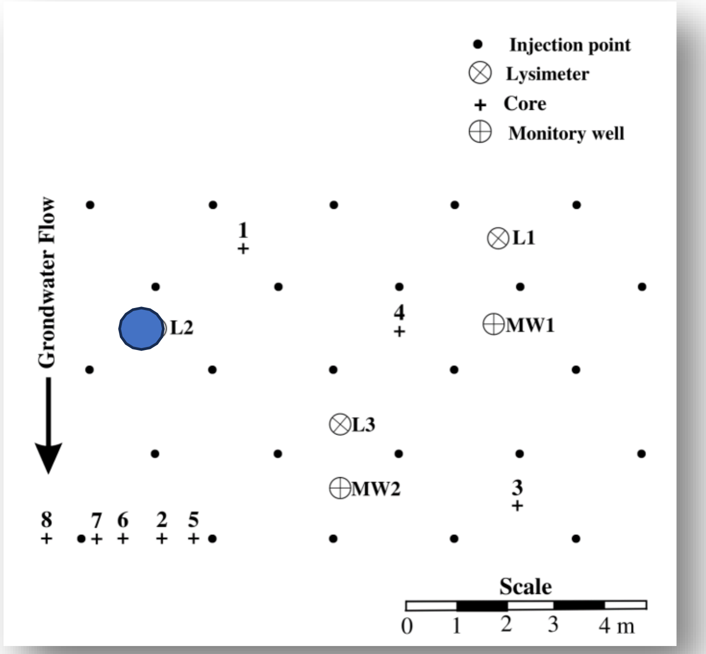
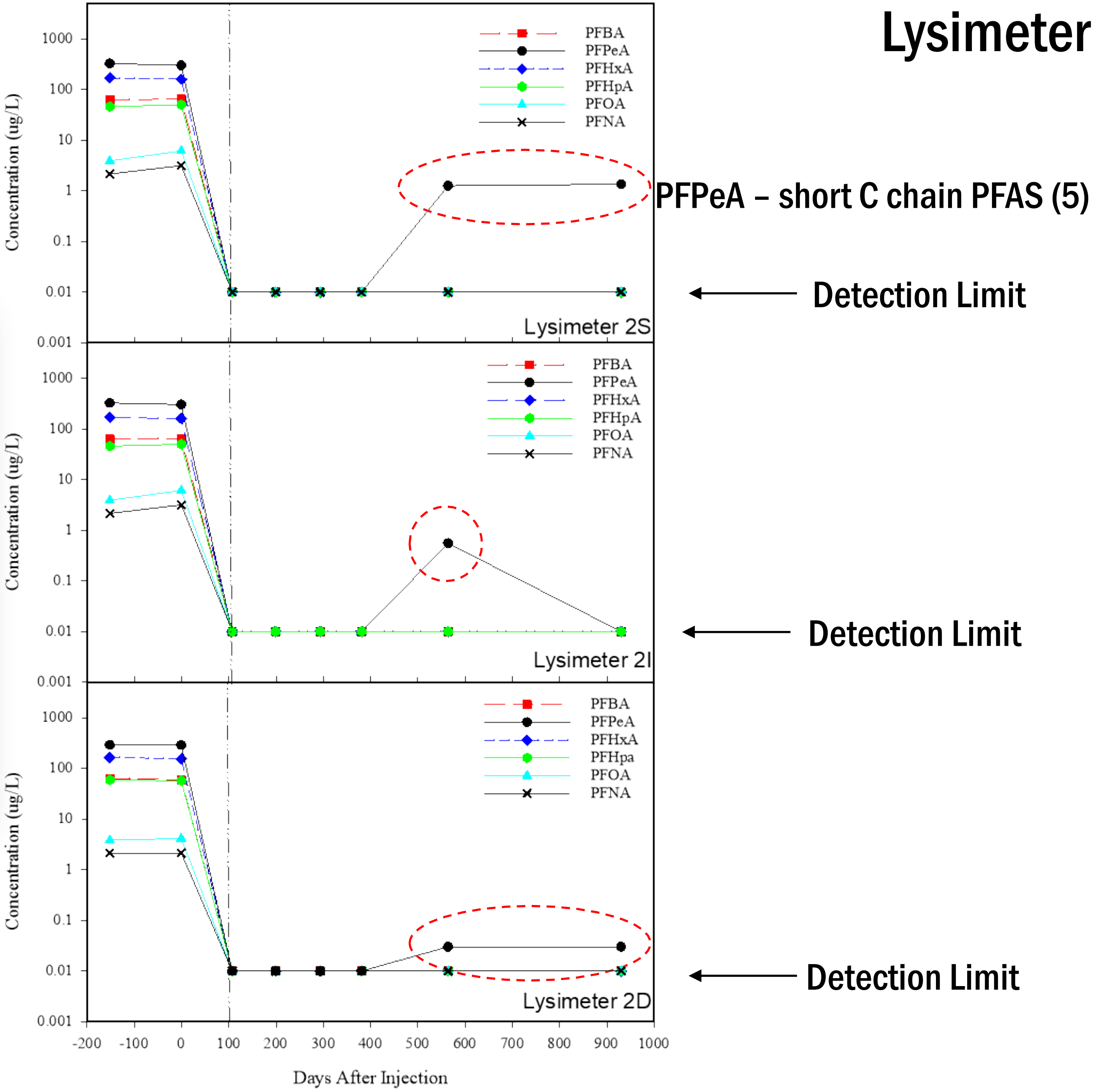
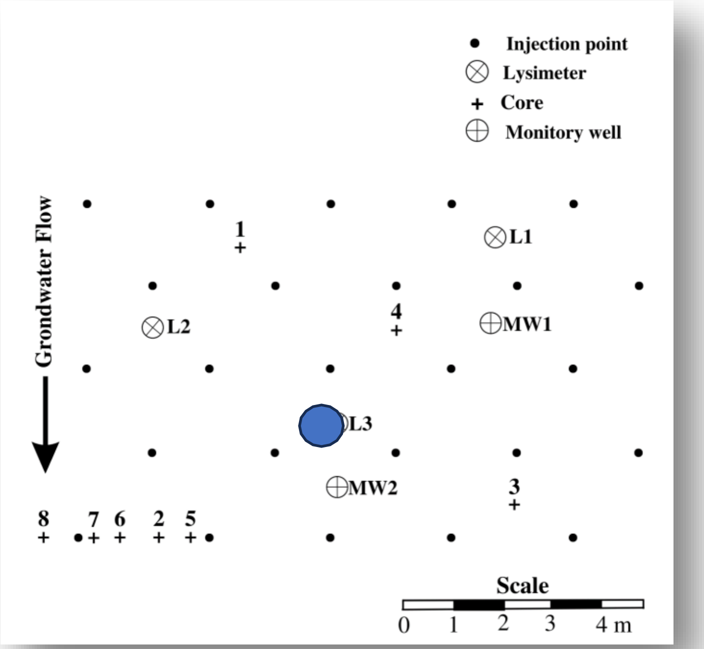
Study Site



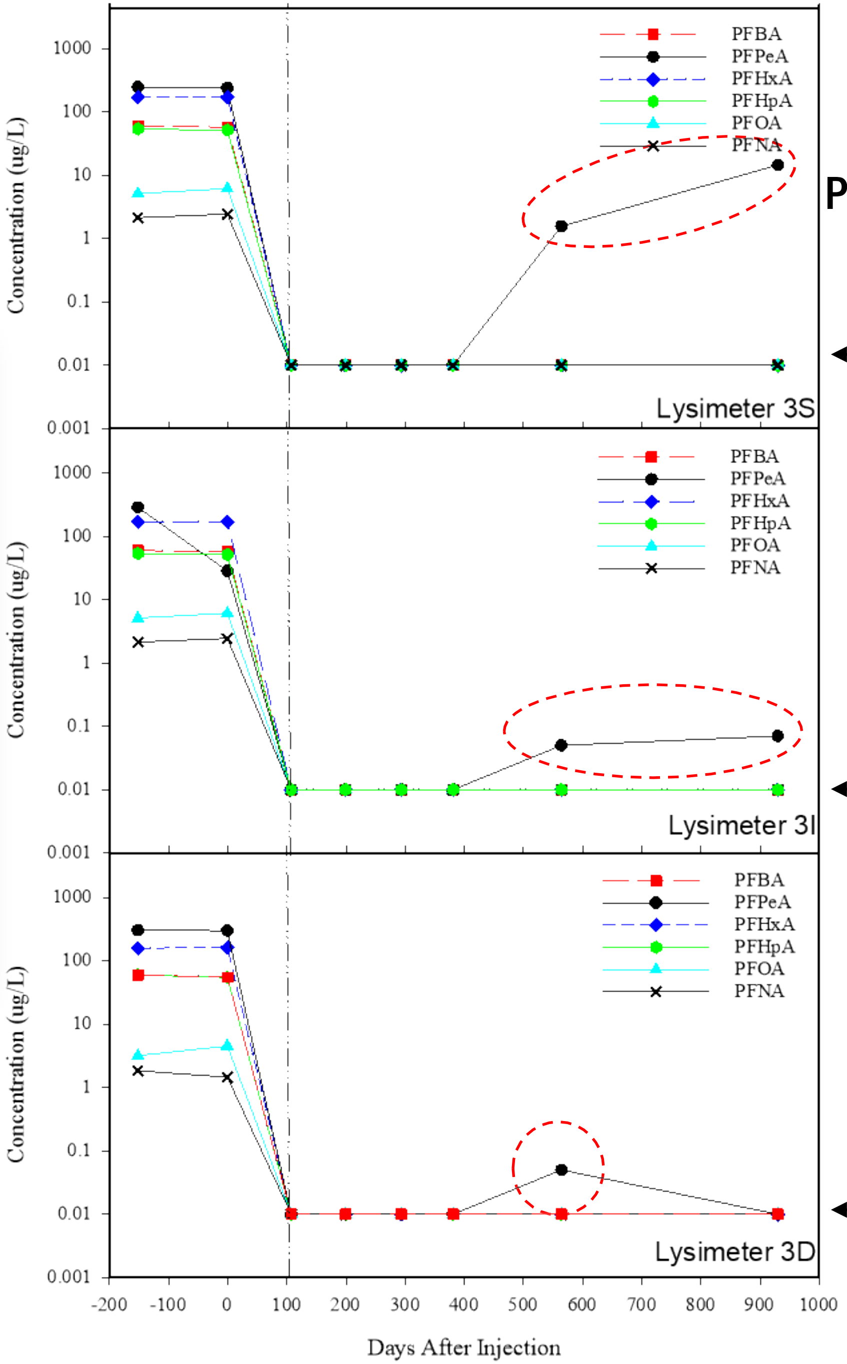
Lysimeter 2



Study Site



Lysimeter 3



PFPeA – short C chain PFAS (5)

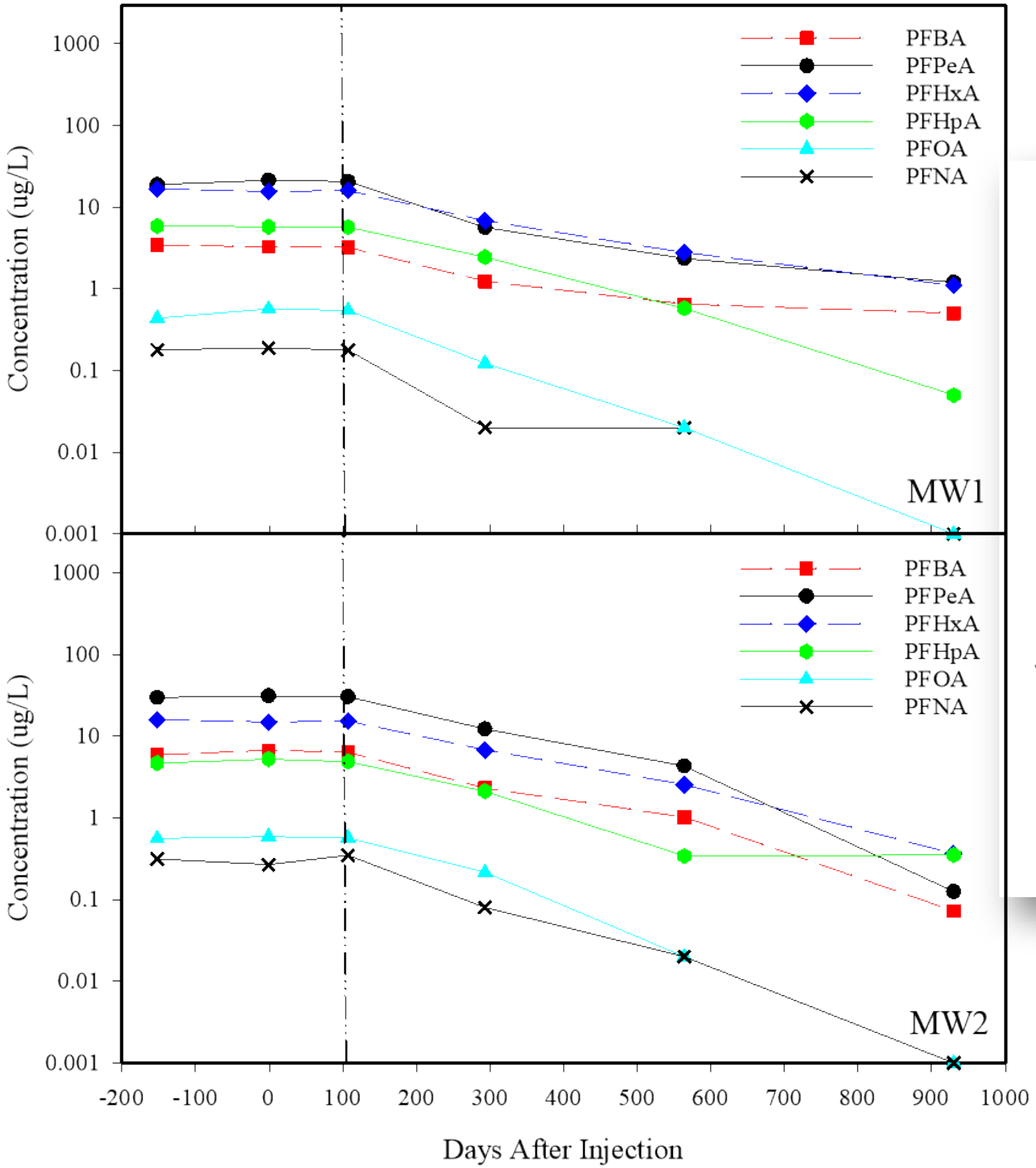
Detection Limit

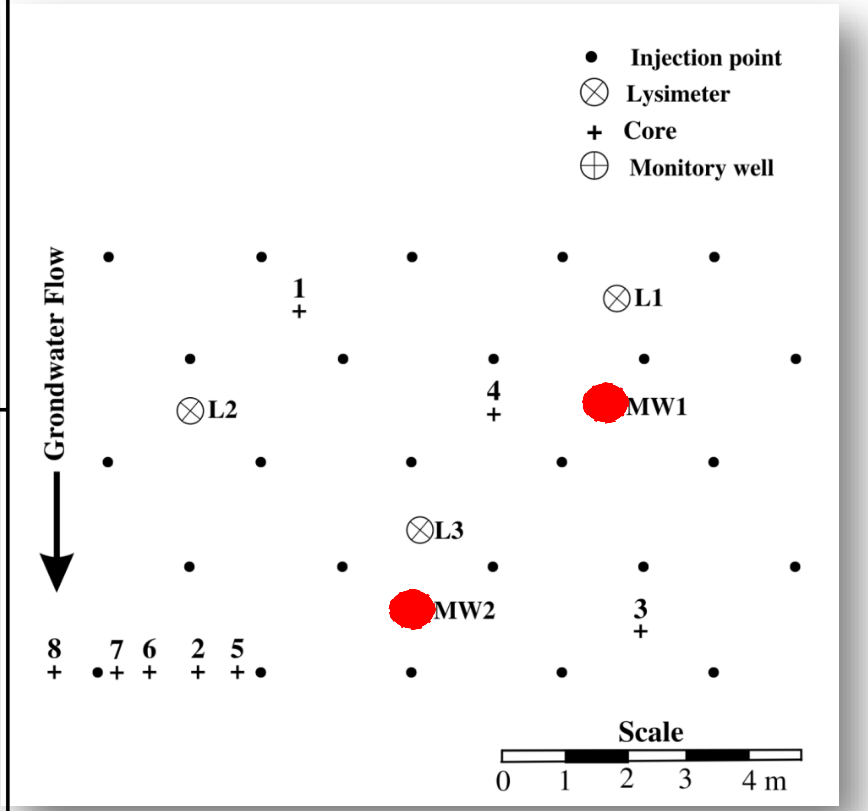
Detection Limit

Detection Limit

Study Site

Groundwater





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Summary

- **Distribution**
  - With TIZ 100% of samples had elevated TOC concentrations post injection
  - Overall within TIZ, TOC concentrations increased by > 3 orders of magnitude
  - Outside of TIZ, less than 9% of samples had elevated TOC concentrations post injectio
  - PlumeStop detected greater than 3.0 m away from injection point
- **PFAS Treatment within Pore Water**
  - Of the six detected PFAS all went to ND within 3 months of injection
  - PFPeA was detected in select lysimeters after 1.5 years
- **PFAS Treatment within Shallow Groundwater**
  - Mass flux of PFAS into the shallow groundwater decreased by >80% (PFBA) to 99.9% (PFOA) over the 30-month monitoring period

On Going Studies

- Fractured Bedrock
  - Central Canada
  - Overburden & bedrock impacted by foam
  - PlumeStop™
  - C6 > ND, breakthrough of C4 & C5 in rock
- Saline Aquifer
  - Middle East,
  - Bulk petroleum hydrocarbon facilities
  - PlumeStop ™
  - 36 months, ND for PFAS
- Long-term Testing
  - Central Ontario site, > 8 years
  - PlumeStop™

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On Going Studies

- Laboratory
  - Isotherm
  - Co-competition studies
  - Analytical issues
  - Column tests
    - U of Toronto & U of Waterloo
  - Numerical modeling
    - Porewater Solutions
    - University of Toronto & Carleton University
  - Field testing (SRDEP)
    - Jacksonville

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On Going Studies

RESEARCH ARTICLE
WILEY

Six pilot-scale studies evaluating the in situ treatment of PFAS in groundwater

Rick McGregor

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Distribution of Colloidal and Powdered Activated Carbon for the *in Situ* Treatment of Groundwater

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Abstract
The use of *in situ* technologies for the treatment of groundwater containing various compounds of concern are widely accepted. These technologies include chemical reduction, chemical oxidation, anaerobic and aerobic bioremediation, and adsorption, among others. One requirement for the successful application of these technologies is the delivery of the remedial reagent(s) to the compounds of concern. A rapidly evolving *in situ* technology is the injection of adsorptive media such as activated carbon and ion-exchange resin including powdered or colloidal activated carbon. Activated carbon has a long-demonstrated history of effectiveness for the removal of various organic and inorganic compounds in above ground water treatment systems. However, due to constraints related to the particle size and physical properties of the activated carbon, the *in situ* application of activated carbon has been limited. Recent developments in the manufacturing of activated carbon have created a smaller particle size allowing activated carbon to be applied *in situ*. To evaluate if powdered and colloidal activated carbon can be effectively distributed in aquifers, the two types of carbon were injected using direct push technology adjacent to each other at four sites with varying geology. Evaluation of distribution was completed by sampling the aquifer prior to and post-injection for total organic carbon. The results of the studies indicated that both forms of activated carbon were effectively delivered to the targeted injection zones with both carbon types being detected at least seven meters away from the point of injection. The colloidal form of the activated carbon showed good distribution throughout the four targeted zones of injection with 93 percent of the samples collected having colloidal activated carbon present within them whereas the powdered activated carbon cells were more susceptible to aquifer heterogeneity with only 67 percent of the samples collected having activated carbon present. Preferential accumulation of activated carbon was

frontiers in Environmental Chemistry
ORIGINAL RESEARCH

The Effect of Heterogeneity on the Distribution and Treatment of PFAS in a Complex Geologic Environment

Rick McGregor[1]* and Leticia Benevenuto[2]

Received: 5 January 2022 | Accepted: 6 January 2022
COMMENTARY
WILEY

PFAS Experts Symposium 2: Statements on available in situ remediation technologies

Stewart Abrams[1] | Rick McGregor[2] | Matthew Burns[3] | John Galasso[4] | Timothy Havranek[5] | John Hesemann[6] | Jeffrey Longsworth[7] | Jeffrey McDonough[8] | Rebecca Mora[9]

DOI: 10.1002/rem.21675
RESEARCH ARTICLE
WILEY

The in situ treatment of TCE and PFAS in groundwater within a silty sand aquifer

Rick McGregor | Ye Zhao
InSitu Remediation Services Ltd, St George, Ontario, Canada

Remediation. 2021;1–11. wileyonlinelibrary.com/journal/rem © 2021 Wiley Periodicals LLC 1

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