

In-Situ Treatment of PFAS at the Air-Water Interface Using Colloidal Activated Carbon

R. McGregor

InSitu Remediation Services

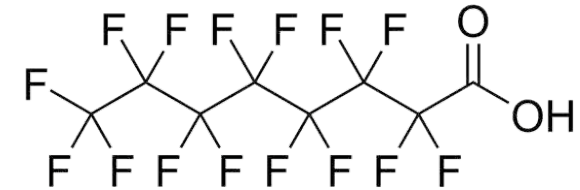
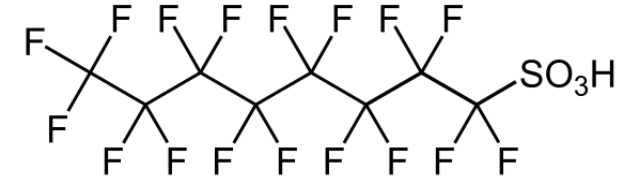
Debora Bueno

Aquífero Serviços de Remediação

March 2023

Agenda

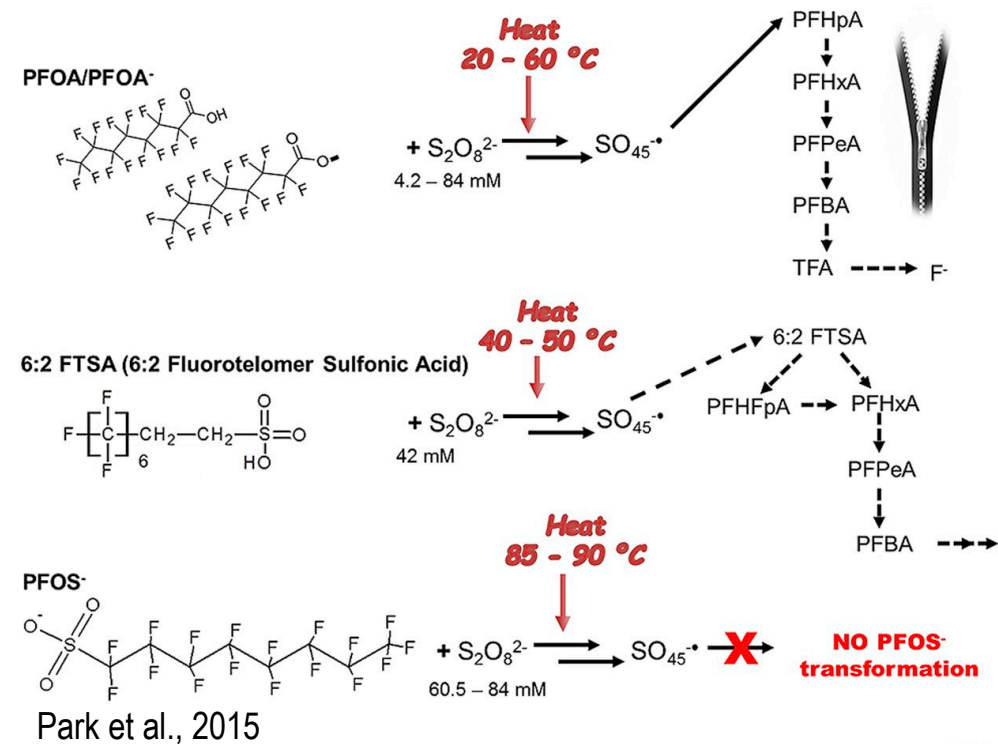
Introduction of PFAS Insitu Remediation
Review of Air-Water Source Zone Study
Update of Ongoing Studies



PFAS Remediation

Challenges:

- Limited demonstrated options
- Resistant to chemical oxidation due to Carbon-Fluoride bond
- Resistant to biodegradation
- Chemox and chem reduction limited
- Low remedial concentrations required
- Sensitive to back & matrix diffusion
- Large diffuse plumes



PFAS InSitu Remediation

Current Approaches

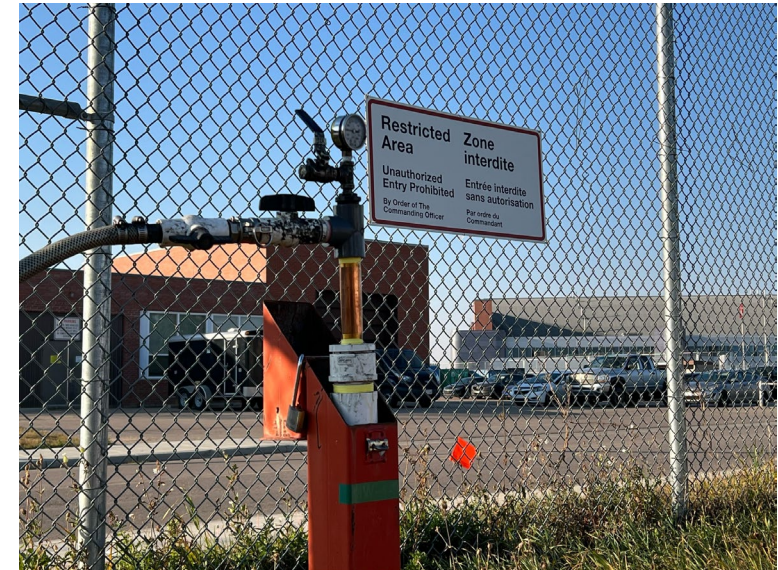
- Ex Situ based
- Pump & Treat
 - Sorptive based
 - Granular activated carbon
 - Ion exchange resin
- Foam Fraction
 - Concentrated waste generated
 - Expensive and never ending



PFAS InSitu Remediation

In Situ Treatment

- Limited demonstrated options
 - Sorptive based
 - Colloidal activated carbon (PlumeStop™)
 - Powder activated carbon
 - Distribution and injection challenges
 - Ion exchange resin
 - Distribution and injection challenges
 - Expensive

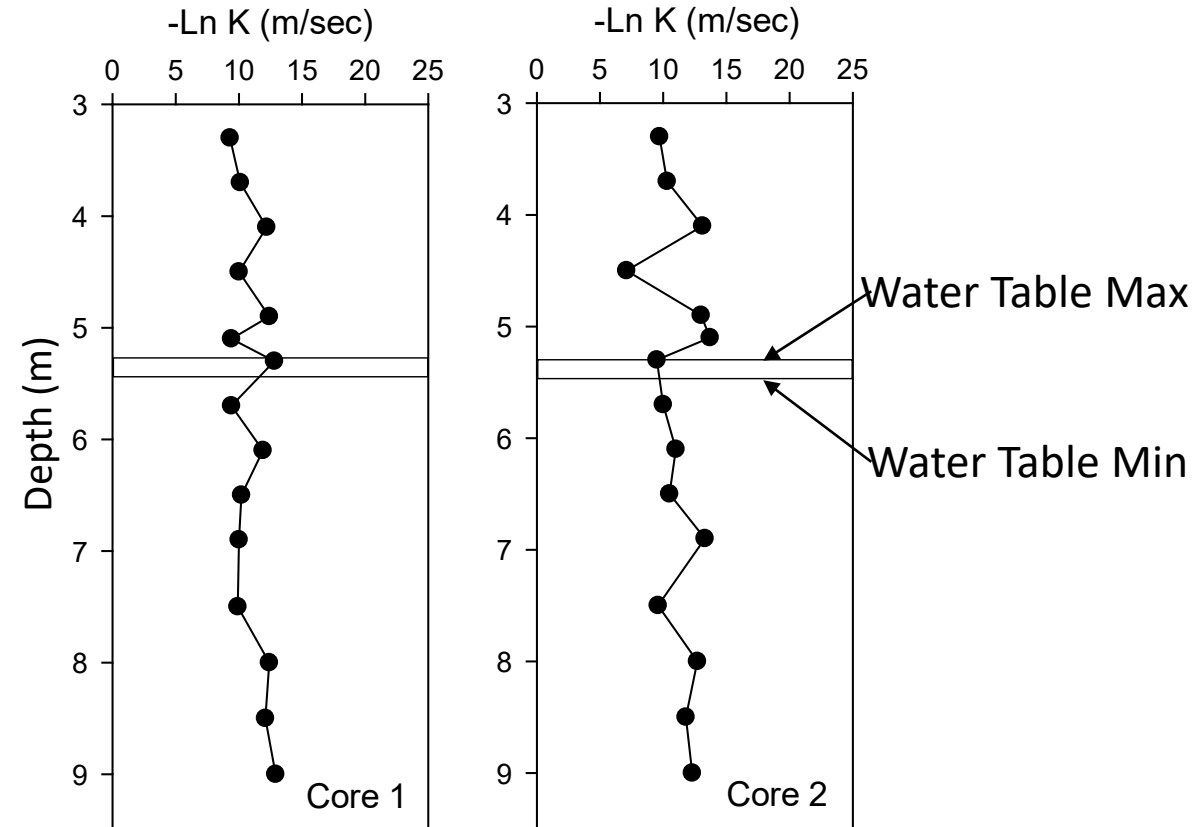


Air-Water Source Zone Site

- 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

Study Site

- Former fire-fighting training area
- Geology
 - Silty sand
- Hydrogeology
 - Unconfined aquifer
 - Water table ~18 ft below surface
 - K: 1×10^{-6} to 9×10^{-4} m/sec
 - Groundwater velocity ~ 50 ft/year
- Geochemistry
 - Iron & sulfate reducing



Study Site

- Shallow groundwater source zone
 - PHC & VOC plume with PFAS present
 - CVOC up to 459 ug/L
 - GRO/DRO 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



Study Site

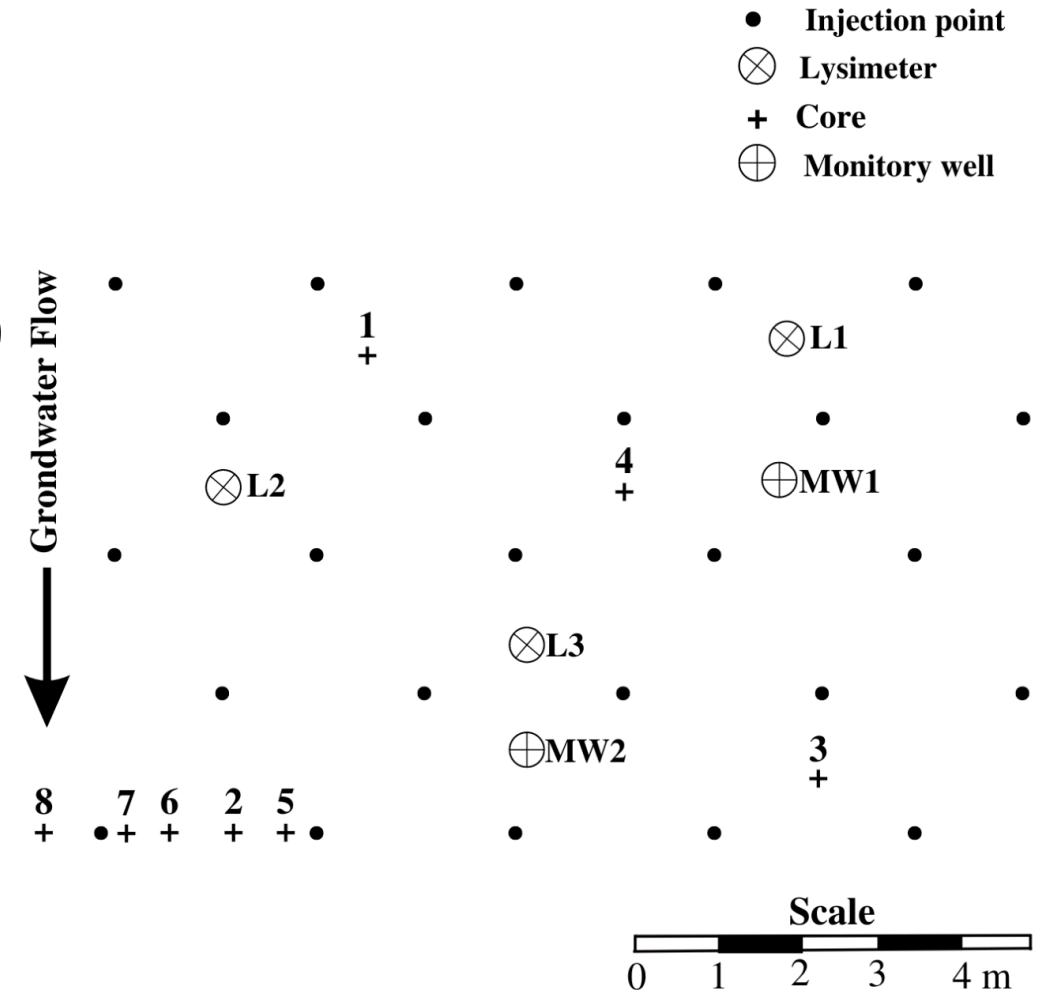
Porewater collected from lysimeters

- 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

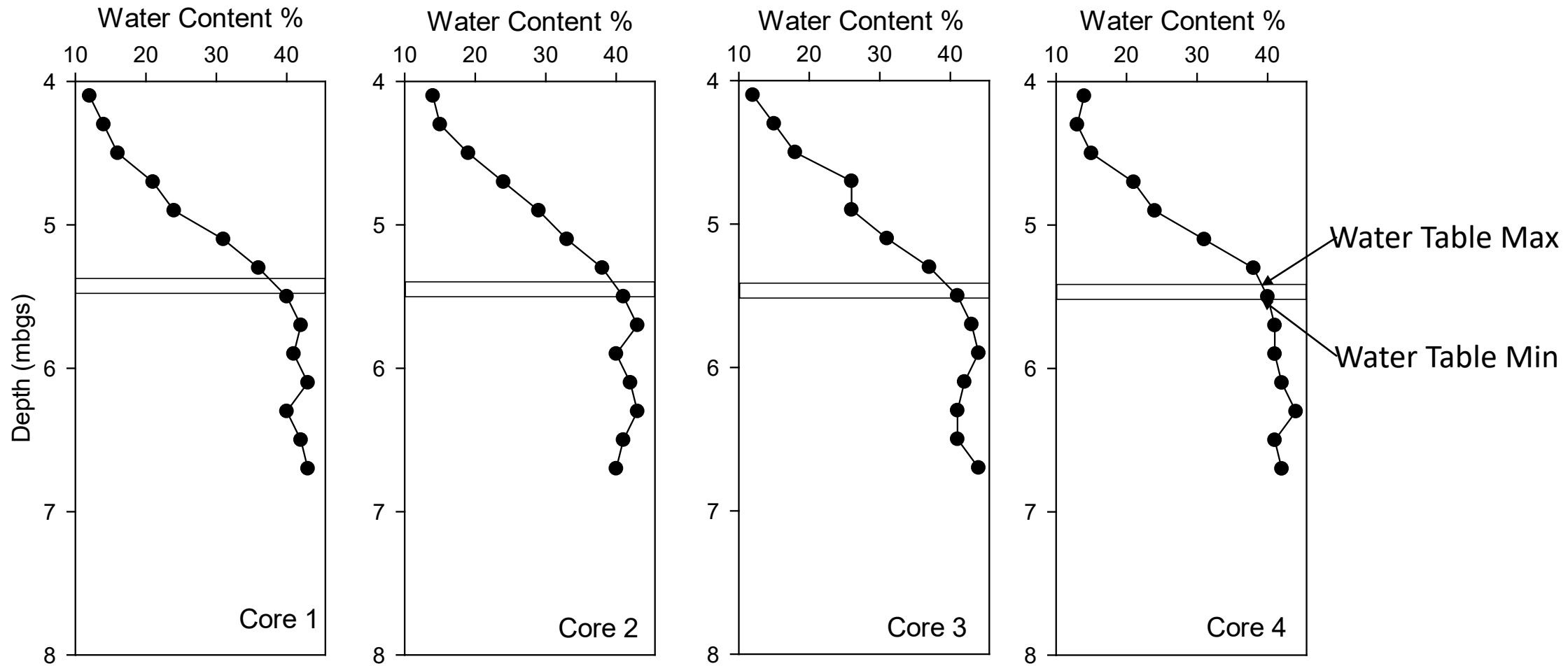
- Test Area:
 - 100 m² area
 - Targeted air-water interface
- Reagents
 - Colloidal activated carbon (PlumeStop™)
 - 800 kg injected in 8,000 litres
- Injection
 - Grid - 6 foot spacing
 - 23 injection points
 - Direct push technology
 - Multiple vertical intervals
 - 20.3 ftbgs & 18.4 ftbgs



Study Site

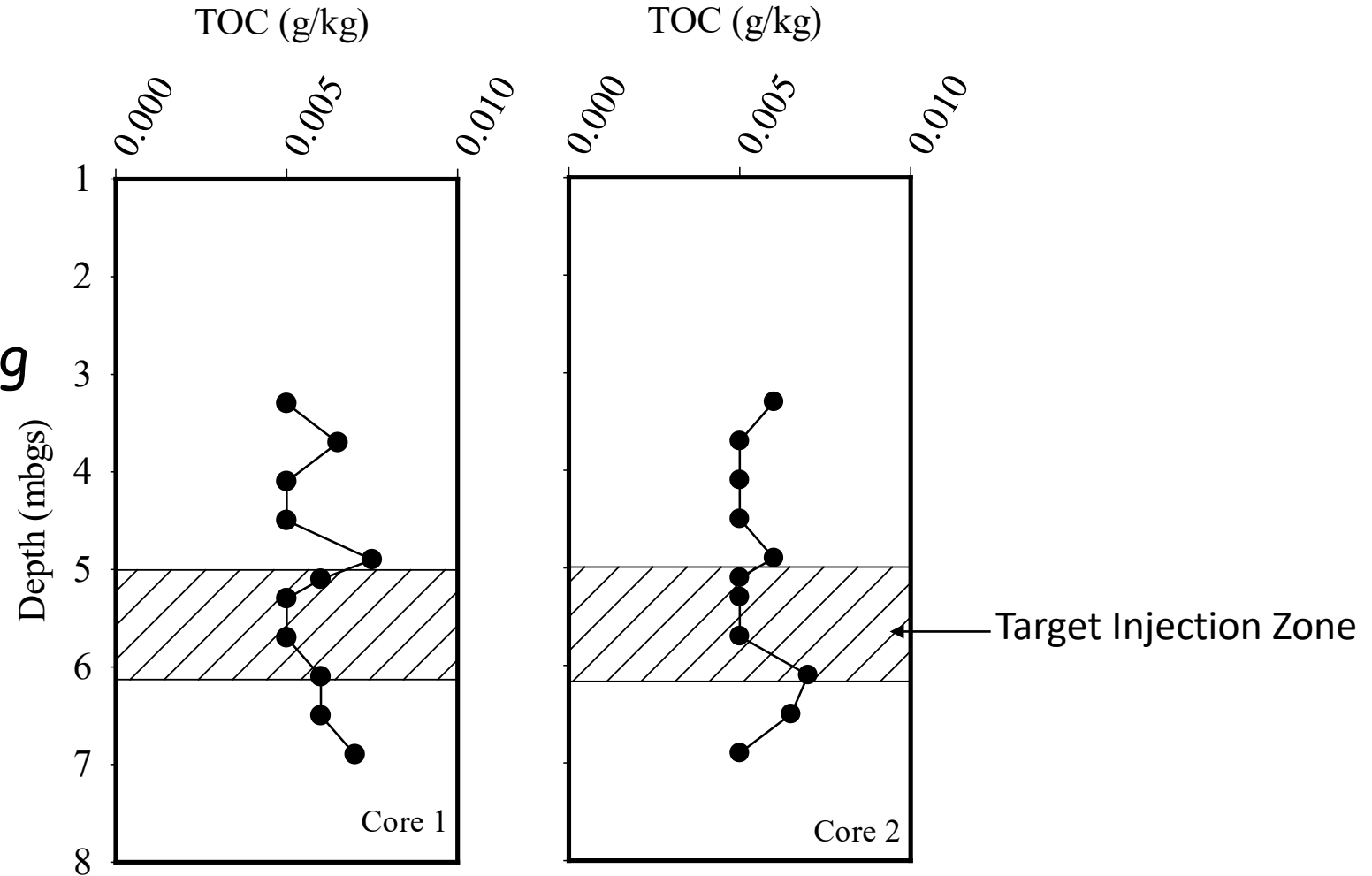
- Groundwater Monitoring
 - Combination of 2" wells (2) and lysimeters (9)
 - cVOCs, GRO, inorganics, general chemistry and PFAS
 - Groundwater
 - Pre-injection (2 events), Days 107, 293, & 564
 - Porewater
 - Pre-injection (2 events), Days 107, 199, 293, 381, & 564
- Aquifer Solids
 - Continuous cores for TOC, pre- & post injection
 - Distribution and "radius" of detection
- Aquifer Testing
 - Moisture content
 - Cores for flexible wall permeameter tests

Study Site



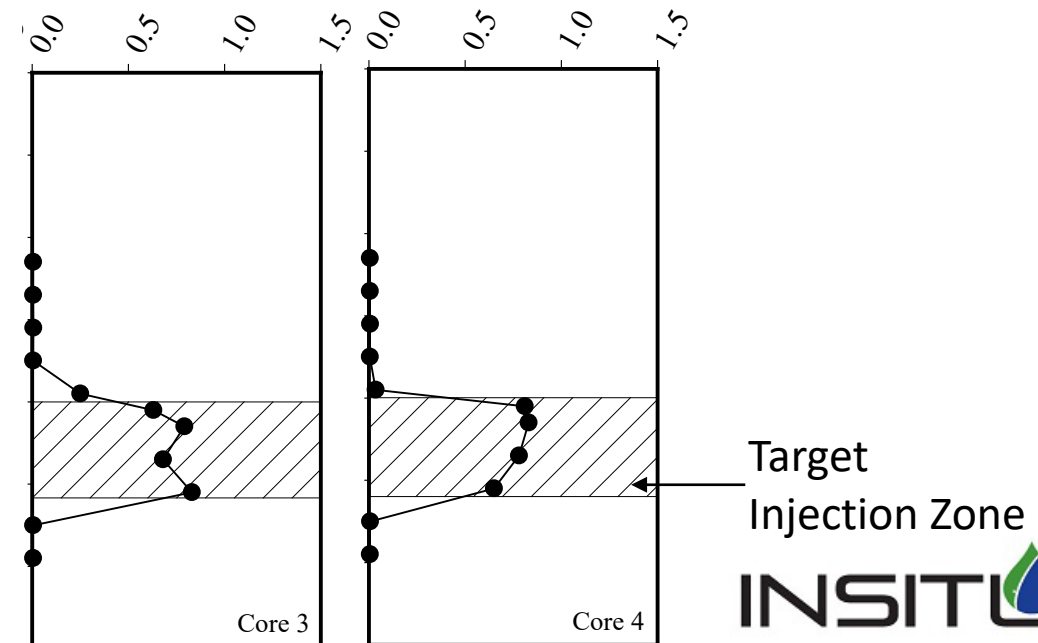
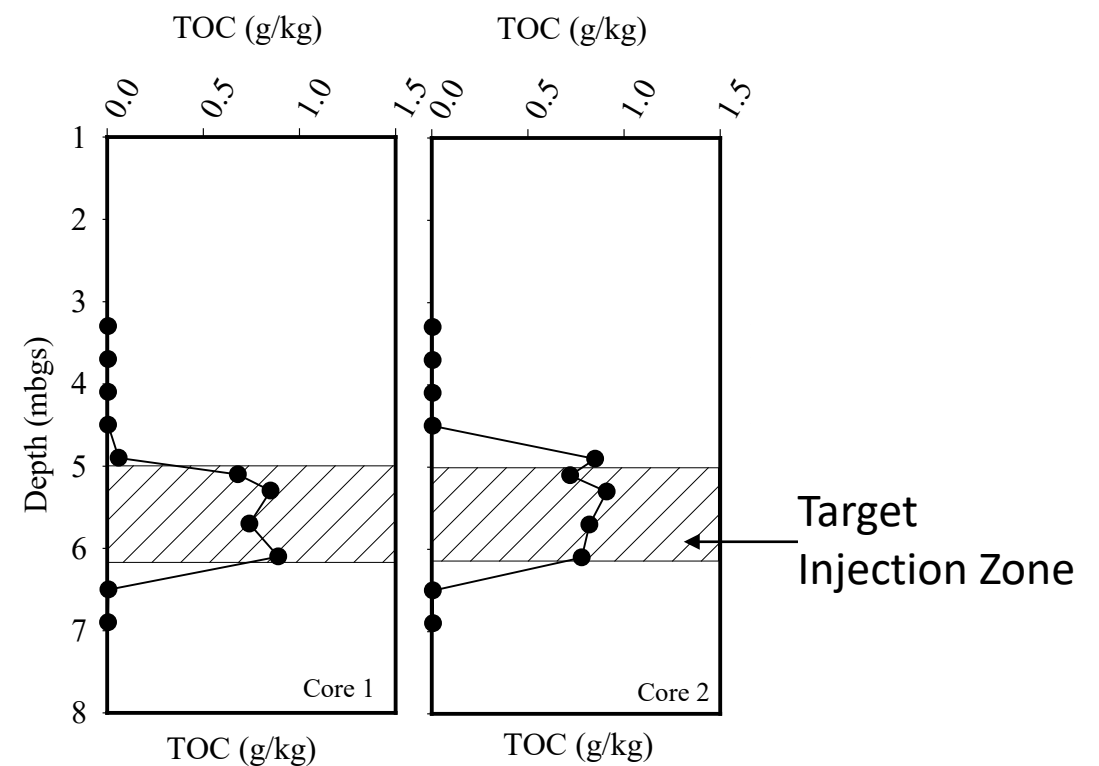
Study Site

- 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

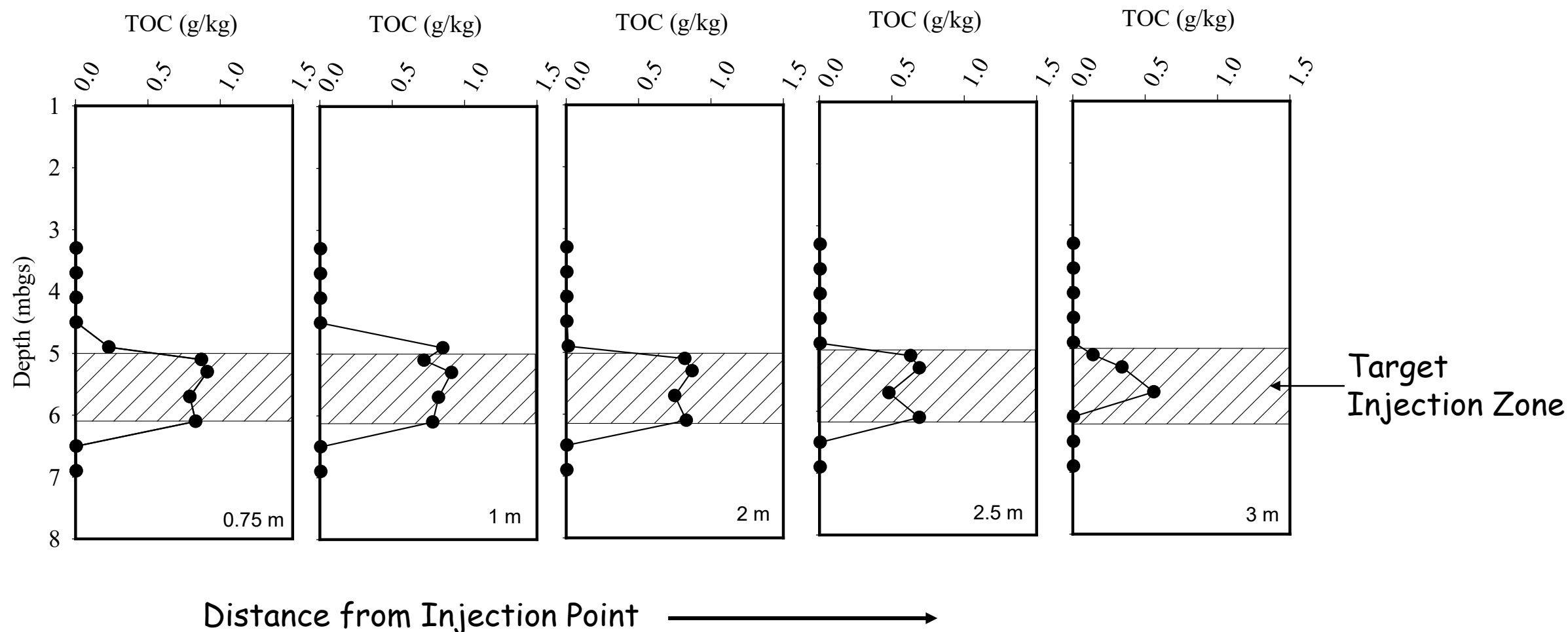


Study Site

- 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

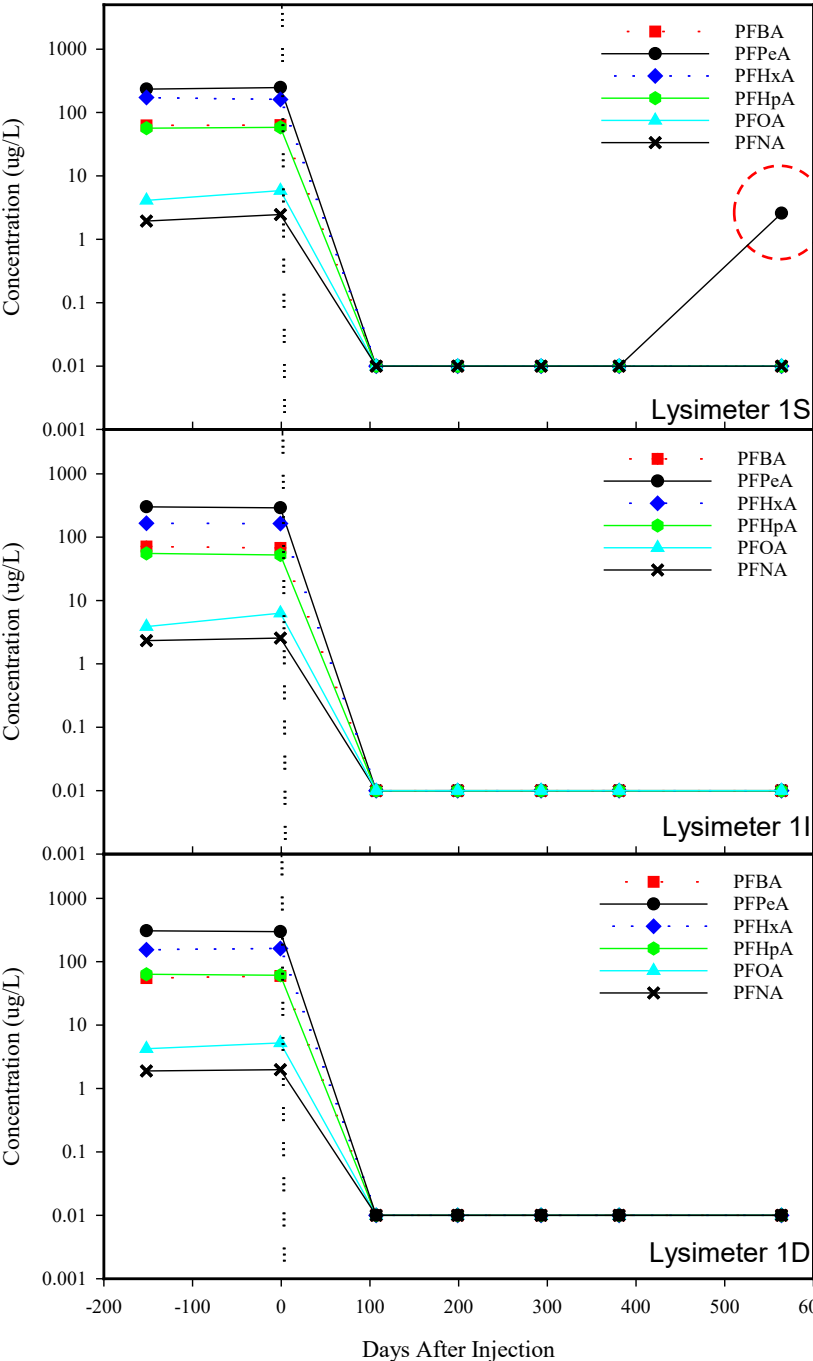


Study Site



Study Site

Lysimeter 1



PFPeA - short C chain PFAS (5)

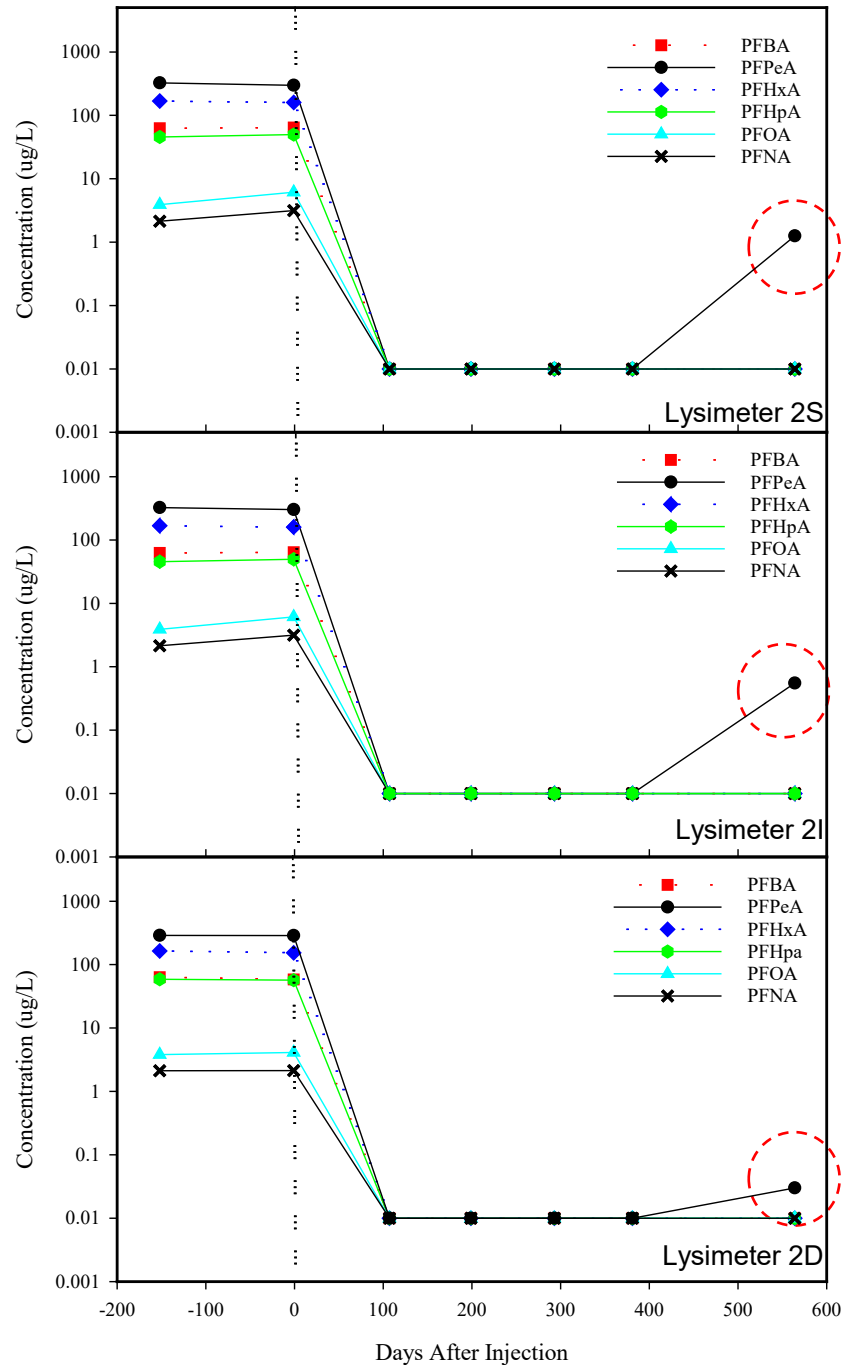
← Detection Limit

← Detection Limit

← Detection Limit

Study Site

Lysimeter 2



PFPeA - short C chain PFAS (5)

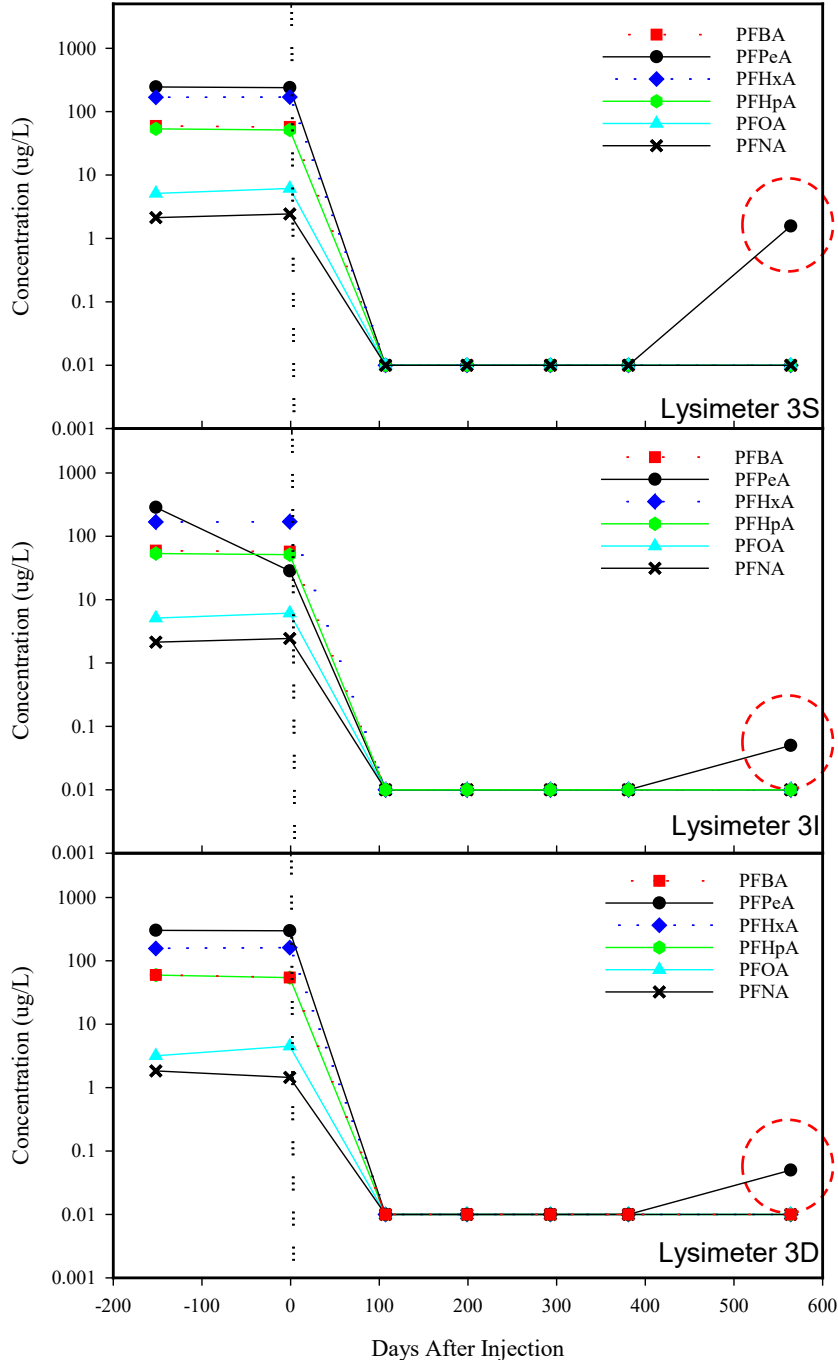
← Detection Limit

← Detection Limit

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Study Site

Lysimeter 3



PFPeA - short C chain PFAS (5)

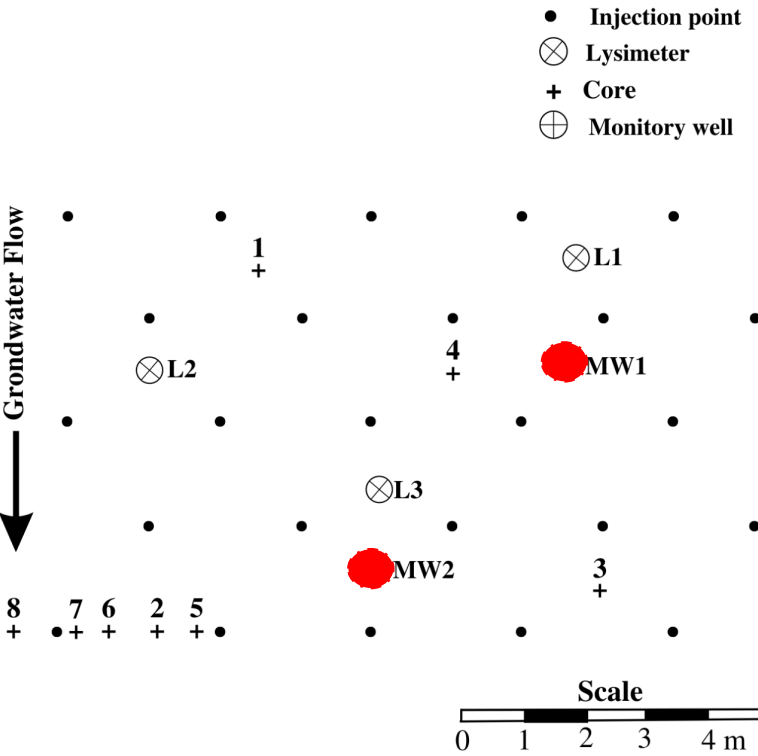
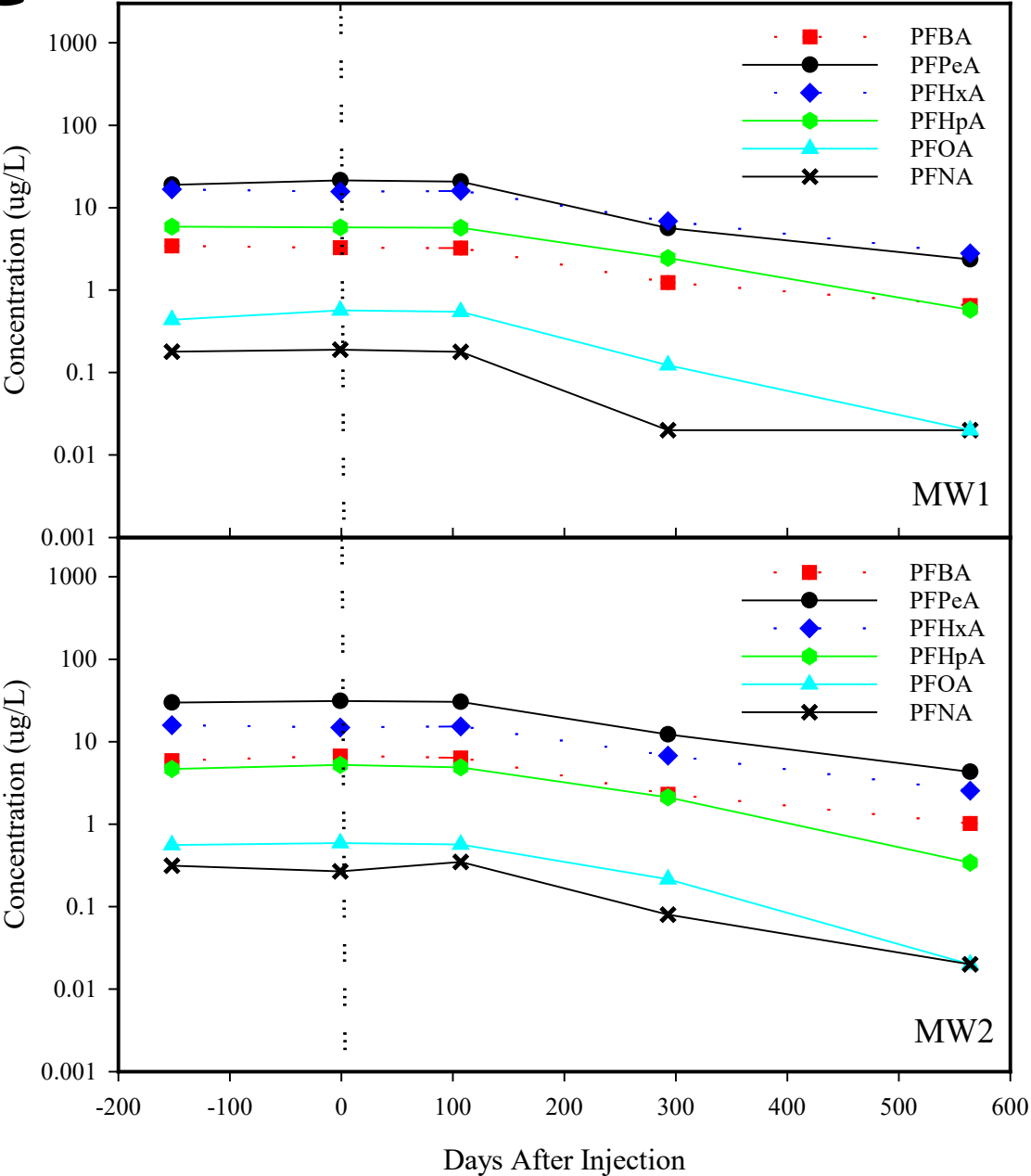
← Detection Limit

← Detection Limit

← Detection Limit

Study Site

Groundwater



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 injection
 - 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 at up to 55 ng/L
- PFAS Treatment within Shallow Groundwater
 - Mass flux of PFAS into the shallow groundwater decreased by 81% (PFBA) to 97% (PFOA) over the 18-month monitoring period

On Going Studies

- Fractured Bedrock
 - Central Canada
 - Overburden & bedrock impacted by foam used to extinguish fire
 - PlumeStop
- Saline Aquifer
 - Middle East,
 - Bulk petroleum hydrocarbon facilities
 - PlumeStop
 - 36 months, ND for PFAS
- Long-term Testing
 - Central Ontario site, > 7 years



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)
 - CFB Borden

Initial PFAS Insitu Site

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RESEARCH ARTICLE

WILEY

In Situ treatment of PFAS-impacted groundwater using colloidal activated Carbon

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Abstract
Poly- and perfluoroalkyl substances (PFAS) have been identified by many regulatory agencies as contaminants of concern within the environment. In recent years, regulatory authorities have established a number of health based regulatory and evaluation criteria with ground water PFAS concentrations typically being less than 50 nanograms per liter (ng/L). Subsurface studies suggest that PFAS compounds are recalcitrant and widespread in the environment. Traditionally, impacted groundwater is extracted and treated on the surface using media such as activated carbon and exchange resins. These treatment technologies are generally expensive, inefficient, and can take decades to reach treatment objectives. The application of *in situ* remedial technologies is common for a wide variety of contaminants of concern such as petroleum hydrocarbons and volatile organic compounds; however, for PFASs, the technology is currently emerging. This study involved the application of colloidal activated carbon at a site in Canada where the PFASs perfluorooctanoate (PFOA) and perfluorooctane sulfonic acid (PFOS) were detected in groundwater at concentrations up to 3,260 ng/L and 1,450 ng/L, respectively. The shallow silty-sand aquifer was anaerobic with an average linear groundwater velocity of approximately 2.6 meters per day. The colloidal activated carbon was applied using direct push technology and PFOA and PFOS concentrations below 30 ng/L were subsequently measured in groundwater samples over an 18-month period. With the exception of perfluoroundecanoic acid, which was detected at 20 ng/L and perfluorooctanesulfonate which was detected at 40 ng/L after 18 months, all PFASs were below their respective method detection limits in all post-injection samples. Colloidal activated carbon was successfully distributed within the target zone of the impacted aquifer with the activated carbon being measured in cores up to 5 meters from the injection point. This case study suggests that colloidal activated carbon can be successfully applied to address low to moderate concentrations of PFASs within similar shallow anaerobic aquifers.

doi/10.1002/rem.21558

1 | INTRODUCTION

Poly- and perfluoroalkyl substances (PFAS) have been identified as emerging contaminants and have attracted concern from regulatory bodies over the past 20 years because they are widespread and persistent in the environment, have potential for bioaccumulation, and may have adverse effects on the immune system, liver, and development of children/infants (U.S. Environmental Protection Agency [EPA], 2009; Environment and Climate Change Canada [ECCC], 2017a). These compounds are used in metal plating, firefighting, photography, and aviation industries for applications including flame suppressants, foaming agents, and hydraulic fluid additives (Hunter-Anderson, Long, Porter, & Anderson, 2016; Government of Canada, 2008). PFASs are no longer produced in Canada (ECCC, 2016) or the United States

(ECCC, 2017b), but can be imported from China as of 2003 (Butt, Berger, Bossi, & Tomy, 2010). Canada has no current drinking water or groundwater regulations for any PFAS; however, the Federal Soil Quality Guidelines and Groundwater Quality Guidelines for PFOS indicate 0.21 milligrams per kilogram (mg/kg) for fine soil, 0.14 mg/kg for coarse soil, and 68 micrograms per liter (μ g/L) for groundwater for the protection of freshwater life (ECCC, 2017b). The EPA drinking water health advisory level for the sum of perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) concentrations is 70 nanograms per liter (ng/L), while other jurisdictions pose stricter regulations (NGWA, 2017).

The remediation of PFASs is challenging for many reasons, including the highly recalcitrant nature of these compounds which is likely due to multiple stable fluoride-carbon bonds (National Ground Water

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RESEARCH ARTICLE

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Evaluating the longevity of a PFAS *in situ* colloidal activated carbon remedy

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Abstract
The remediation of per- and polyfluoroalkyl substances by injection of colloidal activated carbon (CAC) at a contaminated site in Central Canada was evaluated using various visualization and modeling methods. Radial diagrams were used to illustrate spatial and temporal trends in perfluoroalkyl acid (PFAA) concentrations, as well as various redox indicators. To assess the CAC adsorption capacity for perfluorooctane sulfonate (PFOS), laboratory Freundlich isotherms were derived for PFOS mixed with CAC in two solutions: (1) PFOS in a pH 7.5 synthetic water that was buffered by 1 millimolar NaHCO_3 ($K_f = 142,800 \text{ mg}^{1-2} \text{ L}^2/\text{kg}$ and $n = 0.59$); and (2) a groundwater sample (pH = 7.4) containing PFOS among other PFAS from a former fire-training area in the United States ($K_f = 4,900 \text{ mg}^{1-2} \text{ L}^2/\text{kg}$ and $n = 0.24$). A mass balance approach was derived to facilitate the numerical modeling of mass redistribution after CAC injection, when mass transitions from a two-phase system (aqueous and sorbed to organic matter) to a three-phase system that also includes mass sorbed to CAC. An equilibrium mixing model of mass accumulation over time was developed using a finite-difference solution and was verified by intermodel comparison for prediction of CAC longevity in the center of a source area. A three-dimensional reactive transport model (ISR-MT3DMS) was used to indicate that the CAC remedy implemented at the site is likely to be effective for PFOS remediation for decades. Model results are used to recommend remedial design and monitoring alternatives that account for the uncertainty in long-term performance predictions.

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1 | INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants that are widespread in the environment and are generally persistent (Hatton, Holton, & DiGiuseppe, 2018). Perfluoroalkyl acids (PFAAs) are the main types of PFAS that are analyzed in soil and groundwater at contaminated sites and generally have low regulatory advisory or cleanup levels. Some PFAS precursors are known to undergo aerobic biodegradation (e.g., Avendano & Liu, 2016; Harding-Marjanovic et al., 2015), where transformation products may include PFAAs. PFAAs have not been observed to undergo biological or abiotic transformation reactions, resulting in persistent plumes at many sites (Hatton et al., 2018).

There are two classes of PFAAs: perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs). The most commonly regulated PFAS in the environment are perfluorooctanoate (PFOA), which is a PFOA, and perfluorooctane sulfonate (PFOS), which is a PFSA. Regulatory cleanup criteria for these and other PFAS are

undergoing development; at present, the U.S. Environmental Protection Agency (USEPA) has imposed a Lifetime Health Advisory for PFOS and PFOA individually or in combination, of 0.07 microgram per liter (μ g/L; USEPA, 2016a, 2016b). Health Canada drinking water screening values for PFOS and PFOA are 0.6 and 0.2 μ g/L, respectively (Health Canada, 2018). These low cleanup levels and the persistent nature of PFAAs pose a significant challenge in remediating PFAS sites.

Granular activated carbon (GAC) is effective for *ex situ* treatment of PFAS in groundwater in some cases (McClellan et al., 2017). GAC has a typical particle size range of 500 to 1,000 μ m, and powdered activated carbon (PAC) may have a particle size of 10 to 100 μ m. USEPA (2018) presents a summary of the practice of injecting activated carbon *in situ* as a remediation approach for chlorinated solvents and petroleum hydrocarbons. This includes the high-pressure injection of GAC or PAC, which induces fracturing leading to the heterogeneous distribution of GAC and PAC in thin seams or lenses (USEPA, 2018). Another alternative now being employed is the low-pressure injection of colloidal

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