# Summary of Four Applications of Colloidal Activated Carbon for the In Situ Treatment of PFAS in Groundwater

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InSitu Remediation Services





# Background

- Per & Polyfluoroalkyl Substances (PFAS)
- Emerging Compounds of Concern
  - Perfluorooctane Sulfonate (PFOS)
  - Perfluorooctanic acid (PFOA)
  - Thousands of compounds
  - Carbon-fluoride bond strong
  - Shown to bioaccumulate
  - Analytical challenges
  - Health Advisory Levels 10s of ng/L (ppt)
  - Fate & transport not well understood





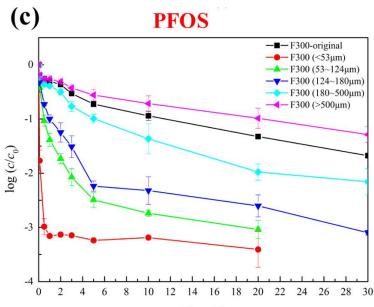
# Background

### In Situ Current Approaches

- Proven
  - Colloidal activated carbon
- Development
  - Ion exchange resin
  - Biochar
  - Powdered activated carbon
  - Sonochemical
  - Foam Fractionization
  - Oxidants



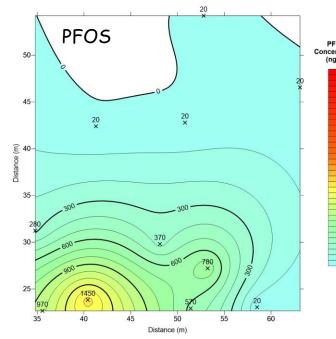


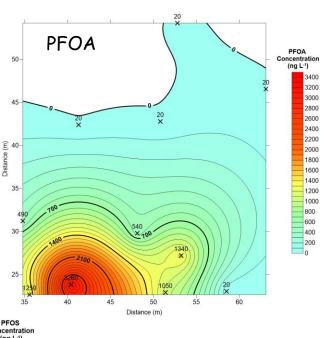


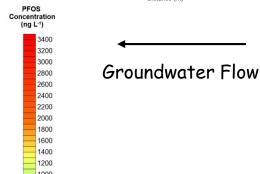
Source: Xiao et al.,2017



- Petroleum Hydrocarbon Spill
  - Source excavated
  - Residue PHCs in soil and groundwater
    - BTEX < 300 ug/L</li>
    - F1 < 2,000 ug/L
    - F2 < 3,500 ug/L
  - PFAS
    - PFOS up to 1,450 ng/L
    - PFOA up to 3,260 ng/L
  - Geology & Hydrogeology
    - Silty sand with sand lens
    - Unconfined
    - $K \sim 2.6 \text{ m/day}$
    - V ~ 1 m/day









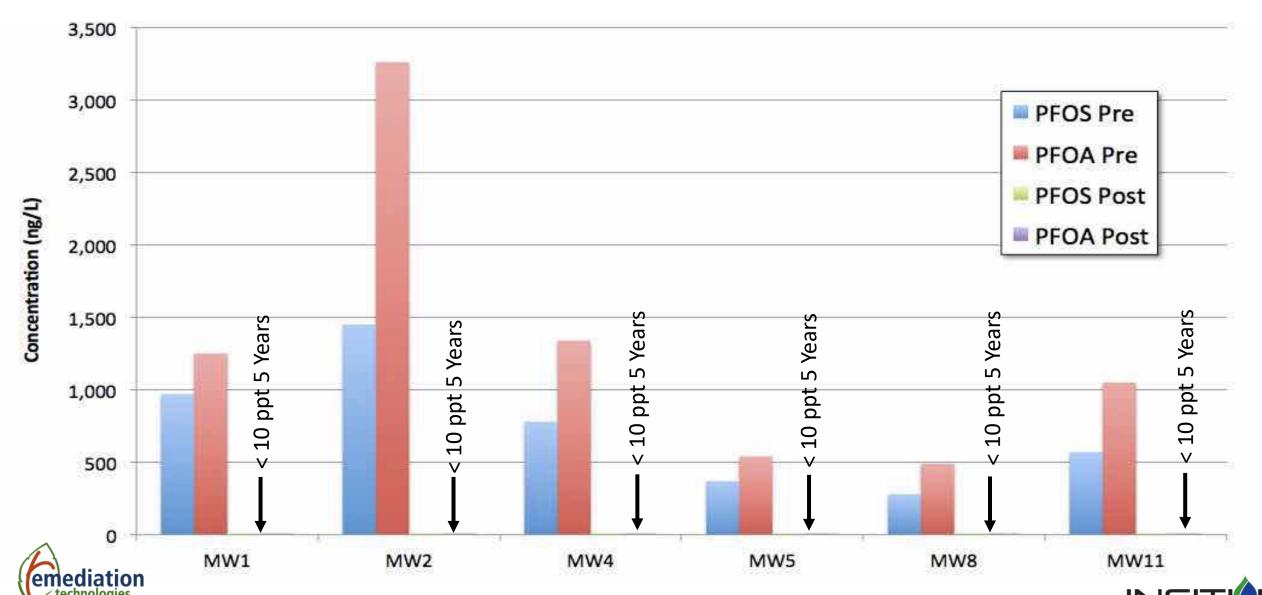


- Based on Pore Volume
  - One event
- Direct Push
- Geology Specific Tools
- Multiple Locations
- Multiple Intervals
- Low Pressure
  - <25 psi</p>
- · Low Volume
  - ~100 to 200 litres/location









- Relatively simple hydrogeologic system
- Successful removal of various PFAS for greater than 5 years
- Successful treatment of PHCs for greater than 5 years
- Modeling suggests CAC should last greater than 50 years

### RESEARCH ARTICLE

### WILEY

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

### Rick McGregor

Poly- and perfluoroalityl substances (PFASs) have been identified by many regulatory age cles as contaminants of concern within the environment. In recent years, regulatory authori water PFAS concentrations typically being less than 50 panggrams per liter (ng/L). Subsurfac ctected in groundwater at concentrations up to 3.260 mg/L and 1.450 mg/L

Quality Guidelines and Groundwater Q

for coarse soil, and 68 micrograms per

The remediation of PFASs is challenge

nology and PFOA and PFOS concentrations below 30 ng/L were iection samples. Colloidal activated carbon was successfully distrib rom the injection point. This case study suggests that colloidal a cessfully applied to address low to moderate concentrations of F

### 1 | INTRODUCTION

Poly- and perfluorgalityl substances (PFASs) have been identified as emerging contaminants and have attracted concern from regulatory lies 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/fetuses (U.S. Environmental Protection Agency [EPA], 2009; Environment and Climate Change Canada ECCCI, 2017al. These compounds are used in metal plating, firefighting, photography. and aviation industries for applications including fume suppressants, foaming agents, and hydraulic fluid additives (Hunter-Anderson, Long, Porter, & Anderson., 2016; Government of Canada, 2008). PFASs are ing the highly recalcitrant nature of thes no longer produced in Canada (ECCC, 2016) or the United States - due to multiple stable fluoride-carbon bo

RESEARCH ARTICLE

WILEY

### 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 car modeling methods. Radial diagrams were used to illustrate spatial and temporal trends in perflu roalkyl acid (PFAA) concentrations, as well as various redox indicators. To assess the CAC adsorby 1 millimolar NaHCO $_3$  (K, = 142,800 mg  $^{1/g}$  L $^g$ /kg and  $\alpha$  = 0.59); and (2) a groundwater s States (K:  $=4.900 \text{ mg}^{1-\alpha} \text{ L}^{\alpha}/\text{kg}$  and  $\alpha=0.24$ ). A mass balance : the numerical modeling of mass redistribution after CAC injection, when mass transition developed using a finite-difference solution and was verified by intermodel comparison for pr nodel (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 rem

### 1 | INTRODUCTION

Per- and polyfkioroalkyl substances (PFAS) are emerging contaminants that are widespread in the environment and are generally persistent (Hatton, Holton, & DKJuiseppi, 2018). Perfluoroalkyl acids groundwater at contaminated sites and generally have low regulatory advisory or cleanup levels. Some PEAS 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 typical particle size range of 500 to 1,000 µm, and powdered activate transformation reactions, resulting in persistent plumes at many sites carbon (PAC) may have a particle size of 10 to 100 um. USEPA (2018)

There are two classes of PFAAs: perfluoroalkyl carboxylates (PECAs) and perfluoroality sulfonates (PESAs). The most commonly hydrocarbons. This includes the high-pressure injection of GAC or PAC regulated PFAS in the environment are perfluorooctanoate (PFOA), which is a PFCA, and perfluoroctane sulfonate (PFOS), which is GAC and PAC in thin seams or lenses (USEPA, 2018). Another alter a PFSA. Regulatory cleanup criteria for these and other PFAS are native now being employed is the low-pressure injection of colloidal

and PFOA individually or in combination, of 0.07 microgram per lite ing values for PFO5 and PFOA are 0.6 and 0.2 µg/L, respective (PFAAs) are the main types of PFAS that are analyzed in soil and (Health Canada, 2018). These low cleanup levels and the persister

PFAS in groundwater in some cases (McCleaf et al., 2017). GAC has a presents a summary of the practice of injecting activated carbon in which induces fracturing leading to the heterogeneous distribution of





- Large Petroleum Hydrocarbon Facility
  - Large BTEX plume with PFAS present
    - BTEX ~ 680 ug/L
    - GRO ~ 3,500 ug/L
  - 22 PFAS analyzed, 6 detected
    - PFBA up to 6,200 ng/L
    - PFHxA up to 16,100 ng/L
    - PFHpA up to 6,080 ng/L
    - PFNA up to 140 ng/L
    - PFOA up to 450 ng/L
    - PFPeA up to 24,000 ng/L







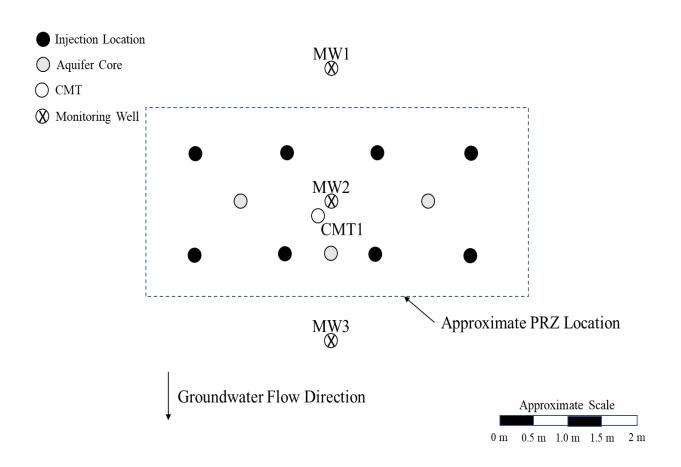
- Geology
  - Fine-grained sand
  - Zone of medium grained sand (~1 inch thick)
- Hydrogeology
  - · Unconfined aquifer
  - Water table ~17 ft below surface
  - Mean K  $5 \times 10^{-5}$  m/sec
  - Groundwater velocity ~ 200 ft/year
- Geochemistry
  - Iron & sulfate reducing







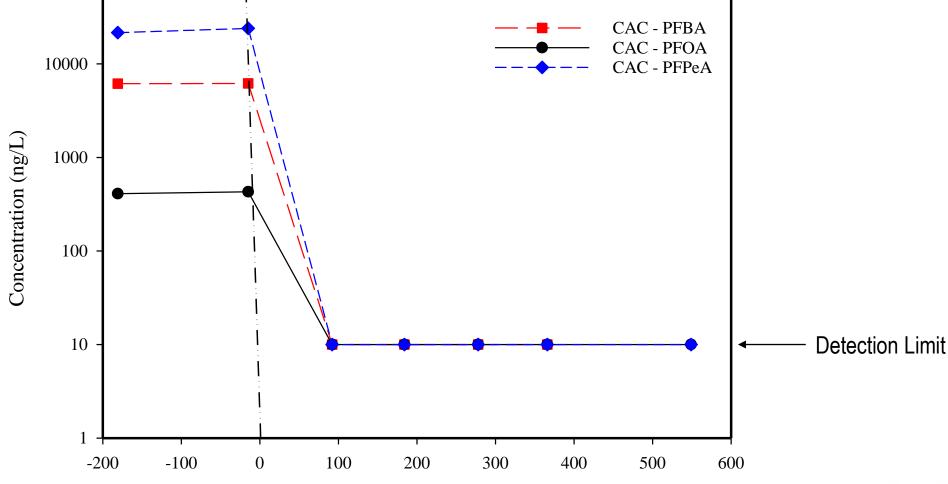
- Six permeable reactive barriers/zones created using:
  - Colloidal activated carbon
  - Powdered activated carbon
  - Biochar
  - Ion exchange resin
  - Sodium persulfate- unactivated
  - Hydrogen peroxide
- Injection
  - Grid 1.5 m spacing
  - Direct push technology
  - Multiple vertical intervals







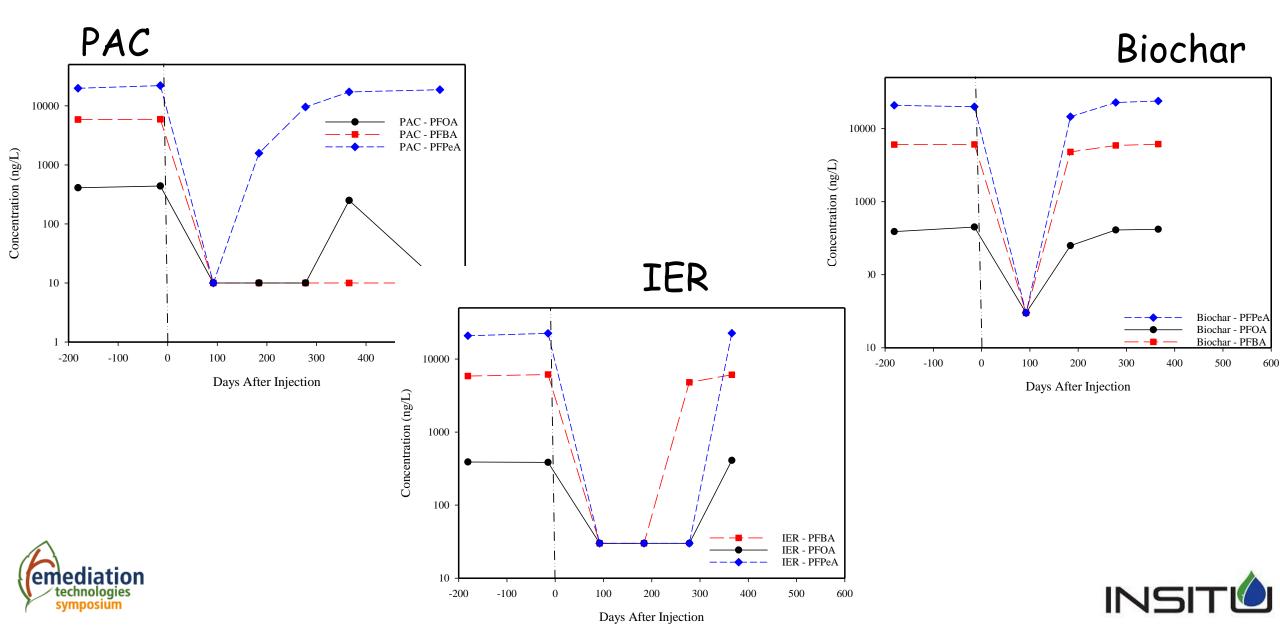
### Colloidal Activated Carbon



Days After Injection







Check for updates

- Breakthrough observed throughout target zone
  - Except for CAC
  - Hydrogen peroxide & persulfate breakthrough in 90 days
  - High C > Low C PFAS
  - Sulphonates > Carboxylates
  - CAC > PAC> IER > Biochar > Hydrogen peroxide
    = persulfate

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RESEARCH ARTICLE

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

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### Abstract

Per- and polyfluoroalkyl substances (PFAS) have been identified by many regulatory agencies as emerging contaminants of concern in a variety of media including groundwater. Currently, there are limited technologies available to treat PFAS in groundwater with the most frequently applied approach being extraction (i.e., pump and treat). While this approach can be effective in containing PFAS plumes, previous studies of pump and treat programs have met with limited remedial success. In situ treatment studies of PFAS have been limited to laboratory and a few field studies. Six pilot-scale field studies were conducted in an unconfined sand aquifer coimpacted by petroleum hydrocarbon along with PFAS to determine if a variety of reagents could be used to attenuate dissolved phase PFAS in the presence of petroleum hydrocarbons. The six reagents consisted of two chemical oxidants, hydrogen peroxide (H2O2) and sodium persulfate (Na2S2O8), and four adsorbents, powdered activated carbon (PAC), colloidal activated carbon (CAC), ion-exchange resin (IER), and biochar. The reagents were injected using direct push technology in six permeable reactive zone (PRZ) configurations. Groundwater concentrations of various PFAS entering the PRZs ranged up to 24,000 ng/L perfluoropentanoic acid, up to 6,200 ng/L perfluorobutanoic acid, up to 16,100 ng/L perfluorohexanoic acid, up to 6,080 ng/L perfluoroheptanoic acid, up to 450 ng/L perfluorooctanoic acid, and up to 140 ng/L perfluorononanoic acid. Performance groundwater sampling within and downgradient of the PRZs occurred for up to 18 months using single and multilevel monitoring wells. Results of groundwater sampling indicated that the PFAS were not treated by either the persulfate nor the peroxide and in some cases, the PEAS increased in concentration immediately following the injection of peroxide and persulfate. Concentrations of PEAS in groundwater sampled within the PAC, CAC, IER, and biochar PRZs immediately after the injection were determined to be less than the method detection limits. Analyses of groundwater samples over the 18-month monitoring period, indicated that all the PRZs exhibited partial or complete breakthrough of the PFAS over the 18-month monitoring period, except for the CAC PRZ which showed no PFAS breakthrough. Analysis of cores for the CAC, PAC, and biochar PRZs suggested that the CAC was uniformly distributed within the target injection zone, whereas the PAC and biochar showed preferential injection into a thin coarse-sand seam. Similarly, analysis of the sand packs of monitoring wells installed before the injection of the



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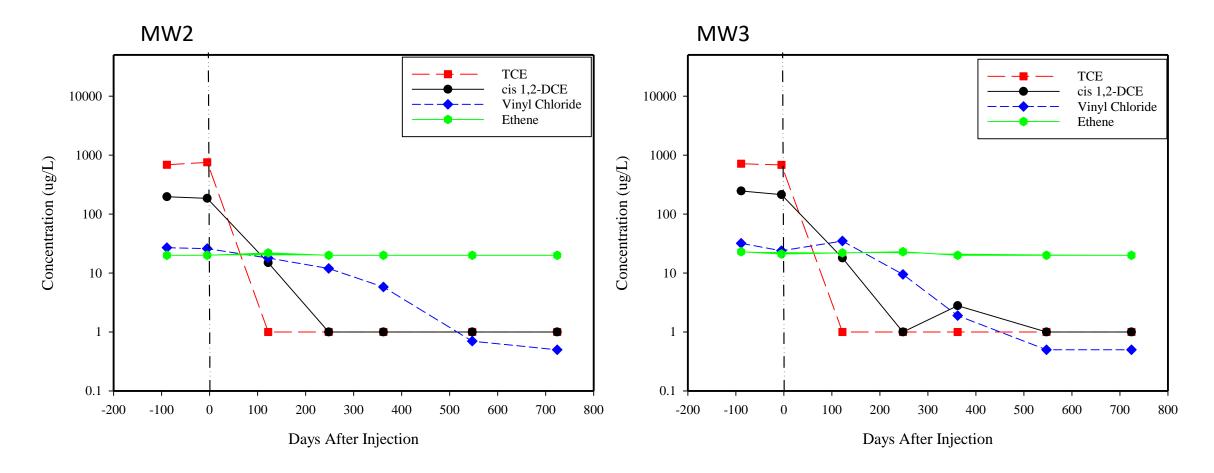


- Industrial Facility China
  - Comingled
    - TCE up to 985 ug/L
    - 1,2 cis DCE up to 258 ug/L
    - Vinyl chloride up to 54 ug/L
  - 5 PFAS detected
    - PFBA up to 795 ng/L
    - PFHxA up to 3,240 ng/L
    - PFOA up to 420 ng/L
    - PFPeA up to 12,800 ng/L
    - PFOS up to 2,140 ng/L

- Geology
  - Silty sand
- Hydrogeology
  - Unconfined aquifer
  - Water table ~3.2 m below surface
  - K:  $5 \times 10^{-6}$  to  $6.3 \times 10^{-4}$  m/sec
  - Groundwater velocity ~ 9 m/year
- Geochemistry
  - Iron & sulfate reducing

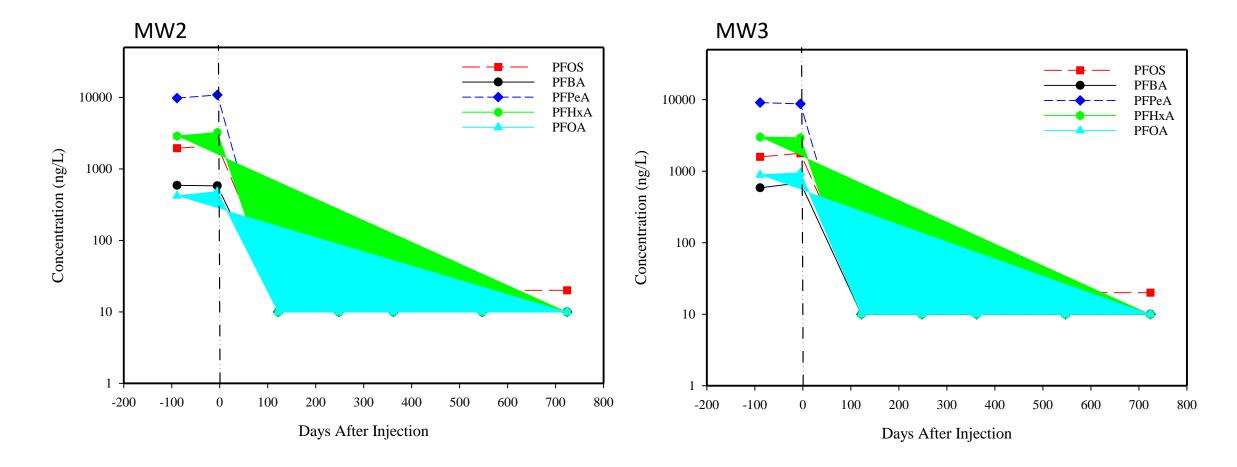
















- Treatment with 3 months of application
  - Comingled with TCE, 1,2 DCE and vinyl chloride
  - Strong reduction conditions, dichlorination of TCE noted, treatment for greater than 2 years
  - Removal of PFAS to below 10 ng/L for greater than 2 years
  - Greater than 99% of samples within target injection zone had CAC present



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RESEARCH ARTICLE

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

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### Abstract

Chlorinated ethenes such as trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride along with per- and polyfluoroalkyl substances (PFAS) have been identified as chemicals of concern in groundwater; with many of the compounds being confirmed as being carcinogens or suspected carcinogens. While there are a variety of demonstrated in-situ technologies for the treatment of chlorinated ethenes industrial site shallow groundwater was impacted with TCE, cis-1,2-DCE, and viny perfluoropentanoic acid. 3240 ng/L of perfluorohexanoic acid. 795 ng/L of pe fluorobutanoic acid. 950 ng/L of perfluorooctanoic acid. and 2140 ng/L of per that the detected PFAS were treated to either their detection, or below the analytical and vinyl chloride indicated that the concentrations of the three compounds de creased by an order of magnitude within 4 months of injection, with TCE decreasing to below the analytical detection limit over the 24-month monitoring period. Cis-1 2-DCE, and vinyl chloride concentrations decreased by over 99% within 8 months of injections, remaining at or below these concentrations during the 24-month more itoring period. Analyses of Dehalococcoides, ethene, and acetylene over time suggest that microbiological and reductive dechlorination were occurring in conjunction with adsorption to attenuate the chlorinated ethenes and PFAS within the aquifer. Analysis of soil cores collected pre- and post-injection, indicated that the distribu

Analysis of soil cores collected pre- and post-injection, indicated that the distribution of the colloidal activated carbon was influenced by small scale heterogeneities within the aquifer. However, all aquifer samples collected within the targeted injection zone contained total organic carbon at concentrations at least one order of manifulde greater than the preinjection total organic carbon concentrations.

### KEYWORDS

colloidal activated carbon, in situ, PFAS, synthetic dye, trichloroethen

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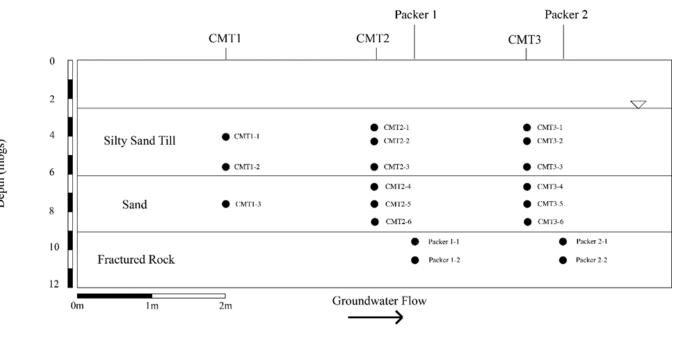
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- Residential/Small Industrial
  - Complex geology
    - Silty sand
    - Sand
    - Fractured rock
  - 5 PFAS detected within the 3 aquifers
    - PFBA up to 795 ng/L
    - PFHxA up to 3,240 ng/L
    - PFOA up to 420 ng/L
    - PFPeA up to 12,800 ng/L
    - PFOS up to 2,140 ng/L

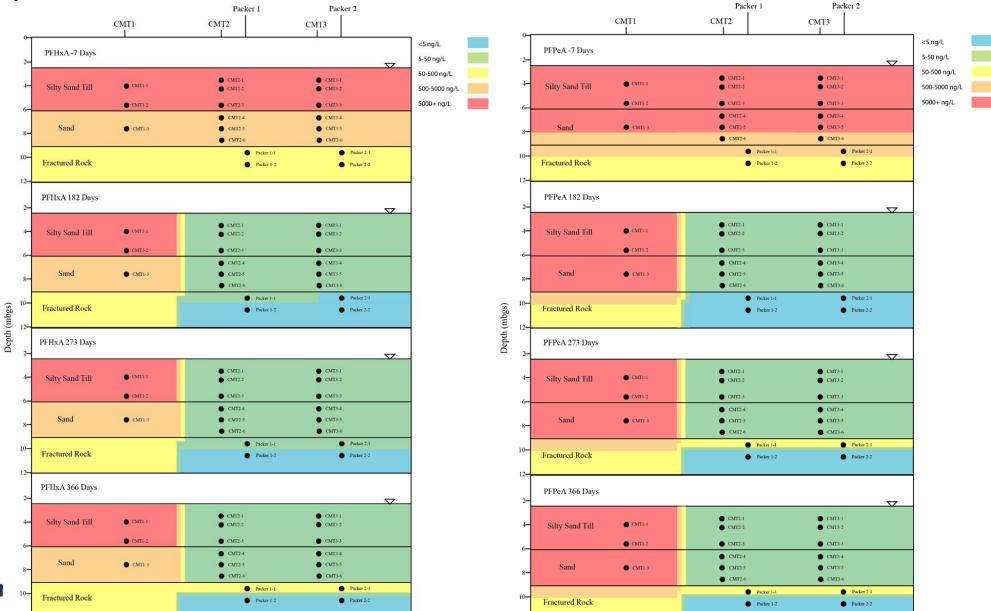






Groundwater Flow

**PFHxA** 



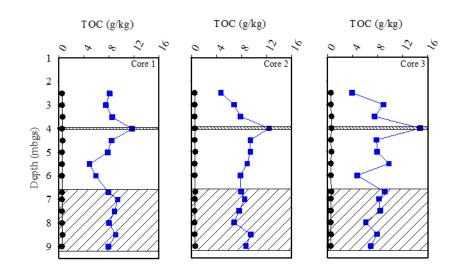
Groundwater Flow





**PFPeA** 

- Removal of PFAS within unconsolidated aquifers within 3 months to below 10 ng/L for greater than 1.5 years
- Greater than 99% of samples within target injection zone had CAC present within consolidation aquifers
- Breakthrough of C4-C5 carboxylic acids within fractured rock aquifer before sulfonic acids







# PFAS Remediation Research Group

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### **Industrial Partners**





