Insitu Treatment of PFAS-Impacted Groundwater: Do We See Desorption or Competitive Sorption Occurring in the Field?

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InSitu Remediation Services

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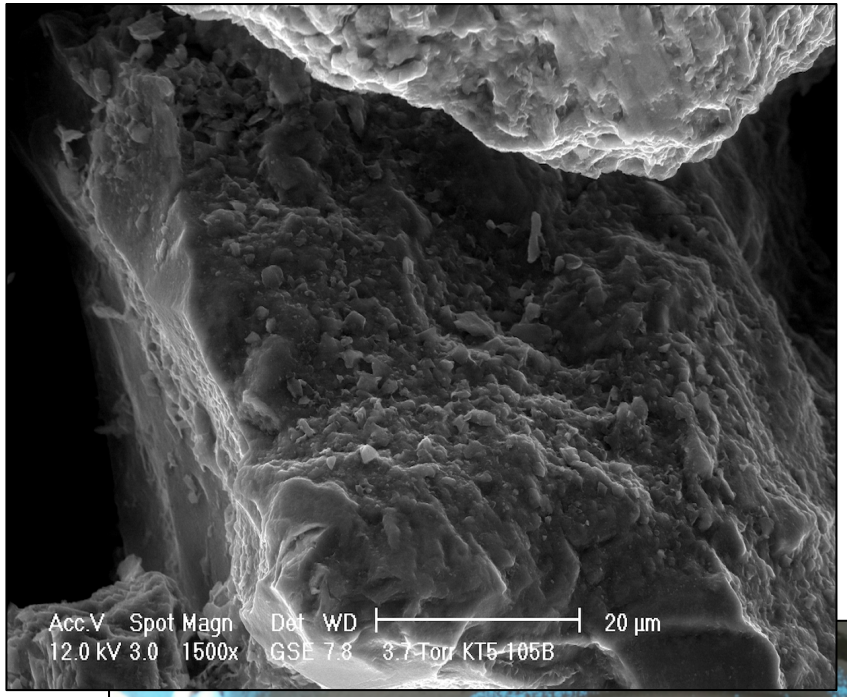
Insitu PFAS Remediation

In Situ Current Approaches

- Proven
  - Colloidal activated carbon (TRL=9)
    - Concerns include
      - » Competition sorption
      - » Desorption
      - » Lifespan
- Development
  - Ion exchange resin (TRL=9)
  - Biochar (TRL=4)
  - Powdered activated carbon (TRL=9)
  - Oxidants



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Study Site

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

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Study Site

- Large Petroleum Hydrocarbon Facility
  - Large BTEX plume with PFAS present
    - BTEX ~ 680 ug/L
    - GRO ~ 3,500 ug/L
  - 22 PFAS analyzed, 6 detected
    - Carboxylic acids
      - 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

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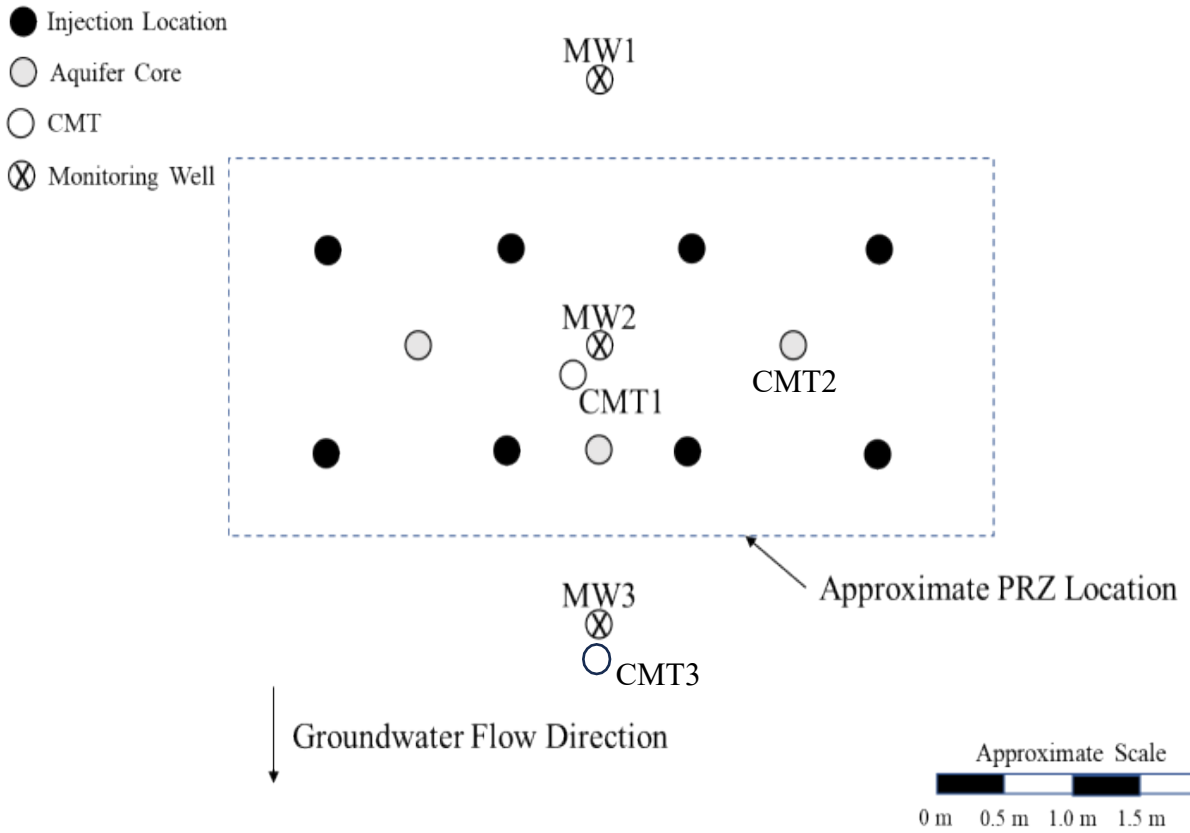
Study Site

- Permeable reactive barriers/zones created using:
  - Colloidal activated carbon
  - Powdered activated carbon
  - Biochar
  - Ion exchange resin
  - Sodium persulfate- unactivated
  - Hydrogen peroxide
- Injection
  - Grid – 5 foot spacing
  - Direct push technology
  - Multiple vertical intervals

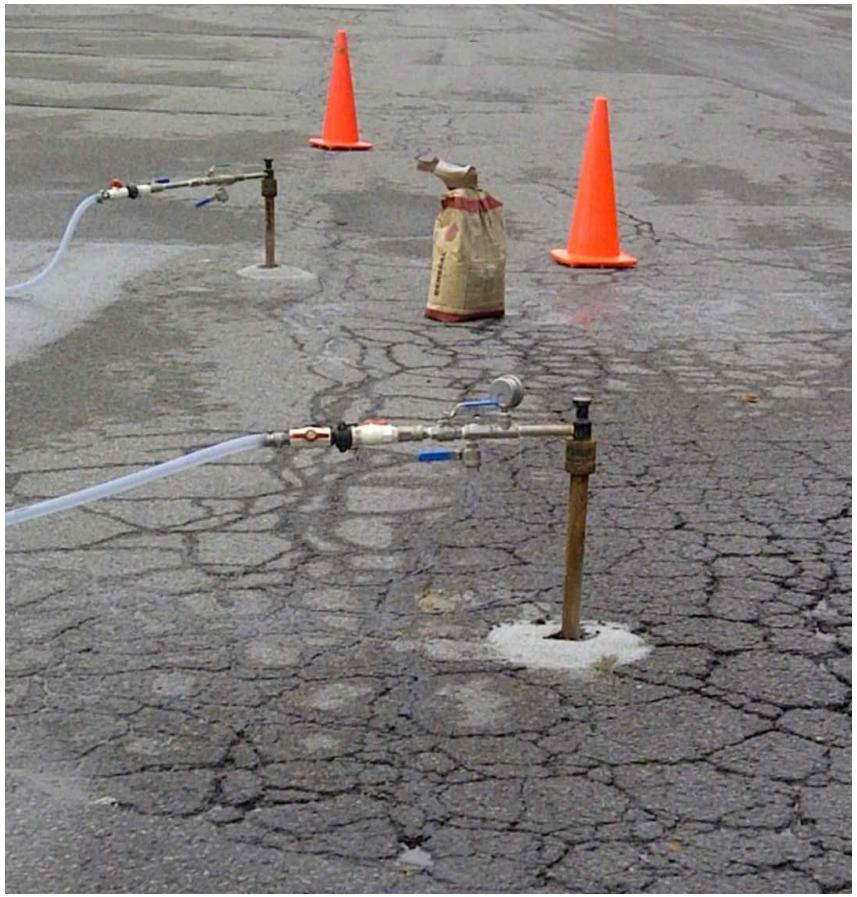


Study Site

- Groundwater Monitoring
  - Combination of 2" and CMT wells
  - BTEX, GRO, inorganics, general chemistry and PFAS
  - Pre-injection: 2 events
  - Post-injection: Days 92, 184, 278, 366, 549 & 1,090
- Aquifer Solids
  - Continuous cores for TOC pre- and post-injection
- Aquifer Testing
  - Pre- and post-injection
  - Cores for flexible wall permeameter tests

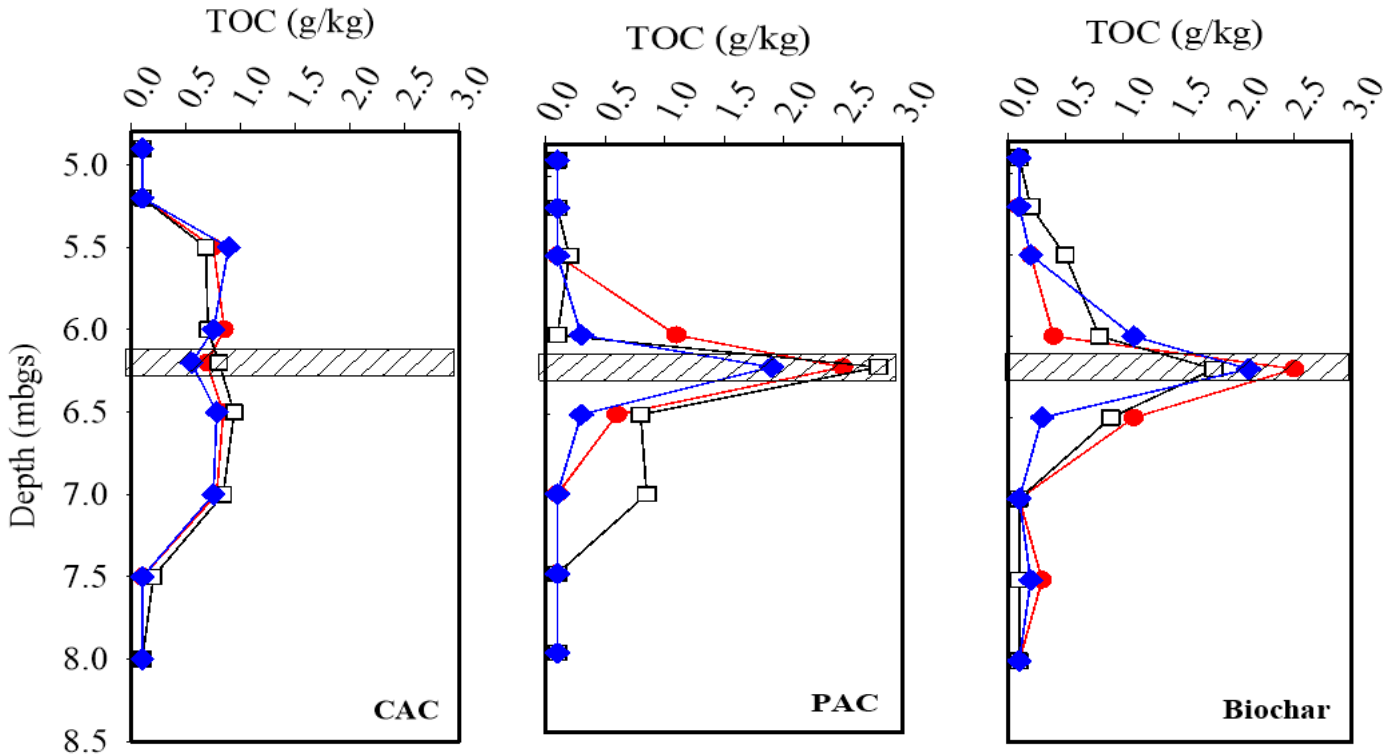
Study Site

- Injection Program
  - Each cell 40 square meters
  - Eight injection points
  - Direct push technology
  - Multi vertical intervals (~ 2 ft)
  - All reagents injected at 10 weight percent
  - Pressures ranged from 20 to 250 psi
    - PAC, Biochar, IER greater than 185 psi
    - CAC, S_2O_8, H_2O_2 less than 35 psi



Pilot Scale Results

- Distribution of reagents

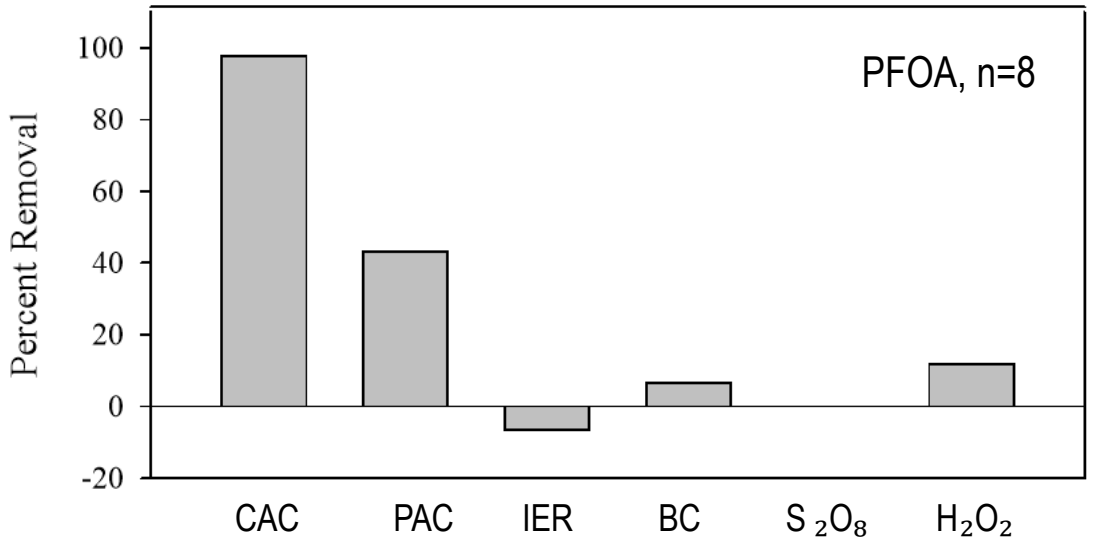


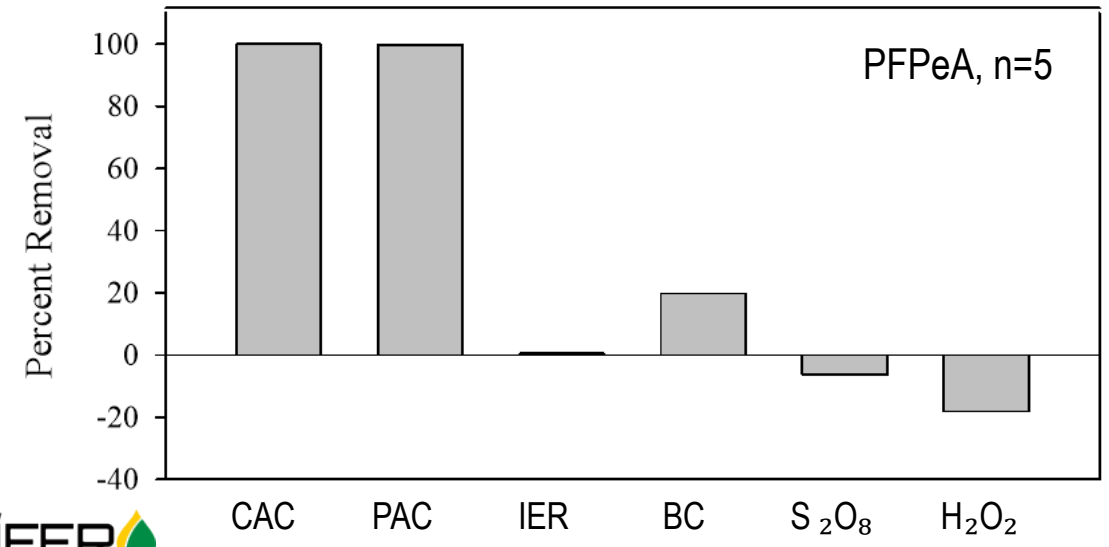
3 cores per test site

Detection limit = 0.1 g/kg

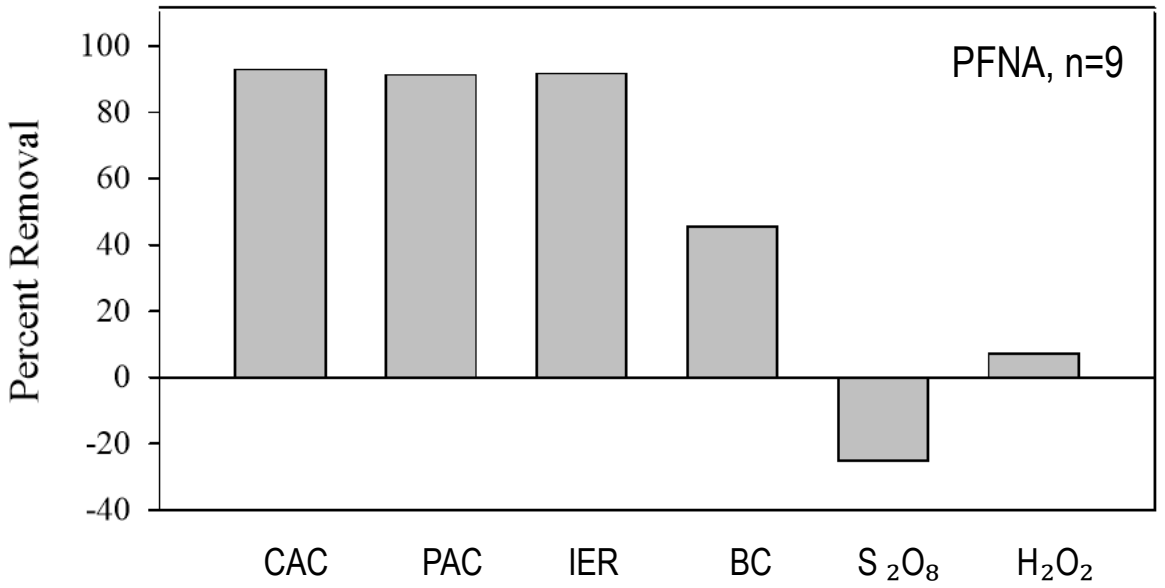
Sand Lens

Pilot Scale Results





Treatment at 366 days



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Pilot Scale Results

- Heterogenetic distribution of reagents except CAC

- PFAS breakthrough observed
  - Except for CAC
  - Hydrogen peroxide & persulfate breakthrough in 90 days
  - Hydrogen peroxide = persulfate > Biochar > IER > PAC > CAC

- Low C PFAS > High C PFAS

- Questions:
  - Will CAC continue to treat PFAS with time?
  - Will competitive sorption occur with PHCs and high C PFAS?
  - Will desorption occur with time?

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Pilot Scale Site

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Or

Remediation Journal

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RESEARCH ARTICLE

WILEY

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

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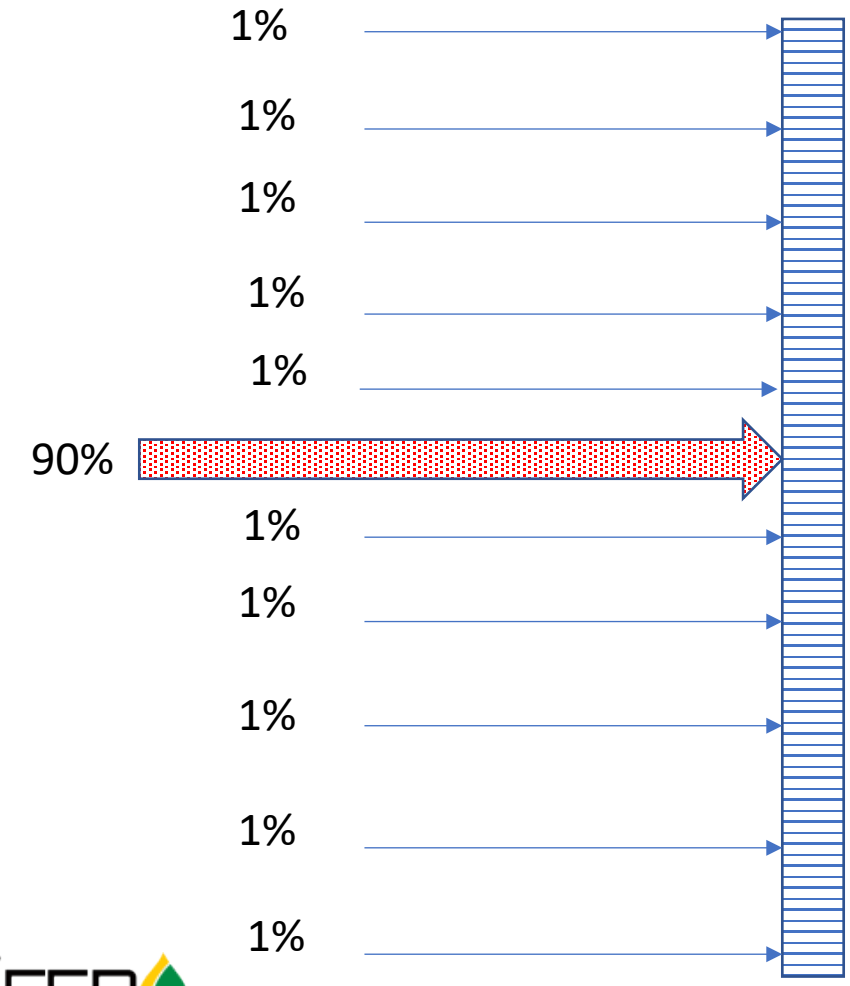
Abstract

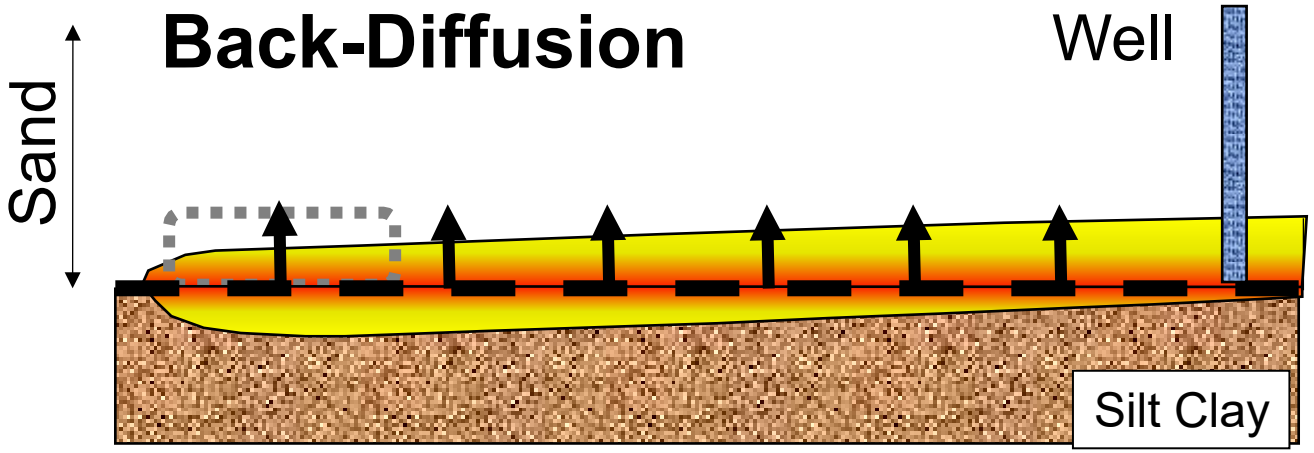
Per- and polyfluoroalkyl substances (PFAS) have been identified by many regulatory agencies as emerging contaminants of concern in a variety of media including groundwater. Currently, there are limited technologies available to treat PFAS in groundwater with the most frequently applied approach being 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 (H_2O_2) and sodium persulfate ($Na_2S_2O_8$), 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 PFAS increased in concentration immediately following the injection of peroxide and persulfate. Concentrations of PFAS 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

Pilot Scale Questions

Flow/Mass Flux Percentage



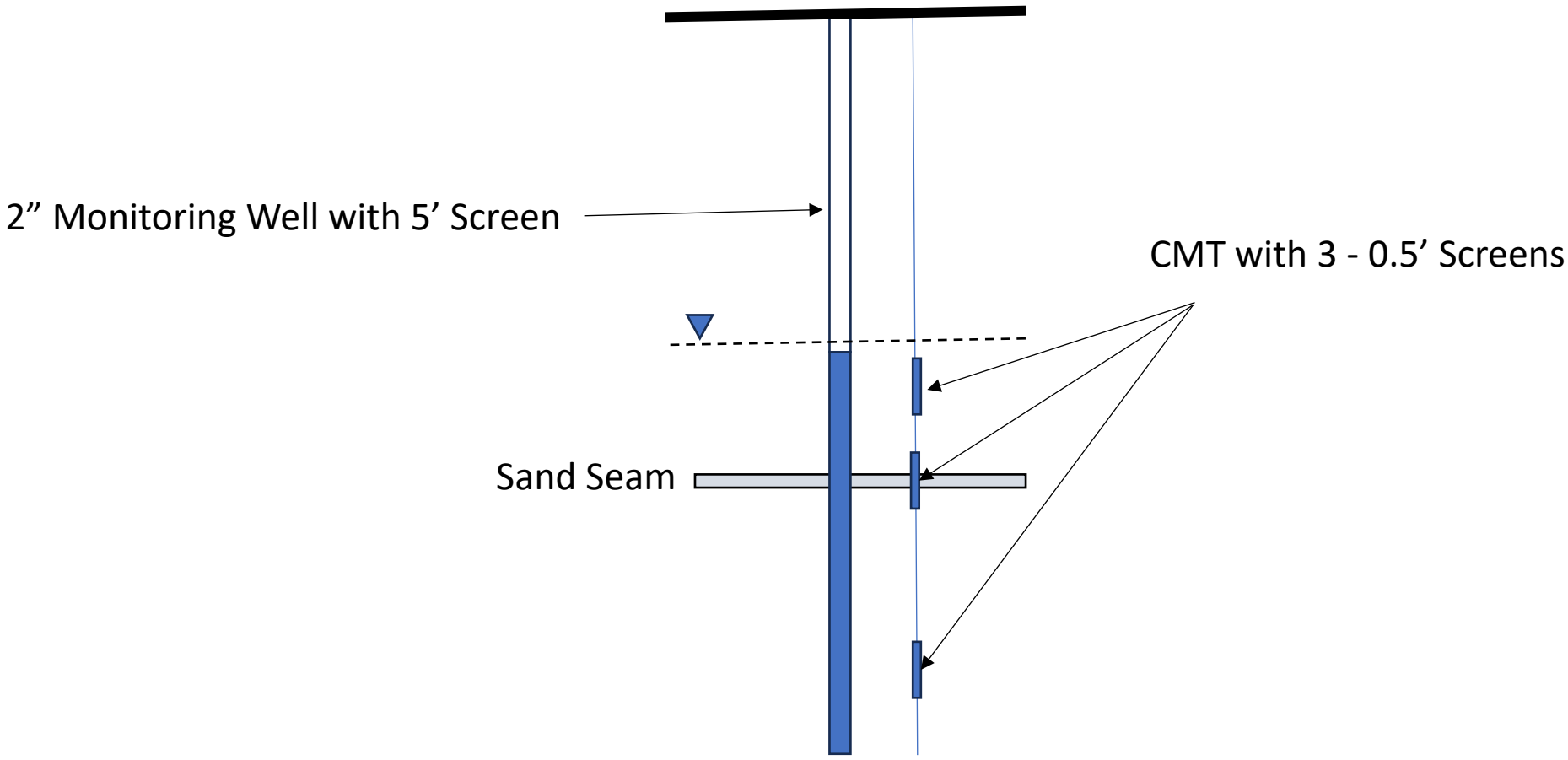
Source D. Reynolds, Geosyntec



Source G. Carey, Porewater Solutions

- Will higher mass flux in sand result in desorption/competition sorption?
- Will long term back/matrix diffusion from finer materials result in desorption/competition sorption?

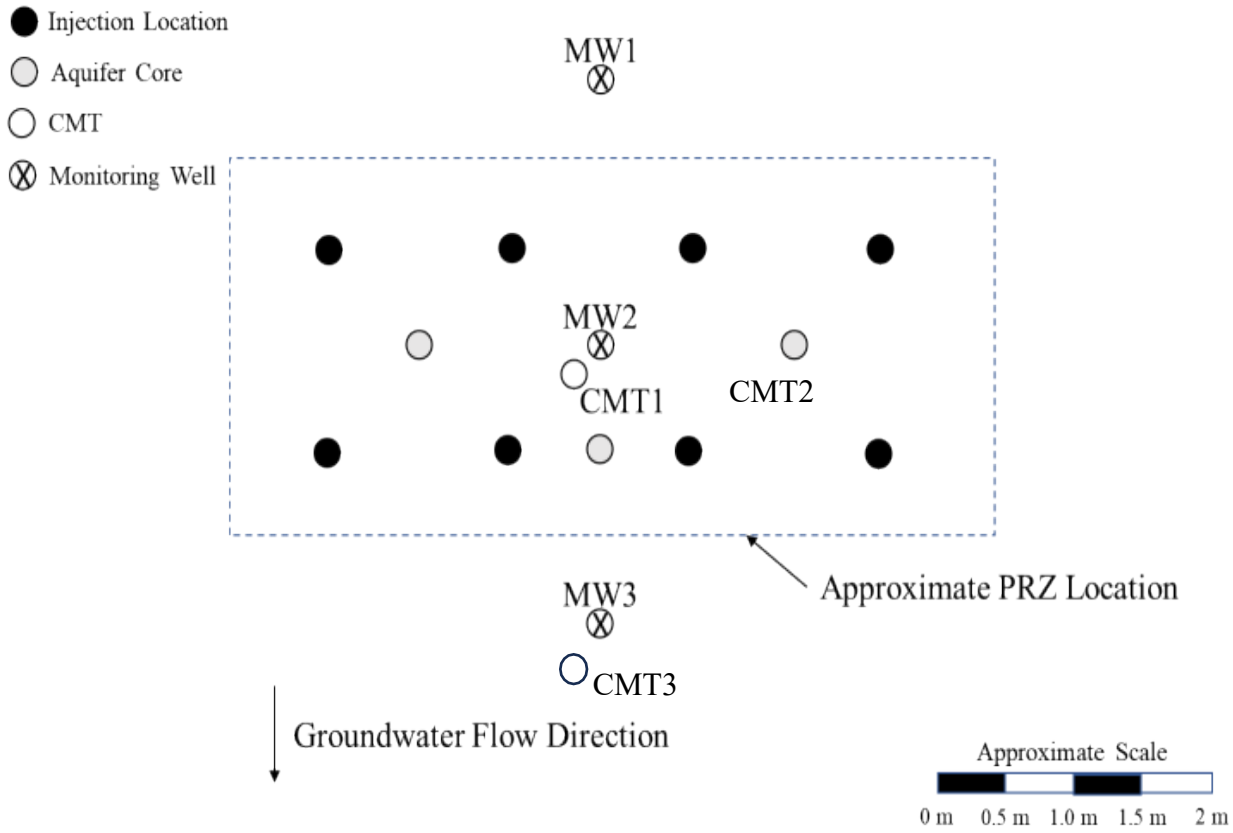
Methodology



Methodology

- Groundwater Monitoring
  - Long-term sampling
    - 2-, 3- & 4-years post injection
  - Compare PFAS from 2" and CMT wells

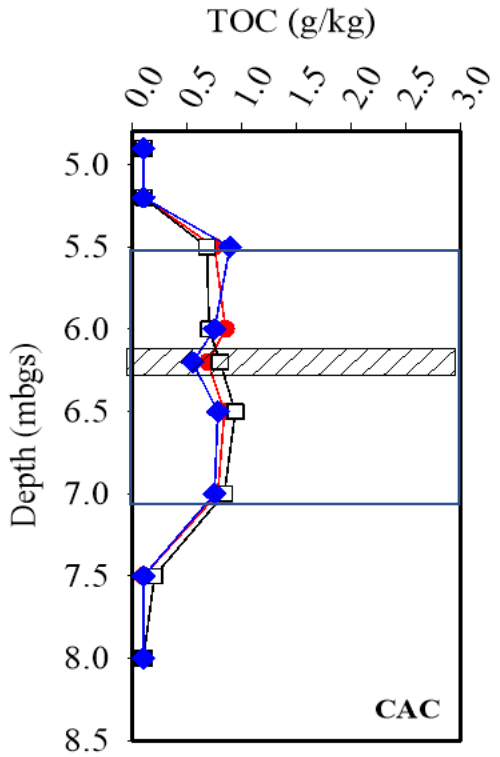
- Aquifer Solids
  - Column tests using influent with high C PFAS and C10-C16 PHCs
  - On going



Results

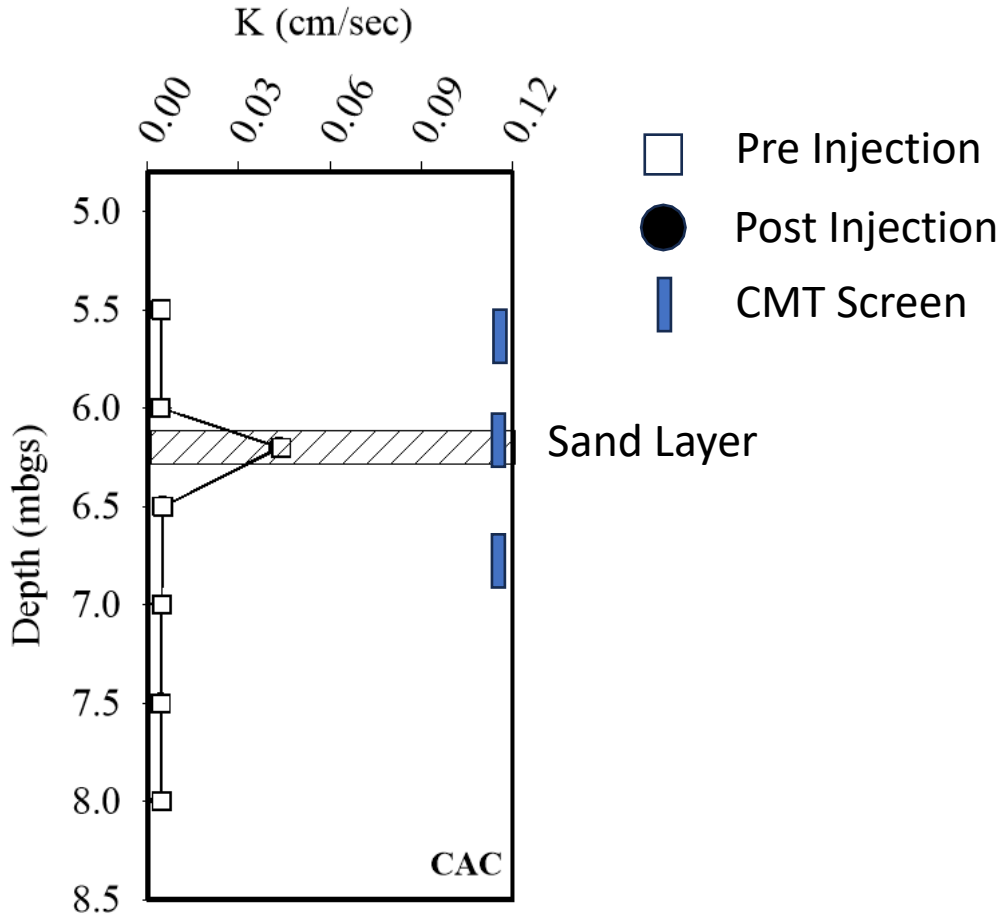
CAC Distribution

- Inside Target Zone - 0.77 g/kg
- Outside Target Zone - 0.11 g/kg
- Pre-Injection - 0.006 g/kg
- 100 % of samples within Target Zone had detectable TOC
- 33 % of samples outside of Target Zone had detectable TOC



Results

Horizontal hydraulic conductivity



- Monitoring with short screened (6") CMT systems indicated that the mass flux of PFAS was controlled by sand seam
- Between 83% and 95% of measured PFAS mass flux was in sand seam

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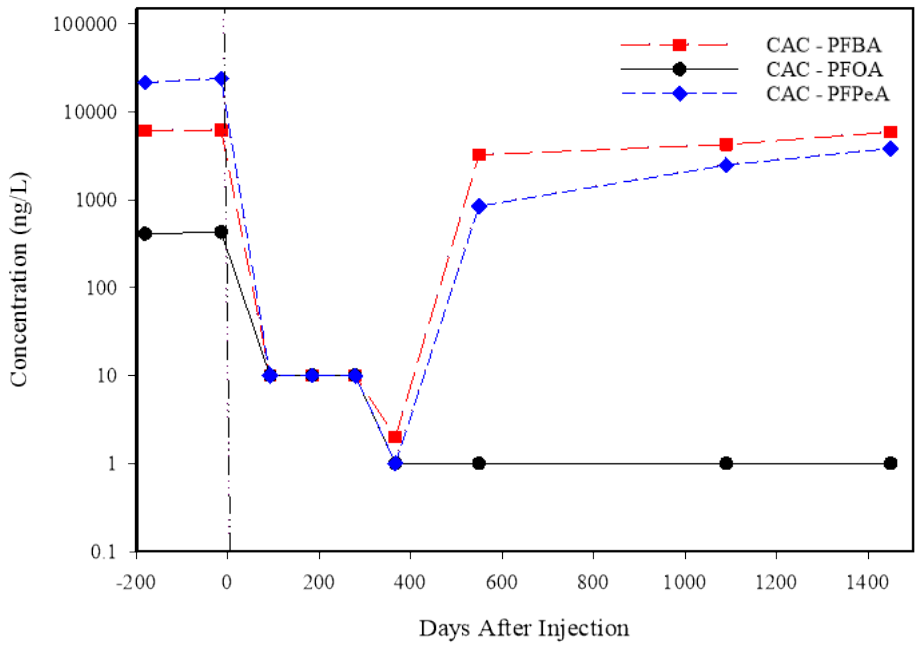
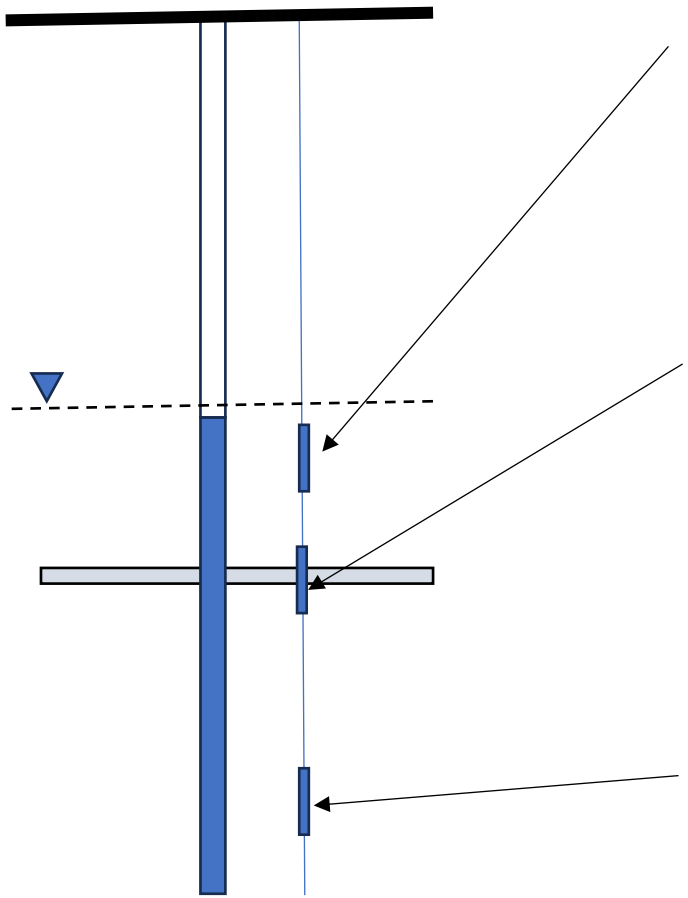
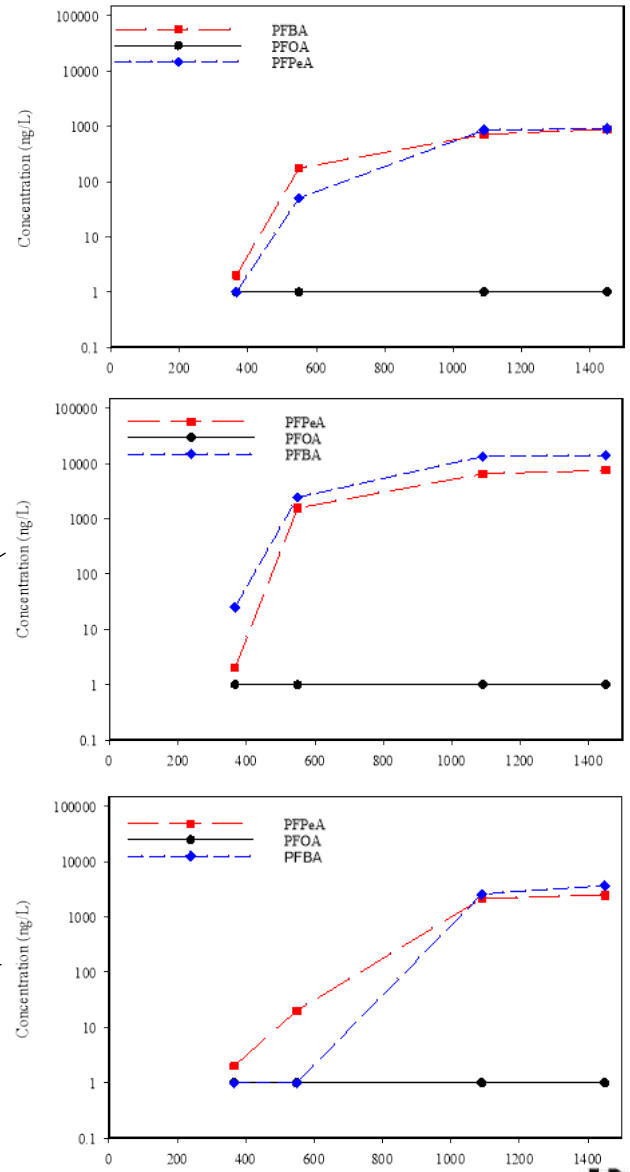
Results

MW2



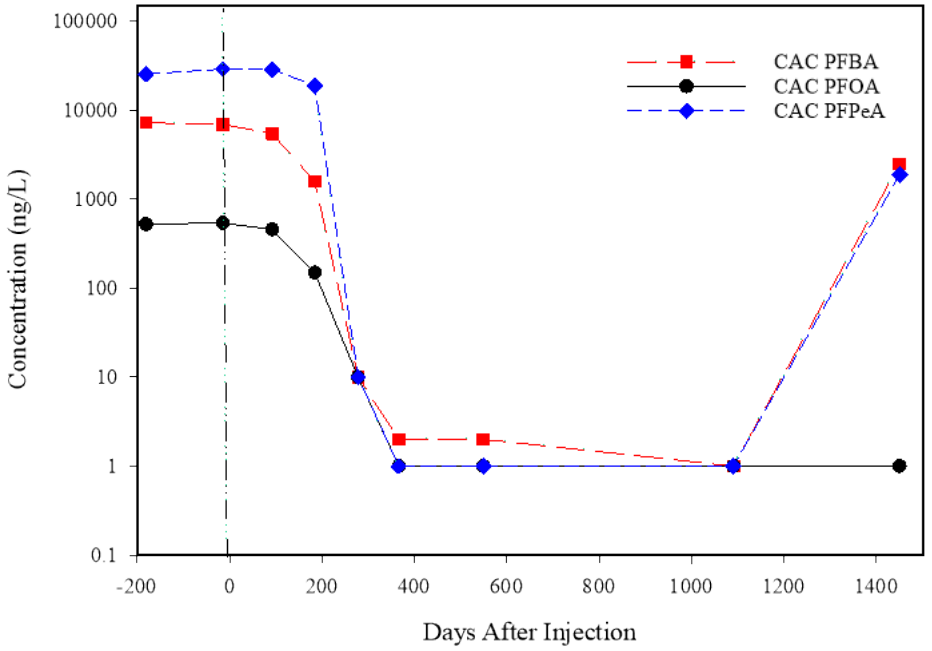


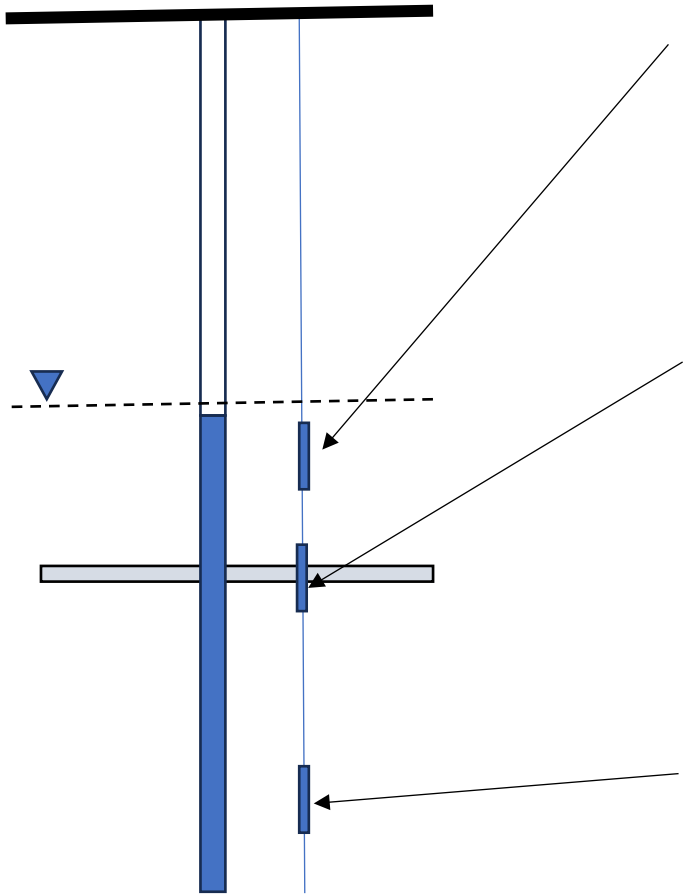
CMT2



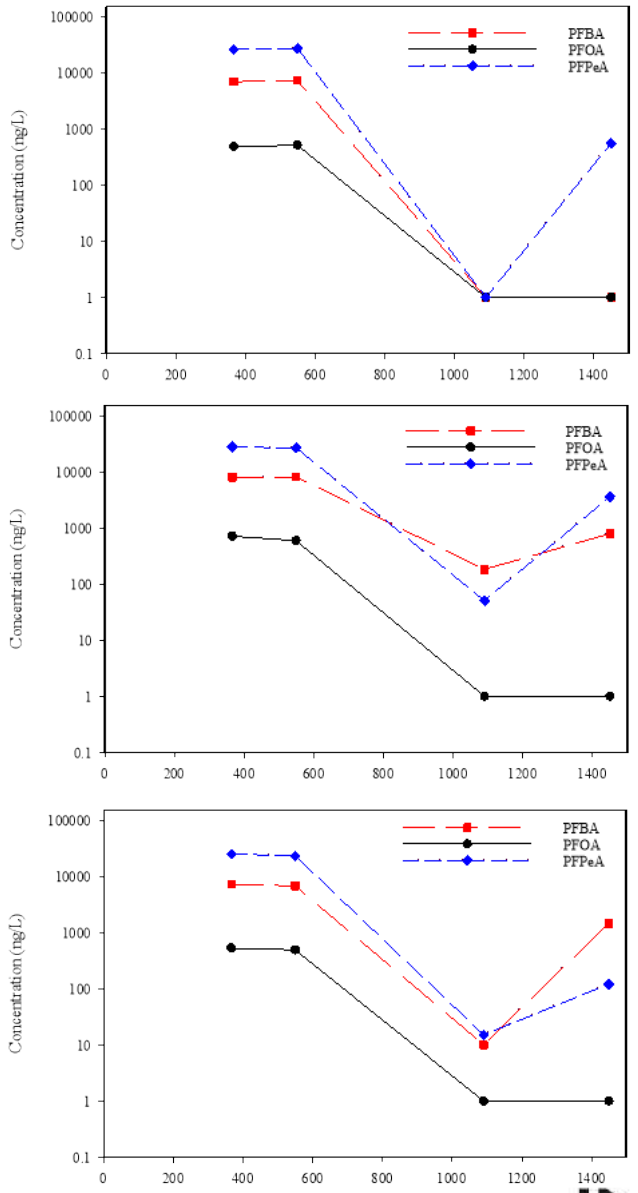
Results

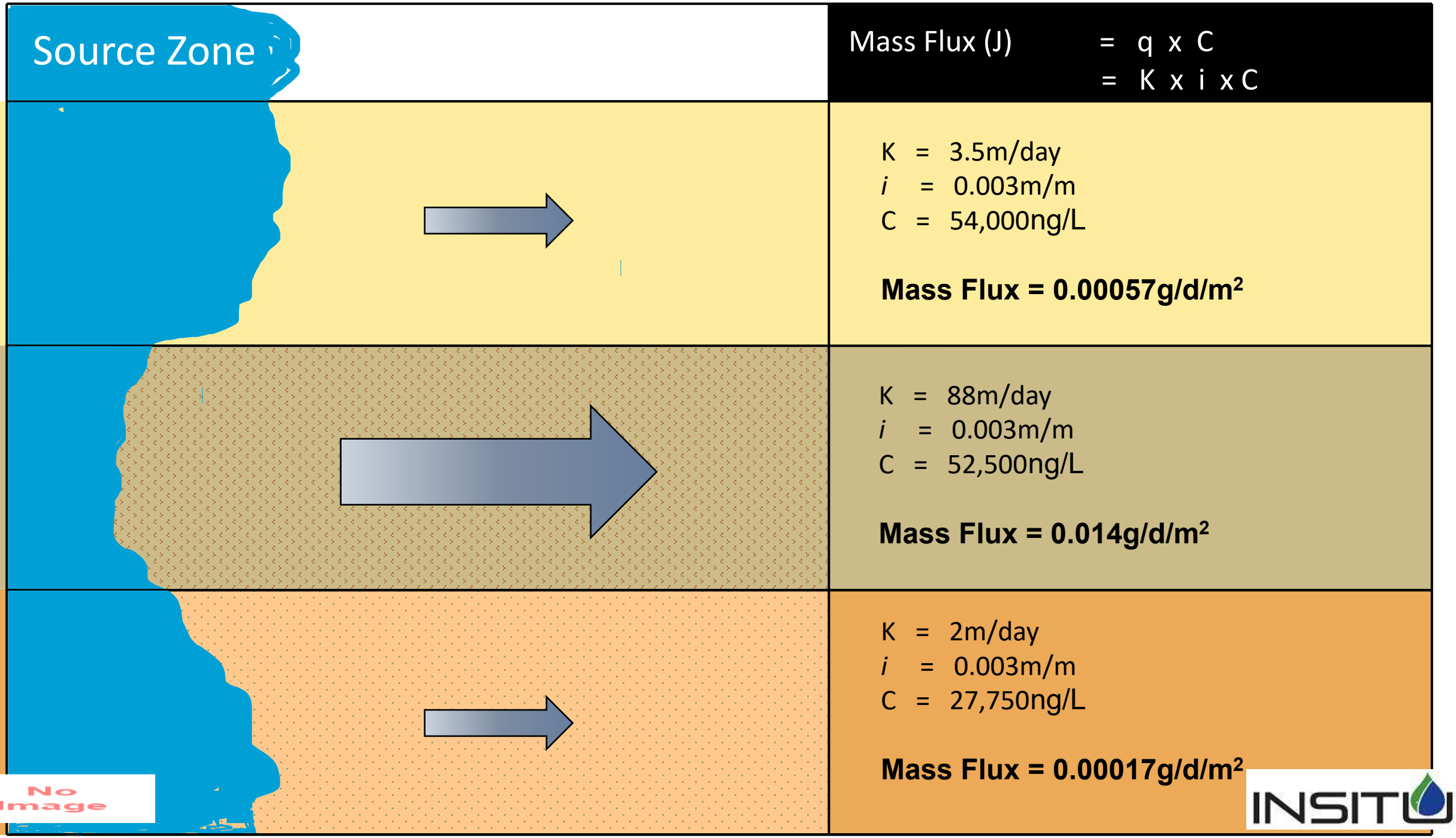
MW3





CMT3




Source Zone
Mass Flux (J) = q x C
= K x i x C
Silty Sand
K = 3.5m/day
i = 0.003m/m
C = 54,000ng/L
Mass Flux = 0.00057g/d/m²
Sand
K = 88m/day
i = 0.003m/m
C = 52,500ng/L
Mass Flux = 0.014g/d/m²
Silty Sand
K = 2m/day
i = 0.003m/m
C = 27,750ng/L
Mass Flux = 0.00017g/d/m²
No Image

Summary

- "Macro" Scale
  - C6 and greater: Non detect after 4 years
  - C4 & C5: breakthrough after 1 year
    - Carboxylic acids
    - PFBA C/Co 95%
    - PFPeA C/Co 16%

- "Micro" Scale
  - C6 and greater: Non detect after 4 years
  - C4 & C5: breakthrough after 1 year
    - Carboxylic acids
    - PFBA C/Co 14% at watertable, C/Co **122** % in sand seam
    - PFPeA C/Co 4% at watertable, C/Co 59% in sand seam

Thank You

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