

NAVFAC Open Environmental Restoration Resources (OER2)

Lessons Learned from In Situ PFAS Sequestration

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Speaker Introduction

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Disclaimer

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OER2 Webinar Series

- **Why Attend?**
 - Obtain and hear about the latest DOW and DON's policies/guidance, tools, technologies and practices to improve the ERP's efficiency
 - Promote innovation and share lessons learned
 - Feedback to the ERP Leadership
- **Who Should Attend?**
 - ERP Community Members: RPMs, RTMs, Contractors, and other remediation practitioners who support and execute the ERP
 - Voluntary participation
- **Schedule and Registration:**
 - Offered quarterly
 - Registration link for each topic (announced via ER T2 email)
- **Topics and Presenters:**
 - ERP community members to submit topics (non-marketing and DON ERP-relevant) to EXWC.T2@us.navy.mil
 - Selected topic will be assigned Champion to work with presenter

Presentation Overview



- **What is PFAS In Situ Sequestration?**
- **Amendments for PFAS In situ Sequestration**
- **Types of PFAS In Situ Applications**
- **Case Studies**
- **Lessons Learned**

What is In Situ Sequestration?

- Injecting, mixing, or applying amendments directly into the ground to bind with chemicals and reduce mobility in the subsurface
- When performed in the vadose zone, can reduce PFAS leaching/mass flux to groundwater
- When performed in the saturated zone, can inhibit migration

Amendments for In Situ Sequestration

Amendments for In Situ Sequestration - Carbon



- **PFAS binding**

- Surface functional groups + microporous regions adsorb PFAS to carbon surfaces

- **Types**

- **Granular Carbon**

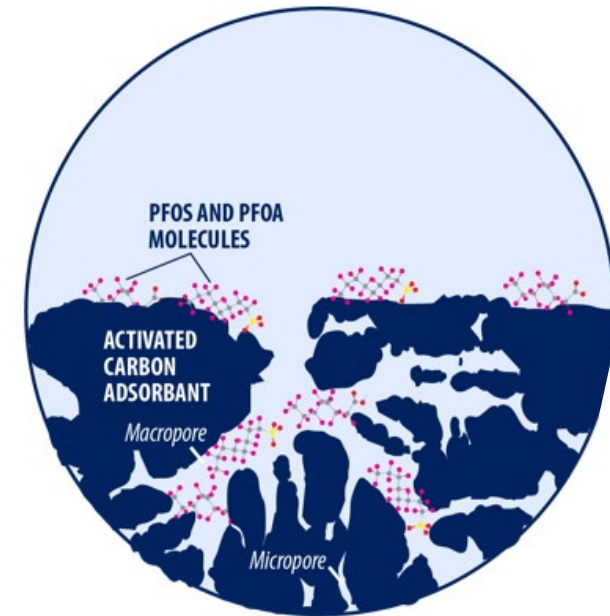
- Largest (~0.2 – 2 mm), about the size of coarse sand
 - More commonly used for ex situ treatment applications

- **Powdered Activated Carbon**

- Medium-sized (<0.18 mm), about the size of silt or fine sand
 - Can be injected into aquifers or mixed into the vadose or saturated zone with large diameter augers or other earth moving equipment
 - Distribution limited

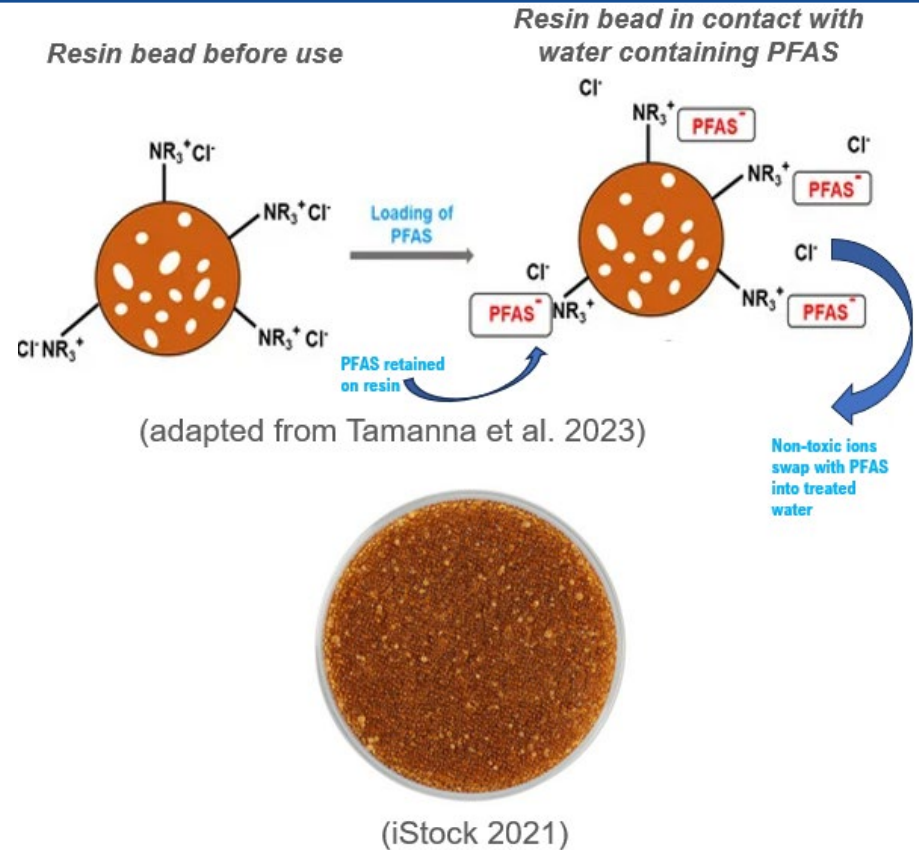
- **Colloidal Activated Carbon**

- Smallest (<5 μm)
 - Can be injected as a liquid suspension or applied to unsaturated soil through surface application with ease of distribution



Amendments for In Situ Sequestration – Ion Exchange (IX) Resins

- Synthetic microbeads (0.3 to 1.2 mm) composed of polymers (e.g. acrylic, polystyrene)
- Contain charged functional groups in the polymer matrix pre-loaded with non-toxic exchangeable counterions
- When PFAS containing water comes in contact with the microbeads, the exchangeable counterions swap out for PFAS
- Anion exchange resins are used for treatment of the current PFAS of interest (PFOA, PFOS, etc.)
- Can be injected, mixed, or used in applications like funnel and gate or trench barriers.
- Efficacy of injection of ground resin is being studied
- Many brands are available (e.g. Purolite, Dowex, CalRes, etc.)



Amendments for In Situ Sequestration – Others You Might Hear About



- **Surface-modified clays (e.g. FLUORO-SORB, Rembind)**
- **Amine-based Polymers (e.g. PolyDADMAC, polyHIPE)**
- **Metal organic frameworks (MOFs)**

- **Not all amendments have been thoroughly demonstrated. Check with your SME first!**

Types of In Situ Sorption Applications

Direct Ground Surface Application



- Colloidal activated carbon can be direct applied through
 - Excavating soils, and spraying in lifts during backfilling operations
 - Creating a boundary wall and flooding it with colloidal carbon, forcing infiltration into the soil
- For sites with thin vadose zones, may reduce mass flux to groundwater
- Most appropriate for sites with higher permeability soils
- Emerging application – will not meet clean up goals for direct exposure; suitable for mass flux reductions

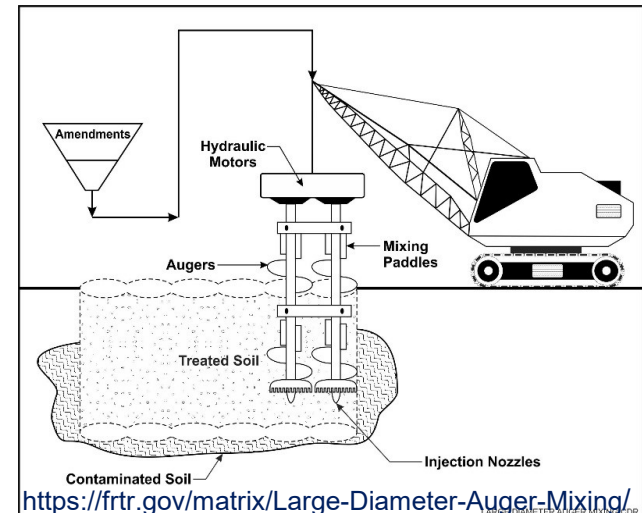


Soil Mixing

- **Aggressive mixing of amendments into the subsurface**
- **Equipment**
 - **Excavators**
 - Suitable for use up to 30 ft bgs
 - Less expensive and most practical option
 - **Large Diameter Augers**
 - For deeper mixing (up to 100 ft bgs)
 - Better vertical uniformity than excavators
 - More expensive and not likely to be many great applications for PFAS sites (more appropriate for DNAPL)
- **For PFAS, mixing is most suitable for use in vadose zone applications and where uniform distribution is key**



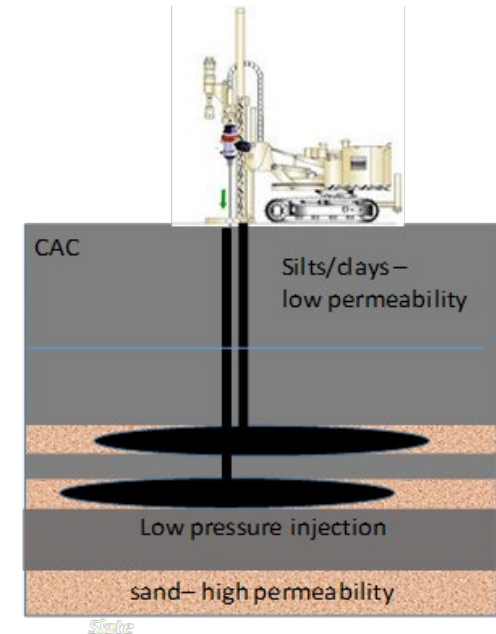
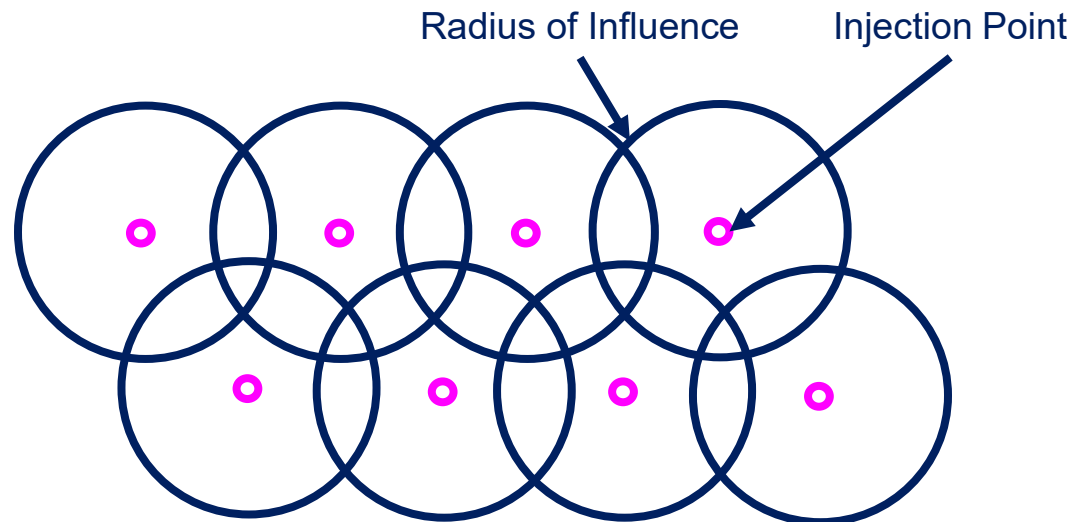
Geo-Solutions, Inc.



Source or Downgradient Barrier Injections

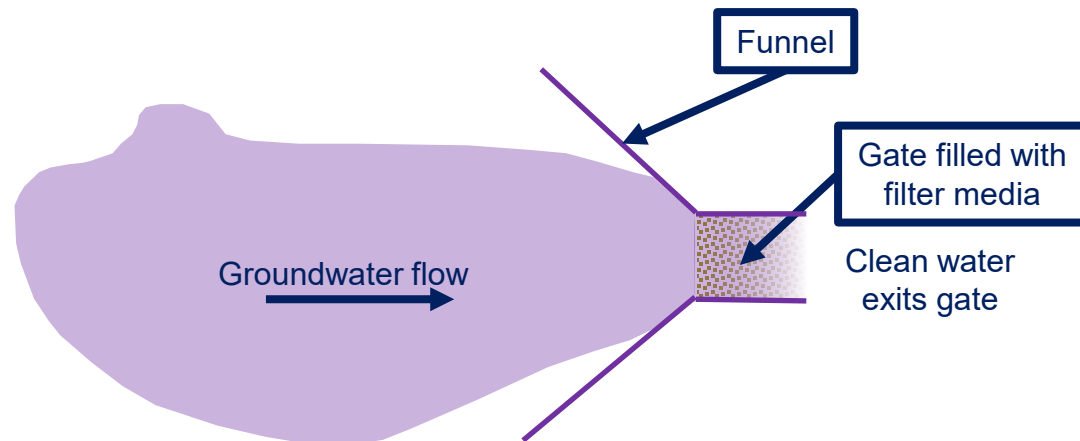


- Direct injection of carbon into the subsurface using DPT
- Can be performed using PAC or CAC, and other amendments
- High and low pressure may be considered



Funnel and Gate

- Makes use of confining units and groundwater flow to capture and filter plume as it travels downgradient
- “Funnel” constructed of slurry wall or sheet pile is keyed into the shallowest confining unit.
- “Gate” filled with filter media (GAC, resin, or other sorbent) is placed between funnel sections
- Groundwater is forced into the gate and treated as it moves downgradient
- Filter media can be removed and replaced when spent (breakthrough occurs above target treatment goals)
- Configurations vary – some are a straight barrier and less funnel shaped
 - May need multiple treatment gates connected to funnel to contain a plume



Case Studies

Case Study 1 – Surface Activation of Colloidal Activated Carbon, Air Station in Southeast



Project Objective:

- Determine the efficacy of surface applied CAC to reduce PFAS mass flux to underlying groundwater

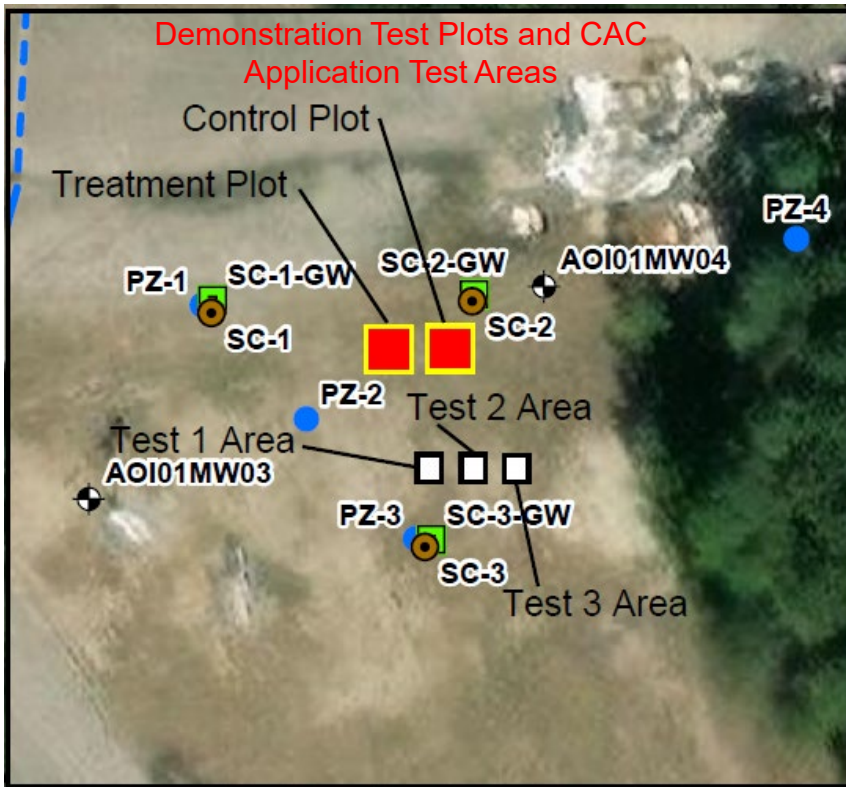
Conceptual Site Model Overview:

- Vadose zone soil concentrations between 500-5,000 $\mu\text{g/kg}$, mostly PFOS
- Groundwater concentrations between 100,000 and 600,000 ng/L , mostly PFOS

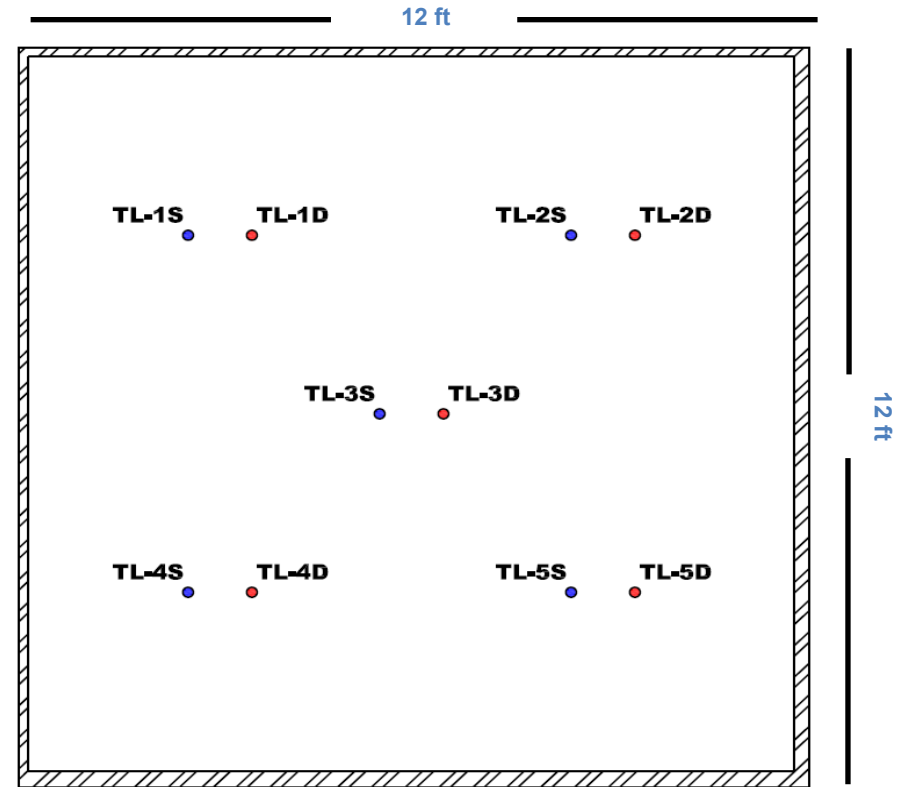
Approach:

- Site characterization, column testing, lysimeter and piezometer installation, field testing of application methods (explored impact of soil and vadose zone injection), and pilot scale surface application, and monitoring

Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



- Piezometer
- ⊕ Monitoring Well
- Discrete Groundwater Location
- Soil Core Location
- Water Utility Segment (Survey)
- - - Water Utility Segment (Approximate)
- Demonstration Test Plots
- CAC Application Test Areas



- **SHALLOW LYSIMETER (2 FT-BGS)**
- **DEEP LYSIMETER (4 FT-BGS)**
- PLASTIC SHEET (OR OTHER) BORDER**

Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



- Sod cutter (remove top 2-3 inches) and turf aerator
- Lysimeters installed in control plot and test plot
- Barrier walls installed in control plot and test plot
- Barrier wall sealed with bentonite



Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



- 1,900 gallons of a 1.5% CAC solution to treatment plot
- 1,900 gallons of GAC pre-treated water to control plot



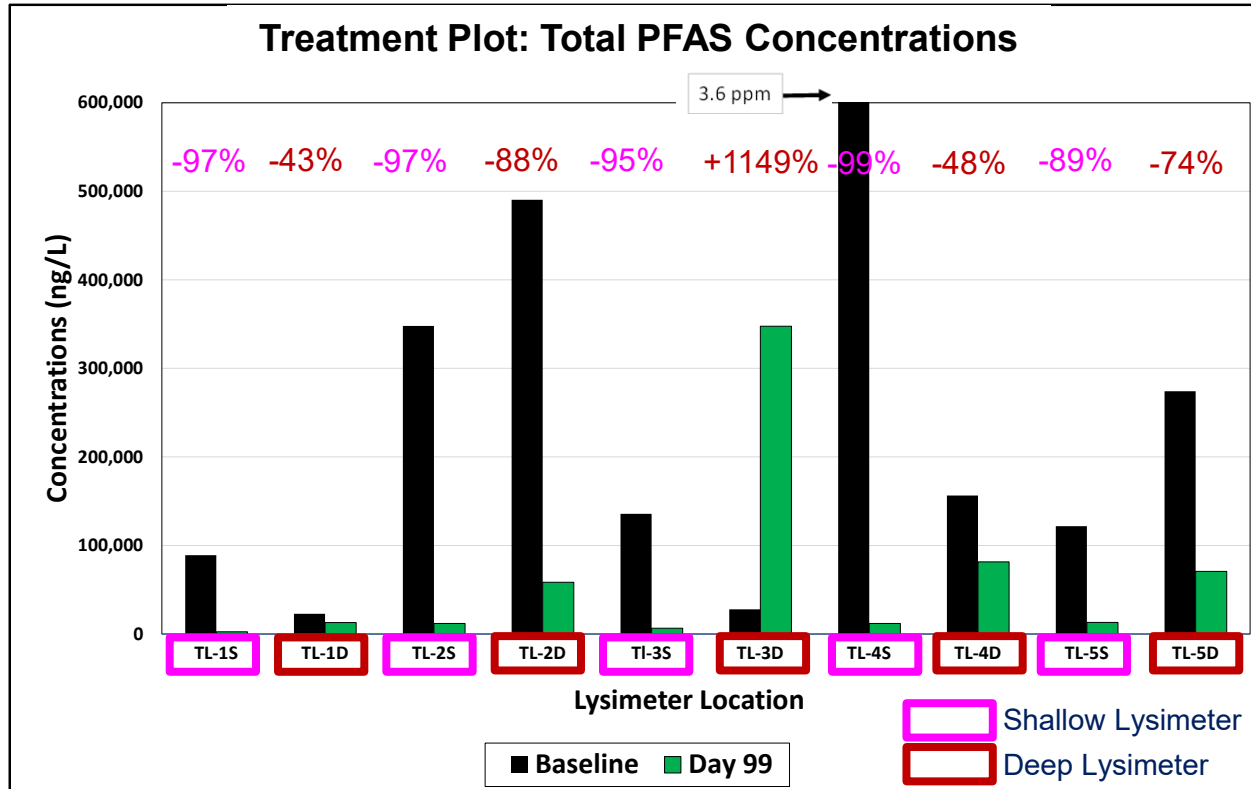
Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



- **Monitoring**
 - Soil cores: CAC abundant to at least 9 inches and some areas to 37 inches (up to 3,900 mg/kg)
 - Migration into formation not even across treatment area due to very slight grade in treatment area
 - Two pore water events completed to date

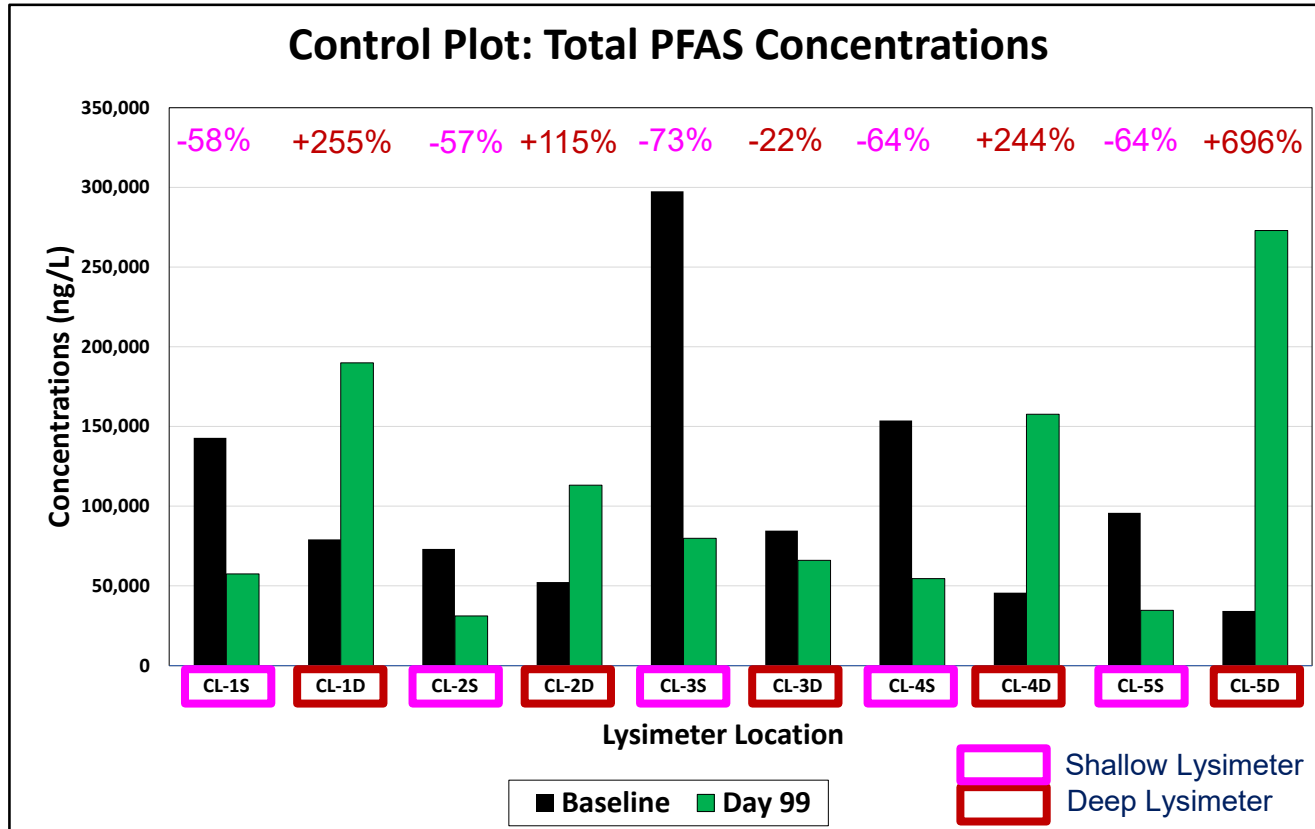


Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



Lysimeter	% change
TL-1S	-97
TL-1D	-43
TL-2S	-97
TL-2D	-88
TL-3S	-95
TL-3D	+1149
TL-4S	-99
TL-4D	-48
TL-5S	-89
TL-5D	-74

Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



Lysimeter	% change
CL-1S	-58
CL-1D	+255
CL-2S	-57
CL-2D	+115
CL-3S	-73
CL-3D	-22
CL-4S	-64
CL-4D	+244
CL-5S	-64
CL-5D	+696

Case Study 1 - Surface Application of Colloidal Activated Carbon, Air Station in Southeast



Take Aways

- **CAC can be surface applied to PFAS impacted soils to reduce mass flux to underlying groundwater**
- **Some ground surface preparation is advisable prior to surface application**
- **Feet of CAC infiltration can be achieved**



NESDI Project 569

Project Objective:

- Evaluate effectiveness of use of CAC for in situ PFAS treatment

Environmental Questions:

- Does CAC distribute sufficiently in aquifers to effectively treat PFAS?
- What is the in situ treatment effectiveness on different PFAS
- What is the long-term adsorption capacity and potential for re-release of PFAS?
- Are there any significant aquifer effects (e.g. CAC in monitoring wells or hydraulic conductivity impacts)

Approach:

- Site characterization, laboratory testing, barrier installation, and monitoring

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic

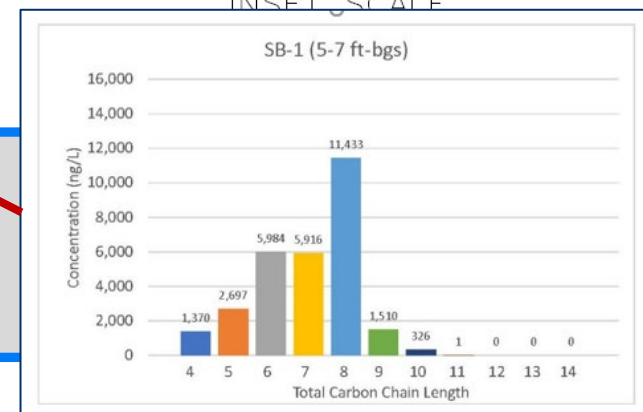
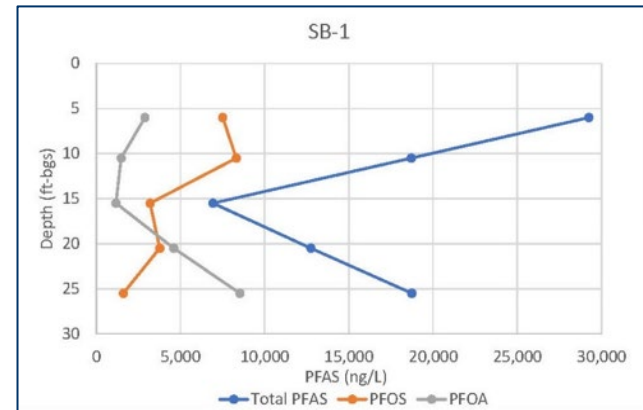
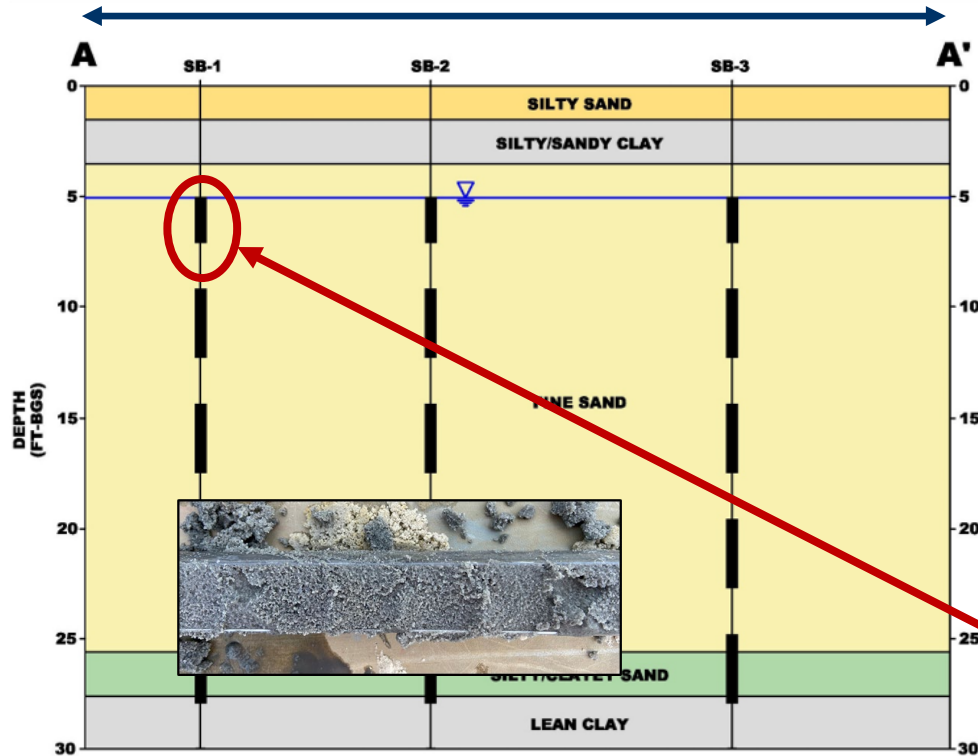
• Conceptual Site Model

- AFFF Storage Area at Installation used for field carrier landing and helicopter training operations
- High permeability sandy formation
- Water table within 6 feet of ground surface
- Relatively homogenous
- Higher PFAS concentrations – up to about 20,000 ppt PFOS in groundwater

PFOS Concentrations in Groundwater (ng/L)



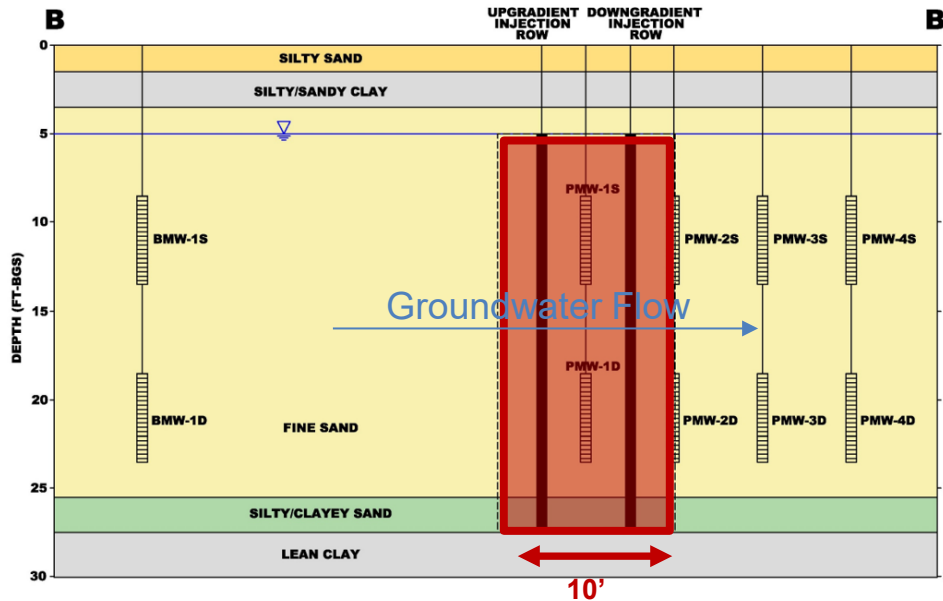
Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



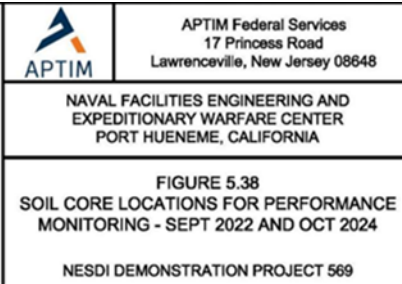
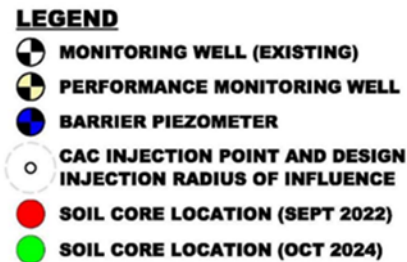
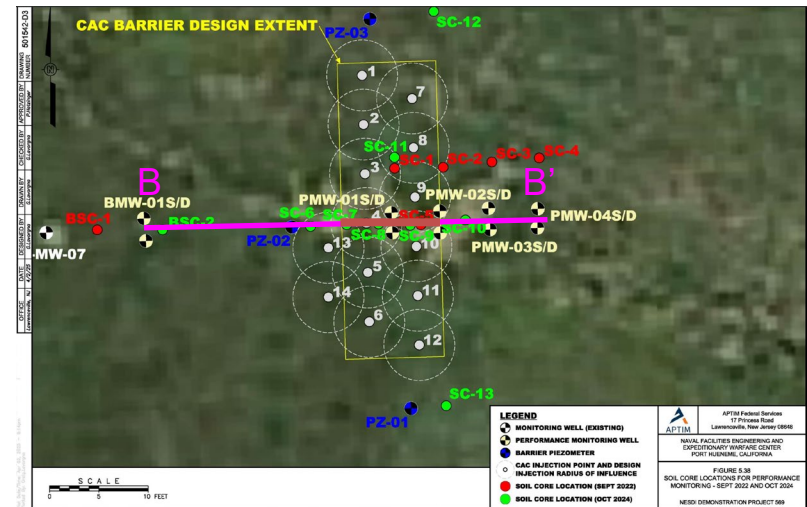
Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



DEMONSTRATION WELL AND INJECTION POINT LAYOUT



30' Long x 10' Wide barrier



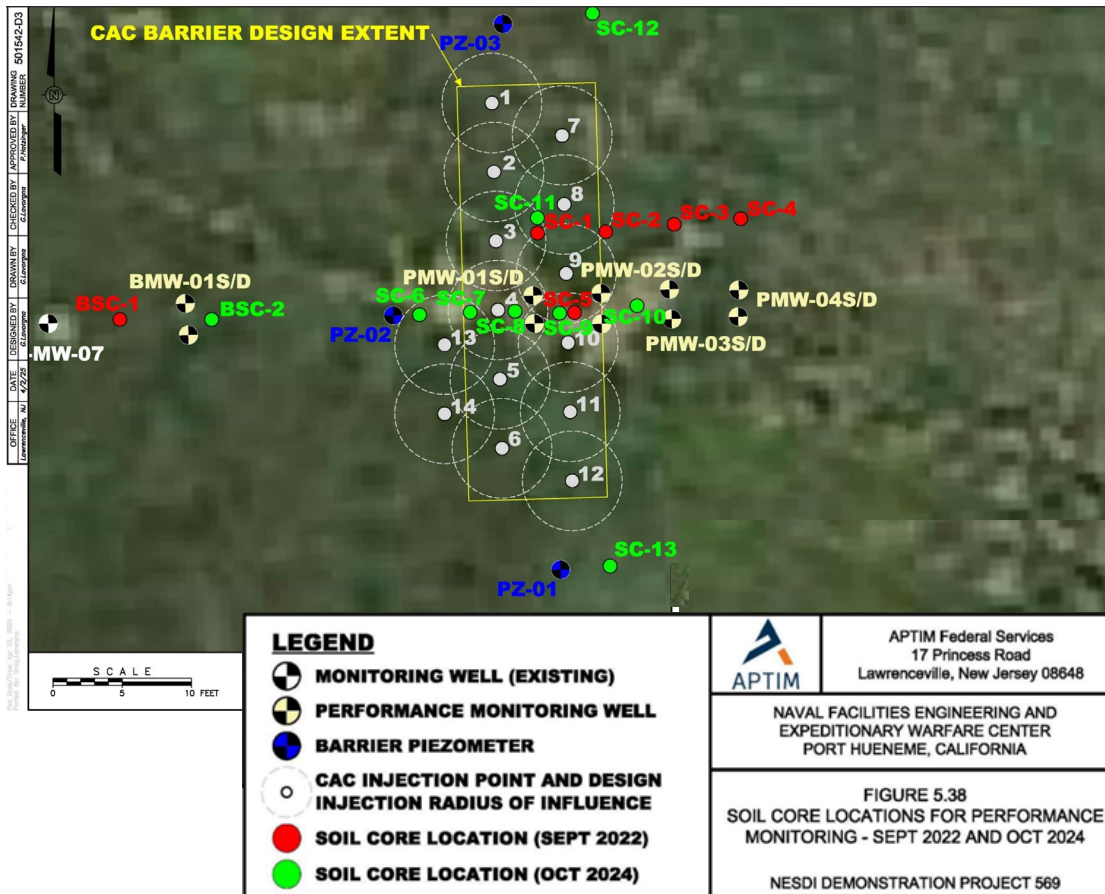
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Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



CAC INJECTION



Quarterly Groundwater Monitoring

- Field parameters (meter)
 - Anions (EPA 300.0)
 - PFAS

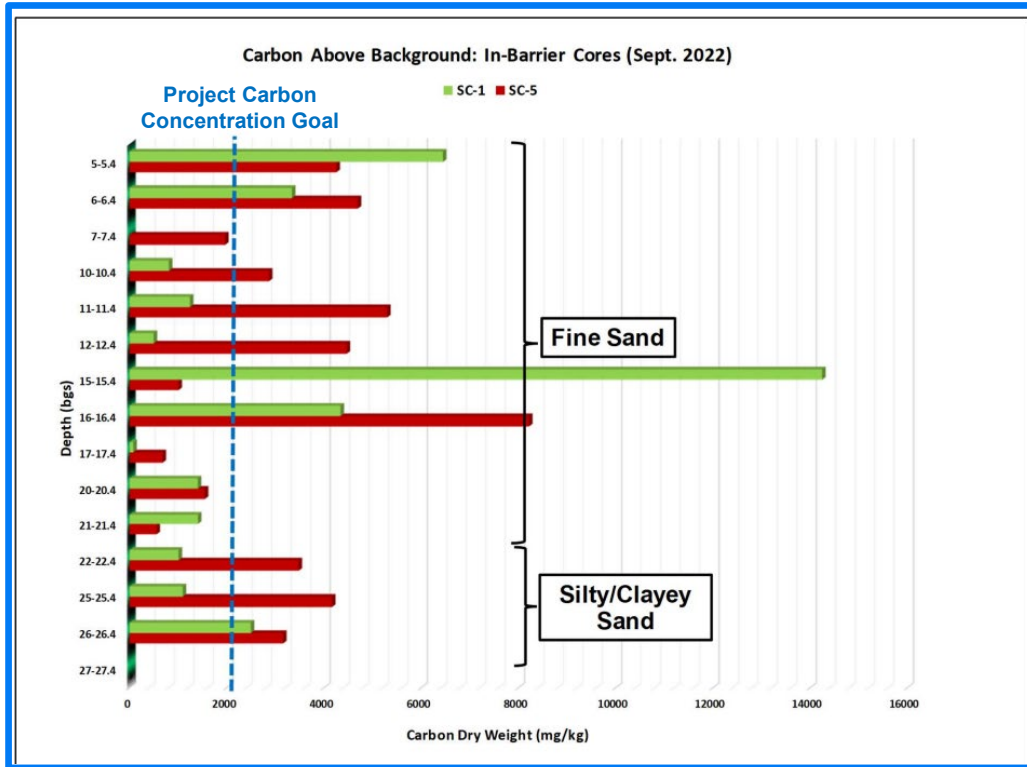
Soil Cores

- 1 & 24-months post injection
- Measure CAC (combustion method)

Passive Flux Meters (6)

- Before barrier Installation
- 1 and 2 years after barrier installation

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic

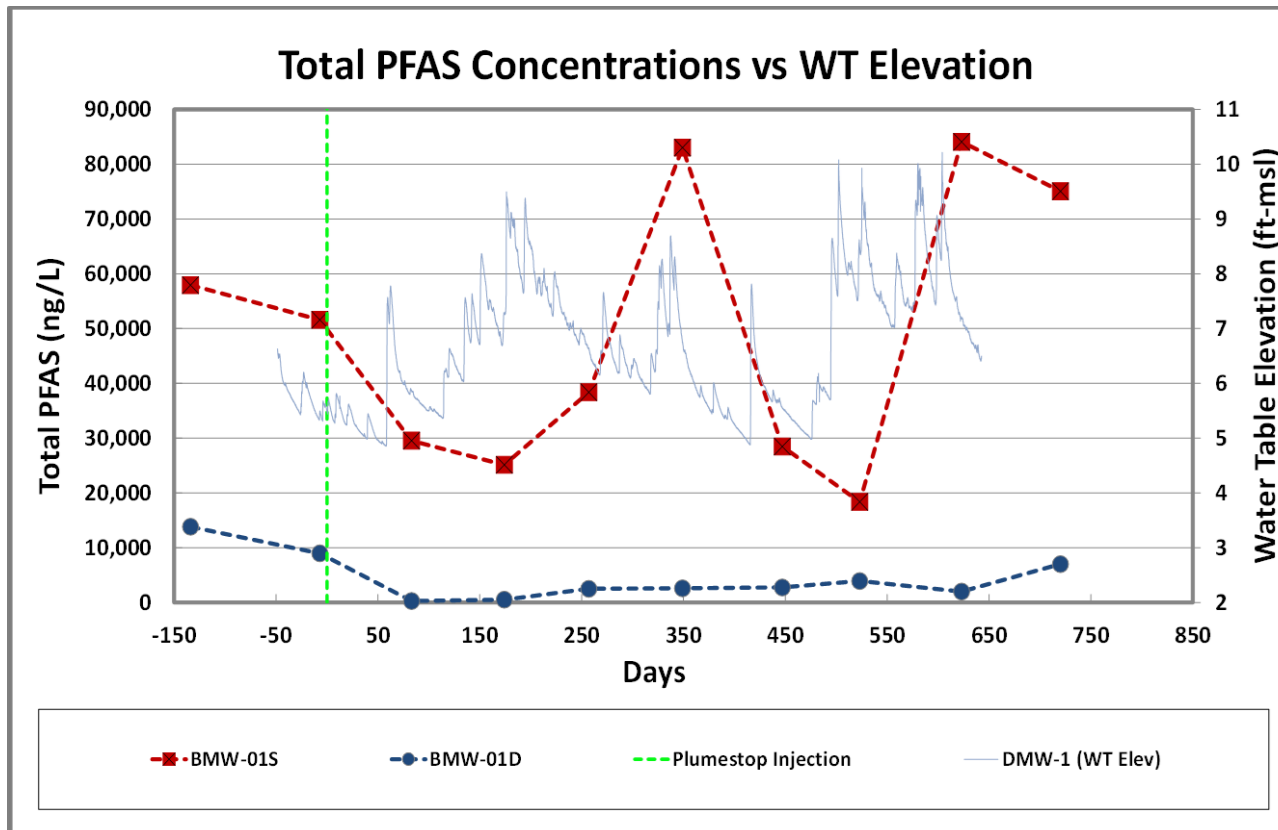


Key Takeaway – Colloidal activated carbon can be effectively distributed in the subsurface using direct injection methods

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



Upgradient Data



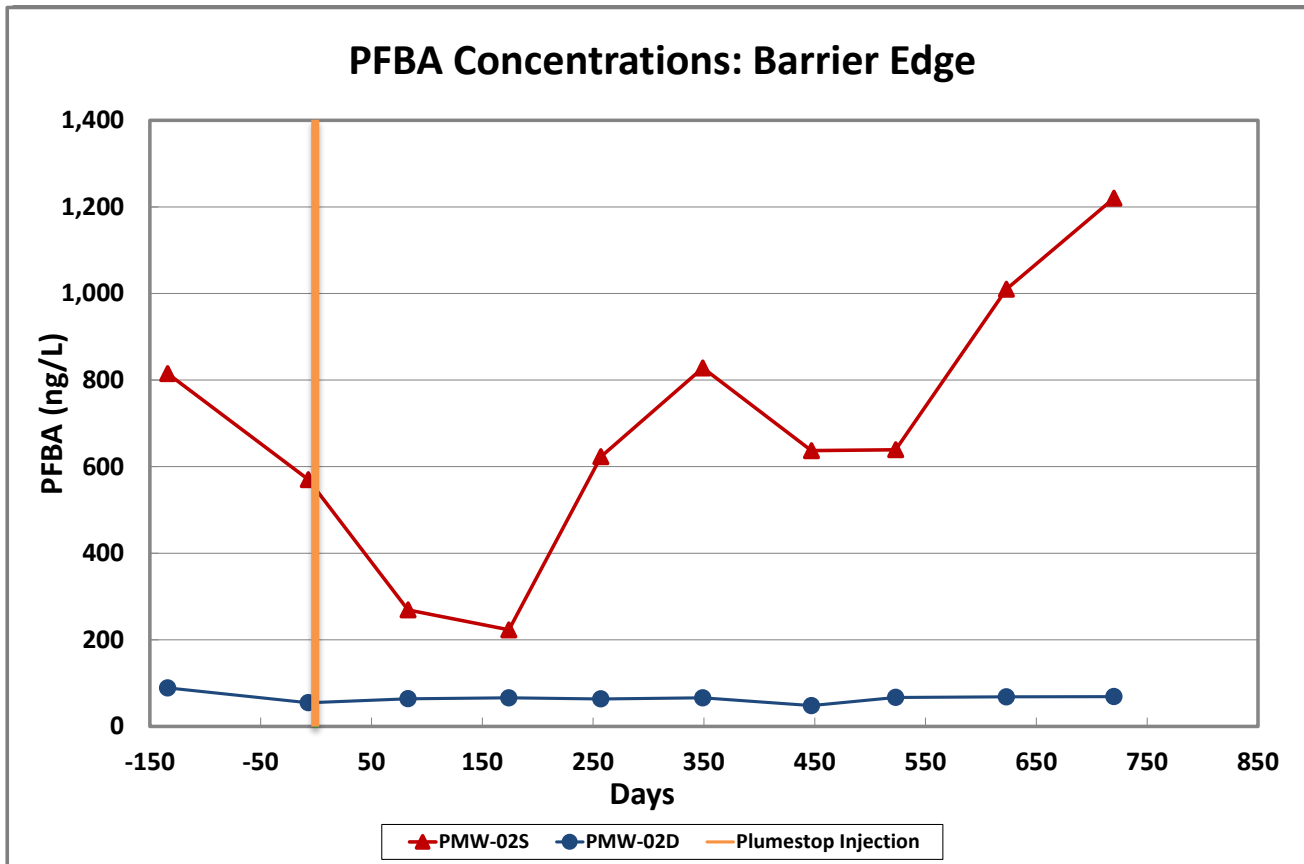
Upgradient– 2 YRS

- Pre-injection baseline
 - Shallow: 52 – 58 µg/L
 - Deep: 9 –14 µg/L
- Over time variability in shallow GW suggests vadose zone impacts - groundwater elevation
- Less variability in Deep Zone

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



PFAS Data - Downgradient Barrier Edge

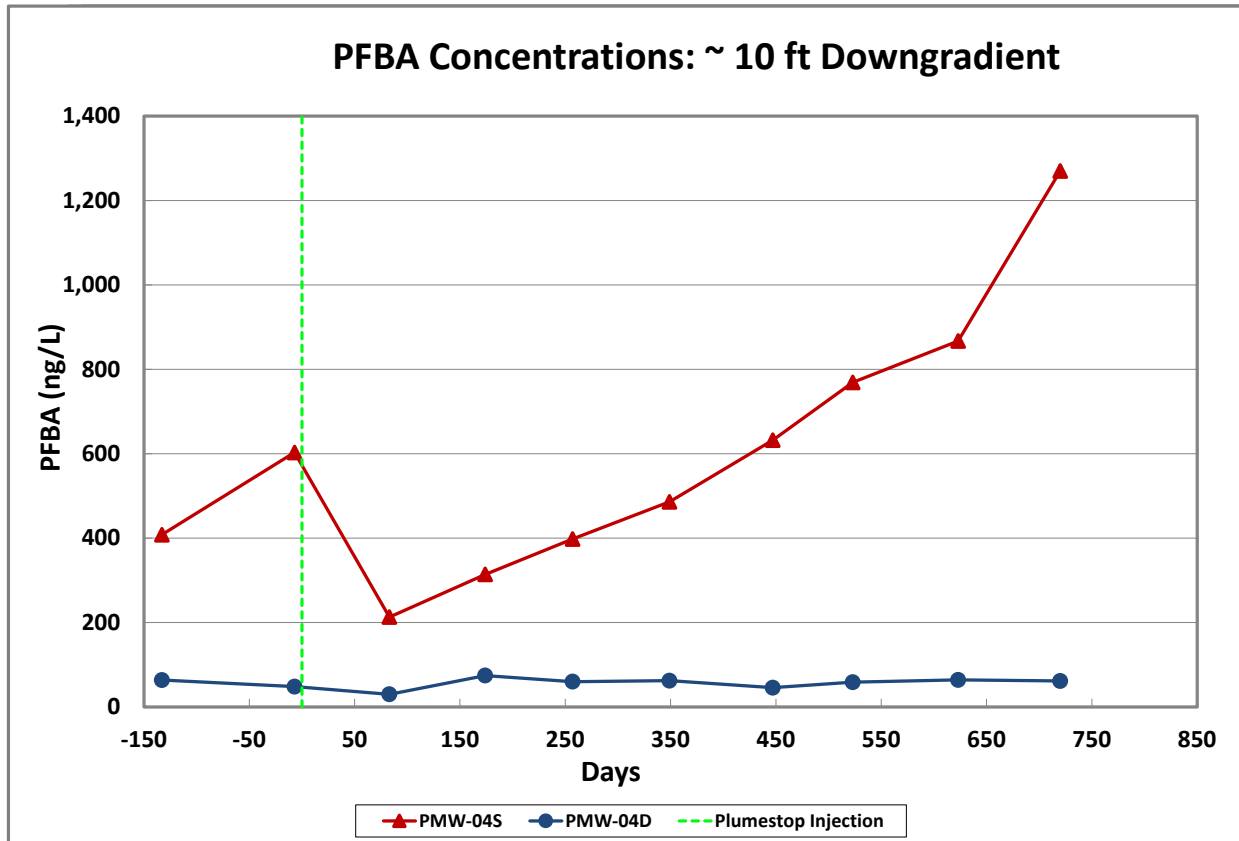


- **2 years after injection**
- 96.8% reduction in shallow zone
- 96.3% reduction in deep zone
- Complete breakthrough of PFBA
- PFPeA, PFHxA also increasing gradually with time (some wells increased to 100-200 ppt after initial reductions)
- Excluding PFBA, 99.85% removal at downgradient edge

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



PFAS Data – 10 ft downgradient



- **2 years after injection**
- 91.2% reduction in shallow zone
- 95.3% reduction in deep zone
- Complete breakthrough of PFBA
- Rate-limited and back-diffusion downgradient of barrier + new vadose zone addition

Case Study 2 – Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of PFAS, Airfield in Mid-Atlantic



Key Takeaways

- Injected CAC barriers can sequester PFAS and reduce downgradient migration of PFAS in groundwater
- Breakthrough of short chained PFAS like PFBA may occur
- If source mass still remains downgradient of treatment, achieving clean up goals may be challenging due to vadose zone leaching and matrix diffusion/desorption

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



ESTCP Project: ER20-5252

Project Objective:

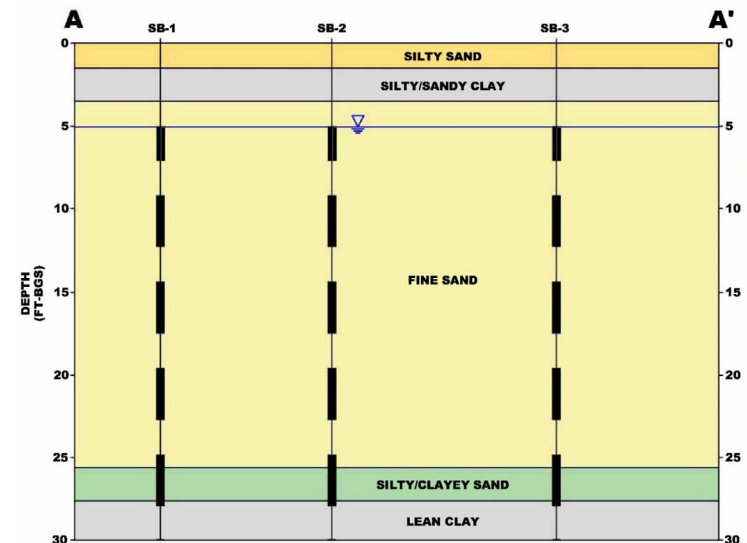
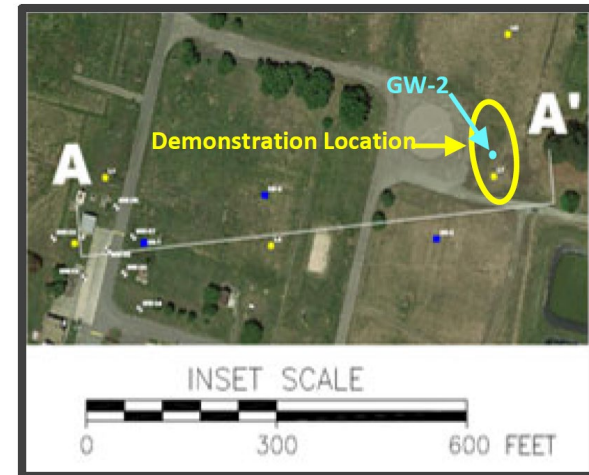
- To demonstrate the long-term and cost effective application of a passive in situ Funnel and Gate Permeable Adsorptive Barrier to capture and remove PFAS emanating from an AFFF source area

Generalized Conceptual Site Model:

- Naval Air Station Fire Training Area
- PFAS in groundwater from AFFF storage/transfer and fire training activities
- Water table 5' below ground surface
- Sandy surficial aquifer
- Confining Unit 27' below ground surface
- Total PFAS (sum of 1633 analytes) up to 365,830 ng/L
- Groundwater migrating off-site toward drinking water receptors (exposure already addressed)

Approach:

- Site characterization, laboratory testing, groundwater modeling, design, installation, monitoring



Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



- Bench scale column testing performed to select adsorptive media
- Three IX resins and one surface modified clay evaluated in columns
- Two of the resins performed similarly, one resulted in resin bed expansion
- The IX resins were more effective in removing PFAS compared to the surface-modified clay
- Selected Dowex Amberlite PSR2 Plus for Field Scale Demonstration

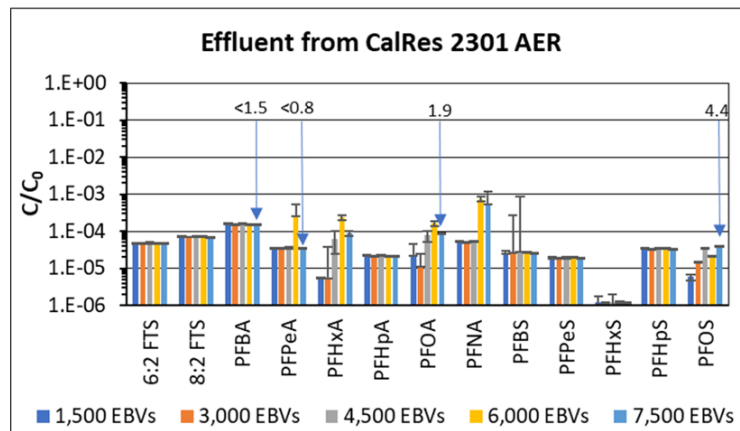


Figure 5.9 PFAS Removal in the CalRes 2301 Columns. Average values plotted. The error bars represent the 95% confidence interval among the three experimental replicates.

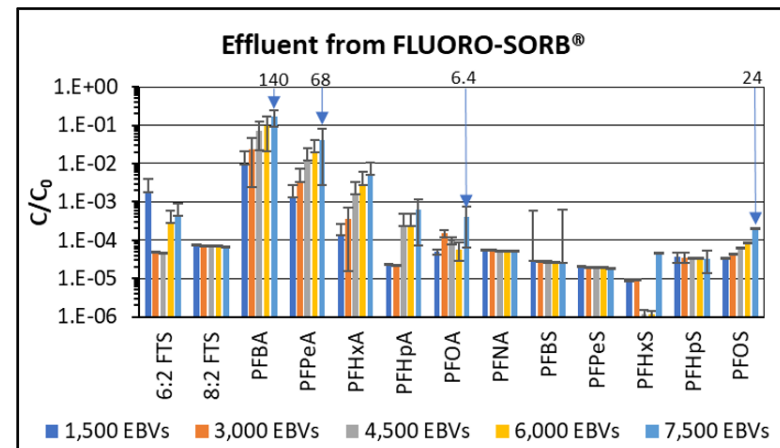
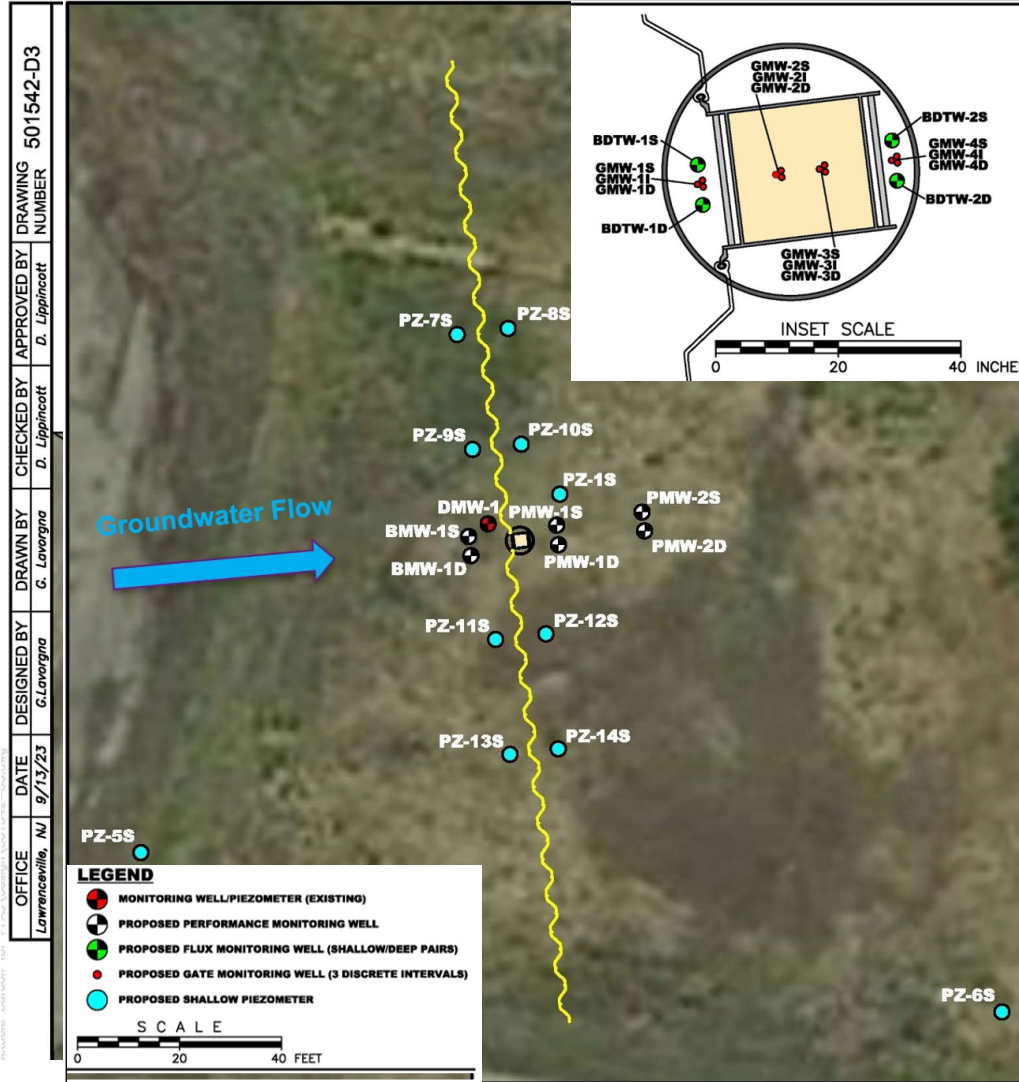
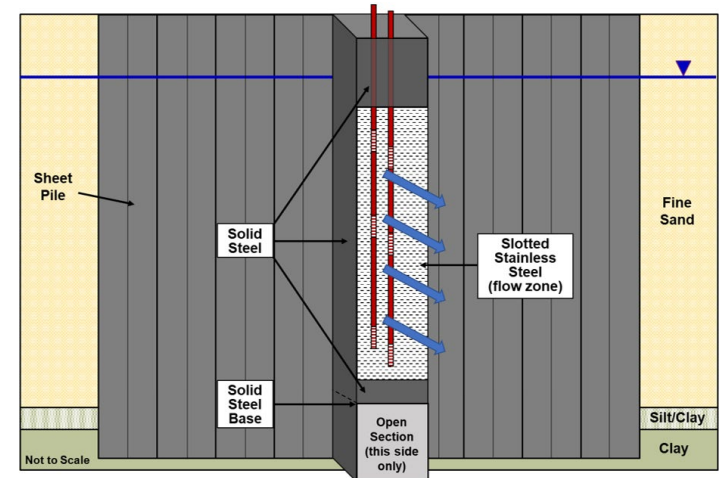


Figure 5.10 PFAS Removal in the FLUORO-SORB® Columns. Average values plotted. The error bars represent the 95% confidence interval among the three experimental replicates.

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for In Situ PFAS Immobilization and Removal, Airfield in Mid-Atlantic



System Design



Anticipate • Innovate • Accelerate



Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic

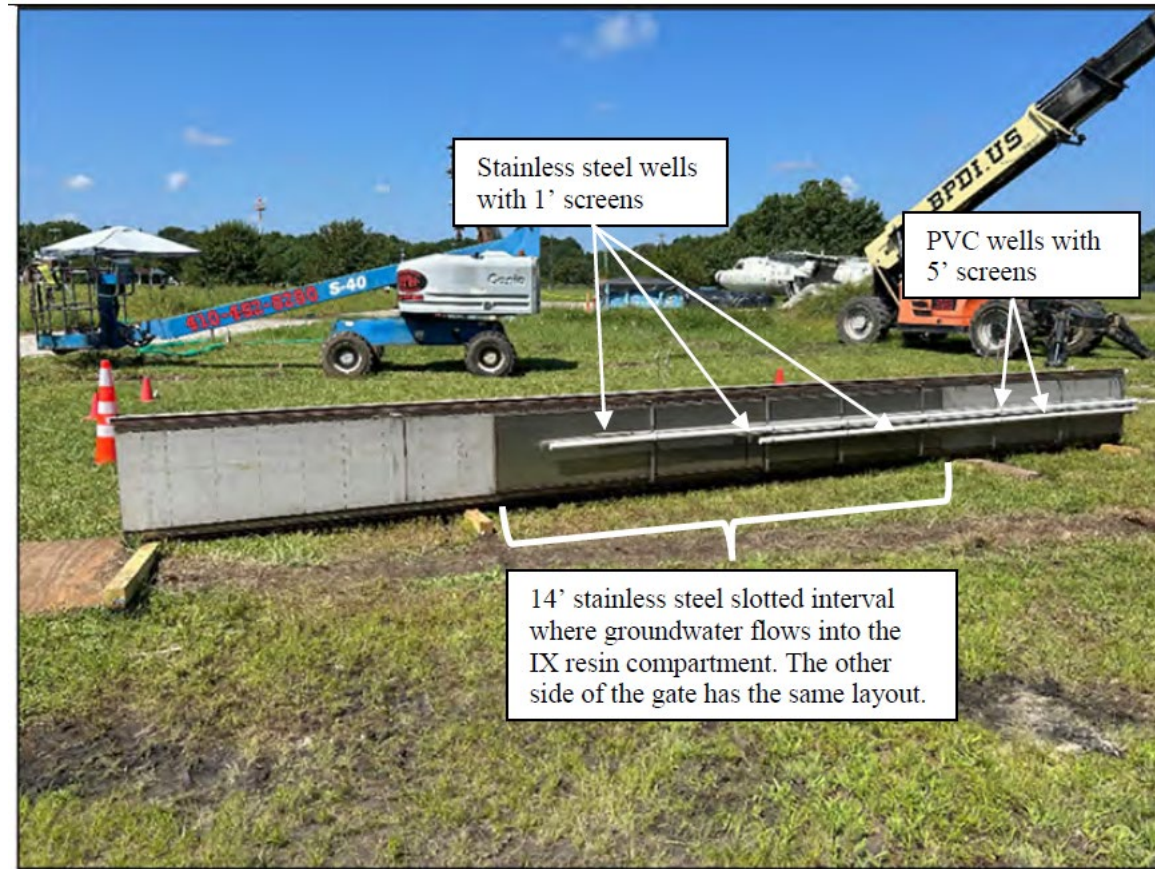


Caisson Installation



Soil Removal from Caisson Using Drill Rig

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



Gate prior to installation

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



Gate Installation



Sand Filter Installation

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



Sheet Pile Installation

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic

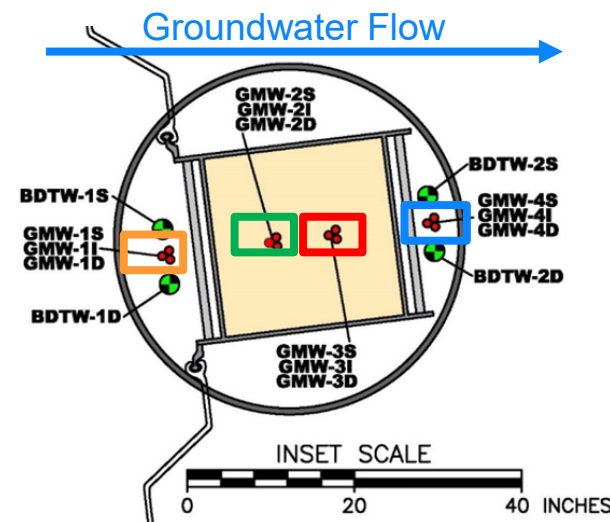
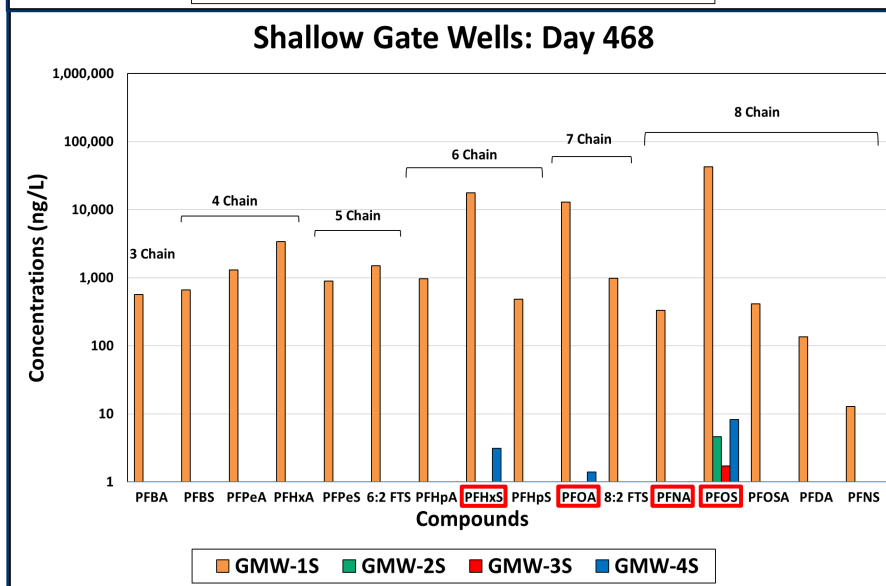
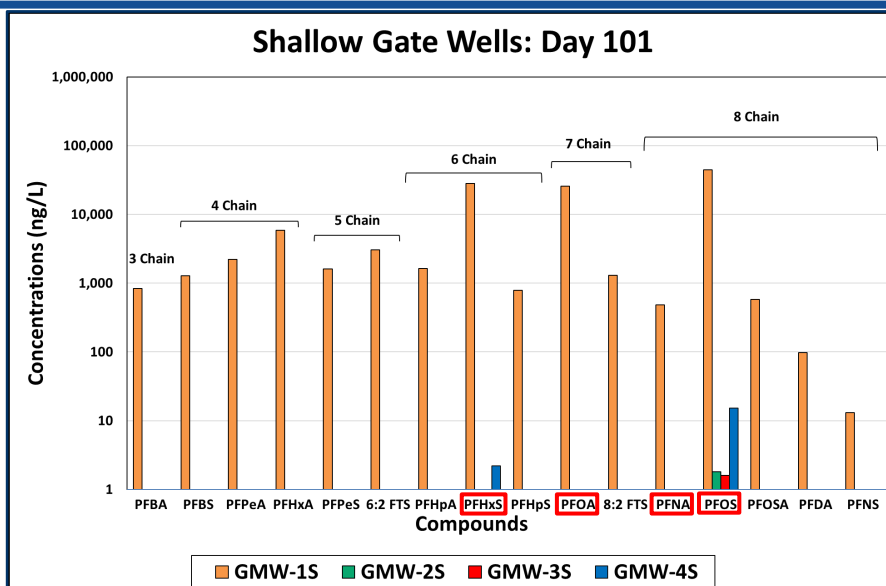
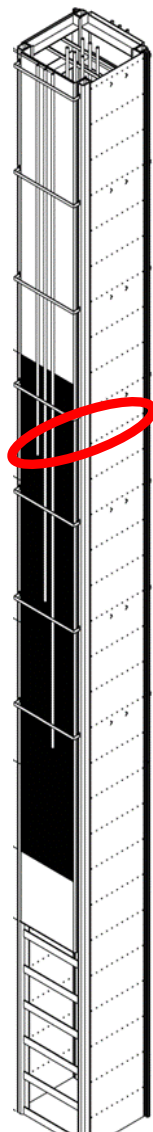


Completed Gate



Completed Wall at Surface

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic

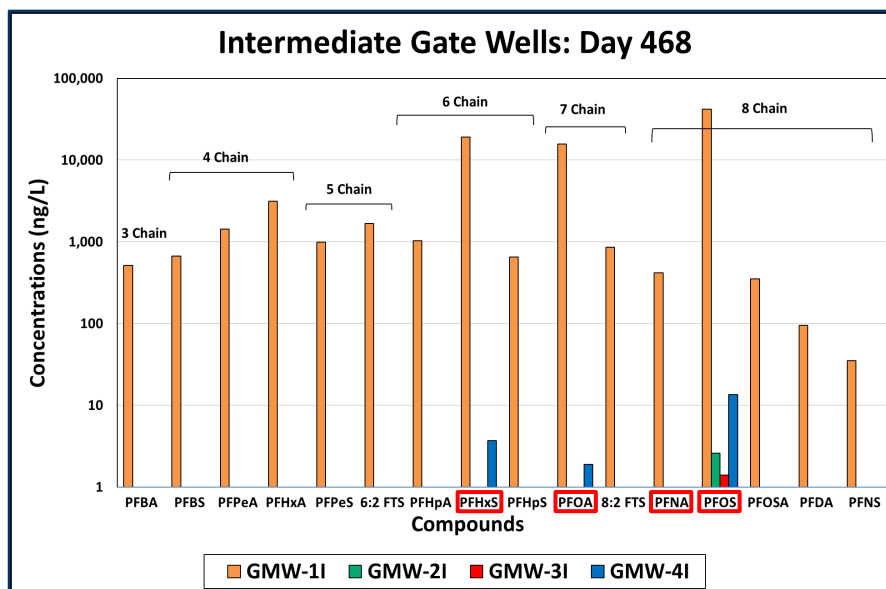
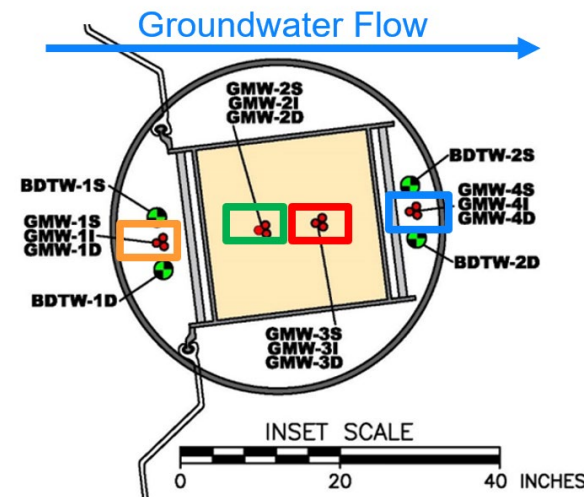
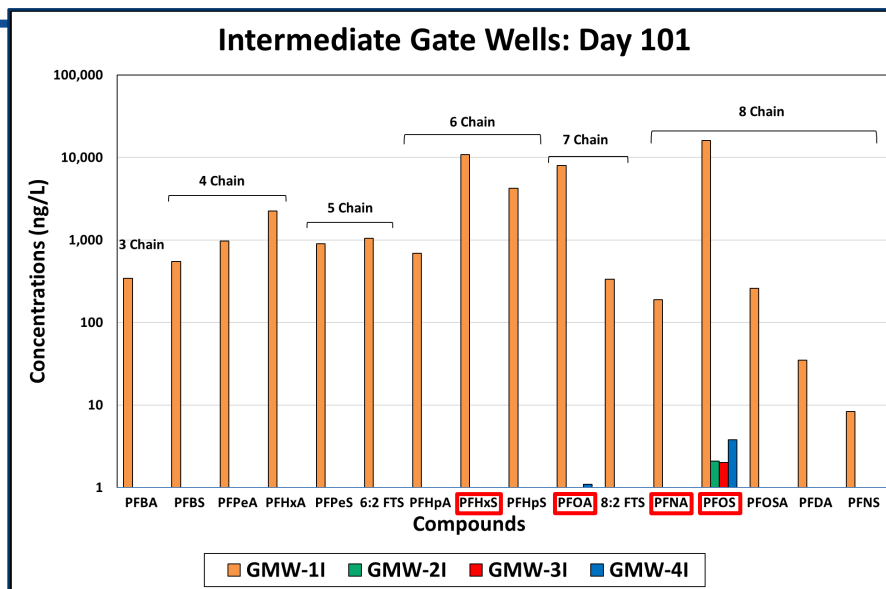
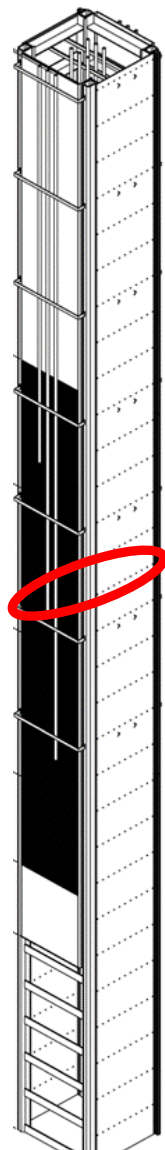


Shallow Gate Wells

- Up to 5 orders of magnitude decrease in gate and effluent well
- Short-chain PFAS removed
- MCLs* achieved:
 - PFHxS: 11 out of 12 samples
 - PFOA: 12 out of 12 samples
 - PFNA: 12 out of 12 samples
 - PFOS: 6 out of 12 samples*

*MCLs have not been established as groundwater clean up goals for this site; however, they were used as performance metrics for this research project.

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



Intermediate Gate Wells

- Up to 4 orders of magnitude decrease in gate and effluent well
- Short-chain PFAS removed
- MCLs* achieved:
 - PFHxS: 11 out of 12 samples
 - PFOA: 12 out of 12 samples
 - PFNA: 12 out of 12 samples
 - PFOS: 6 out of 12 samples*

*MCLs have not been established as groundwater clean up goals for this site; however, they were used as performance metrics for this research project. 46

Case Study 3 – Funnel and Gate Permeable Adsorptive Barrier (PAB) for *In Situ* PFAS Immobilization and Removal, Airfield in Mid-Atlantic



Key takeaways

- Funnel and gate systems can treat high levels of PFAS to at or near MCLs* for over a year**
- Funnel and gate systems are a passive treatment with low O&M costs**
- Adsorptive media can be exchanged, removing PFAS from the subsurface**
- May need multiple funnels and gates to capture plume**

*MCLs have not been established as groundwater clean up goals for this site; however, they were used as performance metrics for this research project.

Lessons Learned

Lesson Learned: Characterization Recommended Before Designing

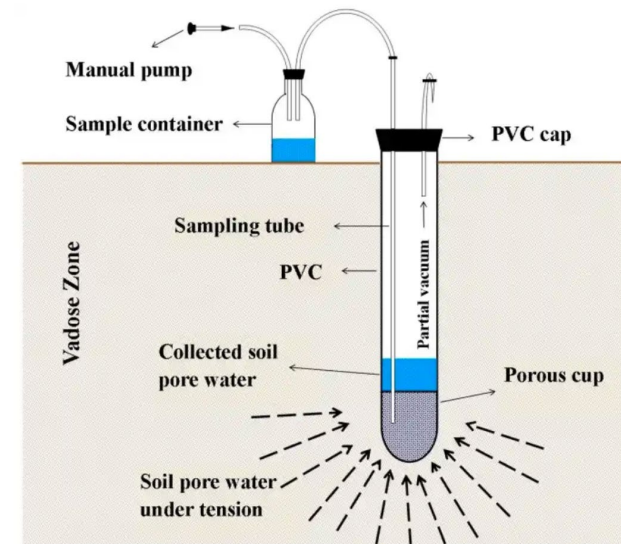


- **PFAS via Method 1633 – target list**
 - Do not use total organic precursor (TOP) assay, total organic fluorine (TOF), non-target analytical list, or other non-standardized PFAS analytical methods without clear objectives, intent for use, and chain of command and SME agreement
- **Groundwater chemistry may impact treatment efficacy**
 - TOC (SM 5310)
 - Metals (especially iron and manganese) (Method 6010D)
 - Anions (Method 300.0)
 - Alkalinity (SM 2320B)
 - Field parameters (pH, ORP, specific conductivity, temperature, turbidity)
- **Co-contaminants (VOCs, petroleum related constituents)**
- **Hydraulic characteristics**
 - Water levels
 - Hydraulic conductivity
 - Detailed geologic characterization (especially soil type/grain size)
 - Tidal study (coastal sites)

Lessons Learned: Recommendations for Monitoring System Performance



- For materials that can be seen with the eye, soil cores are useful to evaluate distribution
- For all barrier remedies
 - Upgradient and downgradient wells to ensure treatment across the barrier
 - Wells along the sides of the barrier to assess potential migration around the barrier
 - Capture multiple depths as appropriate based on lithology
 - Understand groundwater flow velocity and direction
 - Several rounds of quarterly monitoring likely needed
 - Keep potential desorption in mind when placing wells
- Lysimeters or another leaching assessment as well as groundwater beneath the application area is recommended for vadose zone applications
 - Pre-treatment samples should be collected for comparison to post-treatment
 - May have difficulty meeting 1633 volume requirements



Suction Lysimeter

Lessons Learned: Recommendations for Monitoring System Performance



- **REMEMBER:**

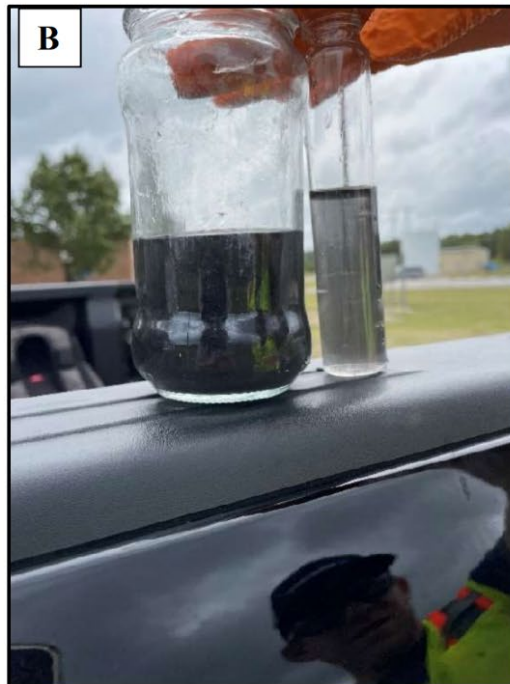
- Eventually adsorption capacity of the treatment media will be reached
- Once in the subsurface, for most application approaches, there is no simple or inexpensive way to extract the amendment
- If there is still mass downgradient of a barrier, it may still contribute to downgradient concentrations for some time
- Important to continue to monitor; reapplication or (when possible) media replacement may be needed

Lesson Learned: Recommendations for Post-treatment Monitoring Analytical Suites

- Pare down list as appropriate based on what you learned during the initial characterization
- PFAS via Method 1633 – target list
- Groundwater chemistry (
 - TOC (SM 5310)
 - Metals (especially iron and manganese) (Method 6010D)
 - Anions (Method 300.0)
 - Alkalinity (SM 2320B)
 - Field parameters (pH, ORP, specific conductivity, temperature, turbidity)
- Co-contaminants (VOCs, petroleum related constituents)
- Soil cores (for distribution)
- Hydraulics (check to see what changed)

Lesson Learned: Managing Migration of Activated Carbon

- Colloidal carbon may migrate readily into monitoring wells or adjacent surface water features/sewer systems
 - May be regulatory concerns with analyzing samples containing carbon
 - Lab may have to do additional processing and charge more for analysis
 - May dissipate after a few quarters of monitoring
- May be perception problems if carbon is observed in surface water



Lesson Learned: Managing Migration of Activated Carbon

- Use of “parking agent” is the most common mitigation approach to address carbon migration to wells and prevent migration to surface water
 - Flocculates the carbon by reducing the repulsion between particles
 - Allows particles to aggregate and settle out
 - Examples: calcium chloride, enzymes
- Parking agents may enhance PFAS adsorption to CAC
- May be regulatory concerns with analyzing samples containing carbon and with potential biases from increased adsorption
- Be sure to get team consensus on approach!

Monitoring Well Location	Flushing Interval (feet)	Clean Water Injected (gallons)	CaCl ₂ Solution Injected (gallons)	CaCl ₂ Injected (pounds)	Total Injected (gallons)	Final Activated Carbon Concentration (ppm)
PMW-01S	13-8	33.5	36.5	34	70.0	0 ppm
PMW-01D	23-18	34.5	36.0	33	70.5	<50 ppm
PMW-02S	13-8	33.5	36.5	34	70.0	<50 ppm
PMW-02D	23-18	43.5	36.5	34	80.0	600 ppm
PMW-03S	13-8	20.0	37.0	34	57.0	0 ppm
PMW-03D	23-18	20.0	37.0	34	57.0	0 ppm
PMW-04S	13-8	N/A	N/A	N/A	N/A	0 ppm
PMW-04D	23-18	20.0	37.0	34	57.0	0 ppm



Lesson Learned – Unanticipated Byproducts

- Project team must ensure injected or added materials do not present other hazards to human health or the environment unrelated to those they are intended to address
- Additives which use amine chemistry are potential contributors of n-nitrosodimethylamine (NDMA), a probable human carcinogen with a tap water RSL and health advisories in several states
- Other possible concerns are additives like cetyltrimethylammonium chloride (CTAC), which may extend carbon life expectancy, but is ecotoxic and should not be used in in situ treatment
- When in doubt, check with an SME!

In Situ Sequestration in CERCLA Remedies



- **Unlikely to be a stand-alone remedy**
 - Reduces mobility but not toxicity or volume
 - Not capable of achieving risk-based clean up goals in source areas
- **Can be useful as an interim action to prevent migration to sensitive receptors**
- **Can be part of a remedial treatment train:**
 - **High Concentration Source Area Example:**
 - Soil removal, groundwater foam fractionation, and supercritical water oxidation of foamate in source area
 - Sequestration barrier to prevent downgradient migration while source treatment is ongoing
 - Monitoring
 - Land use controls
 - **Lower Concentration Source Area Example**
 - Soil cover and groundwater sequestration in low concentration groundwater source area
 - Monitoring
 - Land Use Controls
 - **Other combinations too!**

Key Messages



- In situ sequestration can be a good option to reduce mass flux and PFAS migration depending on the CSM
- In situ sequestration is not suitable to address direct exposure hazards to soil
- Site characteristics (geology, co-contaminants, geochemistry, etc.) may influence effectiveness of treatment
- Media eventually reaches capacity and reapplication or media replacement (where possible) may be needed
- Monitoring is key to meeting treatment objectives
- Set realistic treatment objectives in order to meet long-term protectiveness

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Wrap Up

A short Survey Monkey will be emailed to webinar registrants and participants

Stay tuned for upcoming OER2's via email: EXWC.T2@us.navy.mil

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Thank you for participating!