

PFAS Remediation Using CAC: Field Performance and Cost-Benefit Analysis

Presented by Dr. Grant Carey
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& EMERGING CONTAMINANTS
SUMMIT

OCTOBER 15-17, 2024

U.S. DoD SERDP/ESTCP Project Involvement

ESTCP ER21-3959

An Investigation of Factors Affecting *In Situ* **PFAS Immobilization by Activated Carbon**

ESTCP ER20-5182

Validation of Colloidal Activated Carbon for Preventing the Migration of PFAS in Groundwater

ESTCP ER21-1070

Hydraulic, Chemical, and Microbiological Effects of *In Situ* Activated **Carbon Sorptive Barrier** for PFAS Remediation in Coastal Sites

ESTCP ER24-8200

Two PFAS Remediation Models for Understanding and Managing PFAS in the Saturated Zone

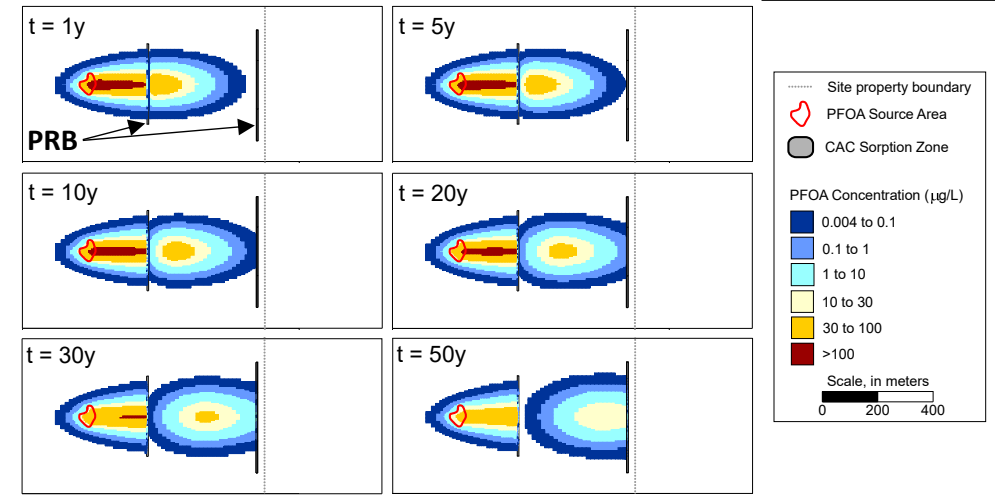
The In-Situ Remediation Model (ISR Model)

- Originally developed in 1998 as BioRedox-MT3DMS
- Field and research projects since 2017
- PFAS-related functionality
 - ✓ PFAS adsorption to CAC
 - ✓ Kinetic sorption
 - ✓ Competitive adsorption
 - ✓ CAC aging
 - ✓ Colloid transport
 - ✓ Branched decay chains

In progress

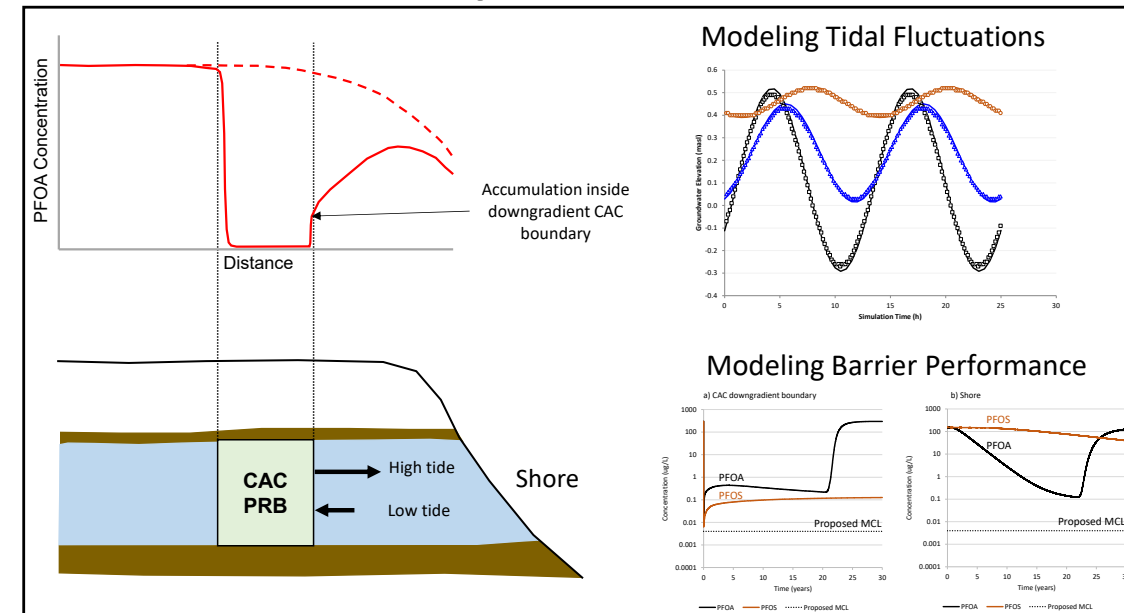
South Dakota Air Force Base

Carey et al. (2023)



Navy Coastal Site

Carey et al. (2024)



Recent ISR Model & PFAS Publications

Application of MT3DMS for Remediation

Grant R. Carey
Steven W. Chapman
Beth L. Parker
Rick McGregor

Simulation of back-diffusion degradation is occurring for scale vertical grid spacing red diffusion in a 3-D model may approach for simulating back some applications. Inexpensive new models, In Situ Remediation (ISR) and comparison of MT3DMS and comparison of growth used to estimate the impact influence on the simulation documented back-diffusion of the back-diffusion contrast simulation with a clay lens had 99.96 percent aqueous TCE used the NCI, on groundwater contamination source zone via a site remediated sites, given that back-diffusion model input and that may vary in back-lenses, retardation coefficient adjacent higher permeability zone of providing containment in the order of meters. The from 3 to 5 mjd based on a 1

Estimating transverse dispersivity based conductivity

Grant R. Carey^{1,*}, Edward A. McBean², Stan Feenstra³, Steven W. Chapman⁴, Beth L. Parker⁵, Rick McGregor⁶

ABSTRACT
A review of state per- and polyfluoroalkyl substances (PFAS) adsorption to four long-chain PFAS (perfluorooctanoic acid (PFOA) followed by perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHx), and perfluorooctanoic acid (PFNA)) are the most frequent. Analysis of 17 field-scale studies of colloidal PFAS sites indicates that in situ CAC injection has short- and long-chain PFAS in the short-term (0-10 years) of organic co-contaminants. Freundlich sorption conditions using a ground forming from (AFF) impacted site. The median literature at 90 AFF-impacted sites were used to a CAC longevity model sensitivity analysis. CAC is insensitive to a wide range of potential conditions. PFOS had the greatest longevity concentrations than the other species because of considerably higher than PFOA and PFHx, proportional to the CAC fraction in soil and the proportional to the influent concentration and

1. Introduction

Sites with NAPL contamination may require expensive, long-term in the subsurface (Parker et al., 2003; Keonangaugh et al., 2013). The layers is proportional to transverse vertical dispersivity (Hunt et al.,

Groundwater Review Paper/ Estimating Tortuosity Coefficient Hydraulic Conductivity

by Grant R. Carey¹, Edward A. McBean², and Stan Feenstra³

Abstract
While the tortuosity coefficient is commonly used, its relationship is demonstrated to not be applicable to textures. The fundamental basis for a correlation between conductivity is demonstrated, although such a correlation is estimating the tortuosity coefficient based on hydraulic conductivity based on results from 17 previously reported diffusion. Analyses of these experimental results confirms that need over a large range of soil textures. The apparent diffusion on hydraulic conductivity.

Evaluating the longevity of a PFAS in situ colloid carbon remedy

Grant R. Carey^{1,*} | Rick McGregor² | Anh Le-Tuan Pham³ | B Seyfollah Gilak Hakimabadi⁴

ABSTRACT
The remediation of per- and polyfluoroalkyl substances (PFAS) at a contaminated site in Central Canada was modeling methods. Radial diagrams were used to fluid mobility and PFAS concentrations, as well as sorption capacity for perfluorooctanoic acid (PFOA) and perfluorobutanoic acid (PFBA) in two solutions: (1) PFOA and PFBA in a 1:1 molar ratio, $K_{oc} = 4.0 \times 10^5 \text{ mL} \cdot \text{kg}^{-1}$ (pH = 7.4) containing PFOS among other PFAS from States ($K_{oc} = 4.900 \times 10^5 \text{ mL} \cdot \text{kg}^{-1}$ and $\alpha = 0.24$). A mass the numerical modeling of mass redistribution in a two-phase system (aqueous and sorbed) to organic includes mass sorbed to CAC. An equilibrium mixing developed using a finite-difference solution and verification of CAC longevity in the center of a source area model (ISRM-T3DMS) was used to indicate that the CAC is to be effective for PFOA remediation for decades. Field data and monitoring alternatives that account for predictions.

1. Introduction

groundwater remediation. The benefits of implementing are discussed. Source area and mid-pore ineffective at attenuating PFAS concentrations within a reasonable timeframe. Among the CAC alternatives, evaluate reactive barrier has the best performance

Longevity of colloidal activated carbon for in situ remediation at AFFF-contaminated airport site

Grant R. Carey¹ | Seyfollah G. Hakimabadi² | Mantak Singh³ | Claire Woodfield³ | Paul J. Van Geel⁴ | Anh Le-Tuan Pham⁵

ABSTRACT
A review of state per- and polyfluoroalkyl substances (PFAS) adsorption to four long-chain PFAS (perfluorooctanoic acid (PFOA) followed by perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHx), and perfluorooctanoic acid (PFNA)) are the most frequent. Analysis of 17 field-scale studies of colloidal PFAS sites indicates that in situ CAC injection has short- and long-chain PFAS in the short-term (0-10 years) of organic co-contaminants. Freundlich sorption conditions using a ground forming from (AFF) impacted site. The median literature at 90 AFF-impacted sites were used to a CAC longevity model sensitivity analysis. CAC is insensitive to a wide range of potential conditions. PFOS had the greatest longevity concentrations than the other species because of considerably higher than PFOA and PFHx, proportional to the CAC fraction in soil and the proportional to the influent concentration and

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been widely used on a global scale for many decades. Because the greatest source of PFAS contamination in the environment today is the use of aqueous film-forming foams (AFFF) for putting out fires. A large number of military and civilian airports have PFAS soil and groundwater contamination due to historical fire training activities. PFAS include polyfluorinated precursors and recalcitrant perfluoroalkyl acids (PFAPAs). PFAS in groundwater in

Analysis of colloidal activated carbon after remediation of a large PFAS plume and source zone

Grant R. Carey^{1,2} | Richard H. Anderson³ | Paul Van Geel⁴ | Keir Soderberg⁵ | Anthony Danko⁶ | Seyfollah Gilak Hakimabadi⁷ | Anh Le-Tuan Pham⁸ | Mia Rebeiro-Tunstall⁹

ABSTRACT
This study evaluated optimal locations for Fluoroalkyl substances (PFAS) in groundwater. New Fluoroalkyl Isotherms for PFAS at a groundwater sample. A hypothetical source area characteristics similar to a site in South Dakota. Modeling indicates that, would still be capable of maintaining contaminant levels in the adsorption zone areal modeling indicates that the future the located core of the plume, and that it will only need to be conducted over-footprint. The benefits of implementing are discussed. Source area and mid-pore ineffective at attenuating PFAS concentrations within a reasonable timeframe. Among the CAC alternatives, evaluate reactive barrier has the best performance

1. Introduction

Colloidal activated carbon (CAC) is an injectable adsorbent that fluoroalkyl substances (PFAS) in the subsurface, serving as an PFAS-impacted sites. However, the effectiveness of the CAC time due to alterations in its physicochemical properties induced study, the effects of CAC aging on surface properties of CAC a

Groundwater solutes influence the adsorption of short-chain PFAS to colloidal activated carbon and impact in situ groundwater remediation

Rachel A. Molé¹, Adriana C. Velosa¹, Grant R. Carey², Xitong Liu³, Guan Anthony Danko⁴, Gregory V. Lowry⁵

ABSTRACT
Adorption of PFAS on engineered colloidal activated carbon (CAC) is examined. CAC surface chemical properties explain trends in PFAS sorption. Ionic strength decreases short-chain PFAS adsorption more than long-chain PFAS. Small molecular weight DOM causes the greatest decrease in PFAS adsorption. Short-chain PFAS barrier lifetimes are significantly lower than long-chain PFAS.

Effects of Physical and Chemical Adsorption on Activated Carbon in the Remediation of a Poly-fluoroalkyl Substance

Liu Jiang¹, Xiaojie Chen¹, Grant R. Carey², Xitong Liu³, Anthony Danko⁴, and Guangbin Li⁵*

1 Department of Civil & Environmental Engineering, MD, 20742, USA
2 Porewater Solutions, 2958 Barlow Crescent, MD, 20742, USA
3 Department of Civil & Environmental Engineering, PA, 15213, USA
4 Department of Civil and Environmental Engineering, PA, 15213, USA
5 Geosyntec Consultants, Inc, 10211 Wincopin Circle, 4th Floor, PA, 15213, USA

Modeling the Influence of Coastal Site Characteristics on PFAS In Situ Remediation

Grant R. Carey^{1,2,*}, Anh Le-Tuan Pham³, Keir Soderberg⁴, Beth Hoeglund⁵

ABSTRACT: Hydrogeologic and geochemical settings were evaluated for a coastal site in the United States to facilitate modeling of the performance of a hypothetical colloidal activated carbon (CAC) *in situ* remedy for perfluorooctanoic acid (PFOA) in groundwater. The average near-shore ionic strength is 84 mM, which was conservatively estimated to result in an increase in the adsorption of PFOA to CAC by about 50% relative to non-coastal sites. A one-dimensional groundwater flow model was constructed and verified to represent the tidally-influenced groundwater velocity fluctuations in the artificial fluid unit at the site. A reactive transport model (ISR-MT3DMS) was used to assess the effects of tidal fluctuations and near-shore geochemistry on CAC performance. This modeling confirmed the hypothesis that tidally-induced groundwater flow reversals near the shore result in the accumulation of PFOA at the downgradient CAC boundary. Slow desorption of PFOA from this downgradient CAC boundary may sustain downgradient plume concentrations above a strict cleanup criterion for a long time; however, there was consistently a large PFOA mass flux reduction (greater than 99.9%) achieved after several decades at the shore. The longevity of a 6-m long CAC permeable reactive barrier downgradient of a high-concentration PFOA source (300 µg/L) was predicted to be on the order of 20 to 40 years. A sensitivity analysis revealed that CAC longevity was substantially greater for perfluorosulfonic acid (PFOS) with a similar source concentration; however, the higher PFOS distribution coefficient (K_d) in soil downgradient from the CAC zone resulted in substantially longer flushing times. It is recommended that short-term remedial action objectives for CAC remedies at coastal sites be based on mass flux reduction targets over a period of several decades, given the demonstrated challenges in trying to achieve very low cleanup criteria downgradient of a CAC zone in the short-term.

Modified competitive Langmuir model for prediction of multispecies PFAS competitive adsorption equilibria on colloidal activated carbon

Mantak Singh^{1,2,*}, Seyfollah Gilak Hakimabadi³, Paul J. Van Geel⁴, Grant R. Carey⁵, Anh Le-Tuan Pham⁶

ABSTRACT
Competitive adsorption of four perfluoroalkyl substances (PFAS), i.e., perfluorooctanoic acid (PFOA), perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHx), and perfluorooctanoic acid (PFNA), on colloidal activated carbon (CAC) was studied and a new predictive model, modified competitive Langmuir model (MCLM), was proposed to predict the competitive adsorption equilibria. The new model is a modification of the competitive Langmuir model (CLM) that gives additional weighting to the molecular weight of the PFAS molecules. A comparative study was done to test the capability of the new model by comparing its predictions to the widely used CLM and ideal adsorbed solution theory (IAST), as well as the experimental data from the batch adsorption experiments on seven different mixtures of the aforementioned PFAS. The models were tested on variations combined two and three PFAS analytes. The analysis showed better predictions by MCLM over the existing models in most of the cases. Additionally, an error analysis was performed to fit the single-solute isotherms that indicated a better fit of the Langmuir isotherm over Freundlich isotherm. Moreover, the study also showed that perfluorooctanoic acid (PFOA) and perfluorobutanoic acid (PFBA) adsorption tend to be higher than perfluorohexanoic acid (PFHx).

1. Introduction

Containment strategies (CS) This contain [15, 34]. The the solid or by the global toxic, and listed these government controlled. Current water exit which are the geologic [41]. Ador

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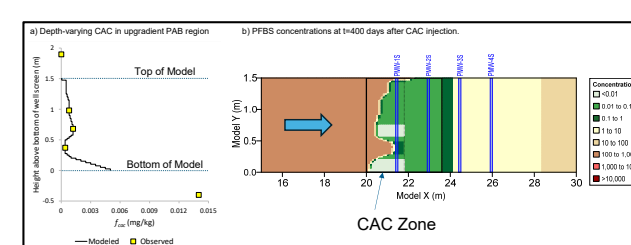
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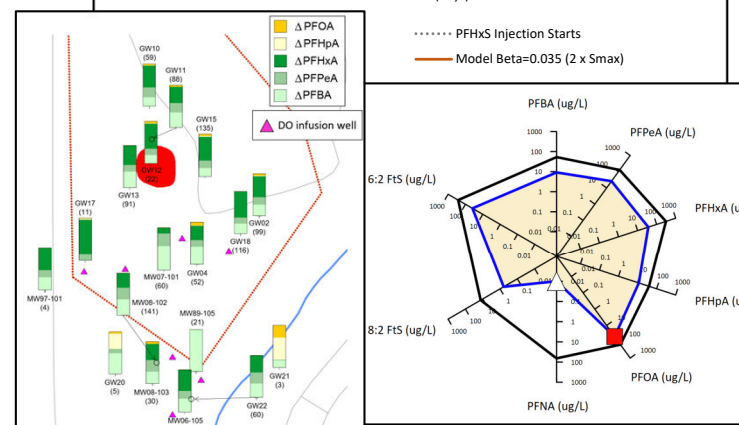
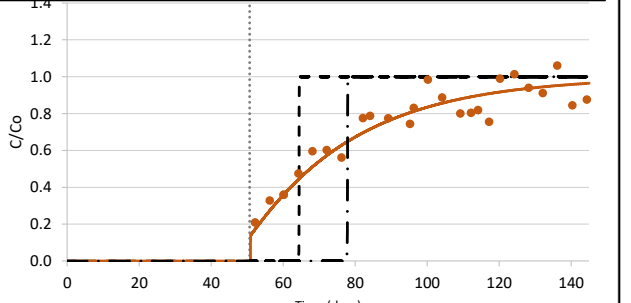
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Papers in progress



Alternative	Downgradient PRB CAC Core/Fringe Concentration	Source Control	Installation Cost*	Total Cost*	Modeled PRB Longevity (y)
1.1	CAC 1000/500 mg/kg	n/a	\$1.6M	\$4.0M	31
1.2	CAC 2000/500 mg/kg	n/a	\$2.0M	\$4.7M	62
1.3	CAC 1000/500 mg/kg plus Re-injection at 15 years	n/a	\$2.4M	\$5.4M	n/a
2.1	CAC 1000/500 mg/kg	Cover	\$2.0M	\$4.9M	35 to 45 (based on 20% to 50% Md reduction)
2.2	CAC 1000/500 mg/kg	Cover + Wall	\$3.2M	\$7.0M	>100
2.3	CAC 1000/500 mg/kg	Soil Stabilization	\$5.6M	\$10.3M	>100



www.porewater.com/PFAS.html

Outline

1 Modeling Field Performance at NESDI Site

- PFAS adsorption isotherms (short- and long-chain)
- CAC Heterogeneity

2 Cost-Benefit Analysis

- Downgradient CAC barrier
- Integrate with source control?

Field Performance at NESDI Site (Eastern USA)

Section 1

Acknowledgements



Dr. Paul Hatzinger, Graig Lavorgna, David Lippincott
APTIM

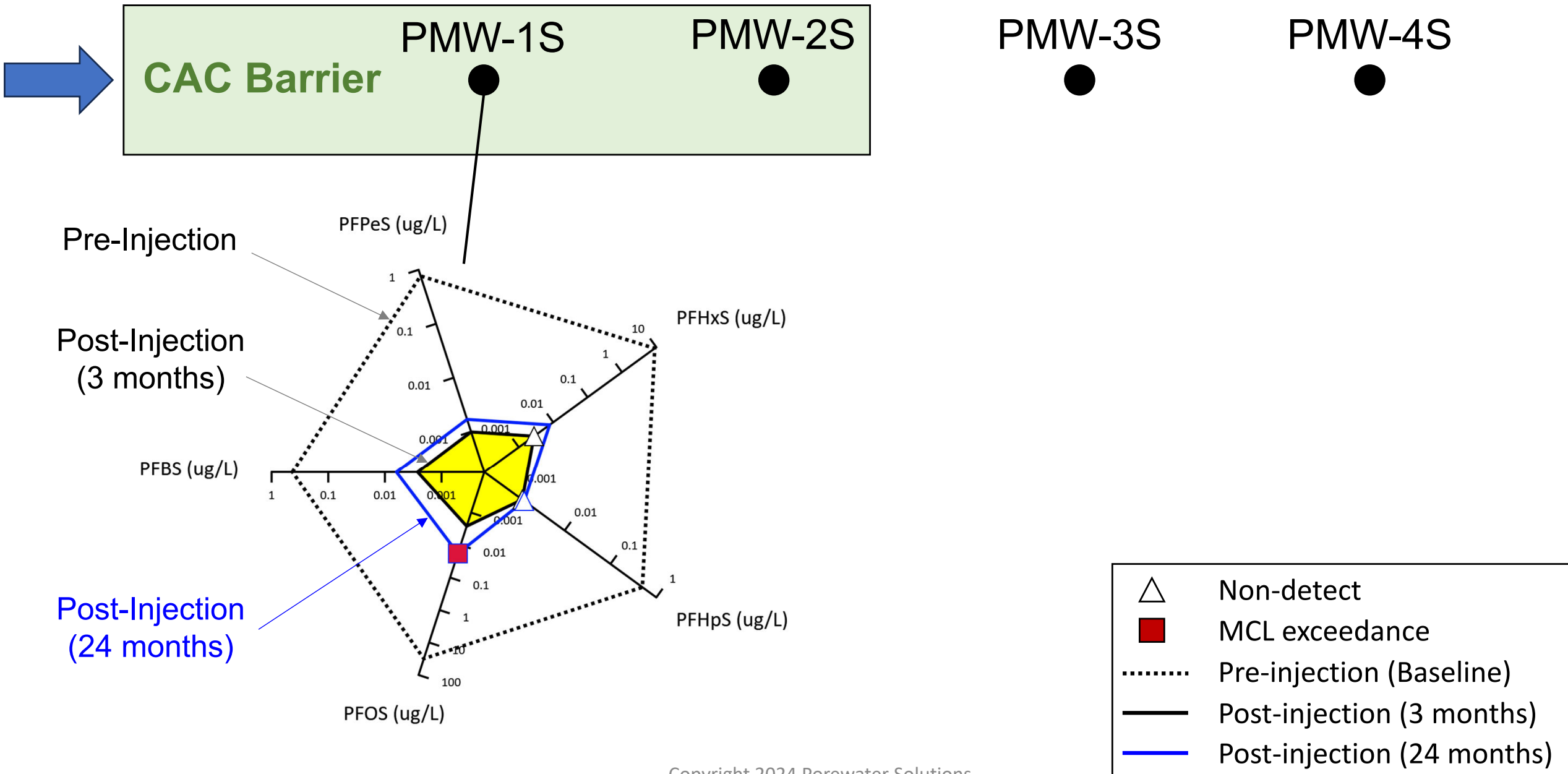


Dr. Anthony Danko
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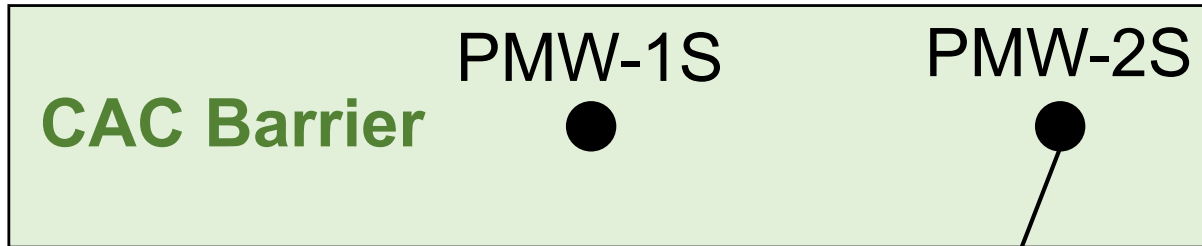
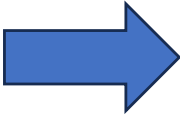


Dr. Brent Sleep
University of Toronto

NESDI PRB Performance: PFSAs



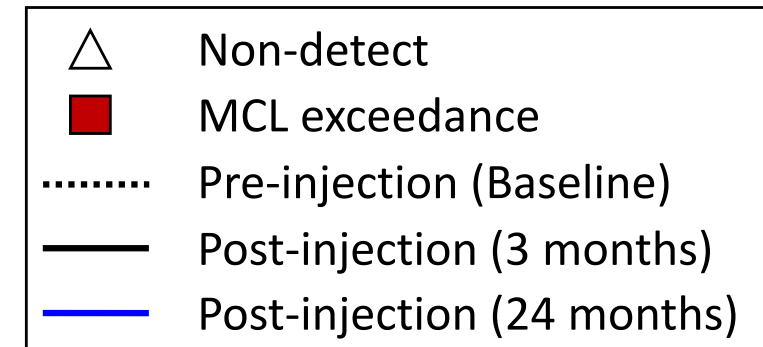
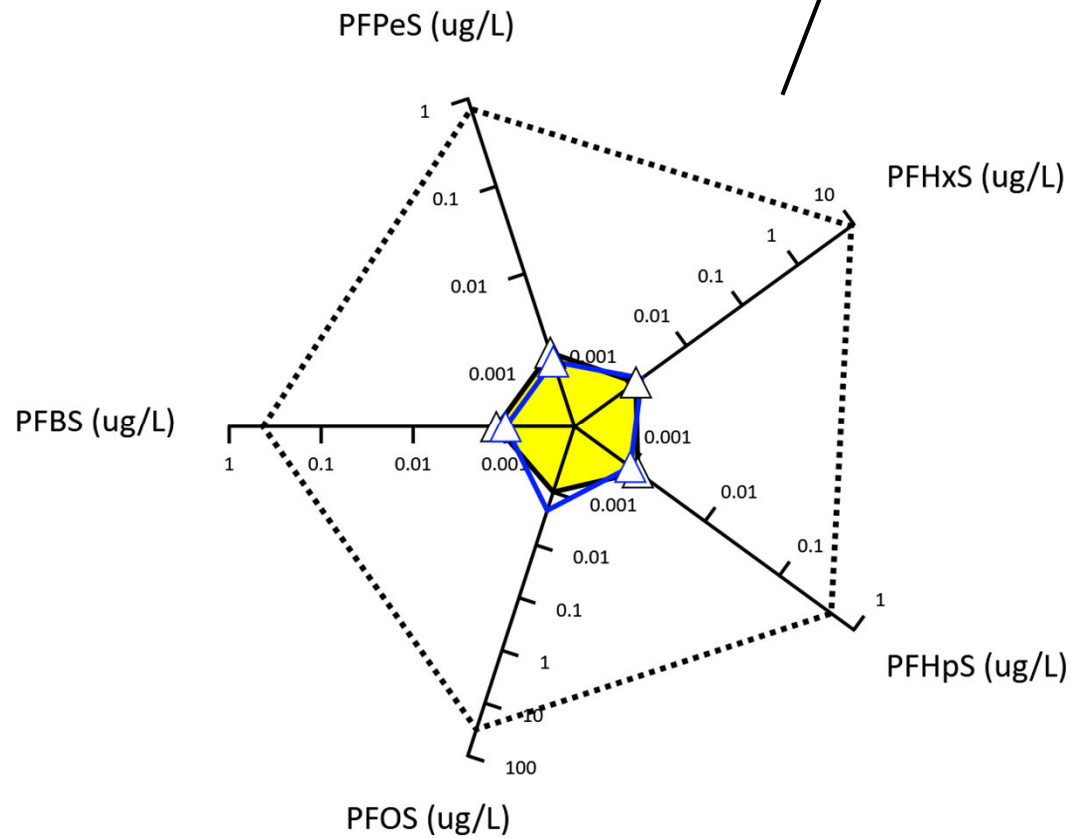
NESDI PRB Performance: PFSAs



PMW-3S



PMW-4S

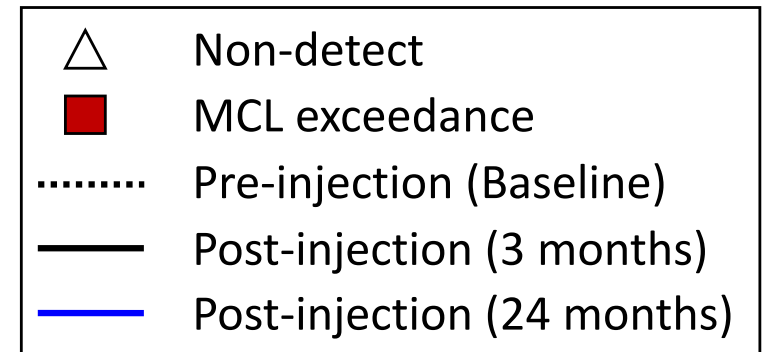
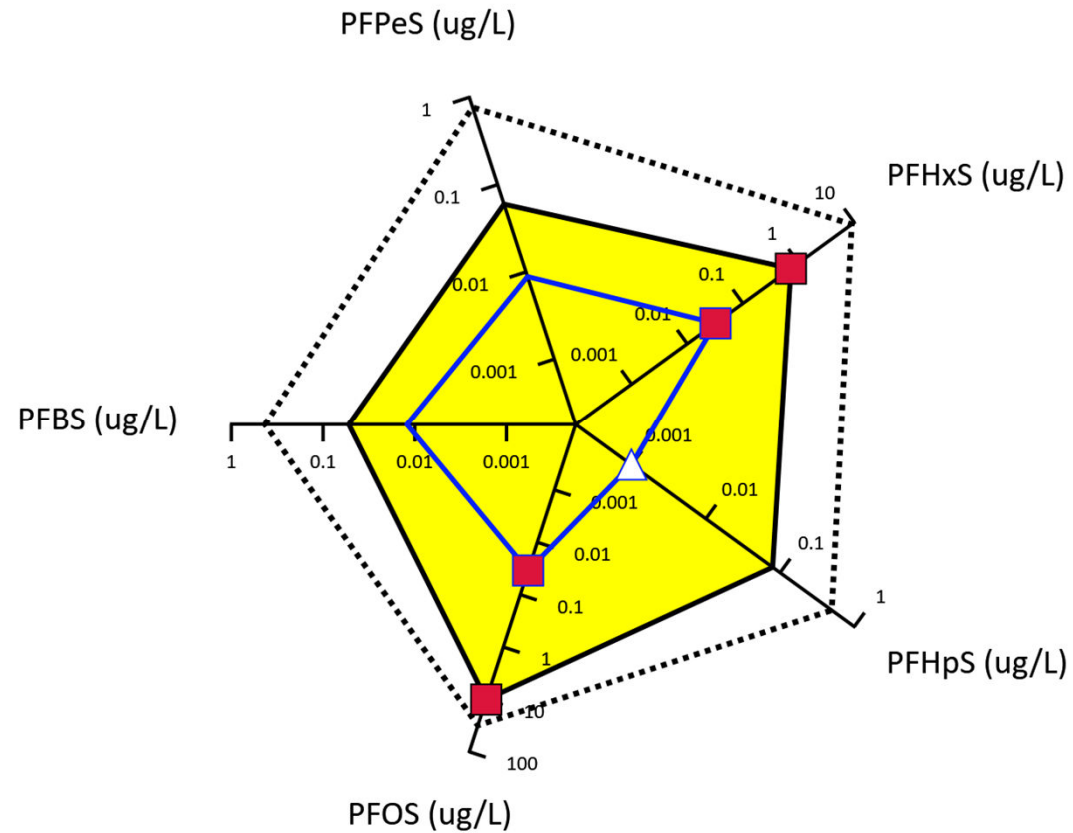


NESDI PRB Performance: PFSAs

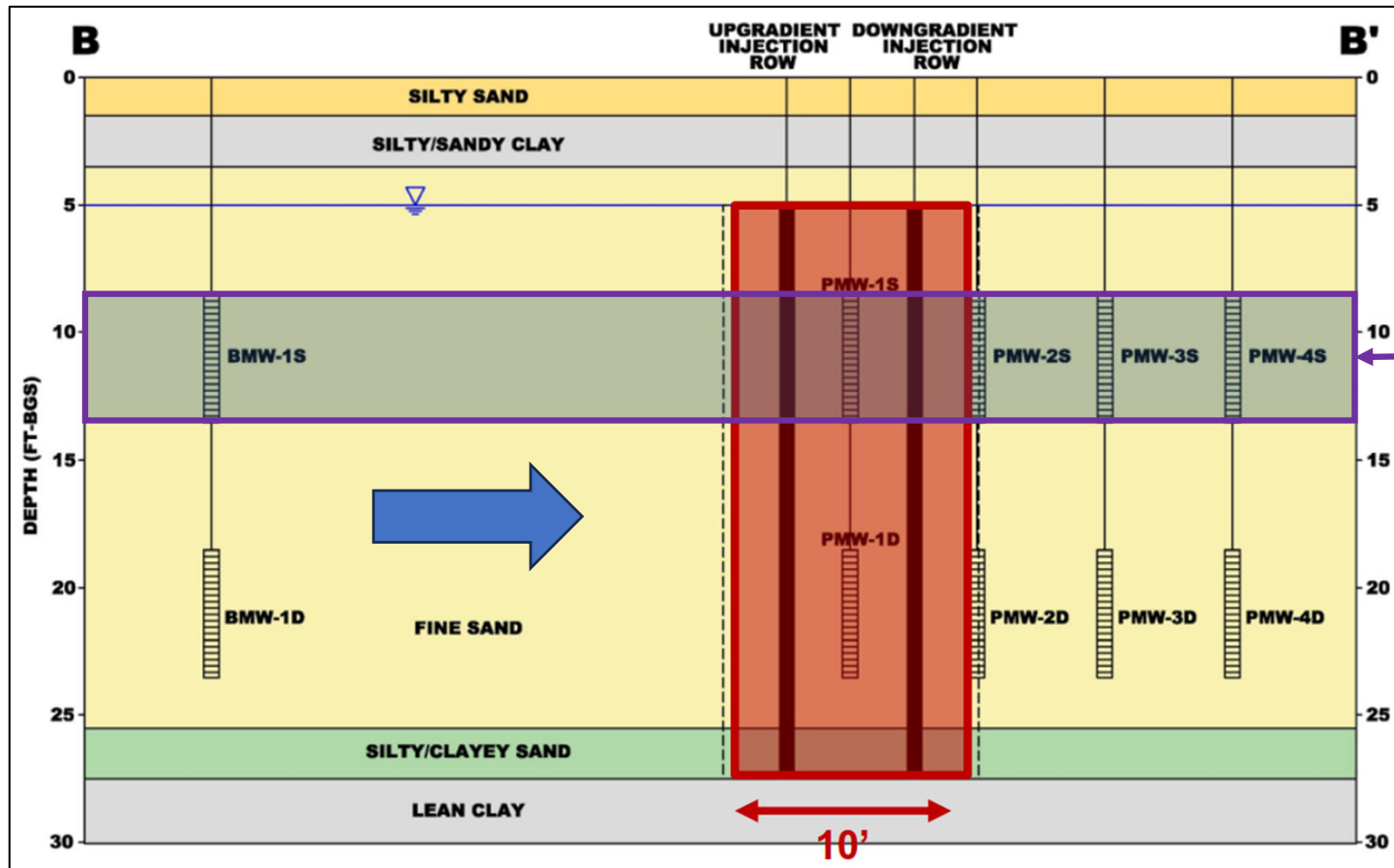
CAC Barrier PMW-1S PMW-2S

PMW-3S

PMW-4S



Eastern U.S. Site CAC Permeable Reactive Barrier



Modeled thickness: 5 ft

Air Force Civil Engineer Center

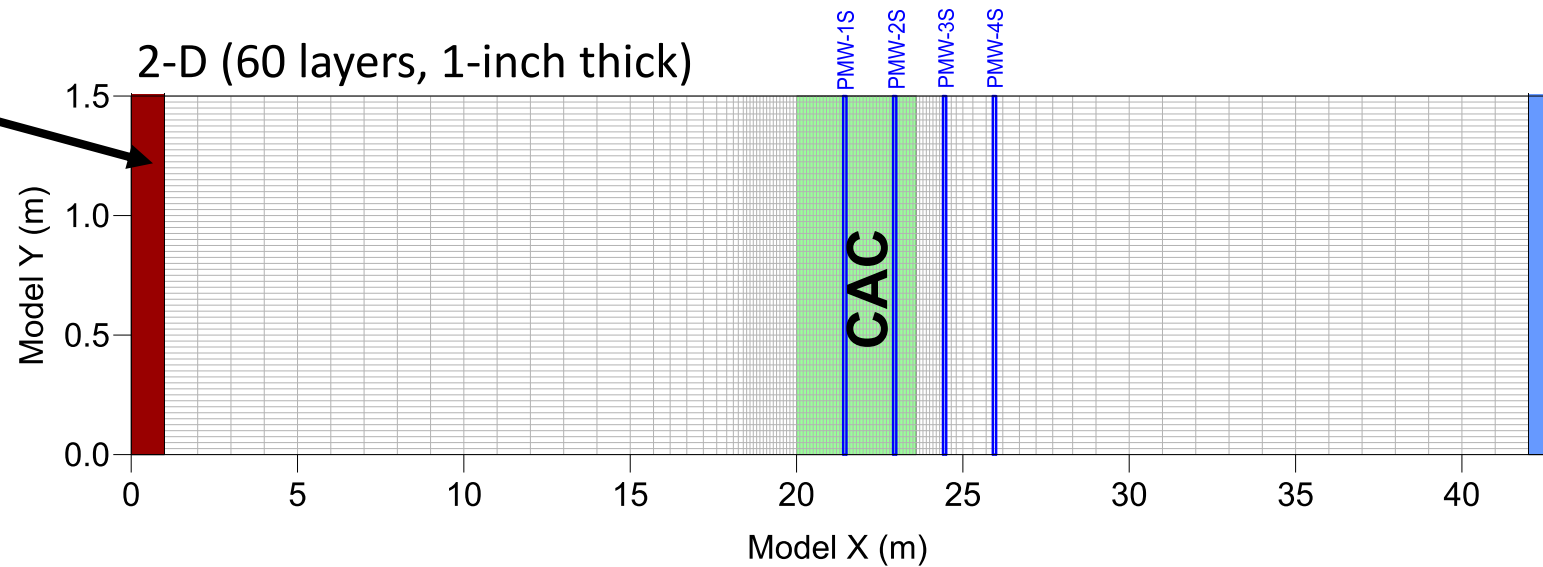
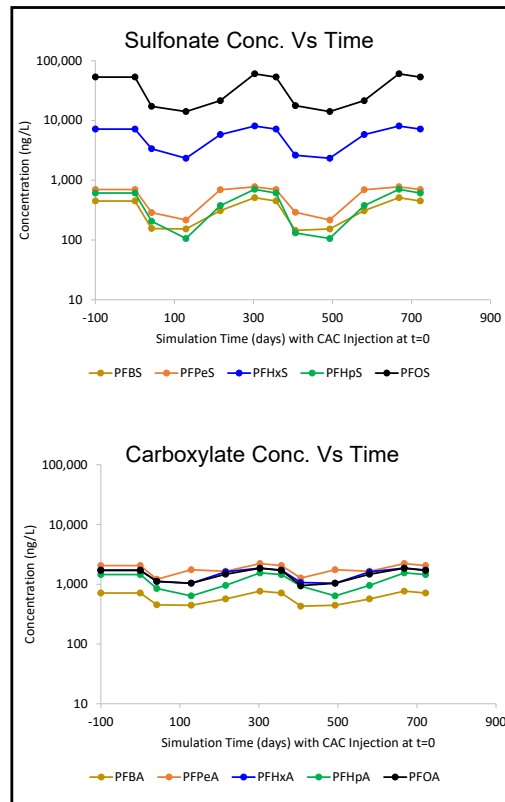


Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of Per- and Polyfluoroalkyl Substances



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NAVFAC EXWC/SH321
September 2023

Model Domain and Boundary Conditions



Carey et al. (2015)

$$\alpha_z = 0.08 \text{ K}^{-0.16}$$

$$\alpha_z = 0.3 \text{ mm}$$

Note: K in m/s

$$K = 150 \text{ ft/y}$$

$$i = 0.001 \text{ ft/ft}$$

$$v = 220 \text{ ft/y}$$

$$f_{oc} = 0.2\%$$

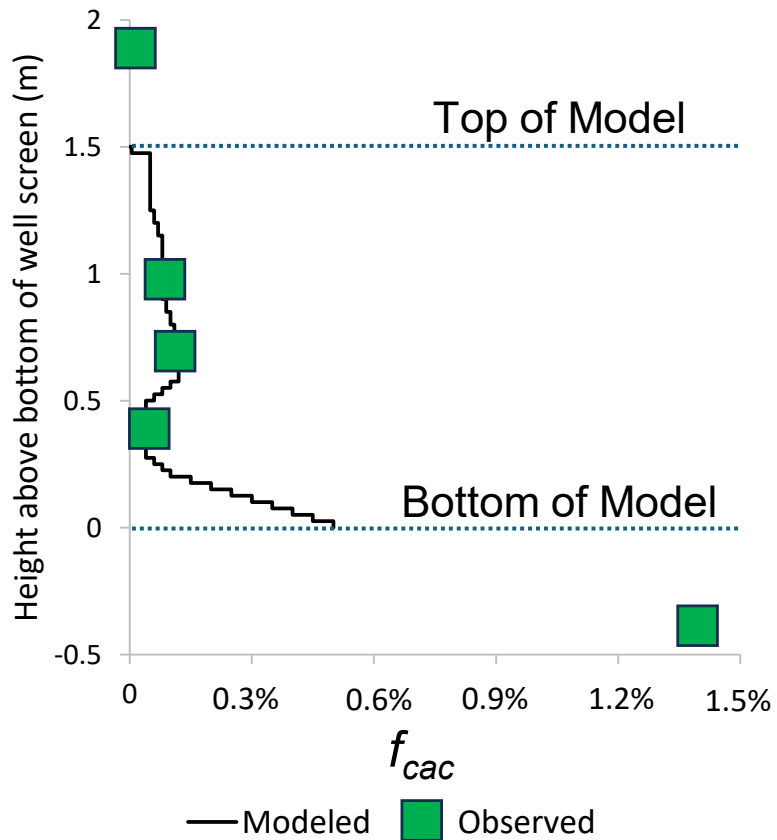
$$\theta_e = 0.25$$

$$\rho_b = 1.6 \text{ kg/L}$$

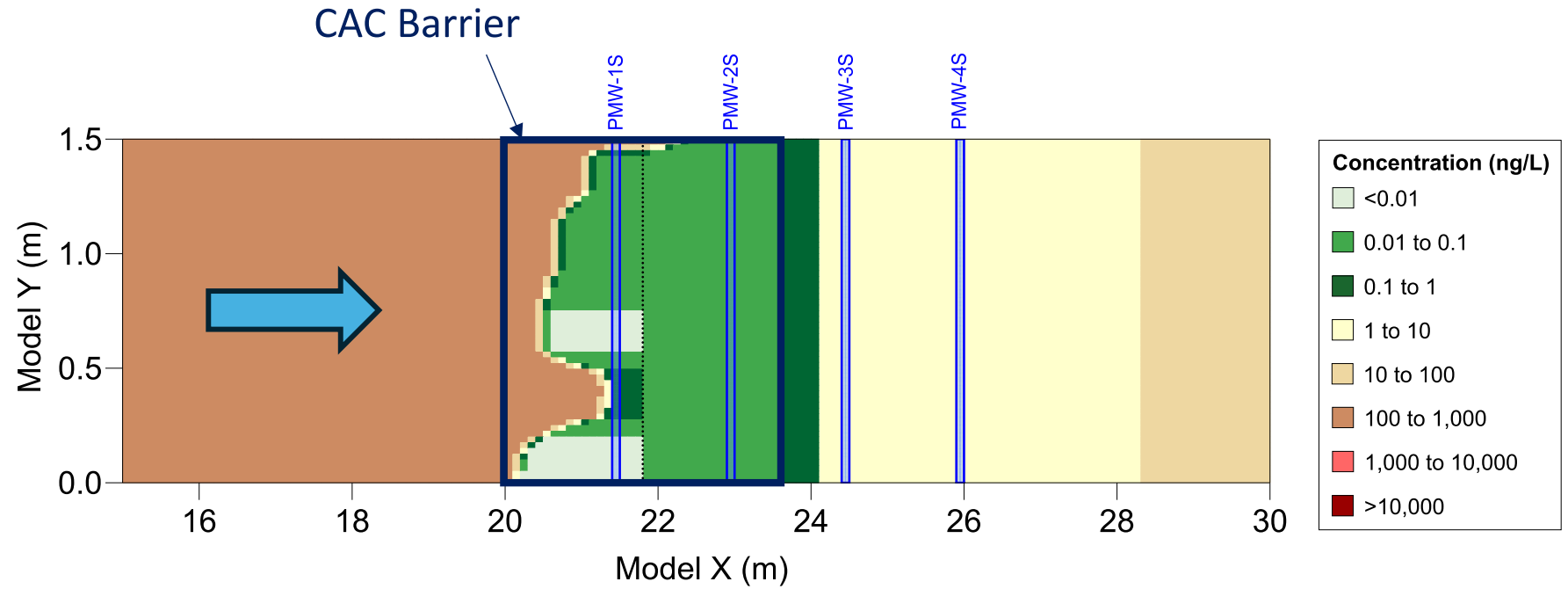
$$\alpha_x = 0.03 \text{ m}$$

CAC Influence on PFAS Transport in Barrier

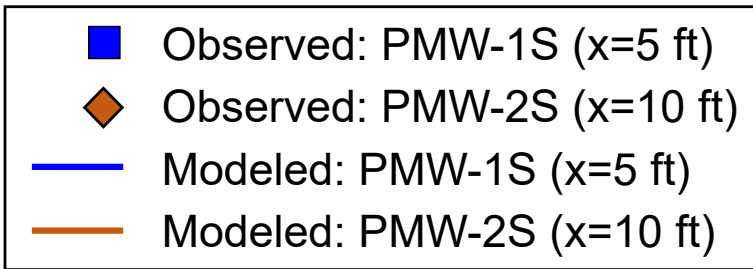
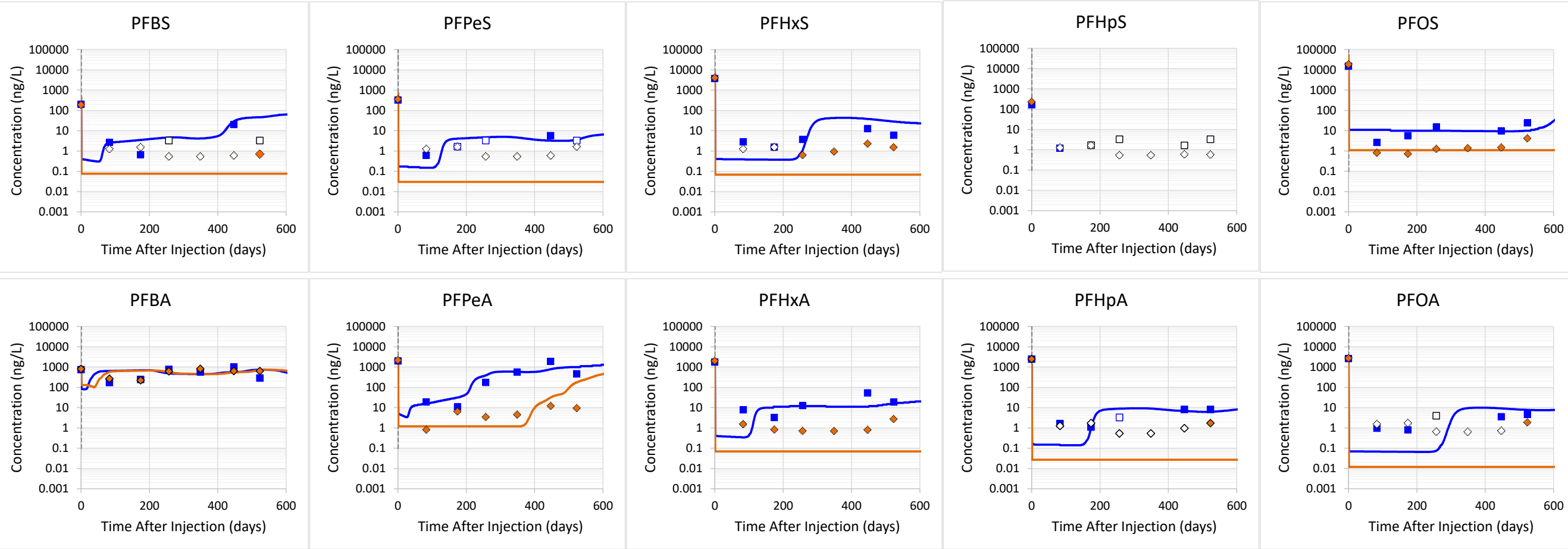
a) CAC Vertical Distribution at x = 5 ft



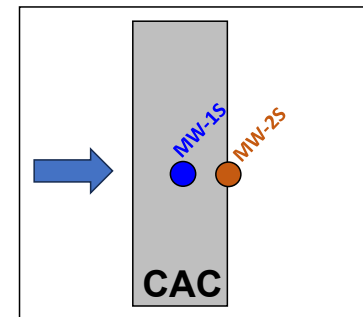
b) Modeled PFBS plume 400 days after CAC injection



Preliminary Isotherm Calibration (First Six Quarters)



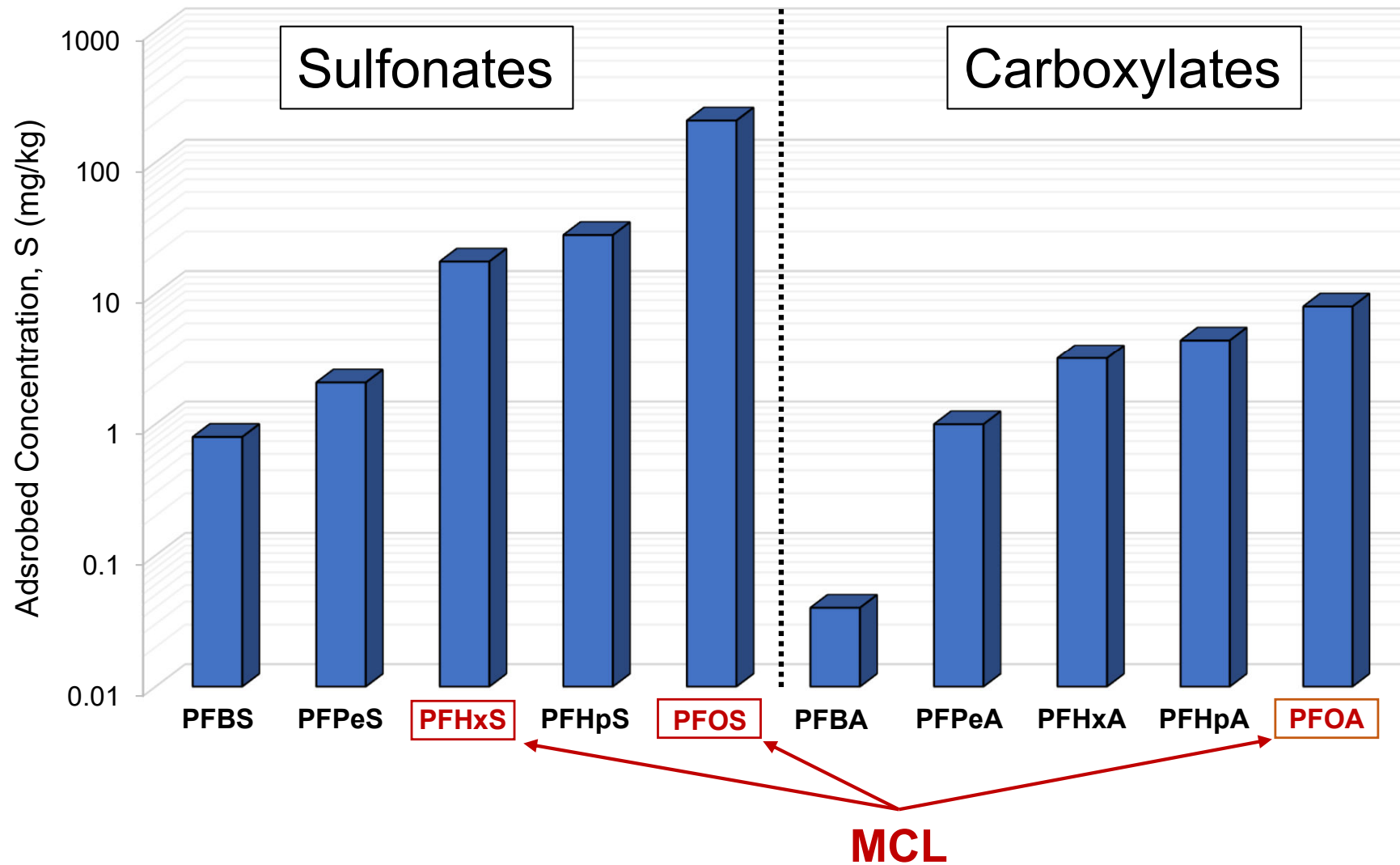
DRAFT



Adsorbed Concentration Based on Calibrated Isotherms

DRAFT

Adsorbed Concentration at Aqueous Concentration $C = 1$ ng/L

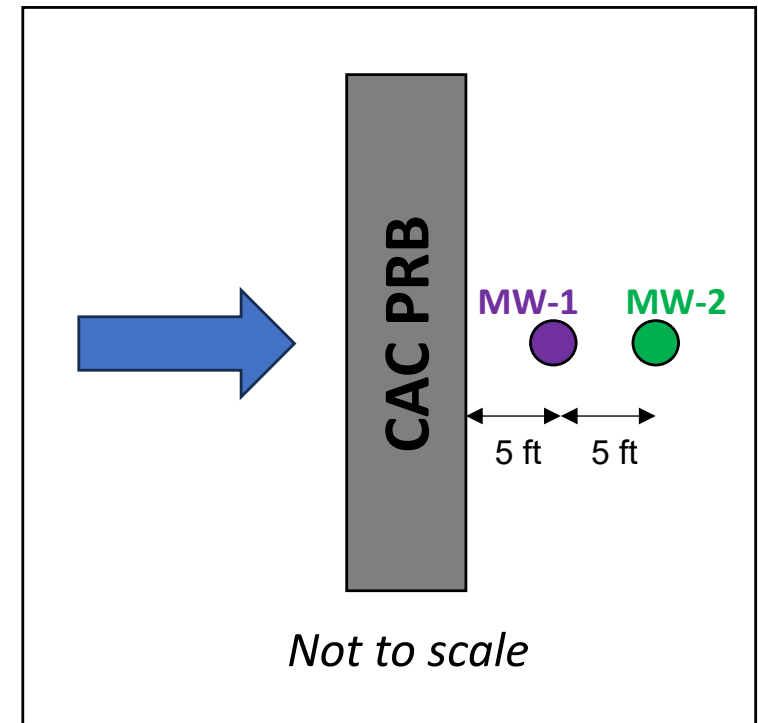
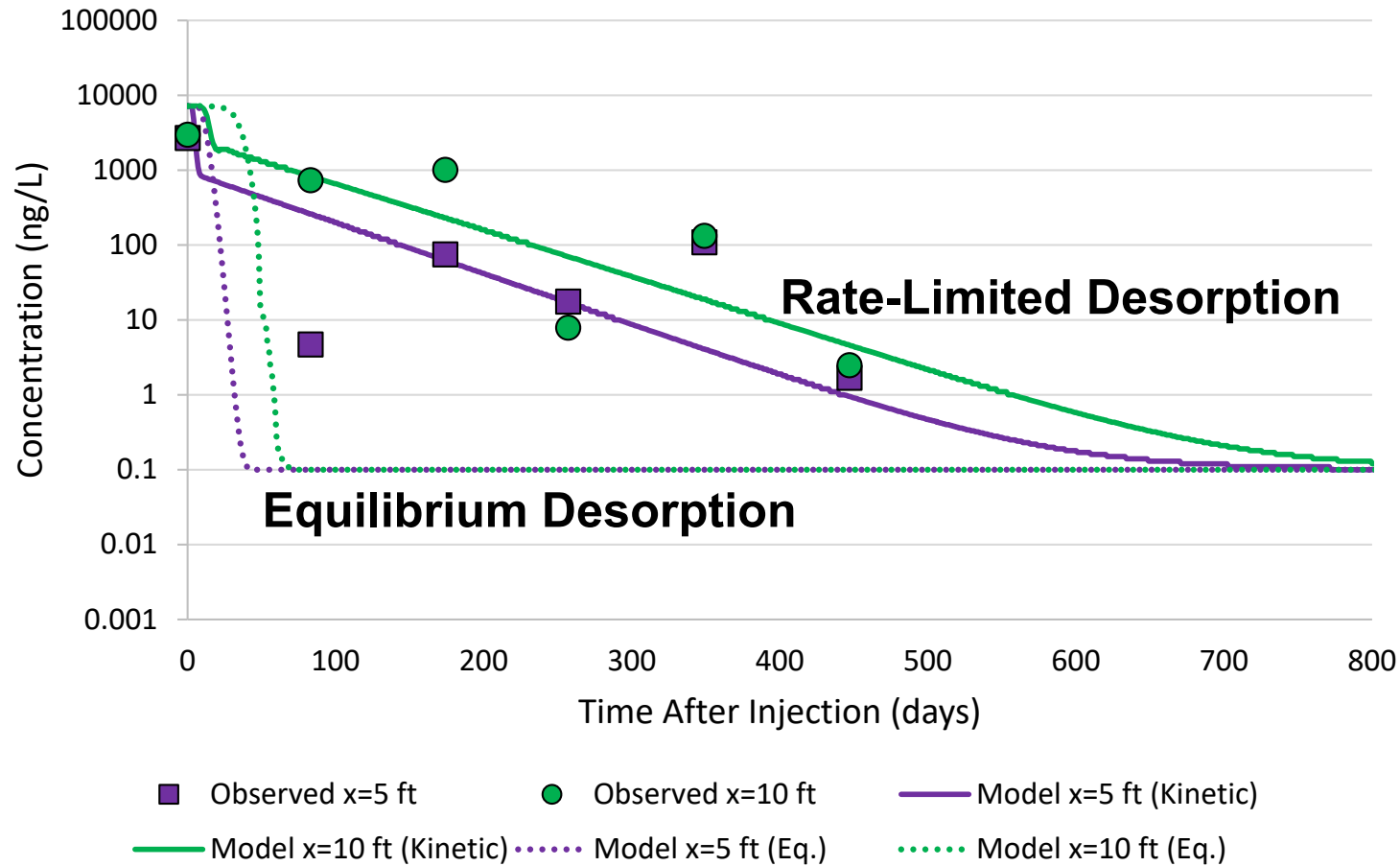


$$S = K_f C^a$$

East US Site: PFAS Desorption Downgradient of PRB

DRAFT

PFHxS: Kinetic vs Equilibrium Desorption



5 ft

Cost-Benefit Analysis

Section 2

Acknowledgements



Matt Vanderkooy, Adam Schneider
Geosyntec Consultants



Dr. Paul Erickson, Keith Gaskill
Regenesis

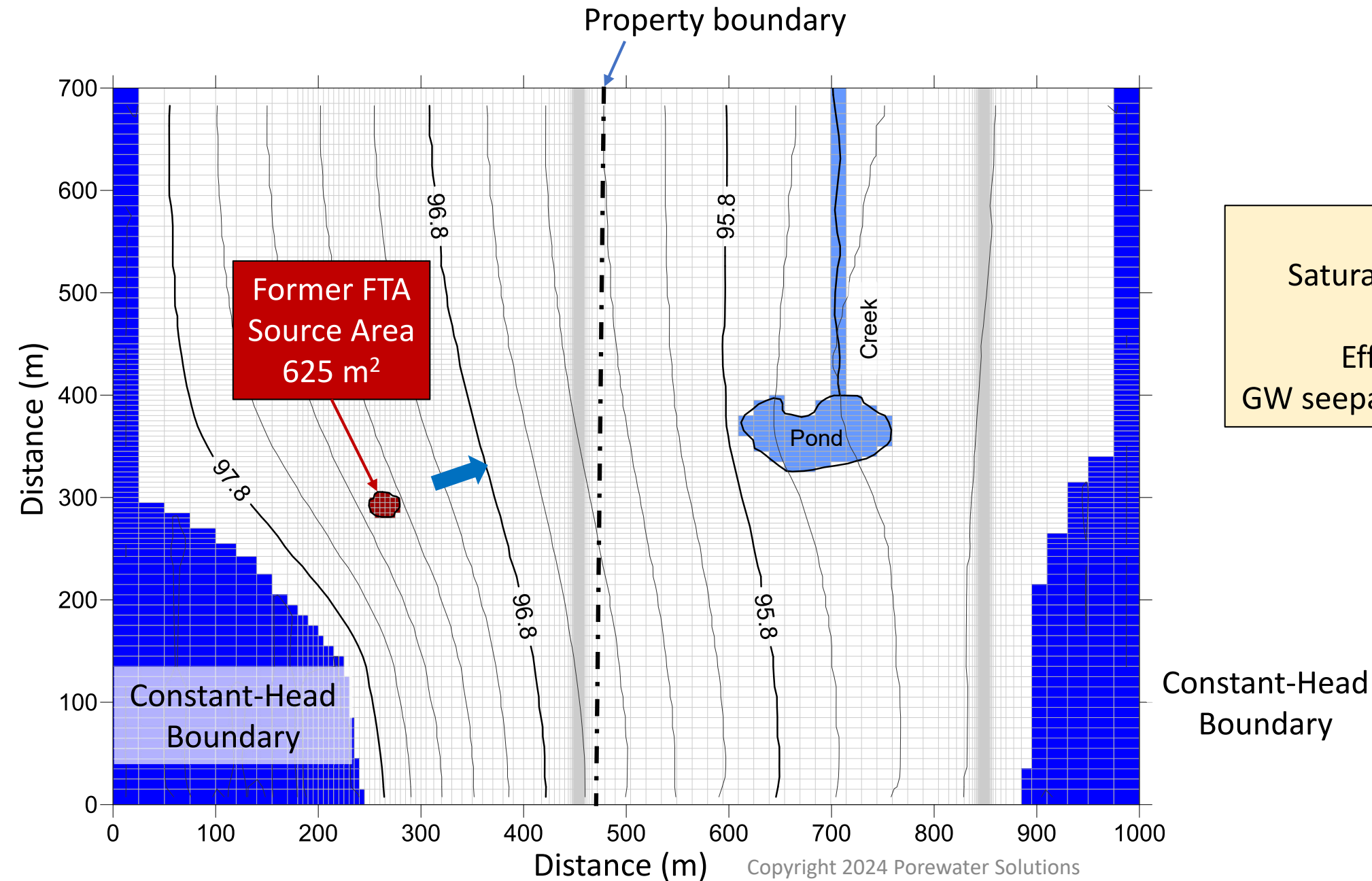


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Hypothetical Site Setting & Model Domain



f_{oc} : 0.1%
Saturated thickness at PRB: 8 m
 $K = 25$ ft/day
Effective porosity = 0.20
GW seepage velocity: ~175 to 200 ft/y

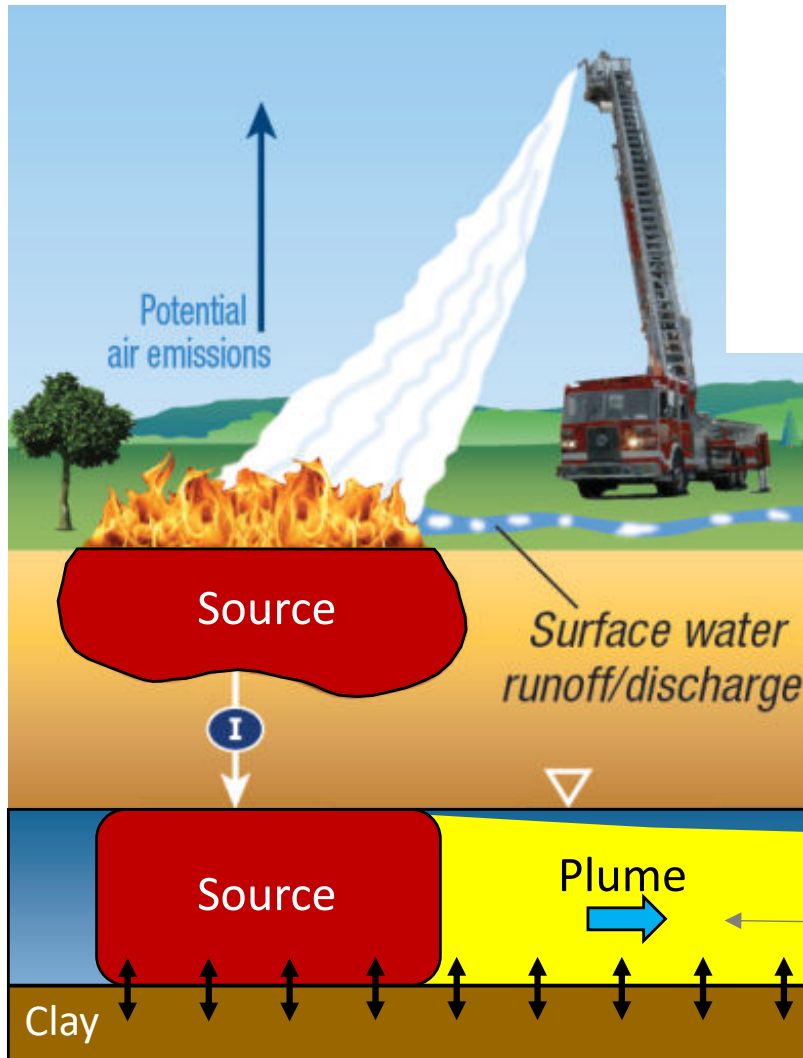
Constant-Head
Boundary

AFFF-Impacted Site Conceptual Model



Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances

Modified from ITRC Fact Sheet, March 16, 2018 (Figure 1)



Near-Source Area

- High PFAS of Concern (POCs), precursors, etc.
- Higher CAC dose needed
- Source zones difficult to delineate

Downgradient PRB Area

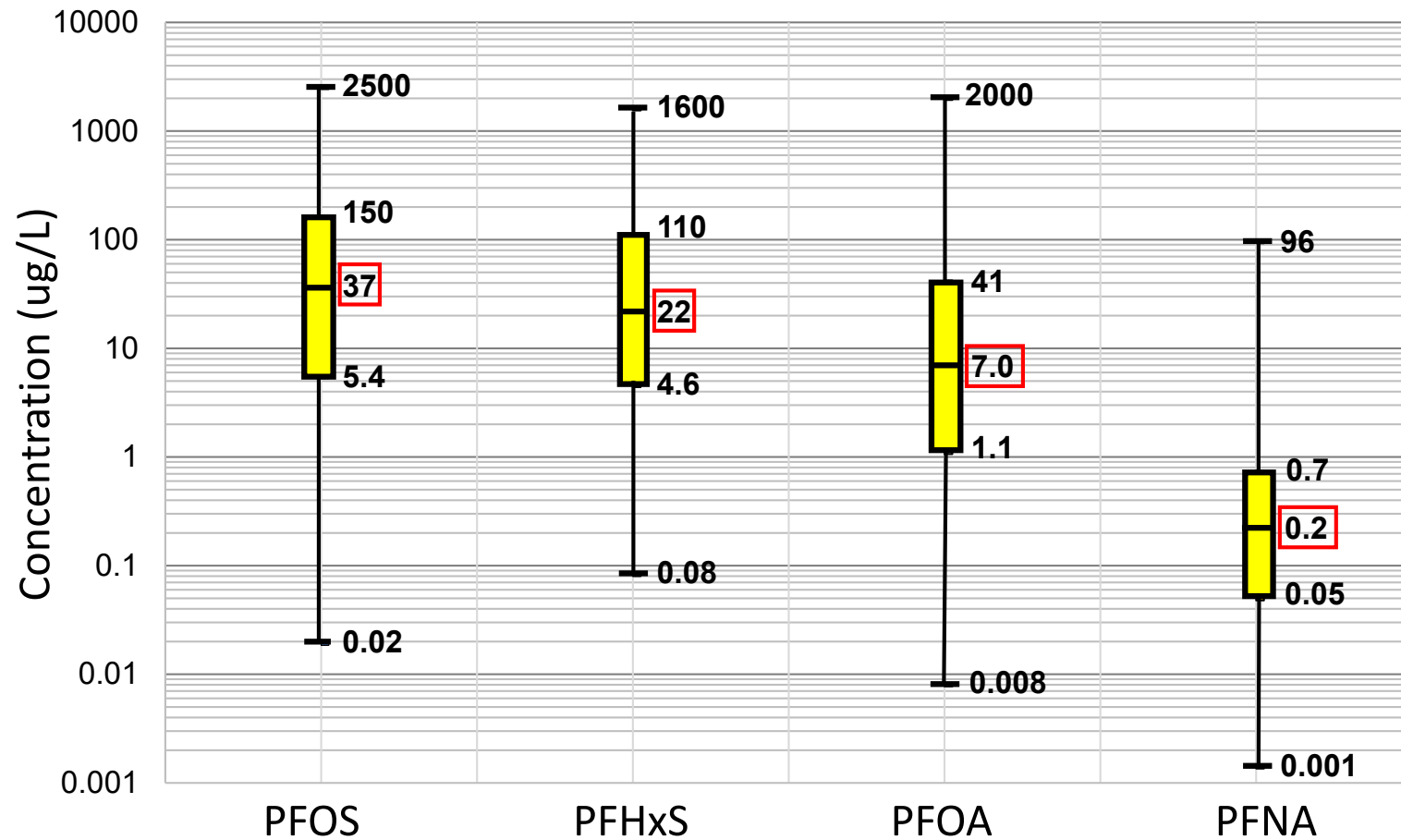
- Lower POCs, lower precursors, etc.
- Lower CAC dose needed

Source Control-Only (long distance to bdy)

- Decades to attain goals at boundary

Desorption, Back-diffusion, Infiltration

Maximum PFAS Statistics for 96 AFFF-Impacted Sites



Carey et al., 2022

PFBS statistics are in Mole et al. (2024)

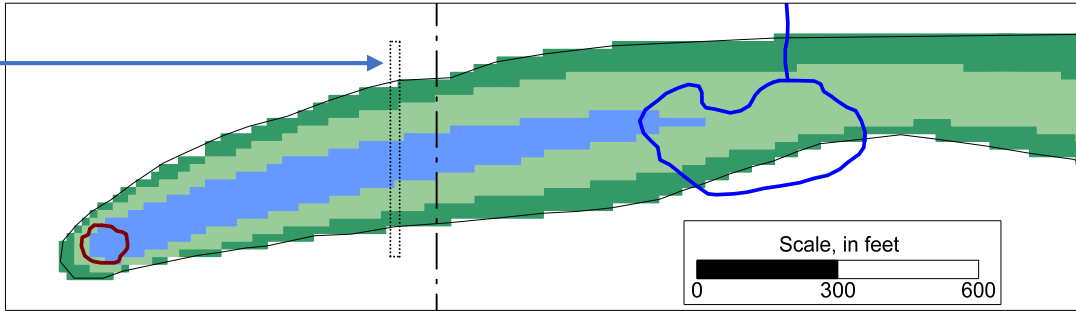
no. PFBS results:	93
Minimum (ug/L):	0.0059
Q1 (ug/L):	0.145
Median (ug/L):	3.0
Q3 (ug/L):	12
Maximum (ug/L):	230

Molé et al., 2024

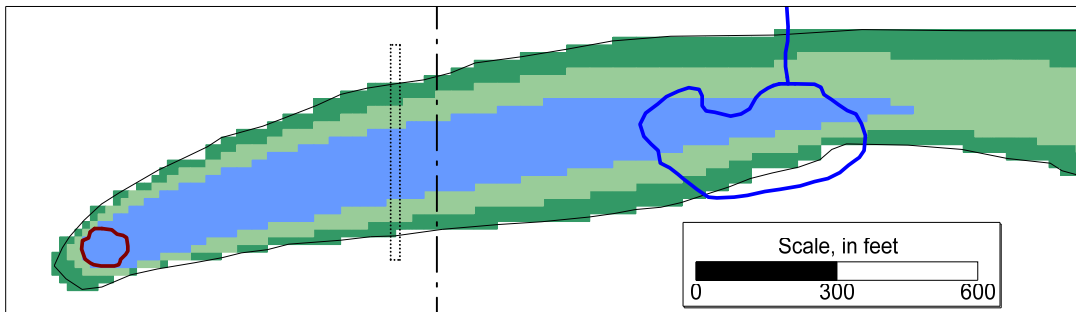
Pre-Remediation Plumes (at end of 50 year simulation)

Proposed downgradient PRB location

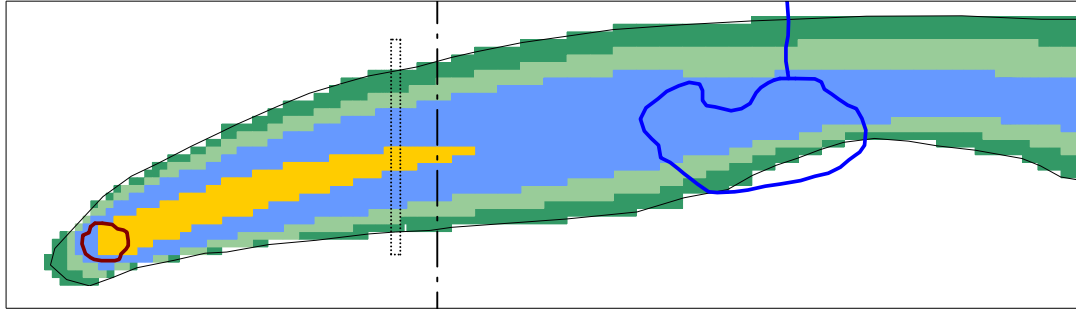
PFBS



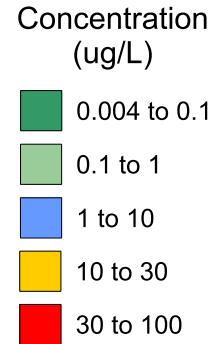
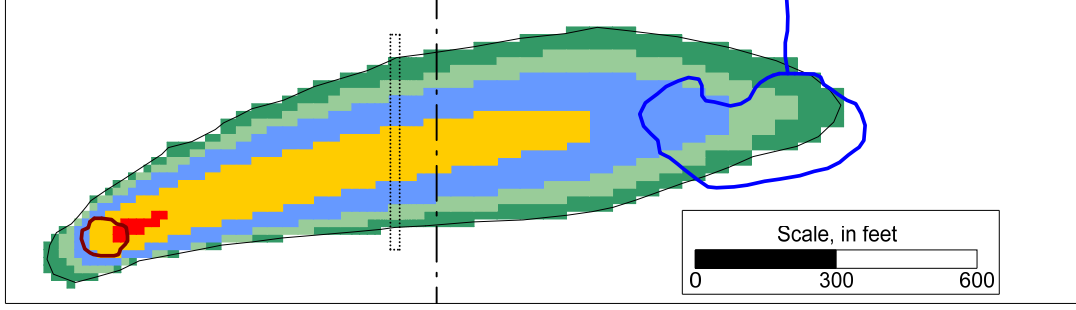
PFOA



PFHxS



PFOS



PFOS plume is expanding over time.

Plumes at t=20 years after CAC Injection

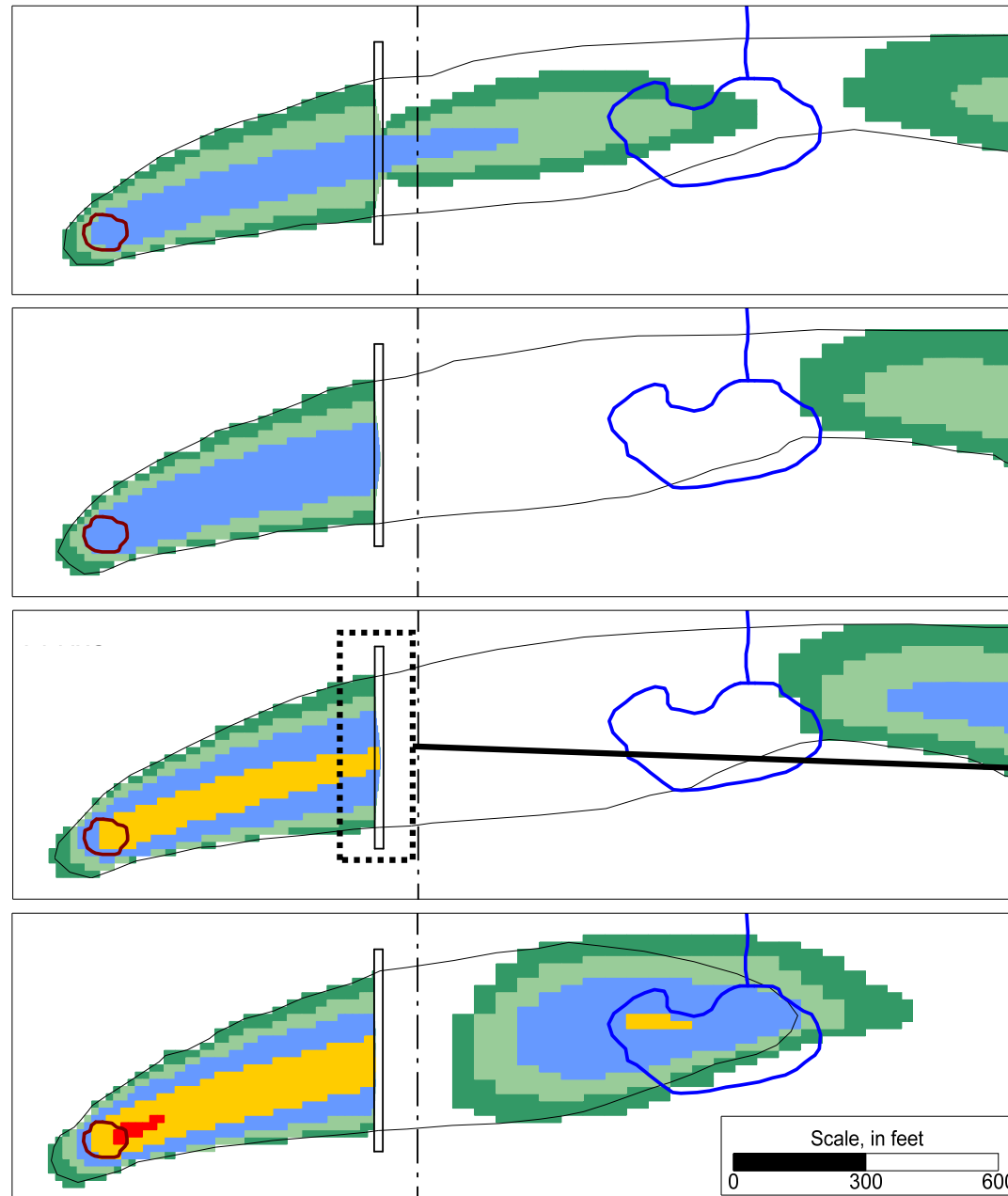
Breakthrough Time

PFBS: 15 years

PFOA: 32 years

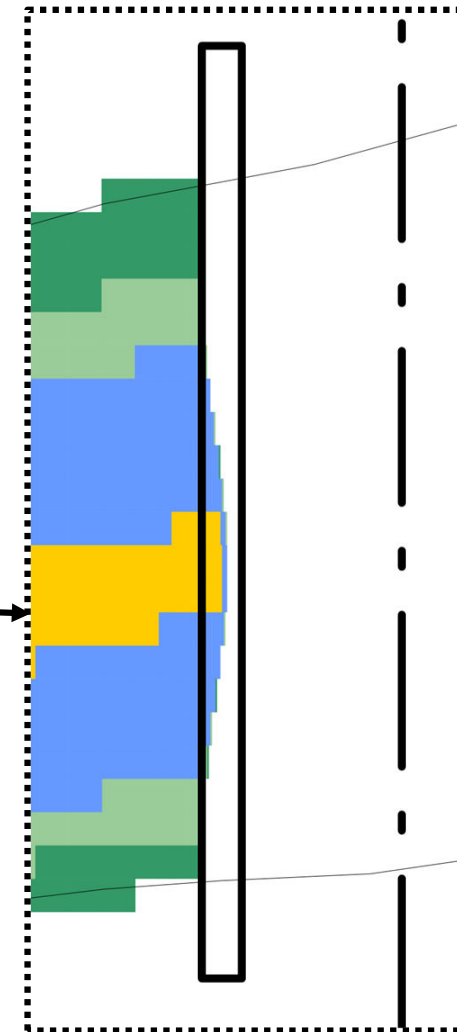
PFHxS: 31 years

PFOS: >>50 years



Barrier width = 20 ft
 $f_{cac} = 0.1\%$ (1000 mg/kg)

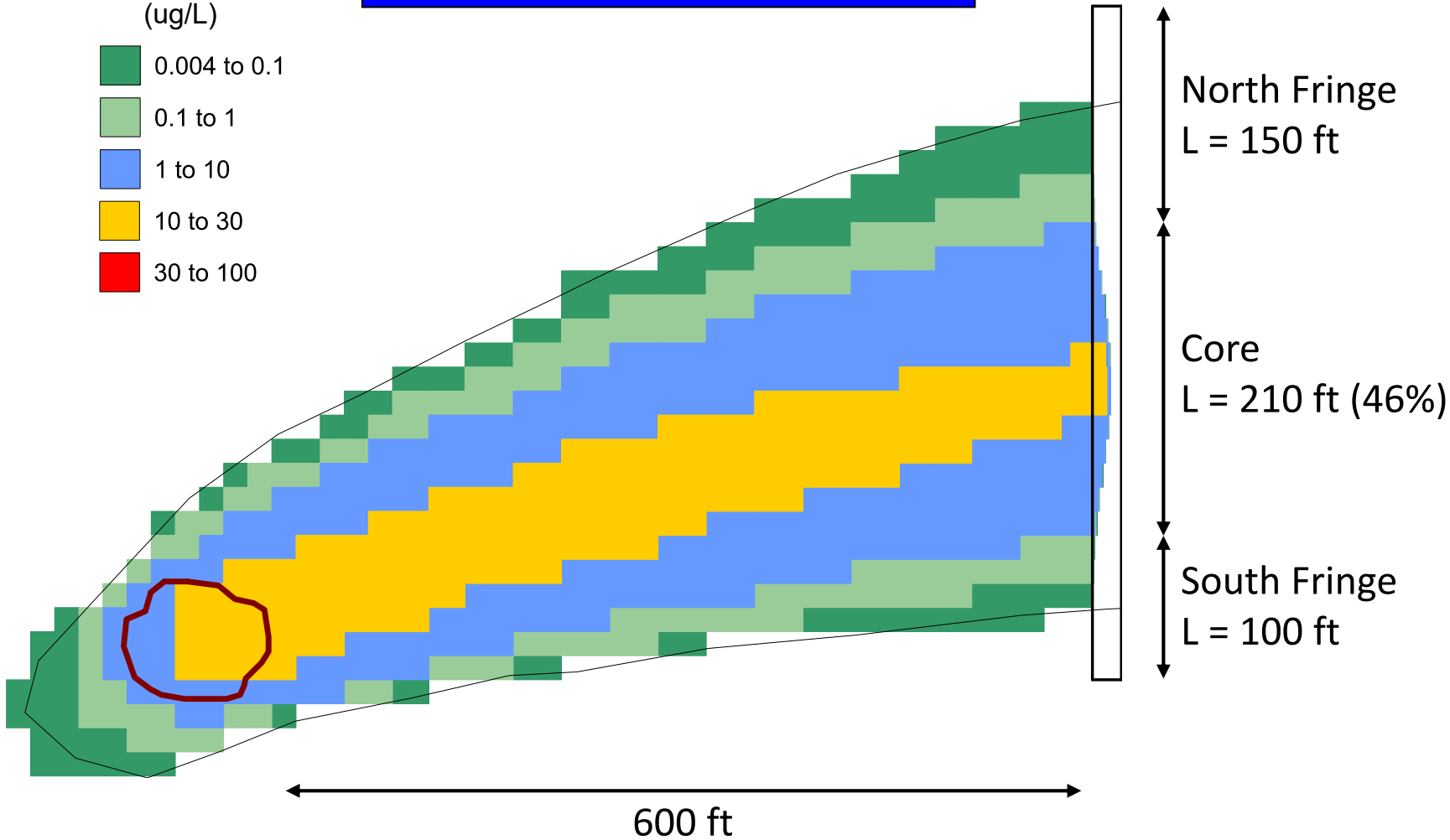
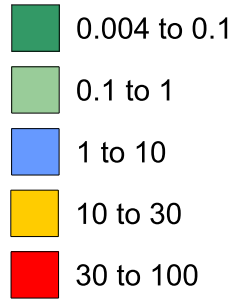
Concentration
(ug/L)



PRB Design with Target Longevity of 30 Years

Annual Average Plume

PFHxS
Concentration
(ug/L)



Total depth: 40 ft
 Saturated thickness: 27 ft
 Total PRB Length: 460 ft
 PRB Volume: 9,200 cy

PRB Component	Proportion of PRB	Target CAC (mg/kg)
Core	46%	1000
Fringes	54%	500

What Happens to CAC PRBs In the Long-Term?

Future options when CAC is spent:

1. Inject follow-up CAC PRB slightly downgradient
 - Low Net Present Value (NPV) cost
2. In the next decade, we may have technologies to treat PFAS-laden CAC in-situ

e.g., smoldering



BOOTH #211
Dave Liefel and Laura Kinsman

Development and Application of Injectable Fuels/Adjuncts for In Situ Treatment of PFAS and Co-Occurring Chemicals in Source Areas by Smoldering Combustion

Objective

The overall objective of this project is to demonstrate the use of an injectable liquid fuel that supports in situ smoldering combustion that causes the destruction and volatilization of per- and polyfluoroalkyl substances (PFAS) and co-occurring chemicals from source areas.

POINT OF CONTACT

David Major, Ph.D.
Principal Investigator
Geosyntec
Phone: (519) 515-0860
Email

PRODUCTS

Webinar

Advances in PFAS Destructive Technologies
5/2/2024

Conceptual Diagram of In Situ Treatment of PFAS

Downgradient PRB Costs

INSTALLATION COST

PlumeStop® + Injection



TOTAL COST

Construction Costs

PlumeStop® + Injection

+ Well Installation

+ Professional Services (26%)

- Detailed design, work plan, H&S plan, permitting (12%)
- Construction mgt and as-built report (8%)
- Health and safety (2%)
- Project management (6%)

+ Contingency cost (30%)

Annual O&M (30 years, NPV, 4.5%)

Downgradient PRB Costs (NPV at 4.5% Discount)

Scenario 1.1: Minimum CAC dose

CAC 0.1% / 0.05% in PRB Core/Fringes

Installation: \$1.6M / Total: \$4.0M

Scenario 1.2: Double Dose & Longevity

CAC 0.2% / 0.05% in PRB Core/Fringes

Installation: \$2.0M / Total: \$4.7M

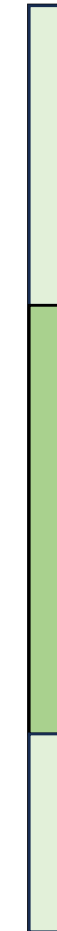
Scenario 1.3: Longevity 50% of Modeled

CAC 0.1% / 0.05% in PRB Core/Fringes

Re-injection at 15 years (NPV)

Installation: \$2.4M / Total: \$5.4M

PRB



CAC: 0.05%

500 mg/kg

CAC: 0.1%

1,000 mg/kg

CAC: 0.05%

500 mg/kg

Site-Specific PFAS Adsorption Testing

- Site-specific chemistry will influence CAC longevity
 - Relative PFAA concentrations
 - PFAS Precursors
 - DOC
 - Other organic chemicals (e.g., DRO)
 - pH
- Site-specific isotherm testing – minor investment (\$15K to \$25K) to increase confidence in CAC dose and remedy longevity



**PFAS-Sorbent
Isotherm Testing
Services**

Contact: BOOTH 215

Sandra Dworatzek

519-515-0839

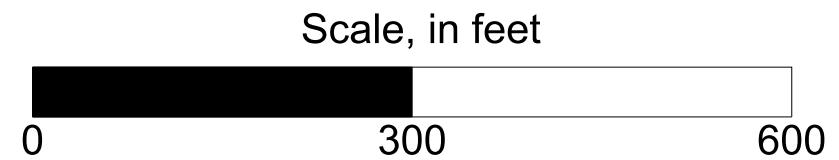
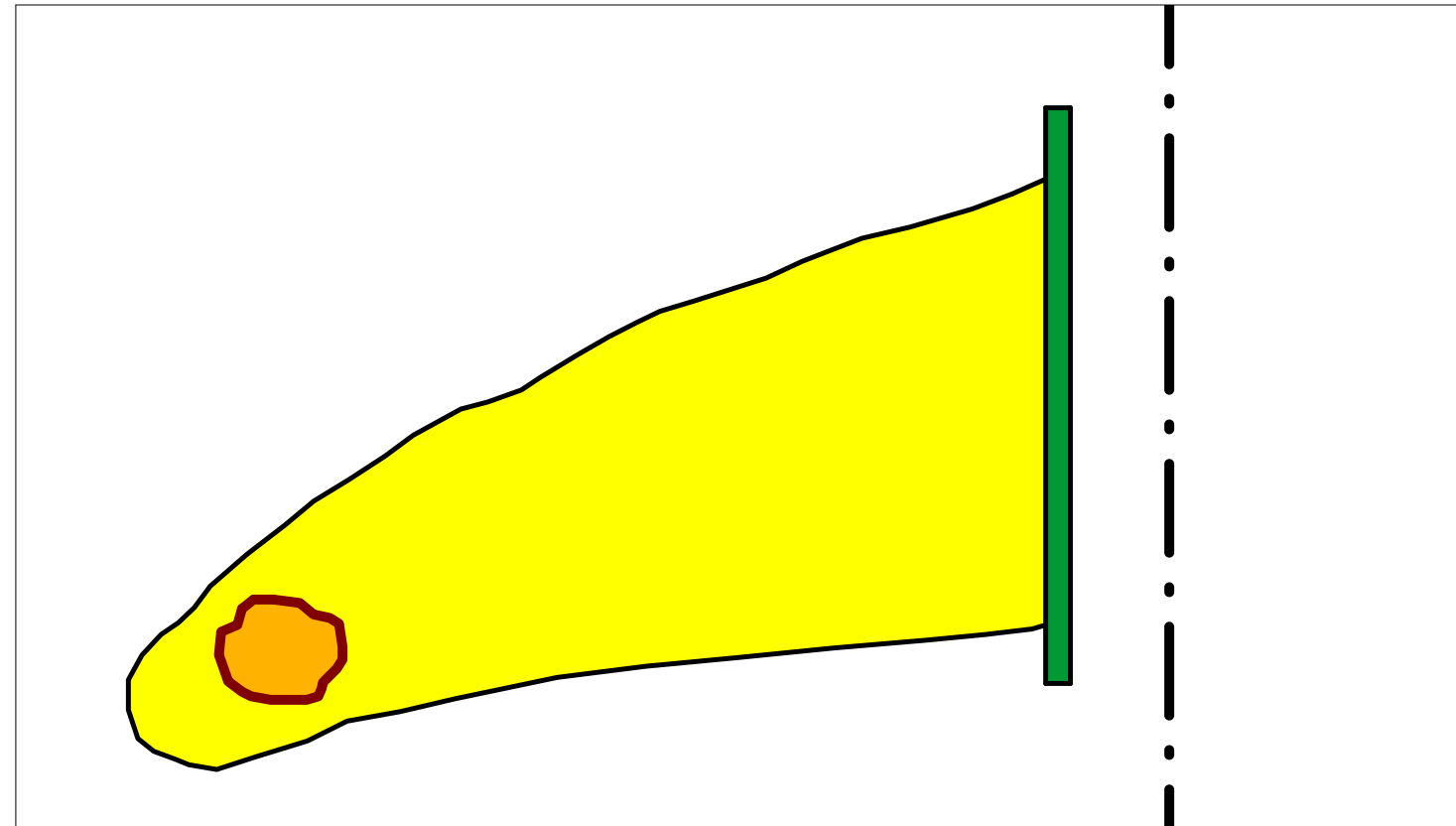
sdworatzek@siremlab.com

Source Control Alternatives

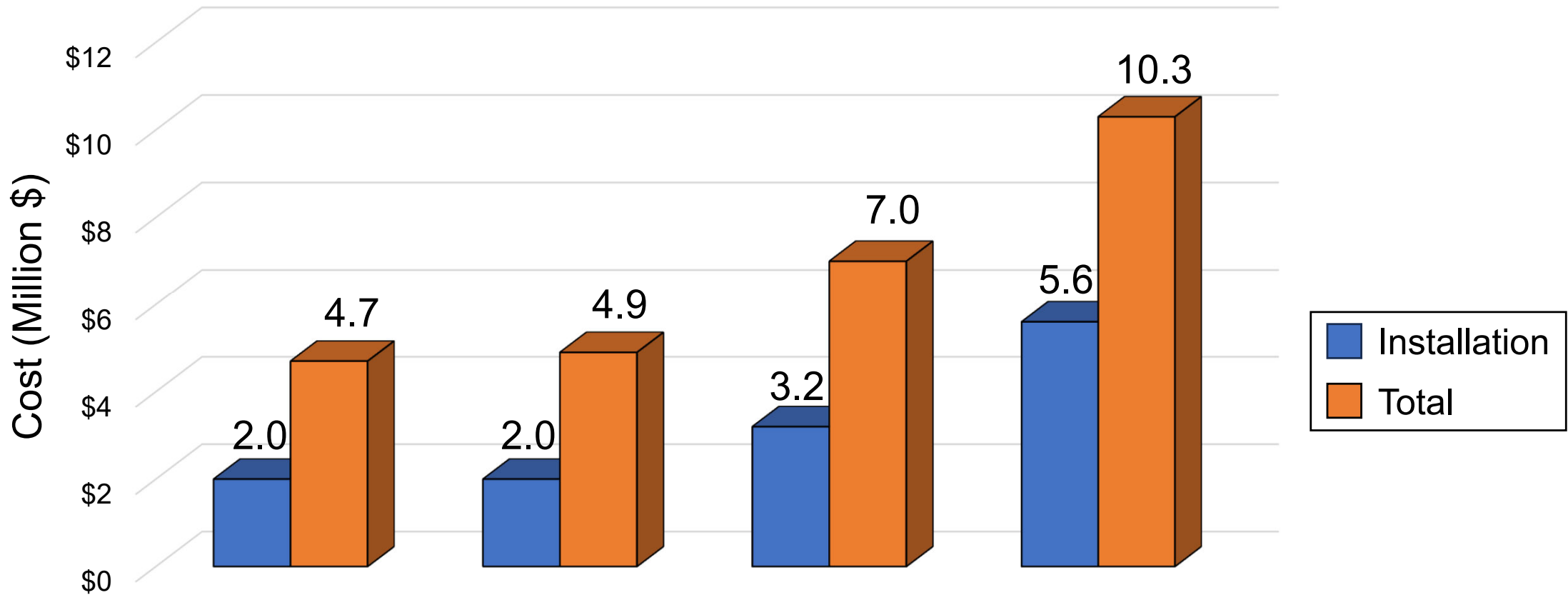
Source Control Alternatives

1. Durable cover
2. Wall + cover
3. In-situ soil stabilization (ISS)

Main benefit: Increased PRB longevity



Integrated PRB and Source Control Alternatives



PRB CAC Dose (%):	0.2 / 0.05	0.1 / 0.05	0.1 / 0.05	0.1 / 0.05
Source Control:	n/a	Cover	Wall + Cover	ISS
Longevity (y):	60	35 to 45	>100	>100

*Vadose zone Md:
20% to 50% of total source*

Md: Mass discharge

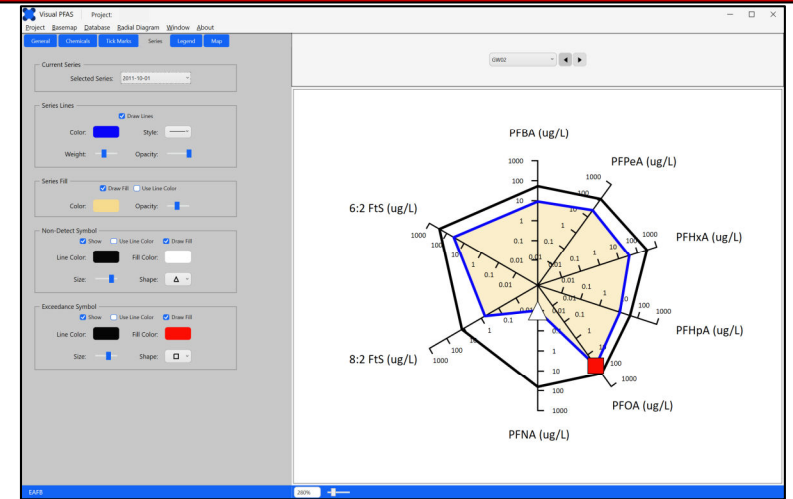
Questions?

Coming January 2025: Visual PFAS™ for Site Characterization and Forensics

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