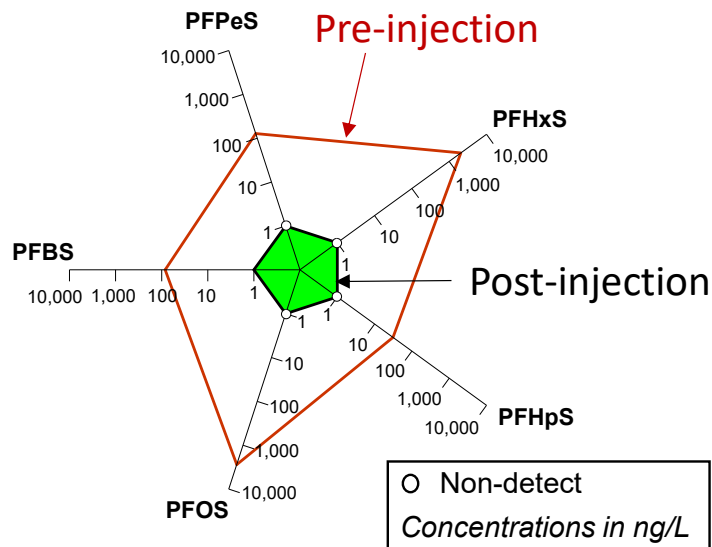
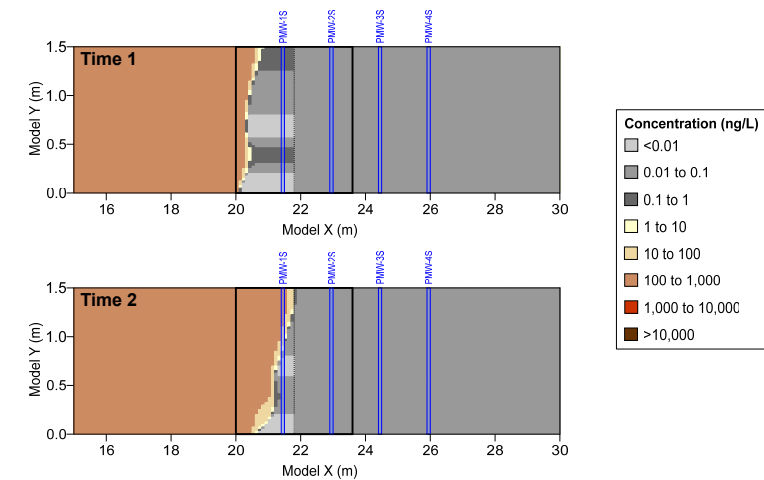


# Case Studies and Long-Term Strategies for PFAS Remediation Using CAC



Presented By  
**Grant R. Carey, Ph.D.**

Porewater Solutions  
Ottawa, Ontario, Canada  
[gcarey@porewater.com](mailto:gcarey@porewater.com)

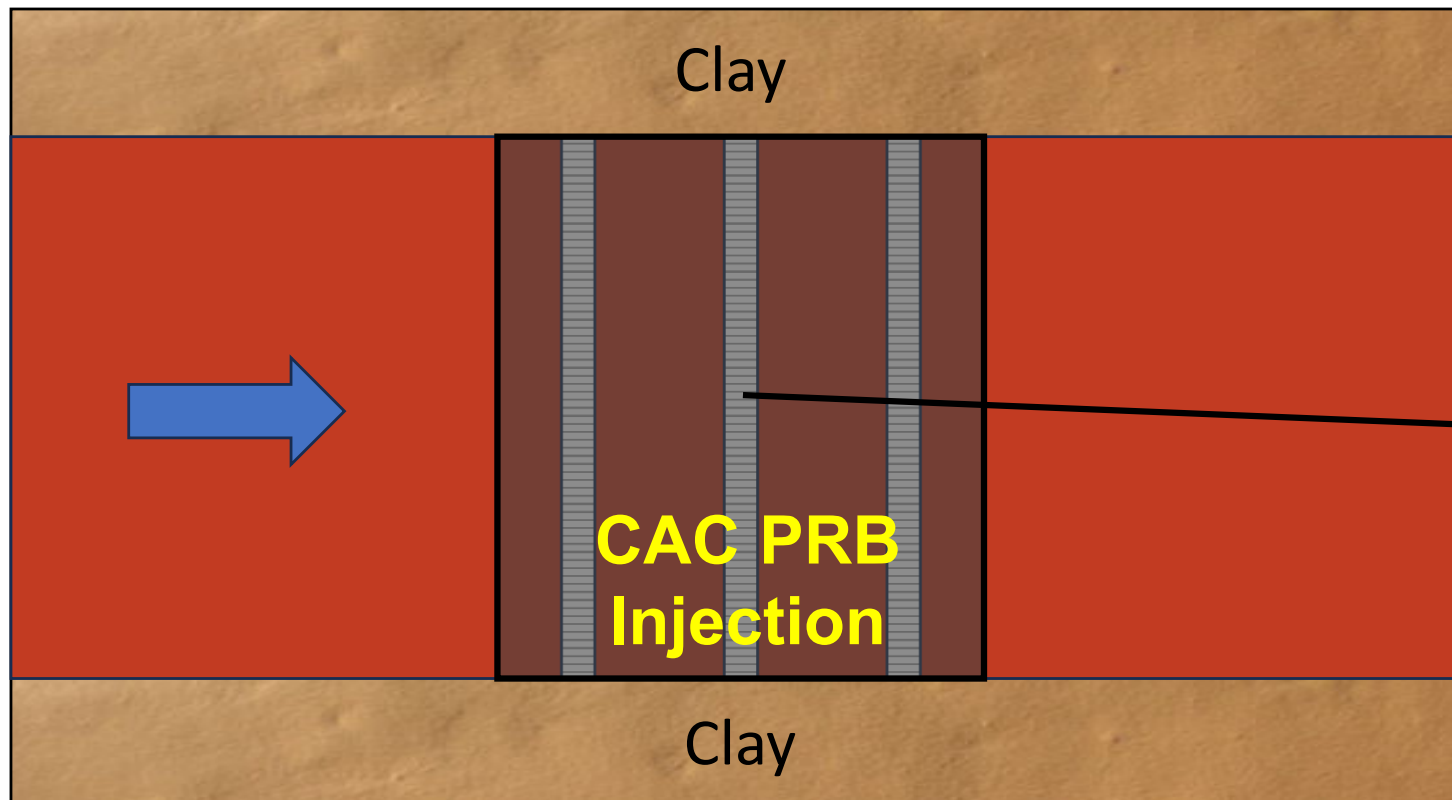


June 2 to 6, 2024

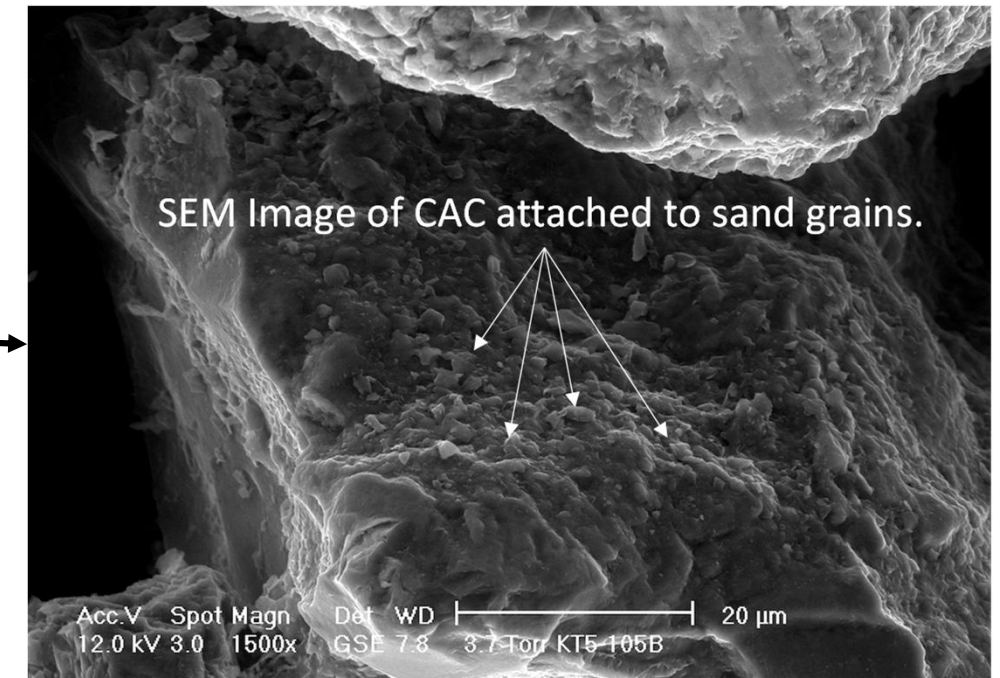
# Remediating PFAS With Colloidal Activated Carbon (CAC)

Typical CAC soil concentration in PRBs: 2,000 mg/kg

Fraction of CAC ( $f_{cac}$ ): 0.2%



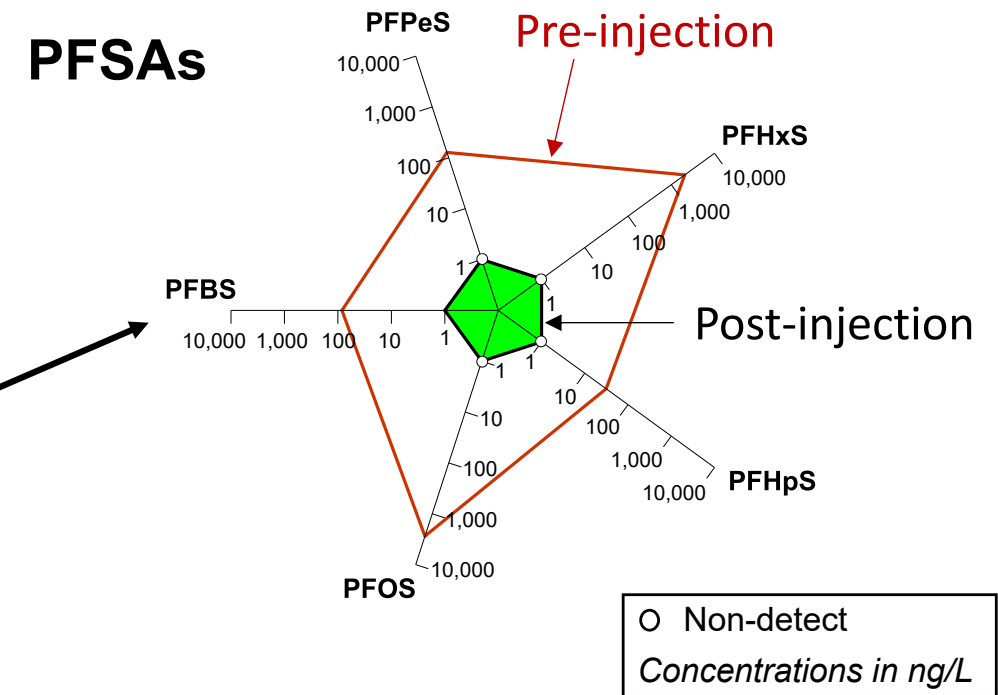
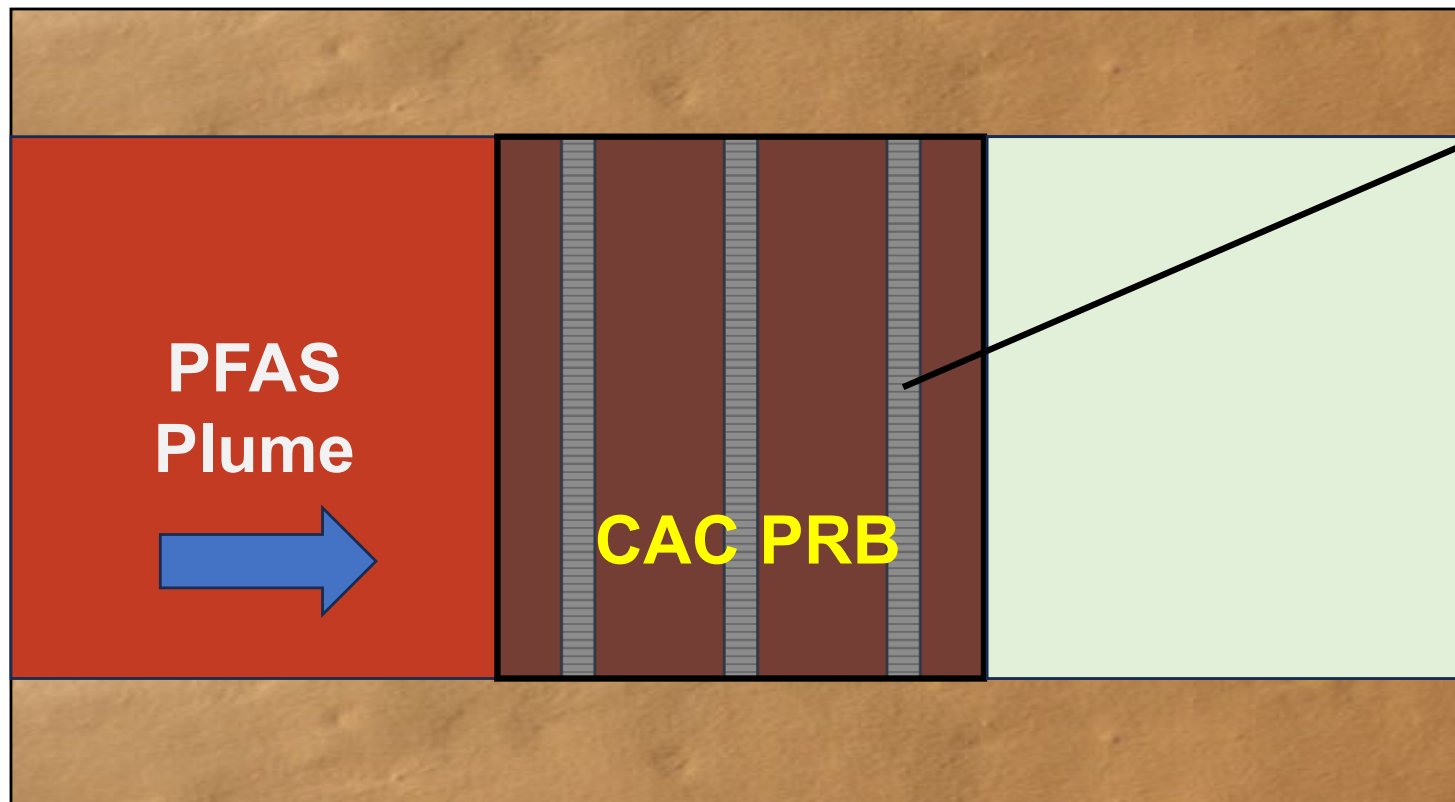
*PRB: Permeable Reactive Barrier*



*Courtesy of REGENESIS*

# Remediating PFAS With Colloidal Activated Carbon (CAC)

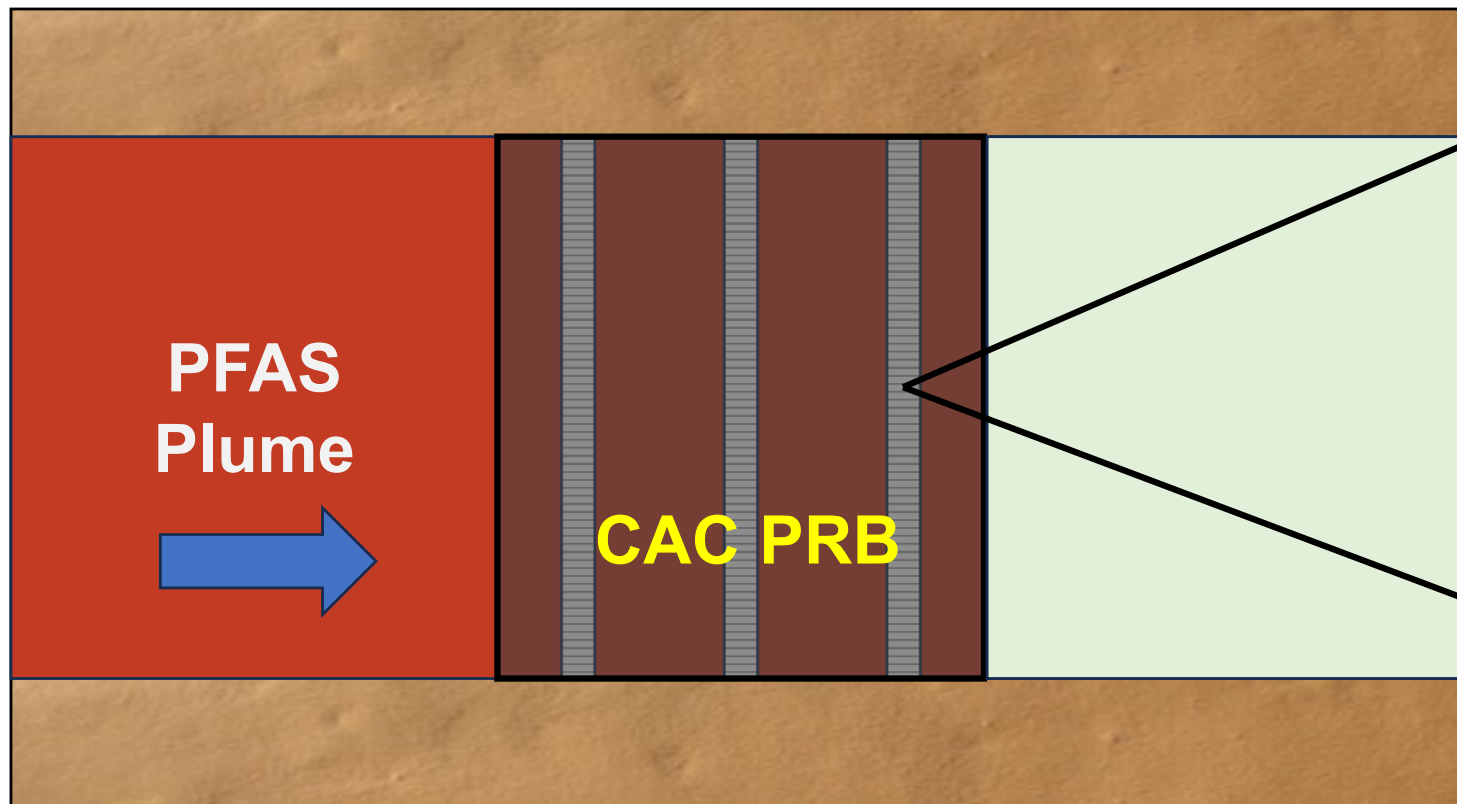
In-barrier monitoring well



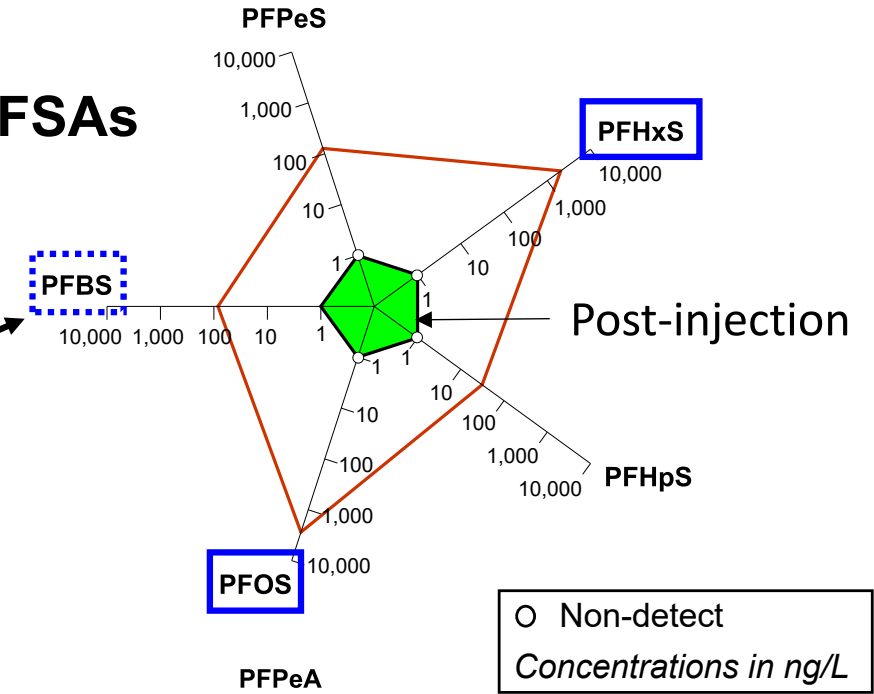
*Note: Radial diagram illustrated using Visual CHEM which was developed by Porewater Solutions.*

More info: [www.porewater.com/PFAS.html](http://www.porewater.com/PFAS.html)

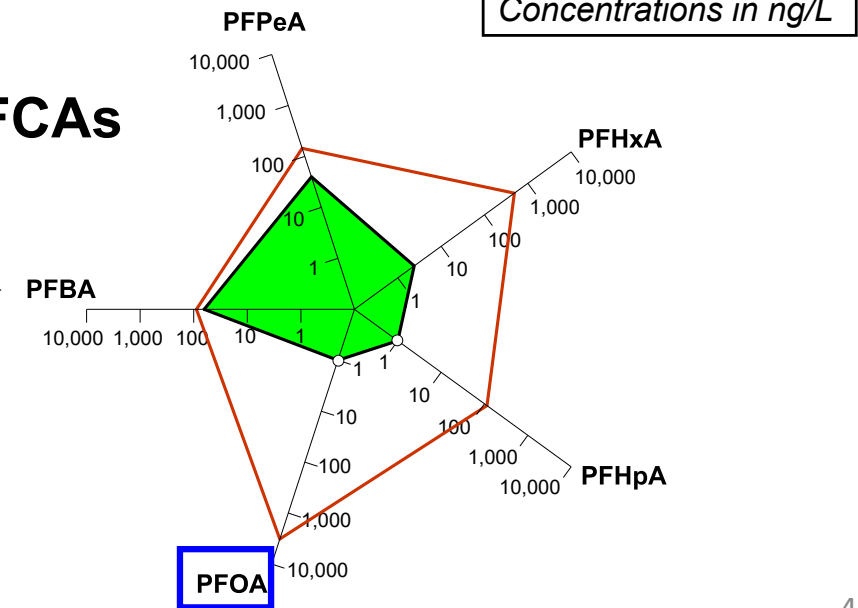
# Remediating PFAS With Colloidal Activated Carbon (CAC)



**PFASs**



**PFCAs**





# 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



# Recent ISR-MT3DMS Publications

## Two papers in progress

### Application of an Advection-Dispersion-Reaction Model for MT3DMS for Modeling Remediation Timeframes

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

Simulation of back-diffusion remediation timeframes is typically required to estimate the scale vertical grouting required to represent diffusive back-diffusion in a 3-D model. A computationally efficient approach for simulating back-diffusion is demonstrated. Incorporation of a local domain model, In Situ Remediation-MT3DMS (ISR-MT3DMS) and comparison with a highly discretized model used to estimate the vertical hydrodynamic gradient on the simulated flux into and out of documented back-diffusion at a Florida site is model of the back-diffusion controlled remediation timeframes with a clay lens having a thickness of 0.2 to 99.96 percent aqueous TCE removal from the clay zone. The source zone in a site treatment may have little back-diffusion, given that back-diffusion will sustain a back-diffusion model input parameters that have and that may require more attention during field testing, retardation coefficient representing sorbed adjacent higher permeability zones. Therefore, prior to providing containment may have an additional time frame due to enhanced transverse advection timeframes are also moderately sensitive to the diffusive dispersivity, but are less sensitive to degradation constant, sorption coefficient, and monitoring. ©2015 Wiley Periodicals, Inc.

**INTRODUCTION**  
The occurrence of back-diffusion at contaminant timeframes for decades to centuries after the

### Estimating transverse dispersivity based on hydraulic conductivity

Grant R. Carey<sup>1,2</sup>, Edward A. McBean<sup>3</sup>, Stan Feenstra<sup>4</sup>  
Received 23 March 2016  
Accepted 19 January 2017

**HIGHLIGHTS**

- Transverse vertical dispersivity (TVD) is inversely proportional to hydraulic conductivity
- TVD is also shown to be inversely proportional to effective grain size
- A novel regression equation for estimating transverse vertical dispersivity is presented
- New transverse vertical dispersivity values are calculated for previous studies
- A previously published equation for estimating TVD where  $\sigma_v$  critical velocity is validated

**ABSTRACT**  
The modeling of depletion timeframes for partially depleting transverse vertical contaminant plumes is a critical step in estimating this parameter over the wider contaminated sites. Transverse dispersivity is a critical threshold for a given contaminant plume. Through the compilation of a number of case studies, a relationship between transverse dispersivity and hydraulic conductivity is established. The critical velocity from 3 to 5 m/d based on a limited number model. The method derived by Kirk and Co. correction factor for dispersivity where  $\sigma_v$

**1. Introduction**  
Sites with NAPL contamination may require expensive, long-term remediation in the subsurface (Parker et al., 2002; Kowalik et al., 2013). The rate of dissolution is proportional to transverse vertical dispersivity (TVD) (Kirk et al., 1988; Johnson

### Longevity of colloidal activated carbon for in situ PFAS remediation at AFFF-contaminated airport sites

Grant R. Carey<sup>1</sup> | Seyfollah G. Hakimabadi<sup>2</sup> | Mantake Singh<sup>3</sup> | Rick McGregor<sup>4</sup> | Claire Woodfield<sup>5</sup> | Paul J. Van Geel<sup>6</sup> | Anh Le-Tuan Pham<sup>7</sup>

**ABSTRACT**  
A review of state per- and polyfluoroalkyl substances (PFAS) remediation at four long-chain PFAS (perfluorooctanoic acid [PFOA], perfluorodecanoic acid [PFDA], perfluorododecanoic acid [PFDDA], and perfluorotetradecanoic acid [PFTDA]) sites indicates that in situ CAC in short- and long-chain PFAS in the short-term levels of organic co-contaminants, competitive sorption conditions using forming foam (AFF) impacted sites. The interest at five AFFF-impacted sites was a CAC longevity model sensitivity analysis to be insensitive to a wide range of conditions. PFOA had the greatest long-chain concentrations than the other species considerably higher than PFOA and proportional to the CAC fraction in the source zone.

**1. Introduction**  
Per- and polyfluoroalkyl substances (PFAS) have been widely used as a global level for many decades. Perhaps the greatest source of PFAS contamination in the environment today is the use of aqueous film-forming foams (AFFF) for firefighting. A large number of military and civilian airports have PFAS soil and groundwater contamination due to historical fire training activities. PFAS include polyfluoroalkyl precursors and reactant perfluoroalkyl acids (PFAAs). PFAAs consist of two classes: perfluorocarboxylic (PFCA) and perfluoroalkyl sulfonates (PFSA).

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

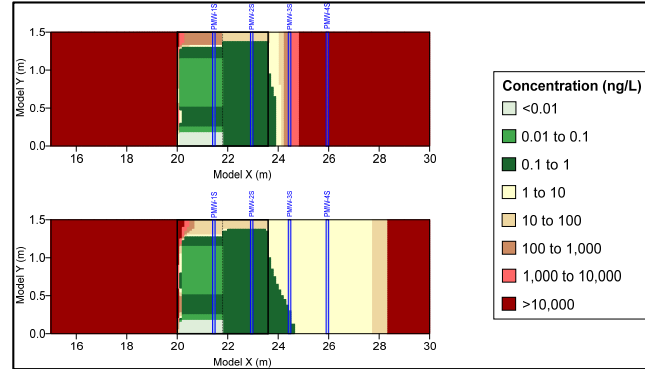
Mantake Singh<sup>1</sup>, Seyfollah Gilak Hakimabadi<sup>2</sup>, Paul J. Van Geel<sup>3</sup>, Grant R. Carey<sup>4</sup>, Anh Le-Tuan Pham<sup>5</sup>

**ABSTRACT**  
Competitive adsorption of four perfluoroalkyl substances (PFAS), i.e., perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDDA), and perfluorotetradecanoic acid (PFTDA) on a colloidal activated carbon (CAC) was studied and a new predictive model, modified competitive Langmuir model (CMLM), was proposed to predict the competitive adsorption equilibria. The new model, a competitive Langmuir model (CMLM) that gave additional weighting to the molecular weight. A comparative study was done to test the capability of the new model by comparing with CSM and ideal adsorbed solution theory (IAST), as well as the experimental adsorption data. The results showed that the CMLM model provided a better fit to the experimental data than the other models. The model also showed that the adsorption capacity of CAC for PFAS is significantly higher than that of PFOA, and the adsorption capacity of CAC for PFAS is significantly higher than that of PFOA.

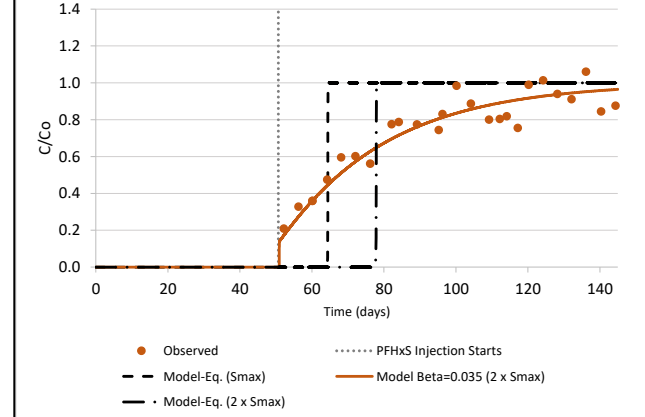
### Modeling the Influence of Coastal Site Characteristics on PFAS In Situ Remediation

Grant R. Carey<sup>1,2</sup>, Anthony Danko<sup>3</sup>, Anh Le-Tuan Pham<sup>4</sup>, Keir Soderberg<sup>5</sup>, Beth Hoagland<sup>6</sup>

**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 tectonic strength is 84 mM, which was conservatively estimated to result in an increase of 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 fill 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 perfluorooctane sulfonic 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.



Column 2 Experimental and Model Results: PFFHS



### Groundwater

#### Review Paper

### Estimating Tortuosity Coefficients Based on Hydraulic Conductivity

Grant R. Carey<sup>1</sup>, Edward A. McBean<sup>2</sup>, and Stan Feenstra<sup>3</sup>

**ABSTRACT**  
While the tortuosity coefficient is commonly estimated using an expression based-relationship is demonstrated to not be applicable, and this is often misapplied. The relationship is demonstrated to be a correlation between the apparent diffusion tortuosity coefficient and hydraulic conductivity, although such a relationship is not typically considered. An estimated tortuosity coefficient based on hydraulic conductivity for saturated, unconsolidated media from 14 previously reported diffusion experiments is presented with a broad range of applications. These experimental results confirm that total porosity is a poor predictor for the tortuosity coefficient in a wide range of soil textures. The apparent diffusion tortuosity coefficient is more related to hydraulic conductivity.

#### Introduction

Although molecular diffusion is a relatively slow process in water, there are circumstances where it may have a significant influence on contaminant transport. For example, back diffusion from low-permeability silts, clays, or rock matrix may cause a substantial increase in remediation timeframes at contaminated sites (Parker et al., 1994; Chapman and Parker, 2005; Sale et al., 2008; Seyfollah et al., 2012). Diffusion also influences the performance of caps on contaminated sediment (USEPA, 1990a; Kubiak and Lanport, 2014) which may be comprised of a wide range of soil textures. pore media relative to diffusive impedance to diffusion is caused (1) hydraulic impedance due to flow paths through connected and (2) (3) and (4) further impede the rate of diffusive transport (Shackelford and Daniel, 1991). hydraulic tortuosity coefficient (τ) is a dimensionless parameter for estimating hydraulic conductivity (K) (e.g., Carmon, 1972; Bear, 1988; related to K).

### Evaluating the longevity of a PFAS in situ carbon remedy

Grant R. Carey<sup>1</sup> | Rick McGregor<sup>2</sup> | Anh Le-Tuan Pham<sup>3</sup> | Seyfollah Gilak Hakimabadi<sup>4</sup>

**ABSTRACT**  
The remediation of per- and polyfluoroalkyl substances (PFAS) at a contaminated site in Central Canada using modeling methods. Radial diagrams were used to model the effect of competitive adsorption of PFAS on the adsorption of PFOA. The results show that the adsorption of PFOA is significantly higher than that of PFOA. The model also showed that the adsorption capacity of CAC for PFAS is significantly higher than that of PFOA.

#### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants that are widespread in the environment and are generally persistent (Hites, Helwig, & Giger, 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 priority or cleanup levels. Some PFAS precursors are known to undergo aerobic biodegradation (e.g., Anderson & Li, 2016; Harding-Margolis 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 (Hilton et al., 2018). There are two classes of PFAAs: perfluoroalkyl carboxylates (PFCA) and perfluoroalkyl sulfonates (PFSA). The most commonly regulated PFAS in the environment are perfluorooctanoic acid (PFOA), which is a PFCA, and perfluorooctane sulfonic acid (PFOS), which is a PFSA. Regulatory cleanup criteria for these and other PFAS are native now being

### Analysis of colloidal activated carbon remediation of a large PFAS plume

Grant R. Carey<sup>1,2</sup> | Richard A. Anderson<sup>3</sup> | Paul Keir Soderberg<sup>4</sup> | Anthony Danko<sup>5</sup> | Seyfollah Anh Le-Tuan Pham<sup>6</sup> | Mia Rebeiro-Tunstall<sup>7</sup>

**ABSTRACT**  
This study evaluated optimal remediation strategies for a large PFAS plume at a contaminated site in Central Canada using modeling methods. Radial diagrams were used to model the effect of competitive adsorption of PFAS on the adsorption of PFOA. The results show that the adsorption of PFOA is significantly higher than that of PFOA. The model also showed that the adsorption capacity of CAC for PFAS is significantly higher than that of PFOA.

#### 1. Introduction

Aqueous film-forming foam (AFFF) containing PFAS has been used historically for fire training activities since the mid-1940s. Eason et al. (2021), resulting in high concentration PFAS source area and groundwater plumes at some military and civilian airports in the United States (Adamsen et al., 2020; Carey et al., 2022). Intestate

### Groundwater solutes influence the adsorption of acids (PFAA) to colloidal activated carbon and impacted remediation

Rachel A. Molé<sup>1</sup>, Adriana C. Veloso<sup>2</sup>, Grant R. Carey<sup>3</sup>, Xitong Anthony Danko<sup>4</sup>, and Gregory V. Lowry<sup>5\*</sup>

**ABSTRACT**  
This study evaluated optimal remediation strategies for a large PFAS plume at a contaminated site in Central Canada using modeling methods. Radial diagrams were used to model the effect of competitive adsorption of PFAS on the adsorption of PFOA. The results show that the adsorption of PFOA is significantly higher than that of PFOA. The model also showed that the adsorption capacity of CAC for PFAS is significantly higher than that of PFOA.

#### 1. Introduction

Common approach for these sites of PFAS is to use activated carbon (CAC) or ion exchange resin. However, the adsorption of CAC or ion exchange resin eventually becomes less effective as the chemicals are spent and must be either disposed of in the landfill, incinerated, or recycled. Inorganic anions decreased adsorption for short-chain PFAA (<7 perfluorinated

# Outline

## 1. PFAS competitive adsorption effects

- 17 Field case studies

## 2. Case Studies of PFAS remediation using CAC

- South Dakota site – CAC PRB placement
- Coastal site – tidal effects, geochemistry
- Eastern US site – short- vs. long-chain, CAC heterogeneity effects

## 3. Long-term PFAS remediation strategies

# PFAS Competitive Adsorption



# Evaluating CAC Effectiveness for PFAS Remediation

Carey et al. (2022)

DOI: 10.1002/rem.21741

RESEARCH ARTICLE WILEY

## Longevity of colloidal activated carbon for in situ PFAS remediation at AFFF-contaminated airport sites

Grant R. Carey<sup>1</sup> | Seyfollah G. Hakimabadi<sup>2</sup> | Mantake Singh<sup>3</sup> | Rick McGregor<sup>4</sup> | Claire Woodfield<sup>3</sup> | Paul J. Van Geel<sup>3</sup> | Anh Le-Tuan Pham<sup>2</sup>

<sup>1</sup>Porwater Solutions, Ottawa, Ontario, Canada  
<sup>2</sup>Department of Civil and Environmental Engineering, University of Waterloo, Ontario, Waterloo, Canada  
<sup>3</sup>Department of Civil and Environmental Engineering, Carleton University, Ontario, Ottawa, Canada  
<sup>4</sup>In Situ Remediation Services Ltd., St. George, Ontario, Canada

**Correspondence**  
 Grant R. Carey, Porwater Solutions, 2958 Barlow Crescent, Ottawa, ON K0A 1T0, Canada.  
 Email: gcarey@porwater.com

**Funding Information**  
 Porwater Solutions, Ontario Centers for Excellence, and Natural Sciences and Engineering Research Council

**Abstract**  
 A review of state per- and polyfluoroalkyl substances (PFAS) guidelines indicates that four long-chain PFAS (perfluorooctanesulfonic acid [PFOS] and perfluorooctanoic acid [PFOA] followed by perfluorohexanesulfonic acid [PFHxS] and perfluorononanoic acid [PFNA]) are the most frequently regulated PFAS compounds. Analysis of 17 field-scale studies of colloidal activated carbon (CAC) injection at PFAS sites indicates that in situ CAC injection has been generally successful for both short- and long-chain PFAS in the short-term (0.3–6 years), even in the presence of low levels of organic co-contaminants. Freundlich isotherms were determined under competitive sorption conditions using a groundwater sample from an aqueous film-forming foam (AFFF)-impacted site. The median concentrations for these PFAS of interest at 96 AFFF-impacted sites were used to estimate influent concentrations for a CAC longevity model sensitivity analysis. CAC longevity estimates were shown to be insensitive to a wide range of potential cleanup criteria based on modeled conditions. PFOS had the greatest longevity even though PFOS is present at higher concentrations than the other species because the CAC sorption affinity for PFOS is considerably higher than PFOA and PFHxS. Longevity estimates were directly proportional to the CAC fraction in soil and the Freundlich  $K_f$ , and were inversely proportional to the influent concentration and average groundwater velocity.

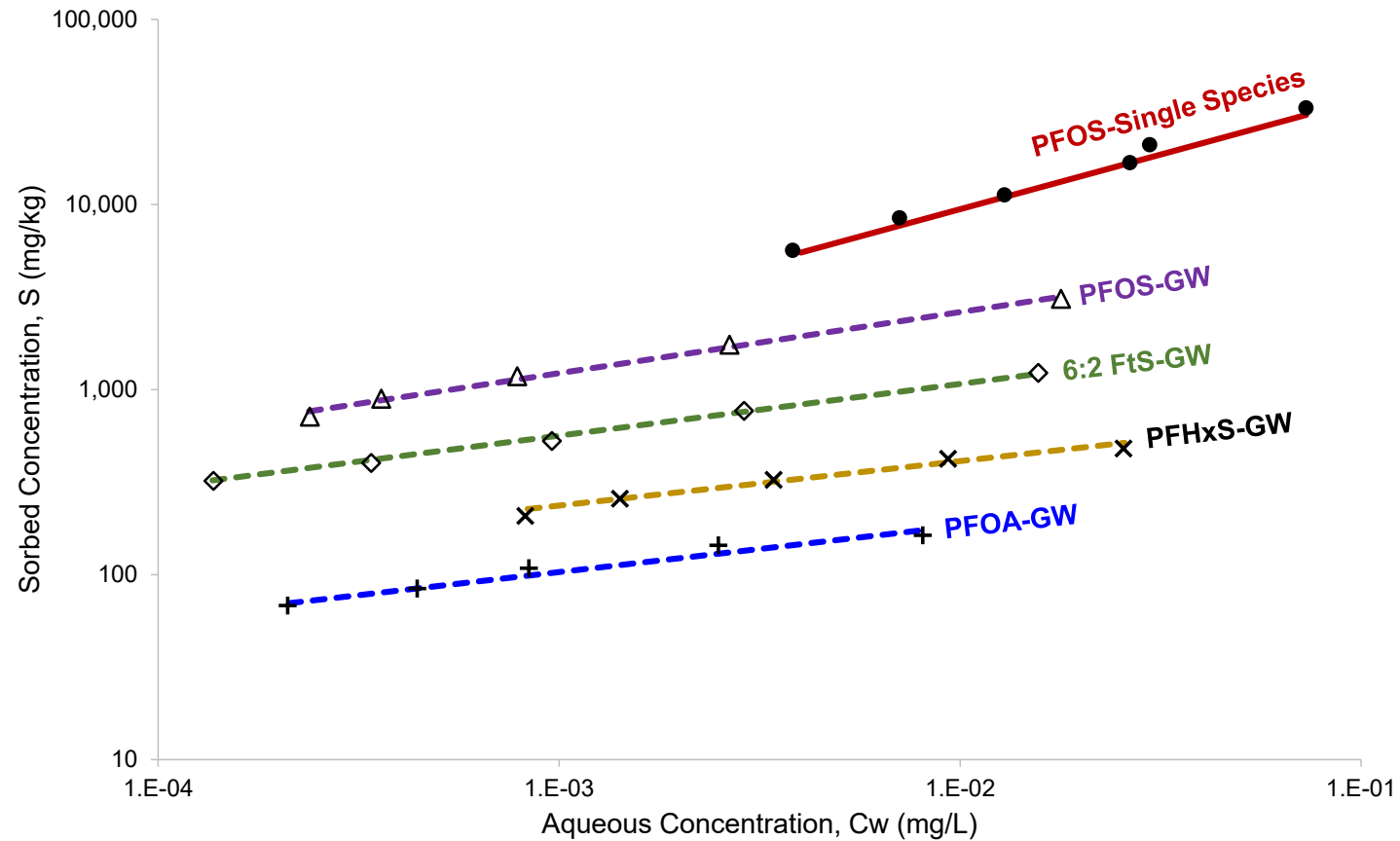
**1 | INTRODUCTION**

Per- and polyfluoroalkyl substances (PFAS) have been widely used on a global level for many decades. Perhaps 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 polyfluoroalkyl precursors and recalcitrant perfluoroalkyl acids (PFAAs). PFAAs consist of two classes: perfluorosulfonates (PFSAs) and perfluorocarboxylates (PFCAs). The fluorocarbon chain length of these PFAAs affects the relative toxicity and hydrophobicity of these compounds. The widespread occurrence of PFAS in the subsurface, combined with their recalcitrance and toxicity, presents a significant groundwater remediation challenge. This challenge is compounded by uncertainty in future regulatory changes anticipated at the federal and state levels, regarding which individual PFAS will be regulated and corresponding clean-up goals.

The most common approach used today for the remediation of PFAS in groundwater involves groundwater extraction with ex situ

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 Remediation, 2022, 1–21. wileyonlinelibrary.com/journal/rem | 1

## Single Species and Groundwater Sample Isotherms (Freundlich)



Dr. Anh Pham

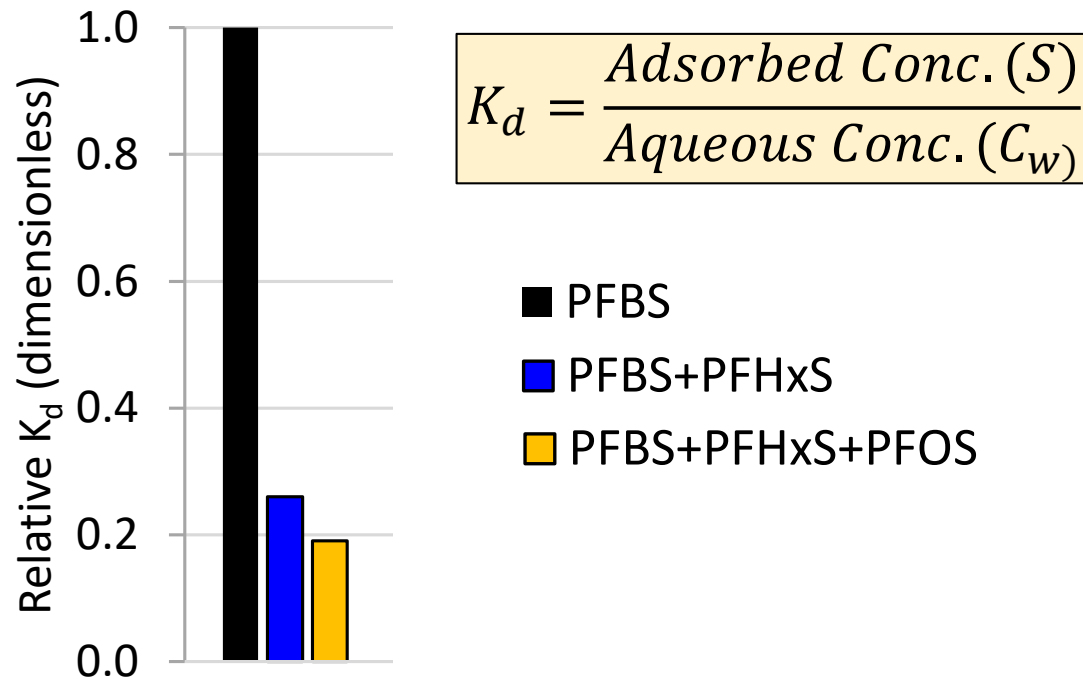


Seyfollah Gilak Hakimabadi

17 Field case studies generated CAC effectiveness, even in the presence of low levels of organic co-contaminants.

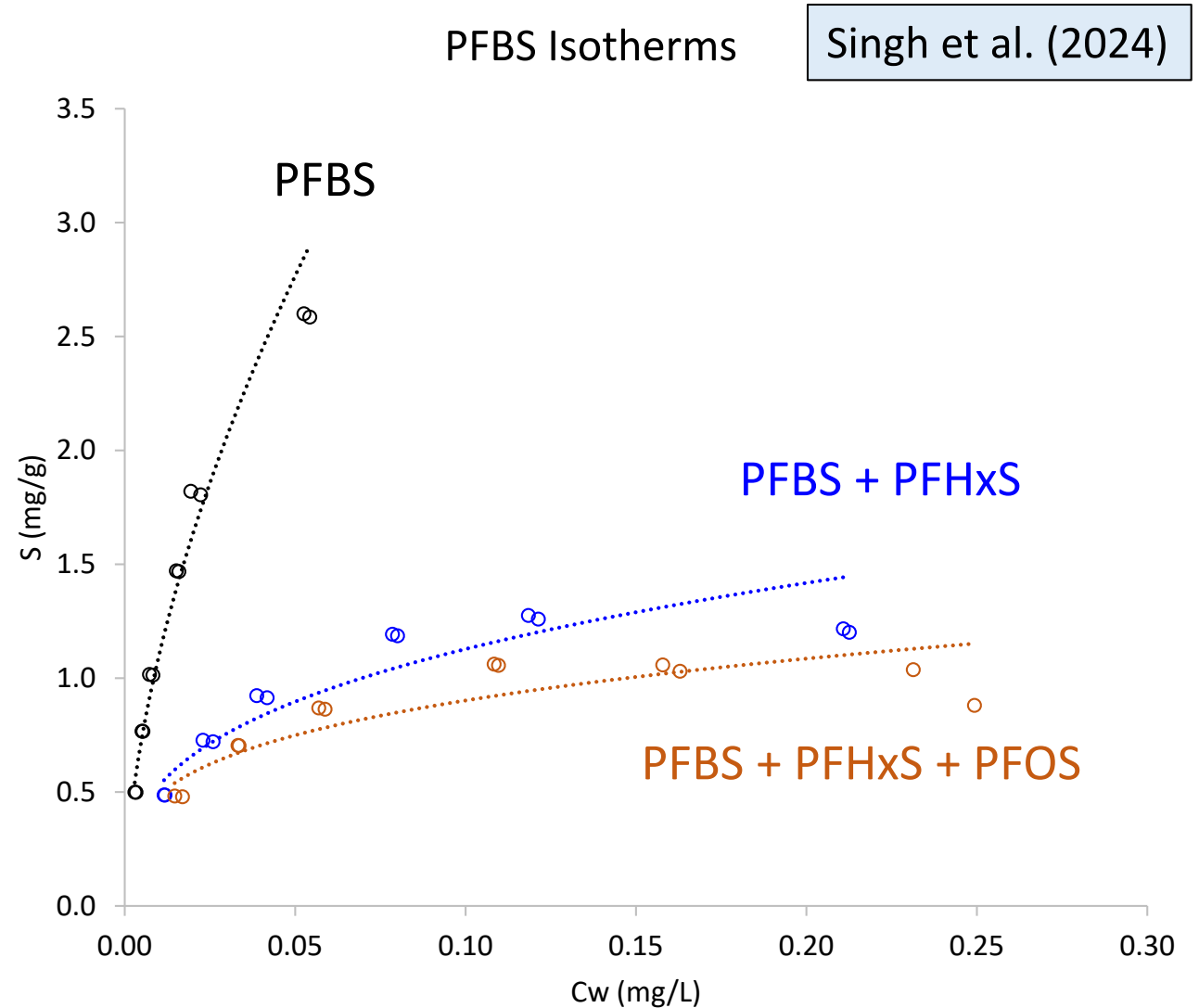


# Influence of Competition on Relative $K_d$

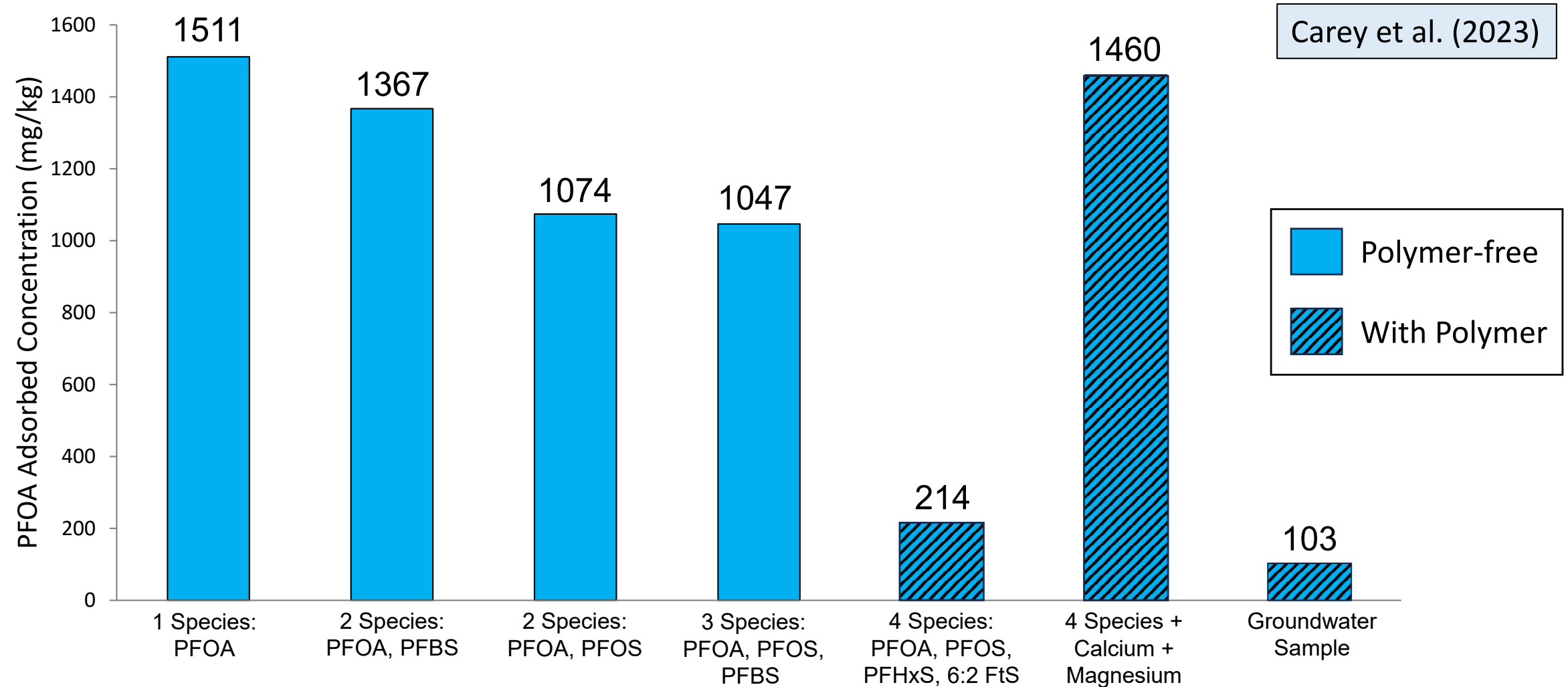


## PFBS Adsorption Trends

- Decreased 3x to 4x from 1 to 2 species
- Decreased 25% from 2 to 3 species



# Effects of Competitive Adsorption



# Chemicals Competing with PFAS for Adsorption

- Long-chain vs. short chain
- Sulfonates vs. carboxylates
- Precursors vs. PFAAs
- Hydrocarbons (if present)
- Natural organic matter (DOC, TOC in groundwater)

**PFAS of Concern: Lower competition in downgradient PRBs vs. source area**

# PlumeStop® Results at 17 PFAS Field Sites

PlumeStop® successfully reduced PFAS mass flux in the CAC zone by orders of magnitude with up to 6 years of monitoring.

Carey et al. (2022)

Concentrations at site (µg/L):

	Average Site	Most-Impacted
PFOS	1.0	152
PFOA	0.9	29

Lithology:

Silty sand or fine sand (13 of 17 sites)

$f_{cac}$ :

0.02% to 0.8% (average 0.2%)

Competitive adsorption observed?

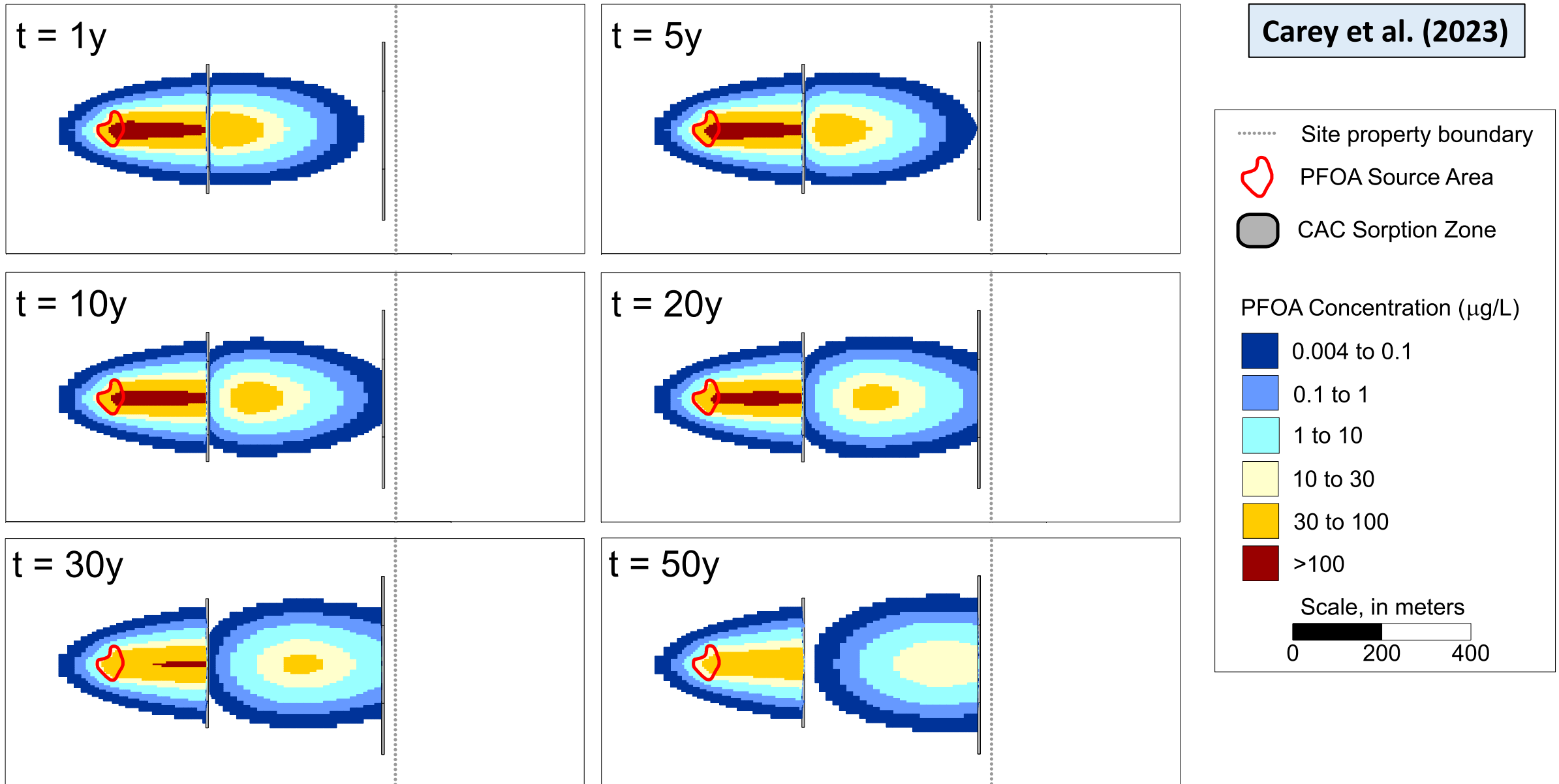
Co-contaminants: No

DOC: Yes, at a landfill

# Case Studies of PFAS Remediating Using CAC

## Section 2

# South Dakota Site: Integrated PRB Alternative

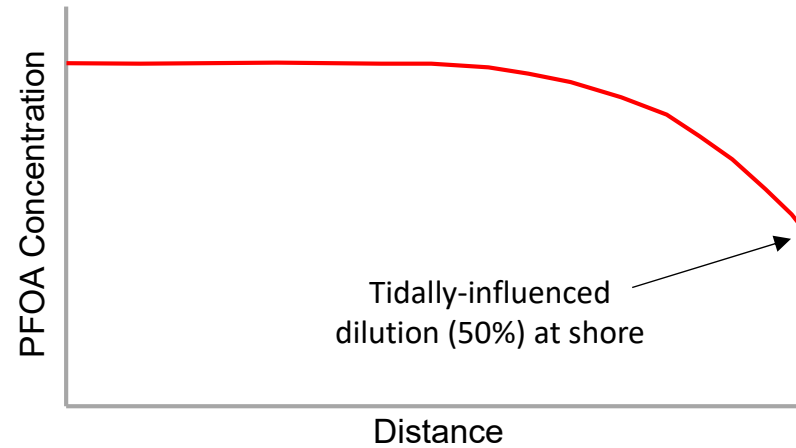




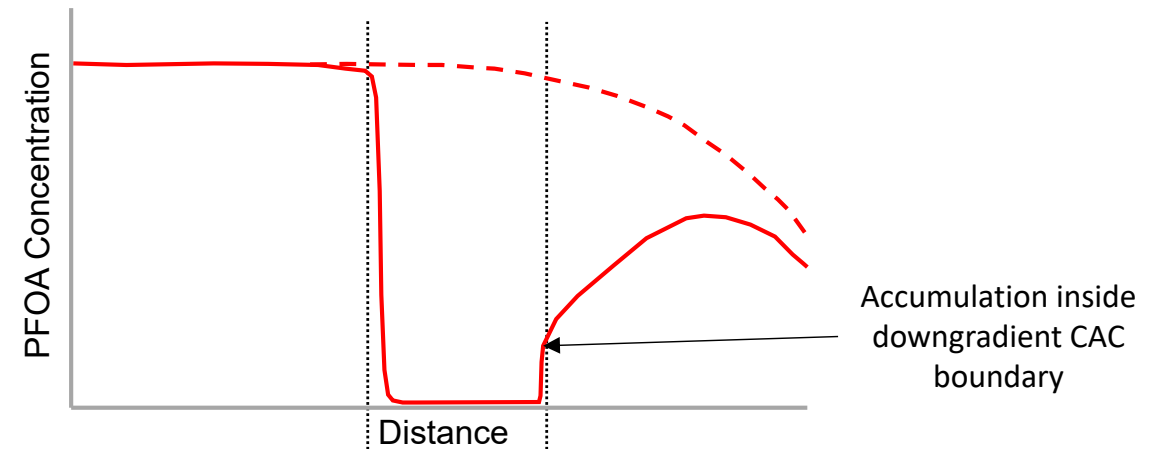
# Coastal Site Conceptual Model

Carey et al. (2024)

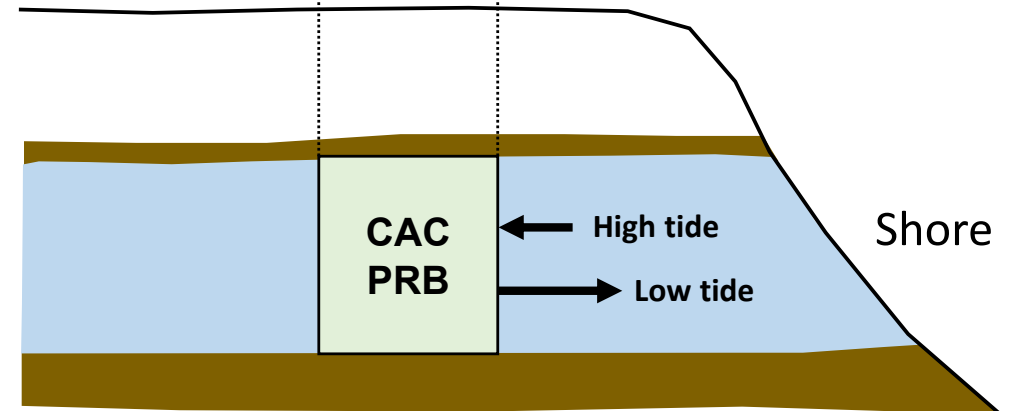
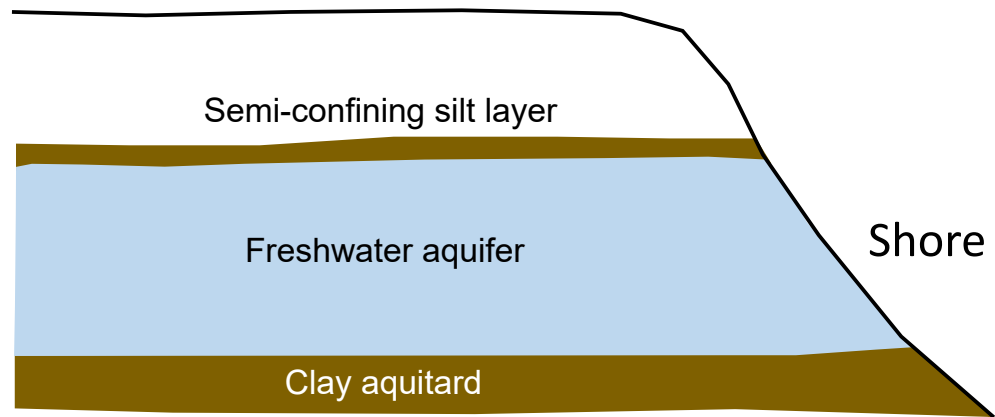
a) Prior to CAC injection



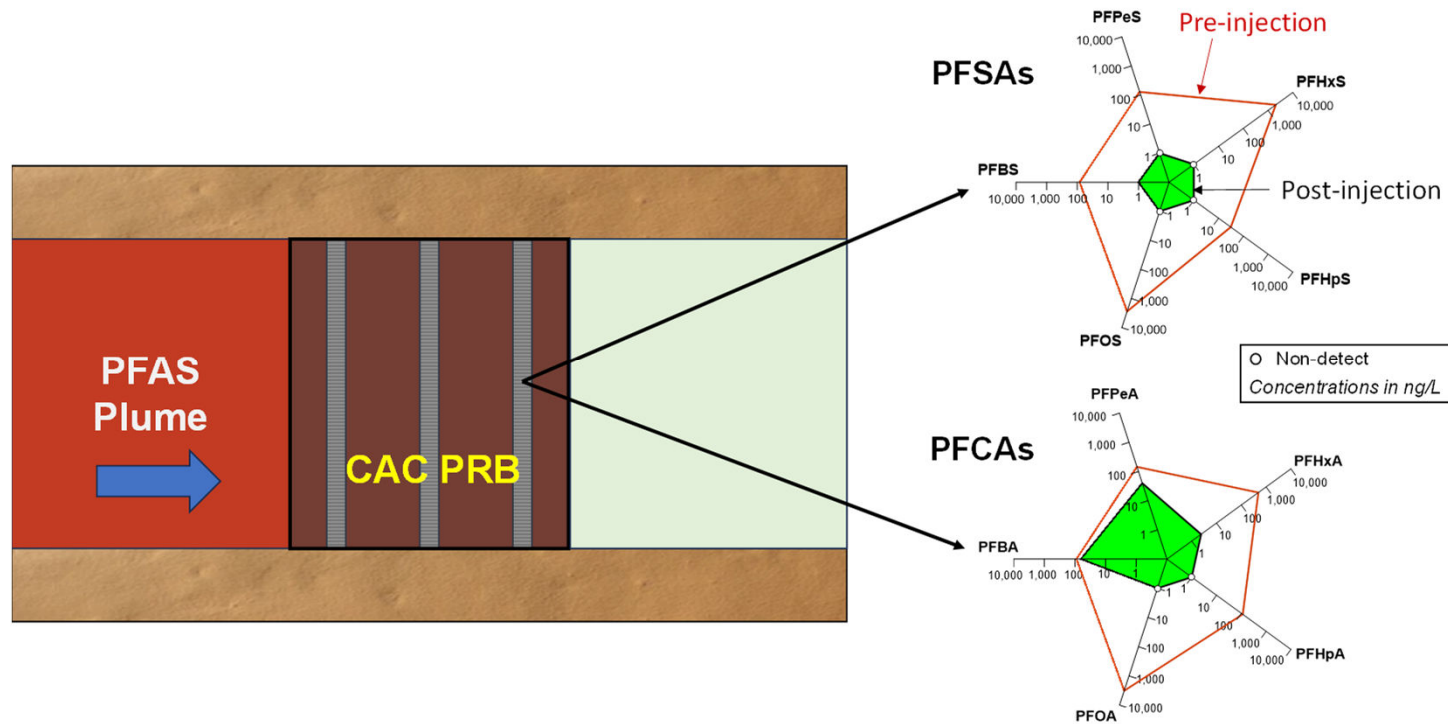
b) Two years after CAC injection



**Source Area**

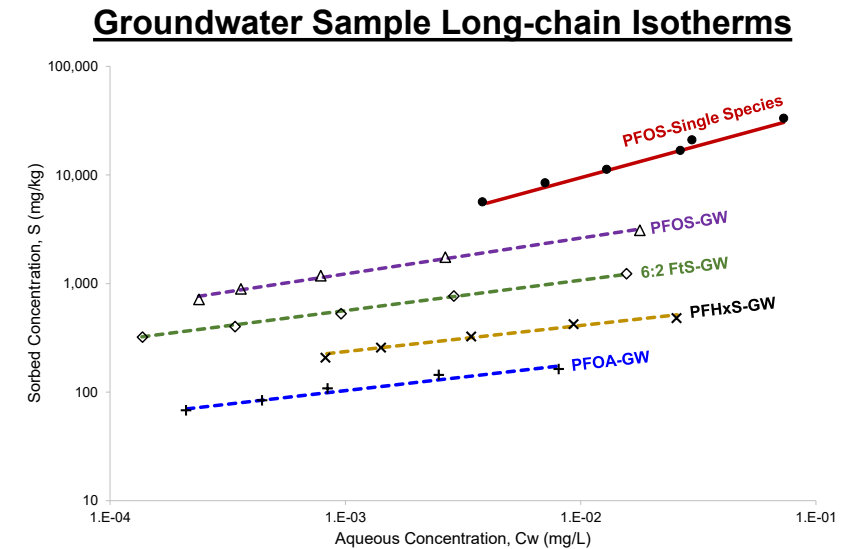


# Model Calibration of CAC Performance at A Field Site

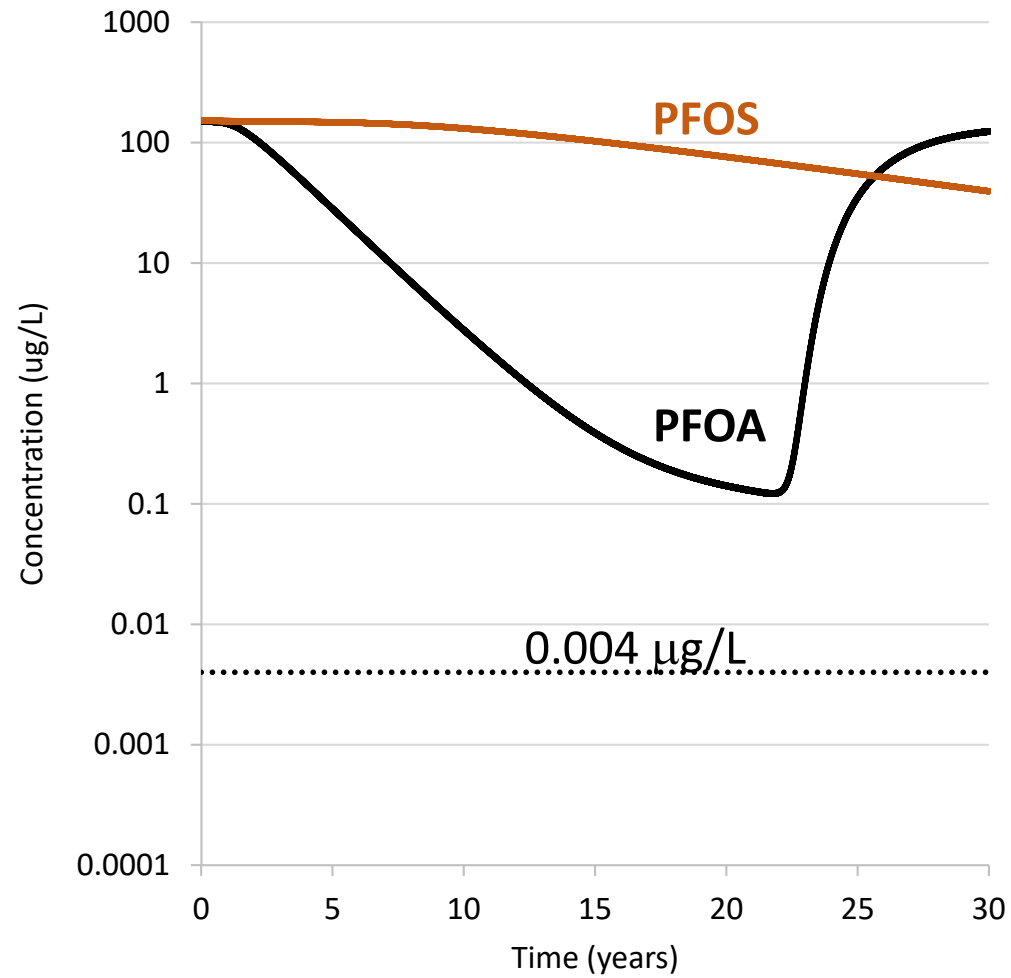
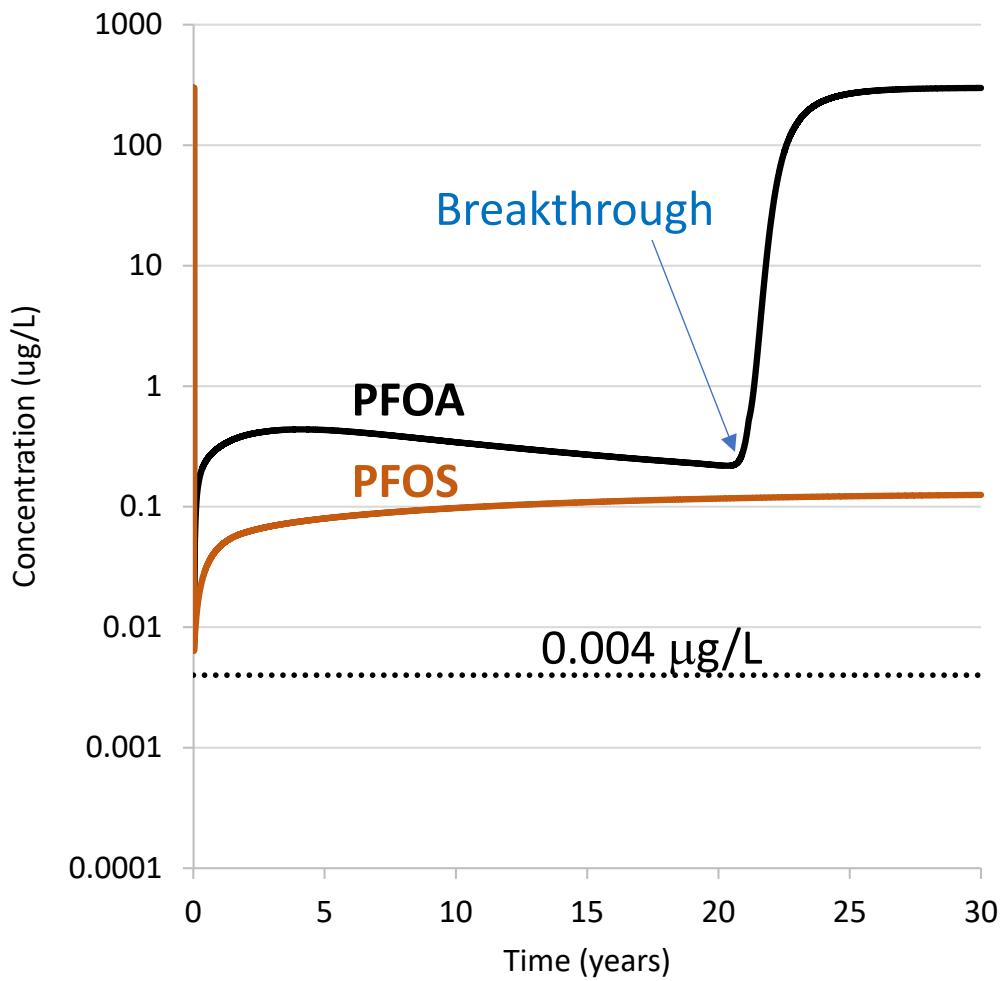
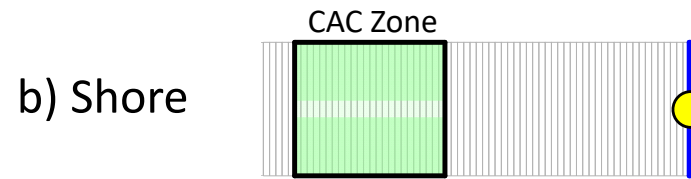
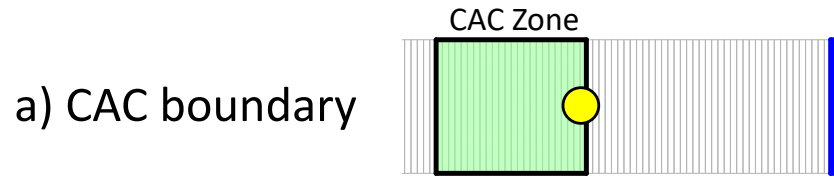


# Modeling Objectives

- Quantify relative adsorption of PFAS to CAC based on:
  - Chain length
  - Sulfonates vs Carboxylates
- Evaluate cause of low-level detections in PRB wells (low ng/L)
- Quantify desorption behavior downgradient of PRB
- Predict PRB longevity

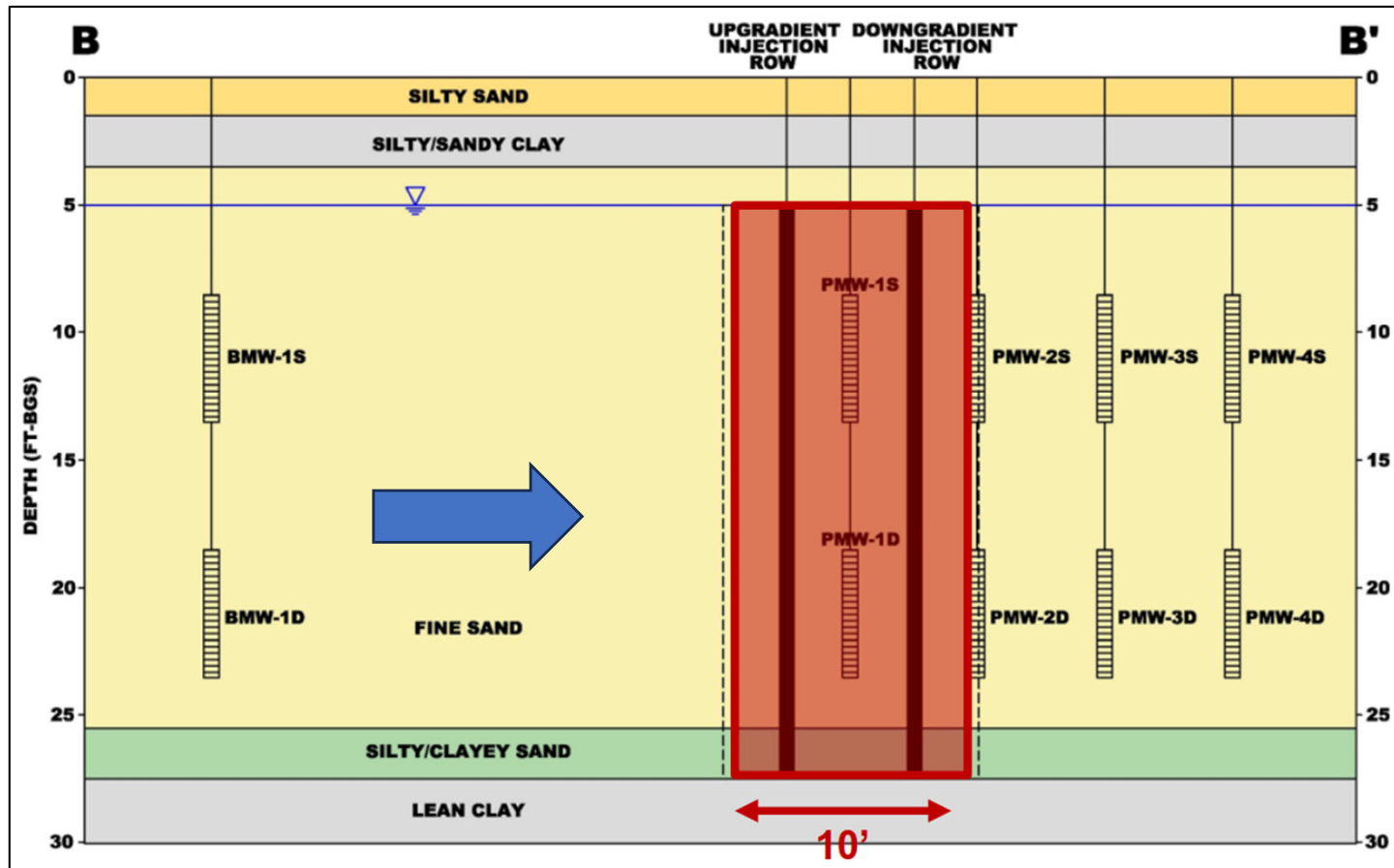


# PFOA vs PFOS Trends



# Eastern U.S. Site CAC Permeable Reactive Barrier

Carey et al. (2024) – in progress



## APTIM

Dr. Paul Hatzinger  
 Dr. Graig Lavorgna  
 Dr. David Lippincott

## Navy

Dr. Tony Danko

## Air Force Civil Engineer Center

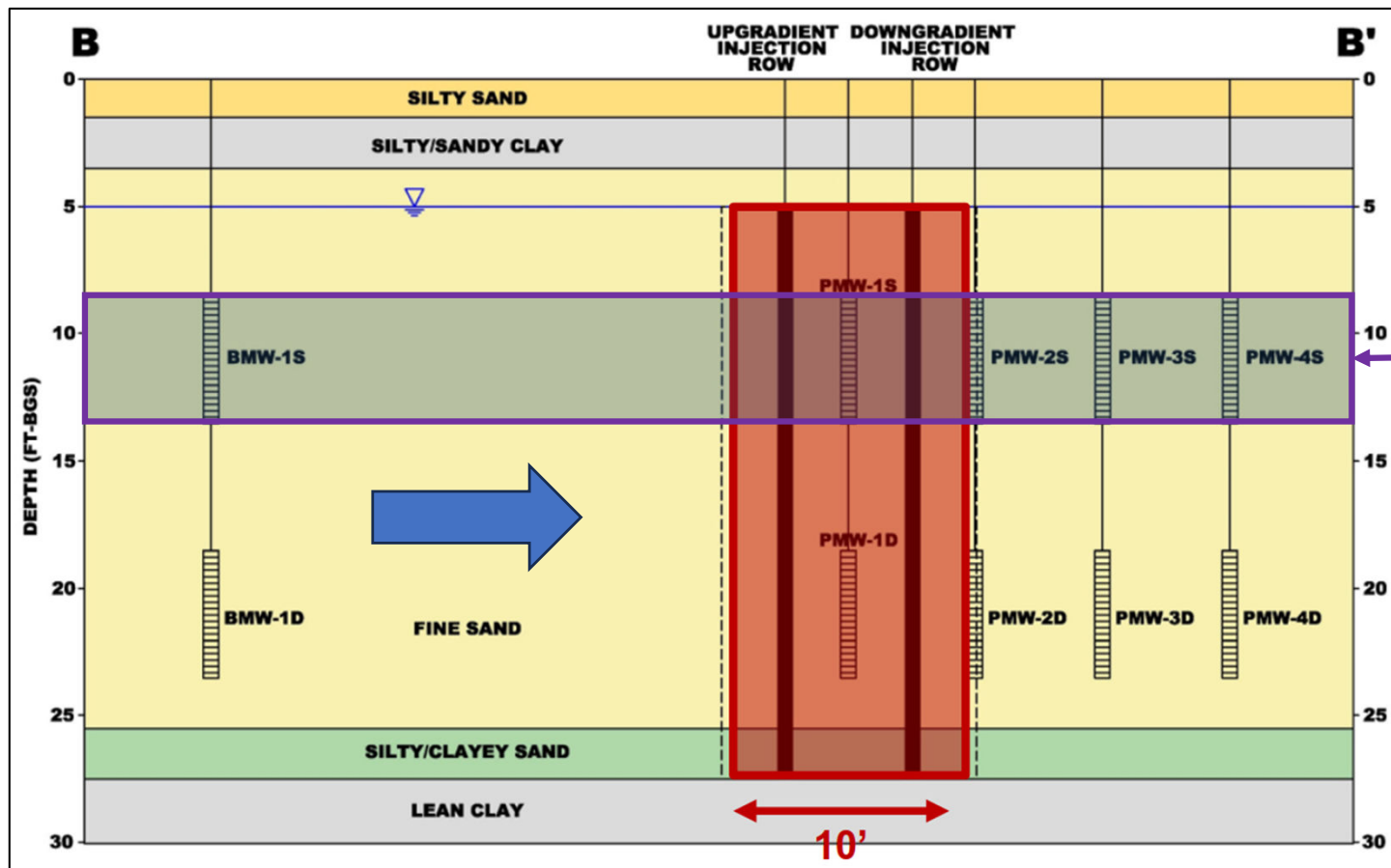


Field Demonstration of Colloidal  
 Activated Carbon for In Situ  
 Sequestration of Per- and  
 Polyfluoroalkyl Substances



Tony Danko, Ph.D., P.E.  
 Environmental Engineer  
 NAVFAC EXWC/SH321  
 September 2023

# Eastern U.S. Site CAC Permeable Reactive Barrier



Modeled vertical extent includes the shallow well screen interval (5 ft thick).

## Air Force Civil Engineer Center



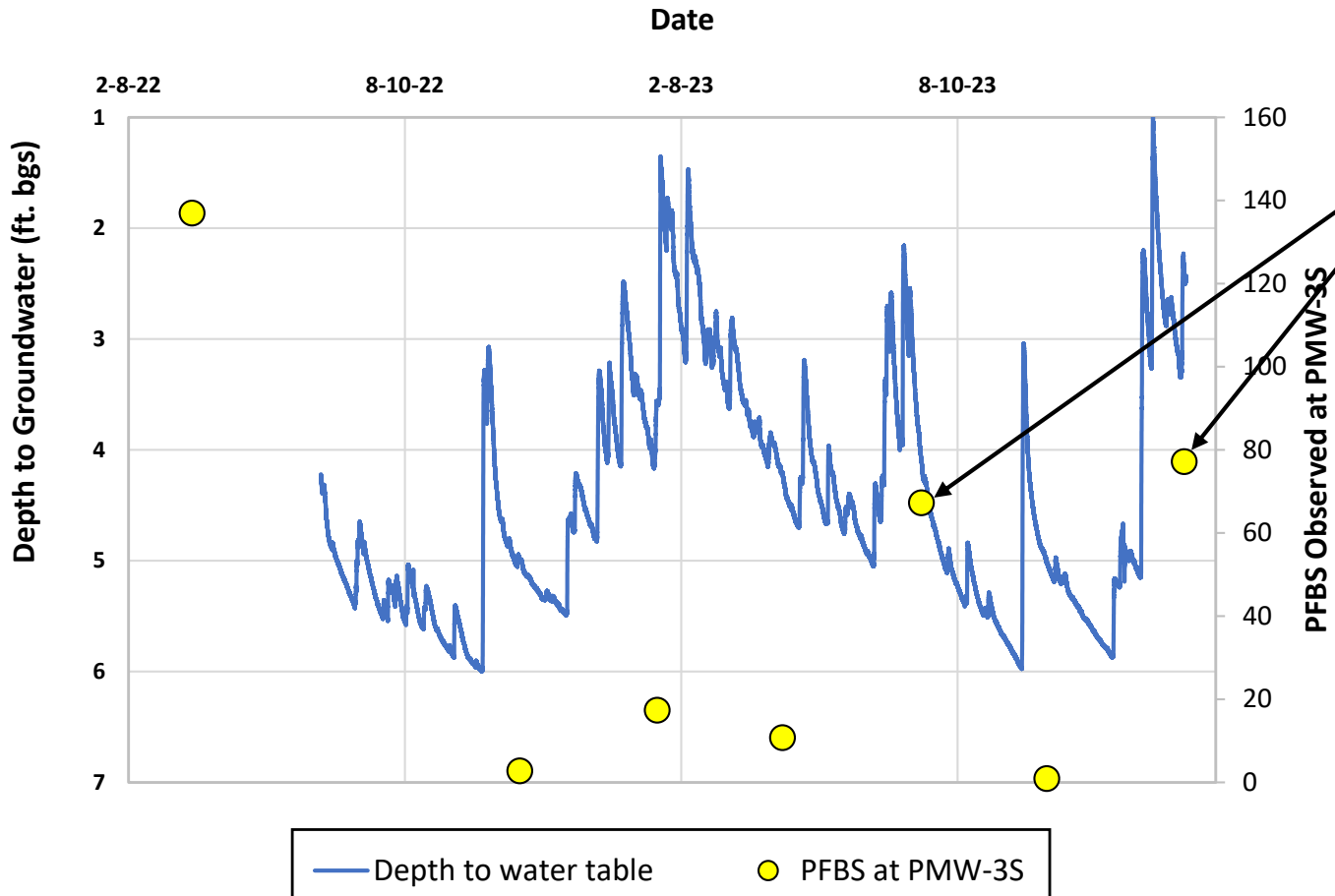
Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of Per- and Polyfluoroalkyl Substances



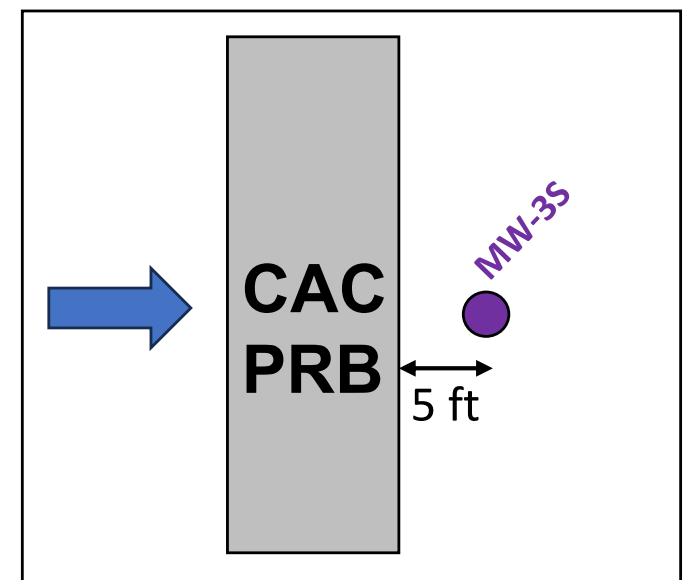
Tony Danko, Ph.D., P.E.  
Environmental Engineer  
NAVFAC EXWC/SH321  
September 2023



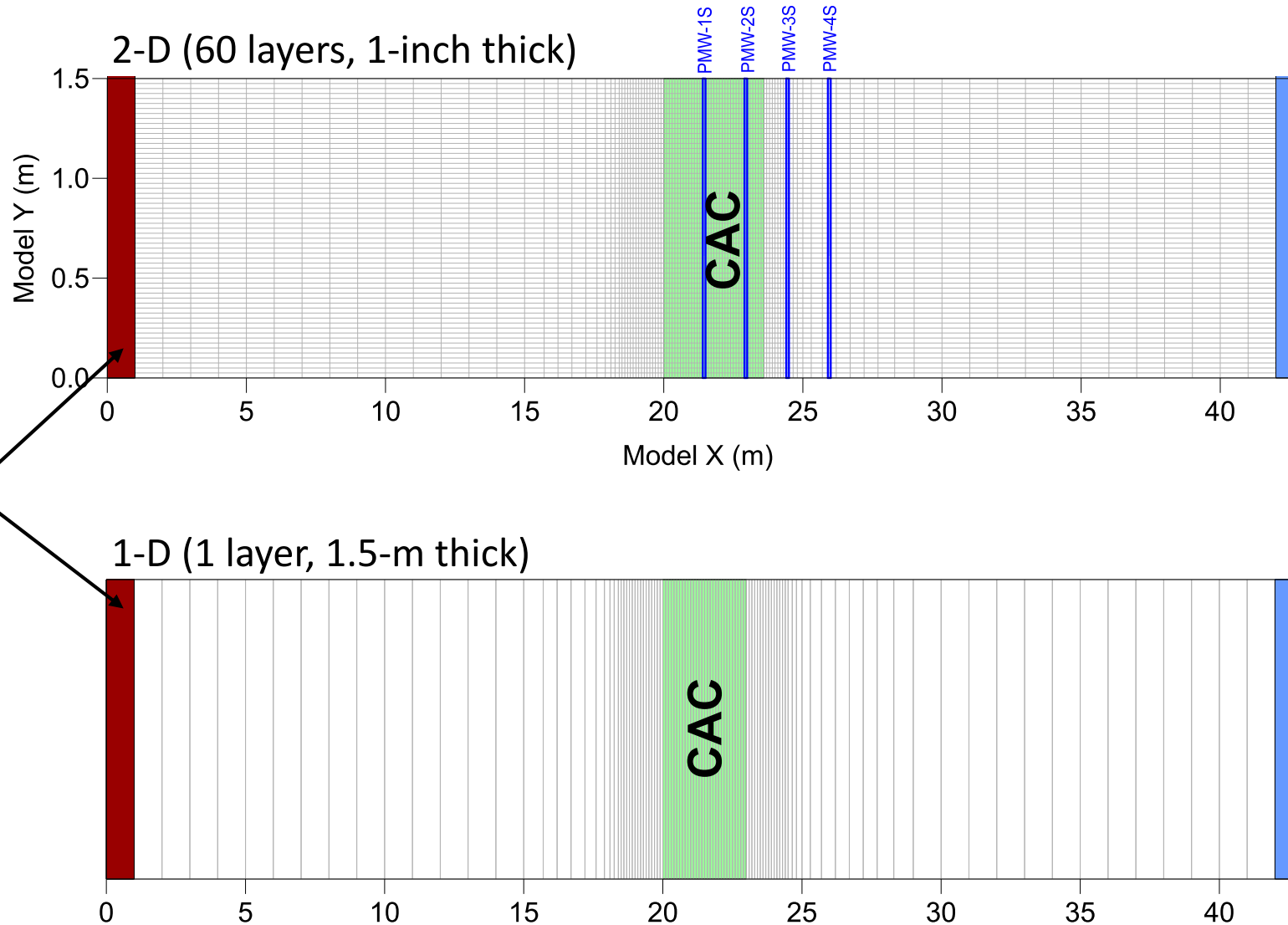
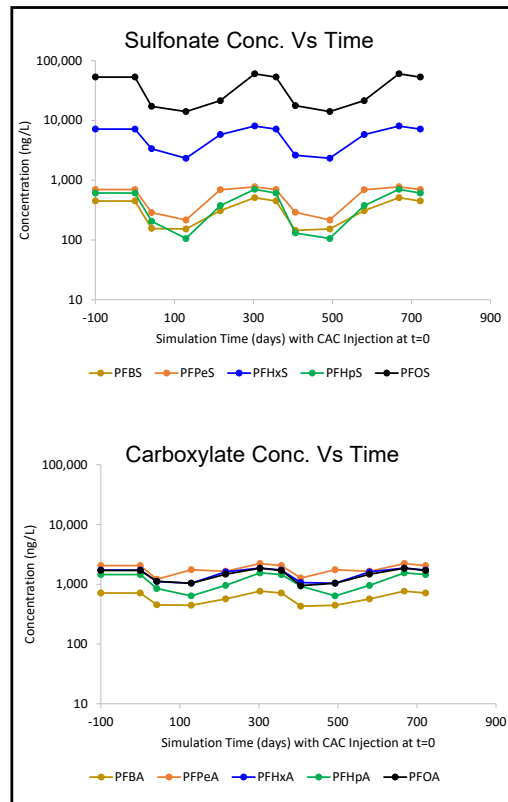
# Downgradient Wells Influenced by Water Table



Spikes in PFBS downgradient from PRB after 2-3 ft rise and fall in water table.



# Model Domain and Boundary Conditions



**Carey et al. (2015)**

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

$\alpha_z = 0.3 \text{ m}$

Note: K in m/s

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

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

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

$f_{oc} = 0.2\%$

$\theta_e = 0.25$

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

$\alpha_x = 0.03 \text{ m}$

# 10 PFAS Solutes Modeled

Class	Solute	Koc (L/kg)	Retardation Coefficient	Maximum GW Conc. (ng/L)	EPA MCL (ng/L)	Exceedance Factor
Sulfonates	PFBS	80	2.0	510		
	PFPeS	105	2.3	777		
	PFHxS	130	2.7	9,100	10	910
	PFHpS	265	4.4	704		
	PFOS	920	12.8	60,300	4	15,075
Carboxylates	PFBA	40	1.5	768		
	PFPeA	50	1.6	2,220		
	PFHxA	80	2.0	1,860		
	PFHpA	100	2.3	1,550		
	PFOA	120	2.5	2,040	4	510

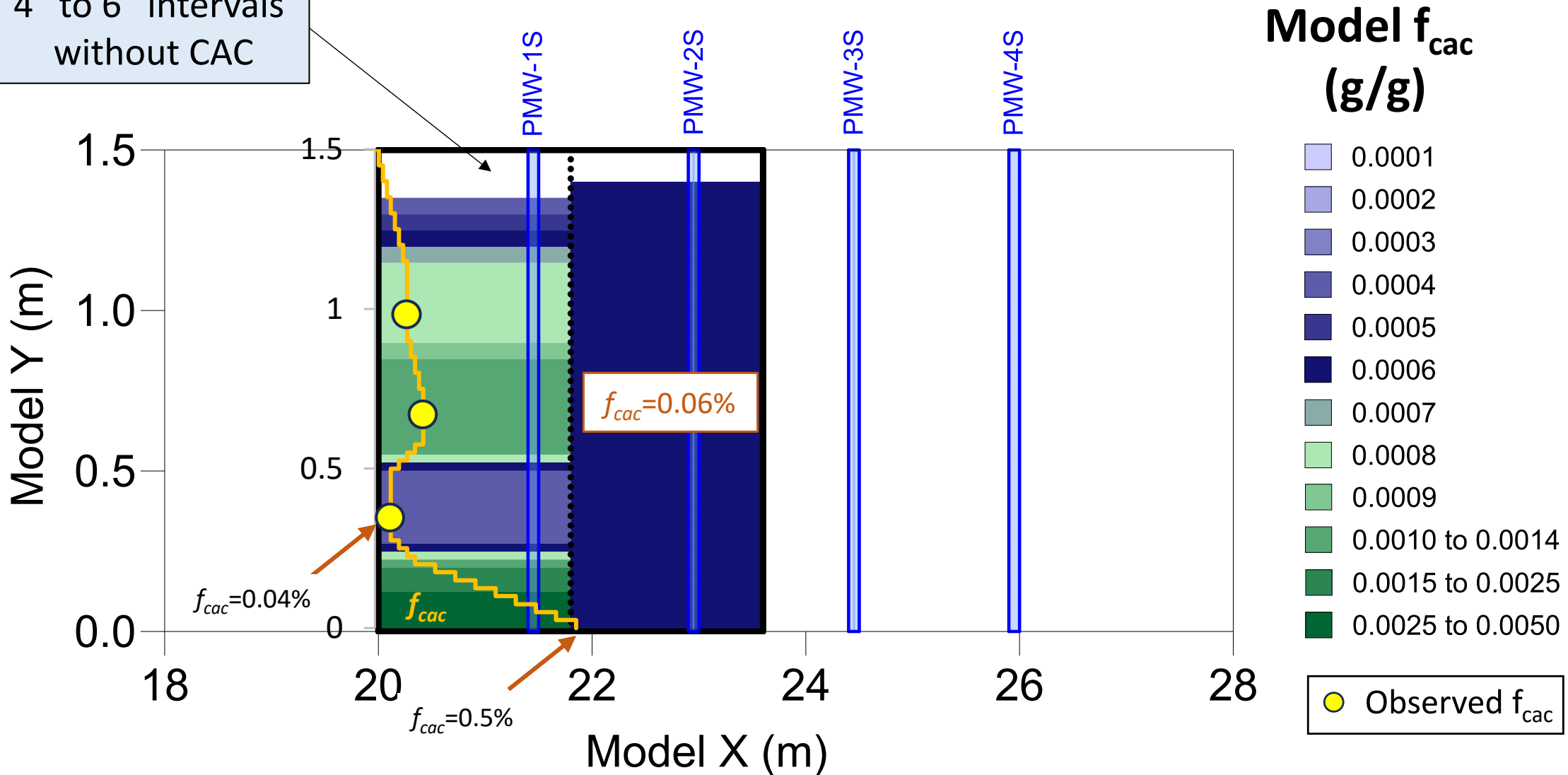
Notes:

1. Koc is based on averages calculated with McGuire et al. (2014) dataset – see Carey et al. (2019) SI.
2. PFNA maximum concentration in groundwater was 552 ng/L, with an exceedance factor of 55.

# Modeled CAC Distribution

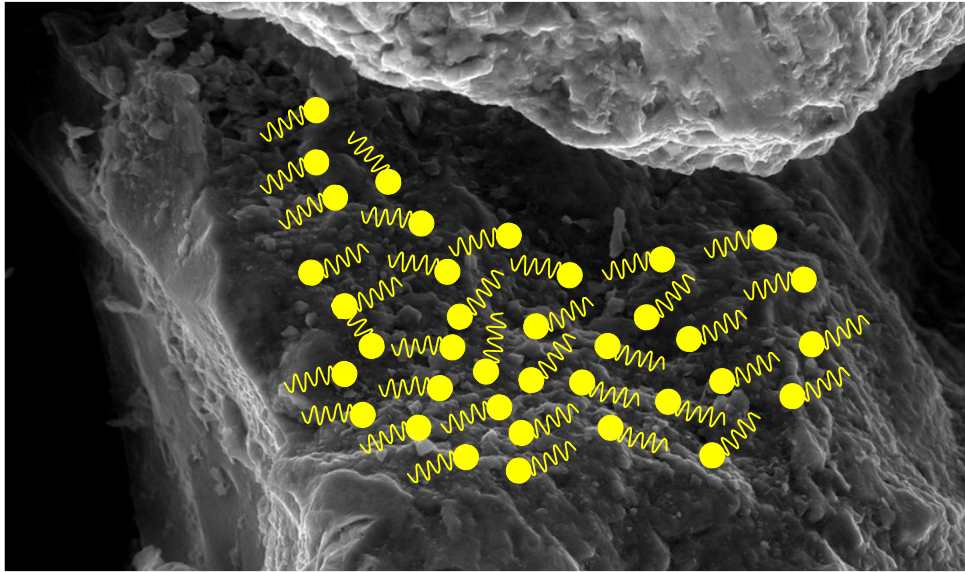
Target fraction of CAC ( $f_{cac}$ ): 0.2% (CAC = 2,000 mg/kg)

4" to 6" intervals  
without CAC

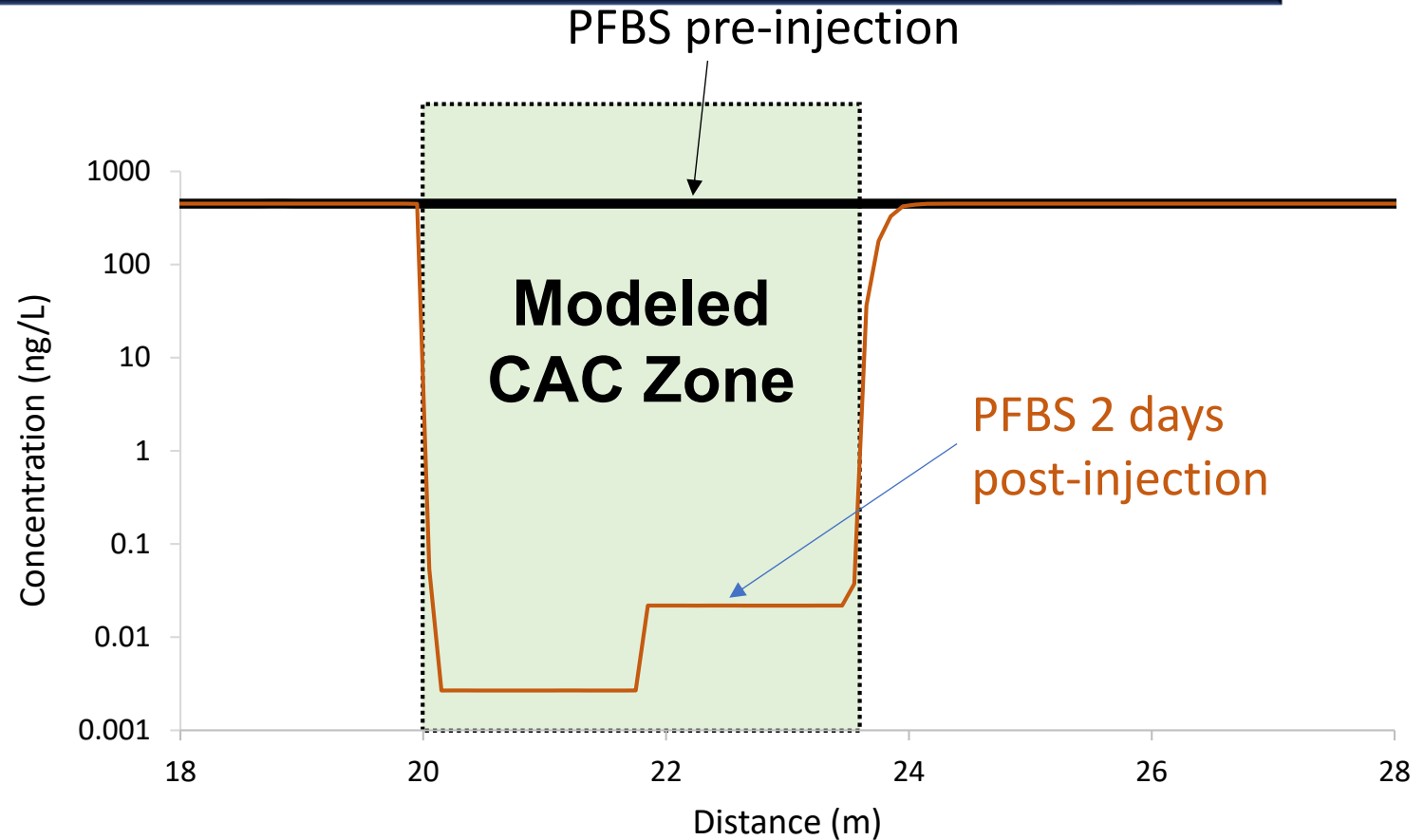
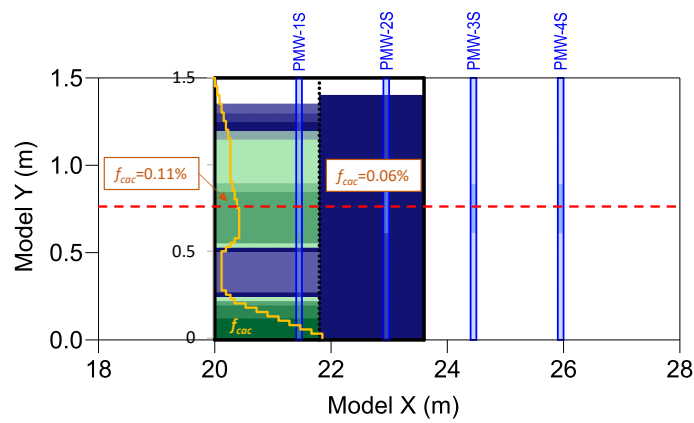


# Modeling CAC Injection: PFAS Concentration

PFAS adsorbed to CAC particles



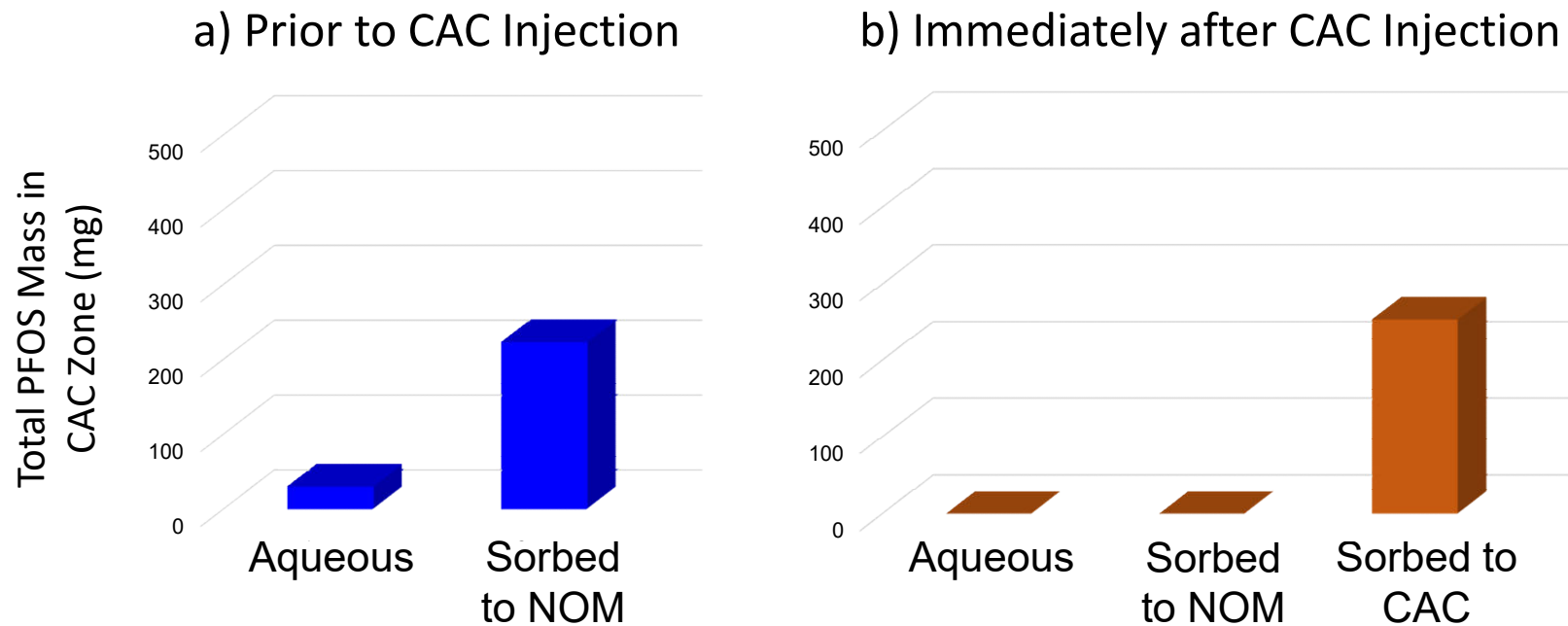
Not to scale – Conceptual illustration only



1. Model first simulates pre-injection plume (stable)
2. CAC Injected in PRB
3. PFAS post-injection Conc. calculated by model (re-equilibration)

# Modeling CAC Injection: PFAS Re-equilibration

## ISR-MT3DMS Mass Balance: CAC Injection



ISR-MT3DMS calculates post-injection PFAS concentrations immediately after CAC injection, based on mass conservation.

### Post-injection C depends on:

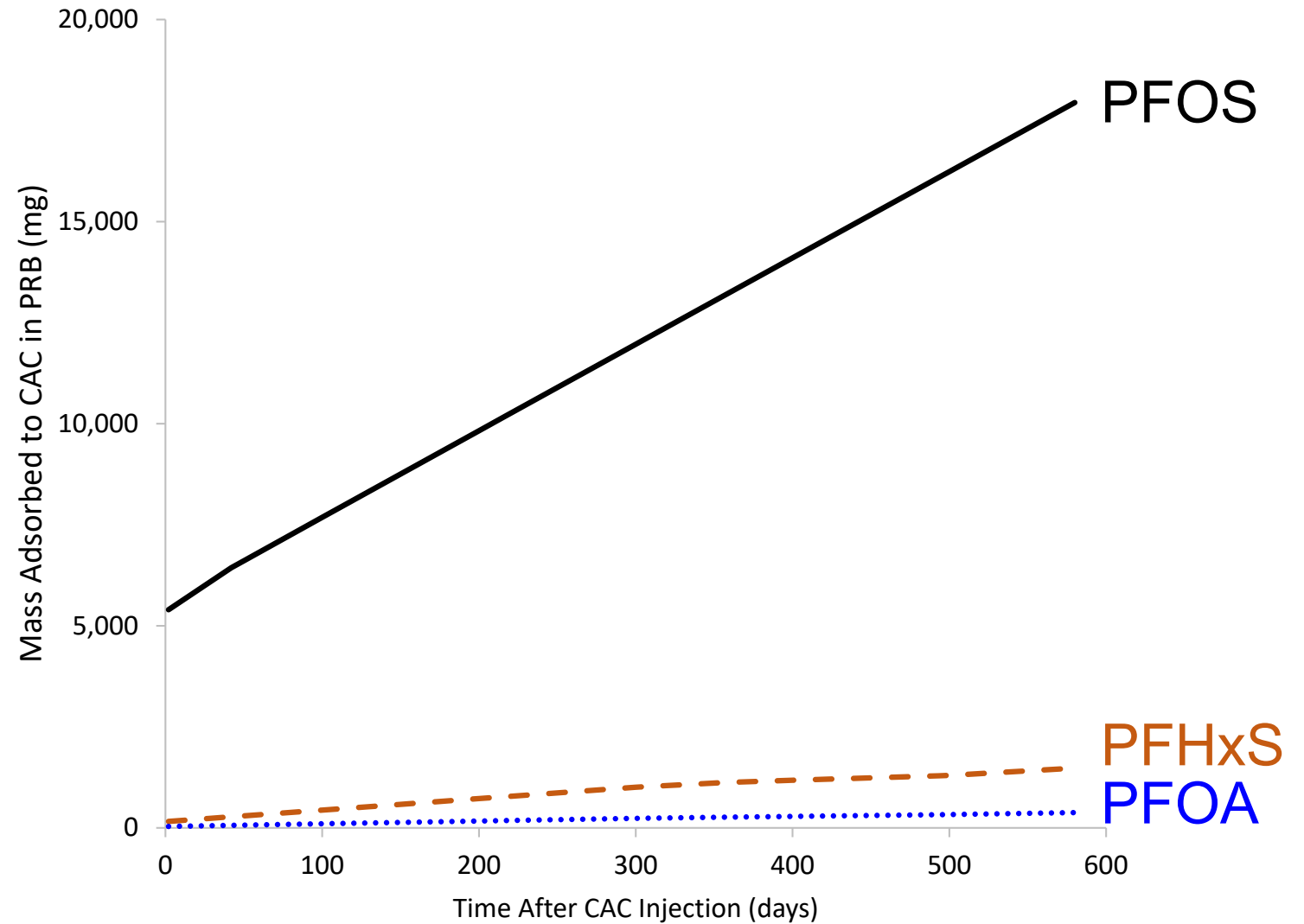
- PFAS adsorption isotherms
- $f_{cac}$
- Pre-injection adsorbed C
  - $f_{oc}, C_w, K_{oc}$

**Design Tip:** Check that calculated PFAS post-injection concentrations are below MCLs.



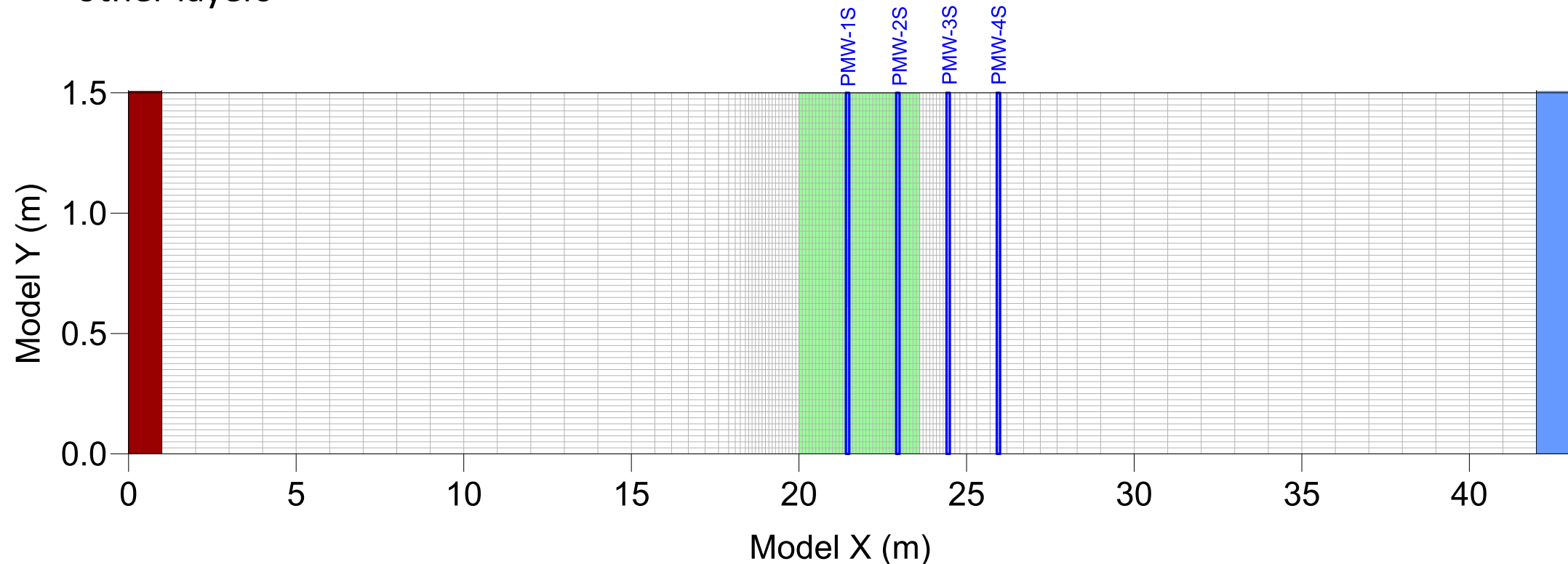
# Model Mass Balance

Solute	Mass Adsorbed to CAC 2 Days Post-Injection (mg)
PFBS	7
PFPeS	12
PFHxS	142
PFHpS	20
PFOS	5,058
PFBA	8
PFPeA	25
PFHxA	26
PFHpA	24
PFOA	32

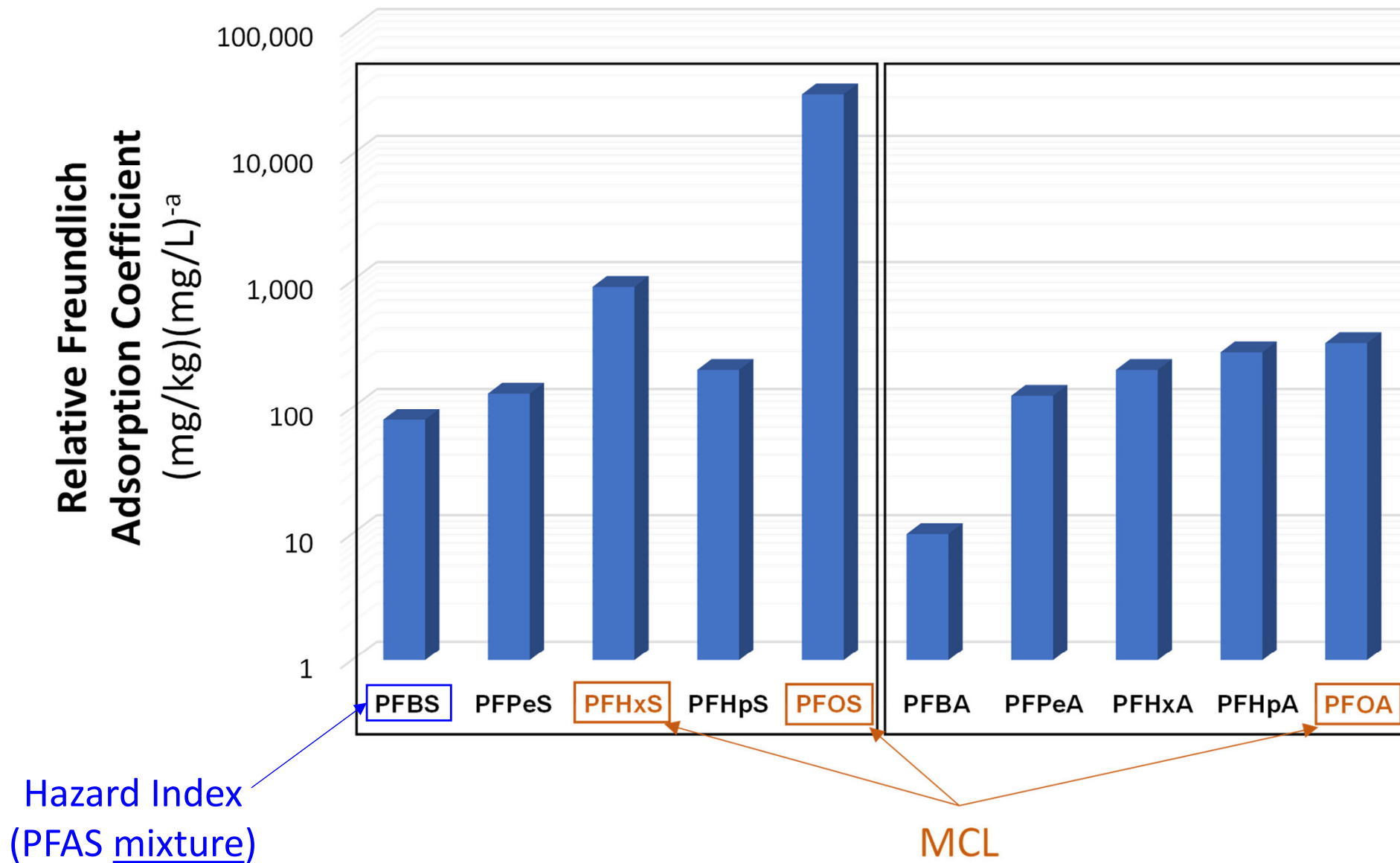


# Multi-Layer Monitoring Wells in ISR-MT3DMS

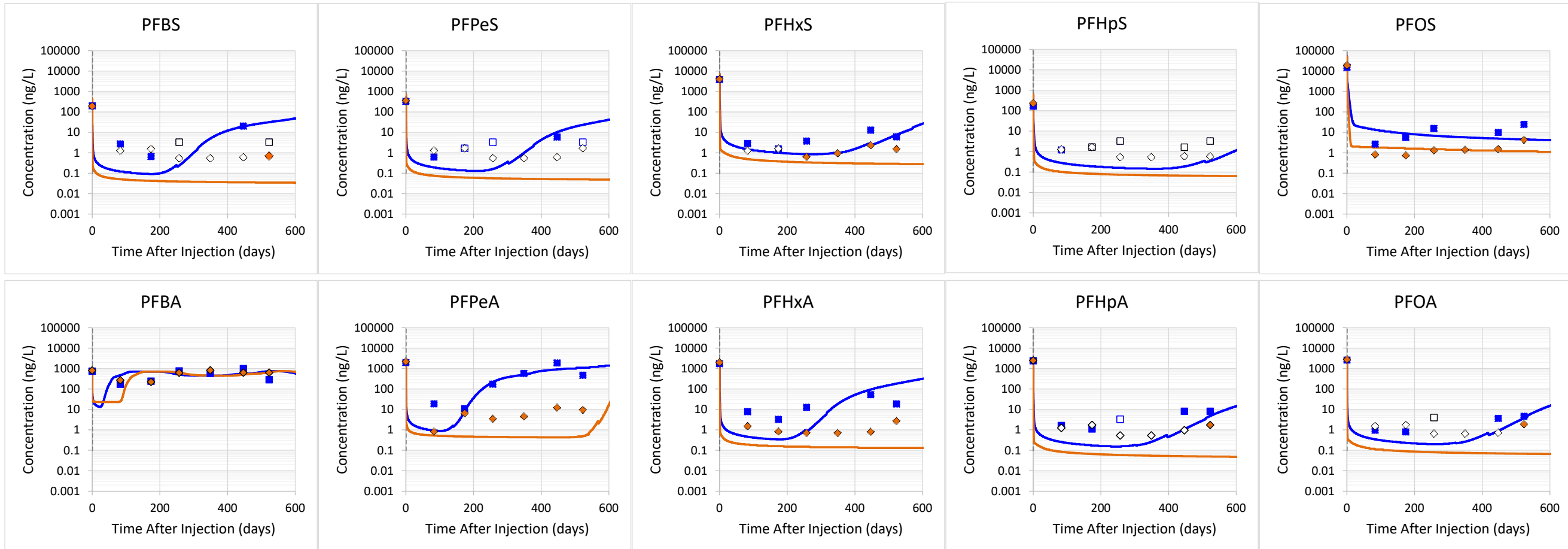
- Monitoring wells screened over 60 layers
- ISR-MT3DMS calculates transmissivity-weighted average concentration over all screened model layers
- Breakthrough in some layers with lower  $f_{ac}$  will be diluted in the well with clean water from other layers



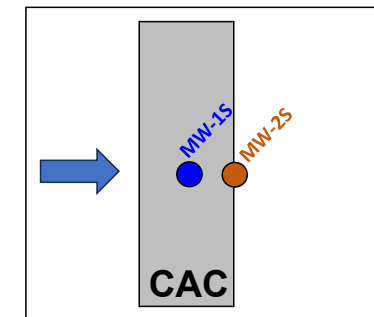
# Eastern US Site: Calibrated PFAS Adsorption Isotherms



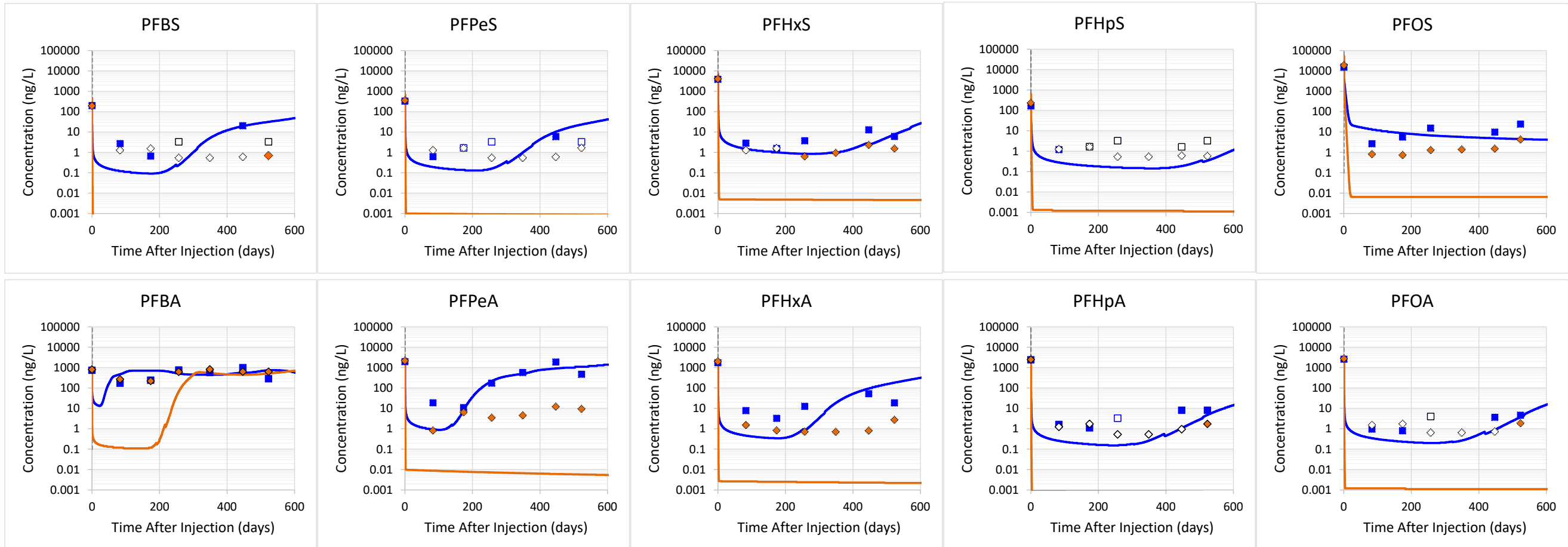
# Modeled PFAS Trends at In-Barrier Monitoring Wells



Symbols: Observed (white fill: ND, color fill: detected)  
 Lines: Modeled  
 Blue: PMW-1S (x=5 ft into PRB)  
 Orange: PMW-2S (x=10 ft into PRB)



# Modeling CAC Injection: Right $f_{cac}$ zone = 0.4%

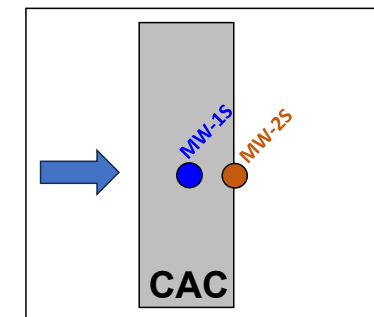


Symbols: Observed (white fill: ND, color fill: detected)

Lines: Modeled

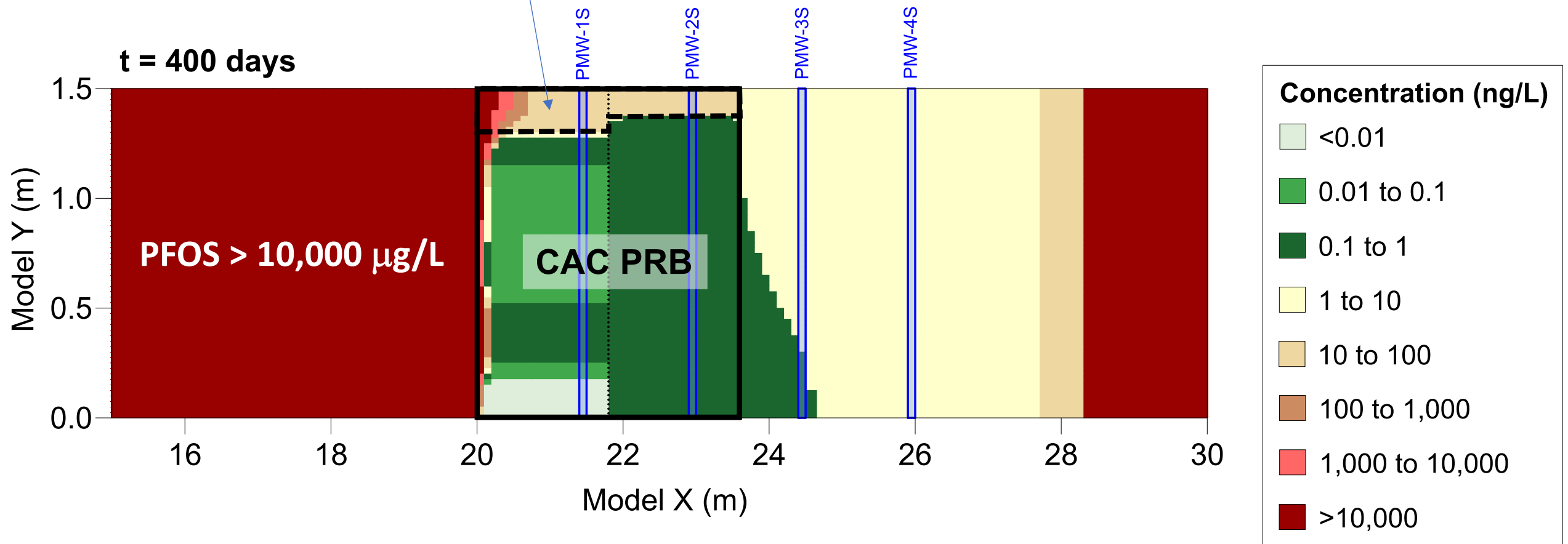
Blue: PMW-1S (x=5 ft into PRB)

Orange: PMW-2S (x=10 ft into PRB)



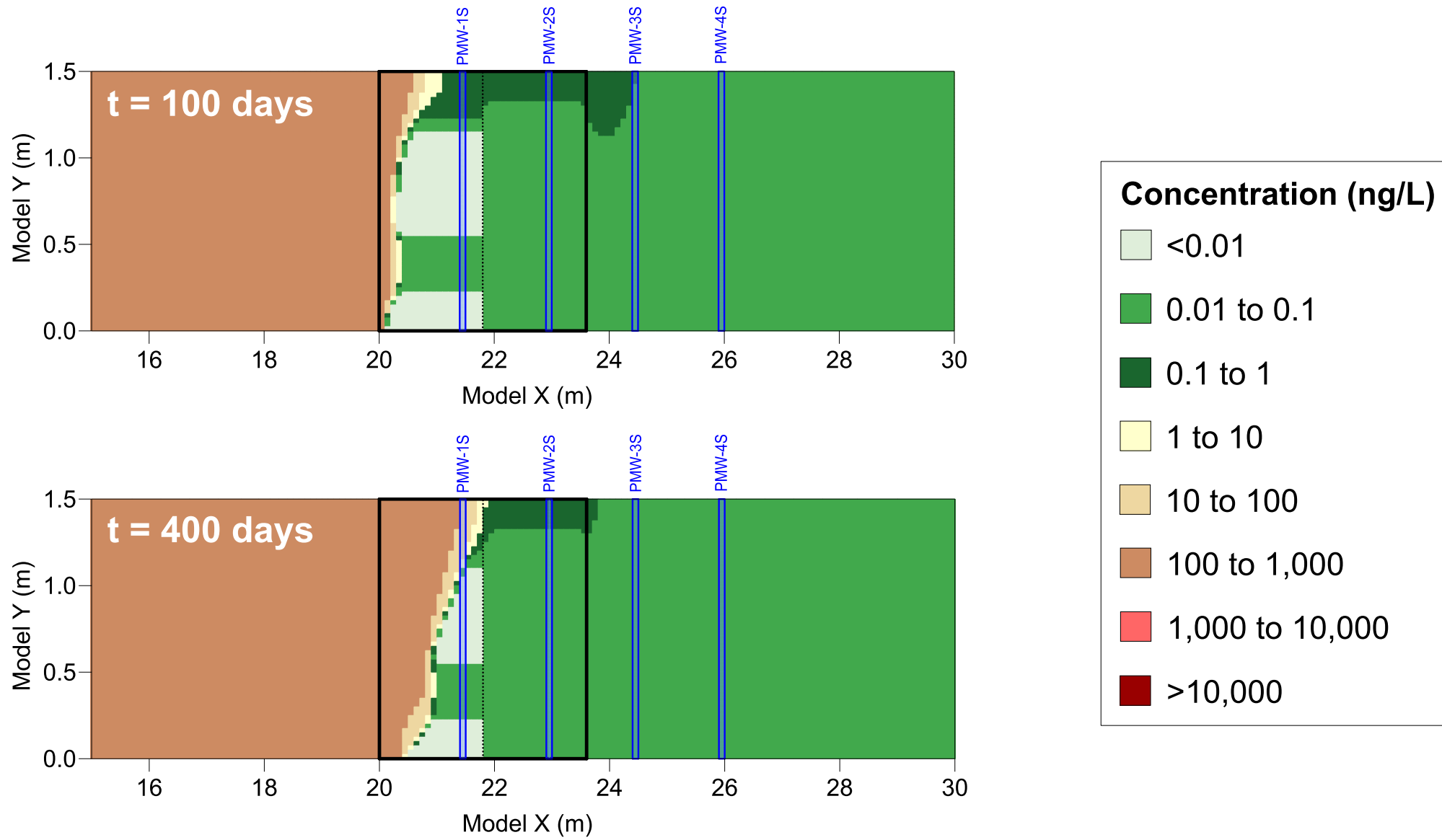
# Modeled PFOS Concentrations in Cross-Section

CAC not present

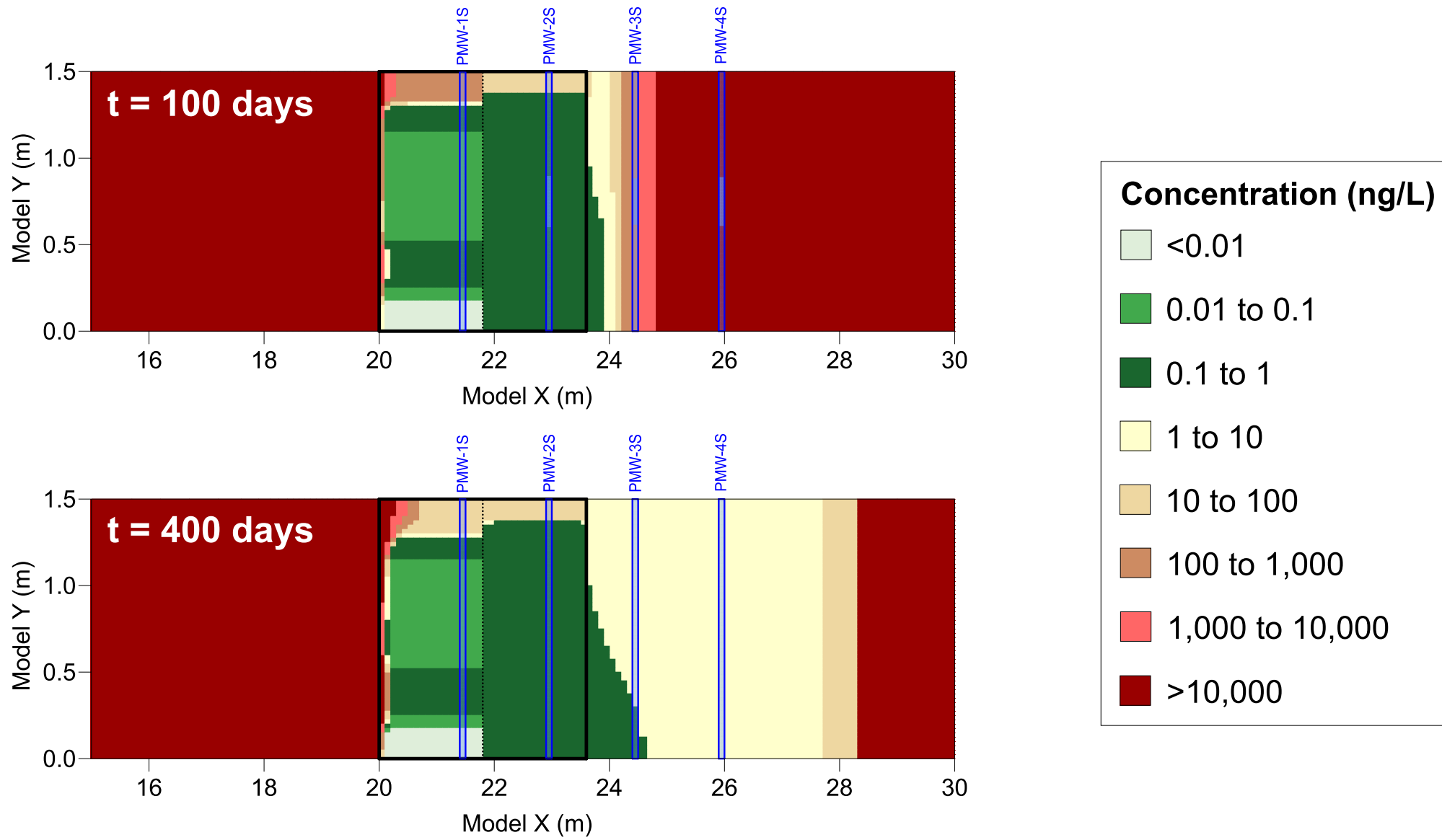


*ISR-MT3DMS calculates the transmissivity-weighted average of PFAS concentrations in multi-layer well screens.*

# Modeled PFBS Concentrations in Cross-Section



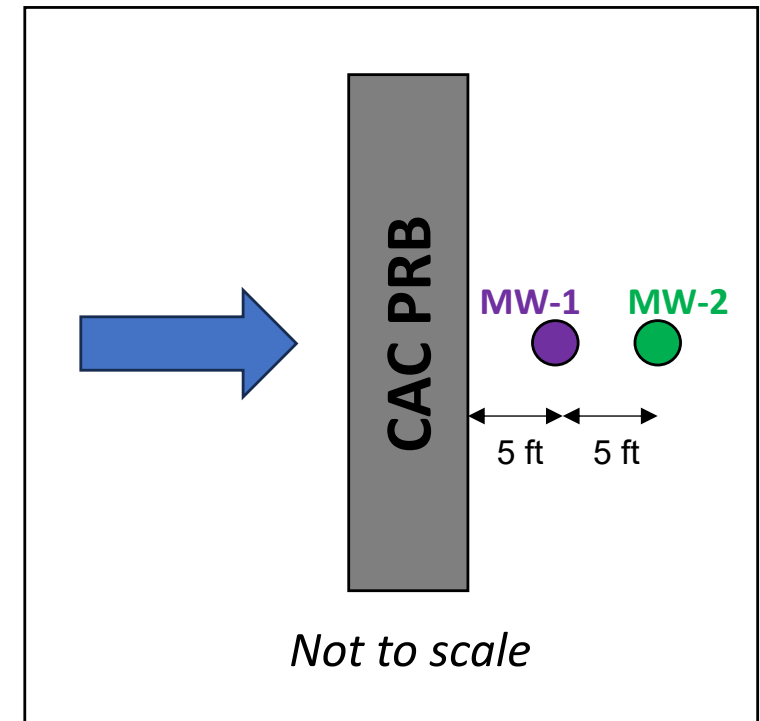
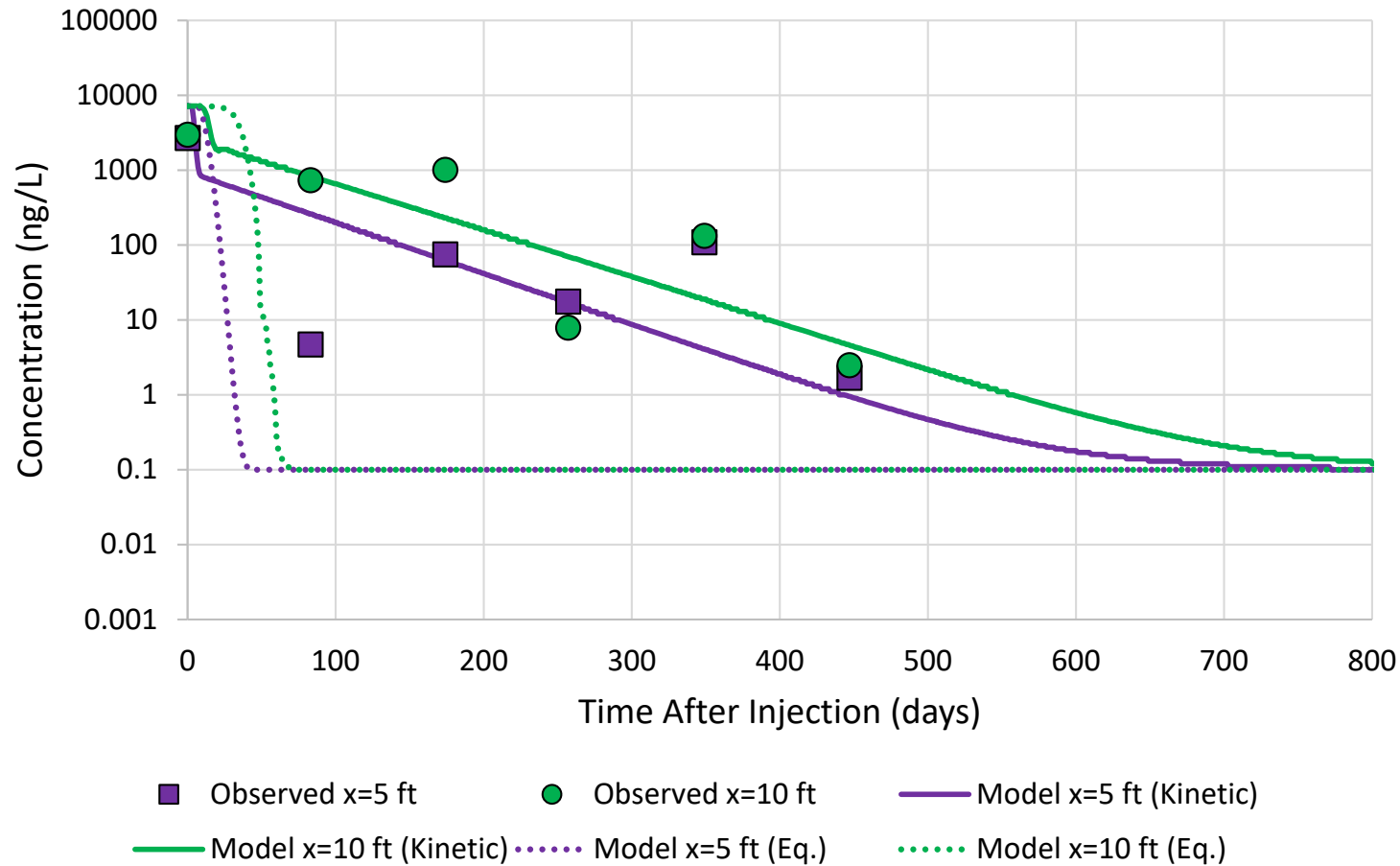
# Modeled PFOS Concentrations in Cross-Section





# East US Site: PFAS Desorption Downgradient of PRB

PFHxS: Kinetic vs Equilibrium Desorption



$$v = 200 \text{ ft/y}$$

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

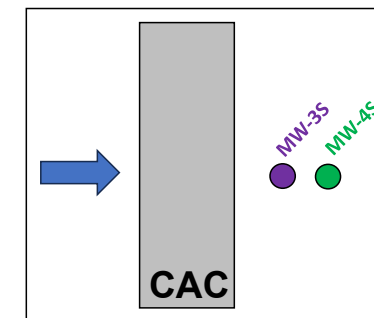
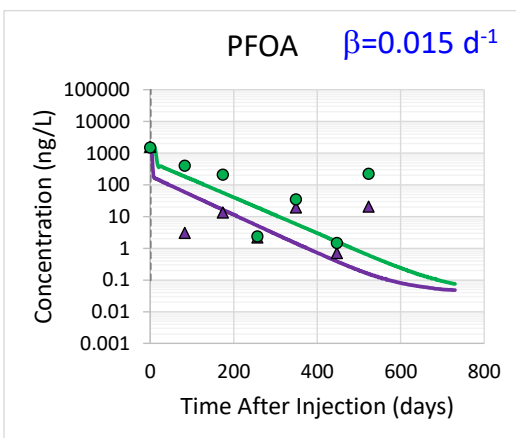
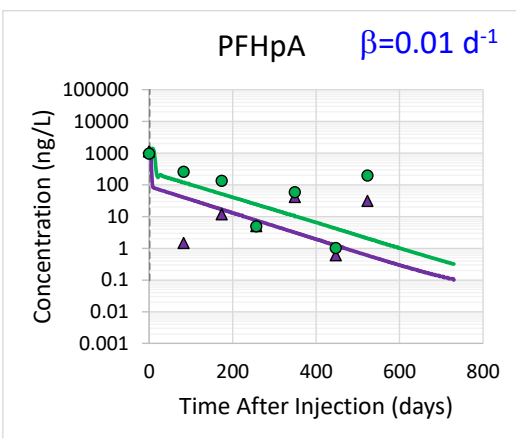
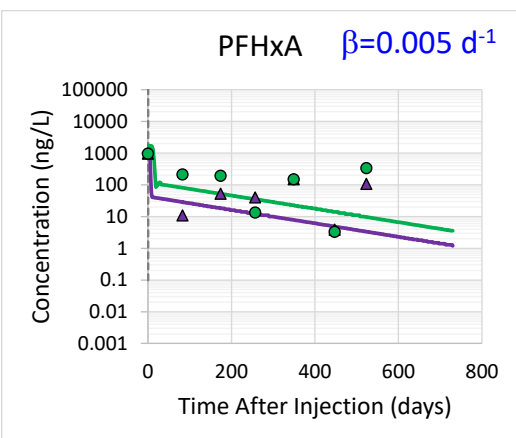
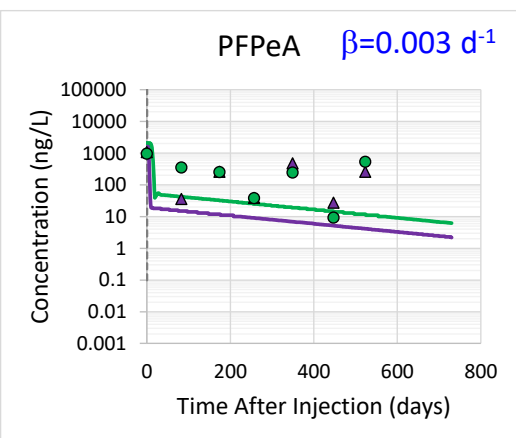
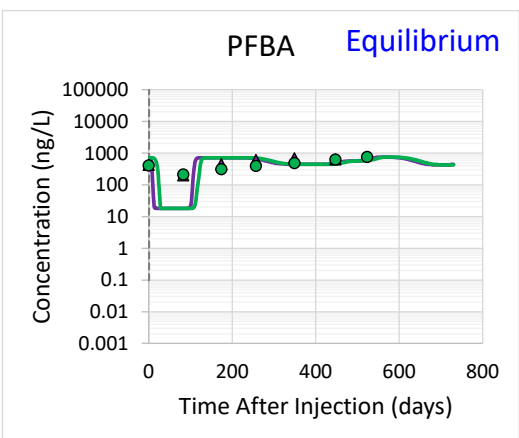
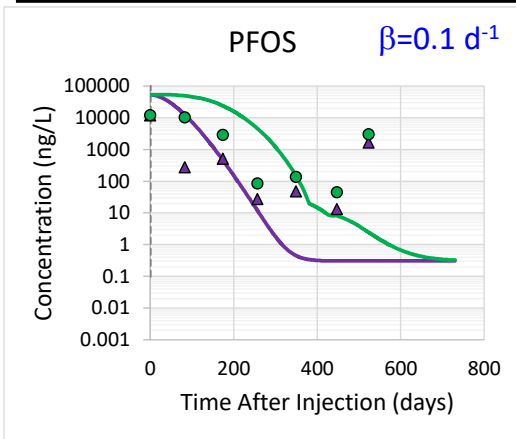
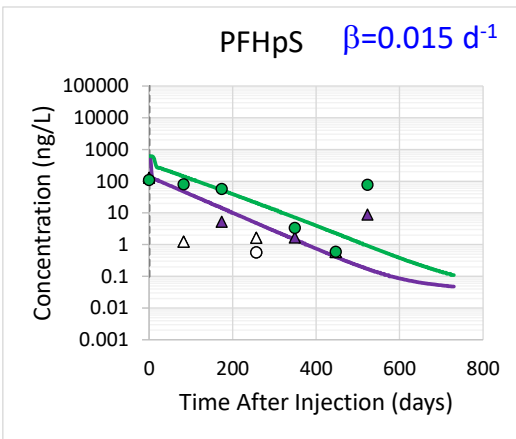
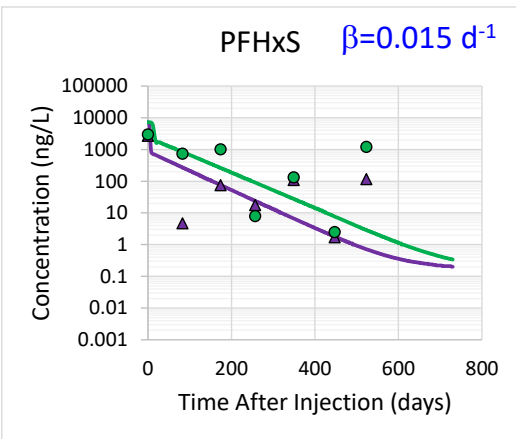
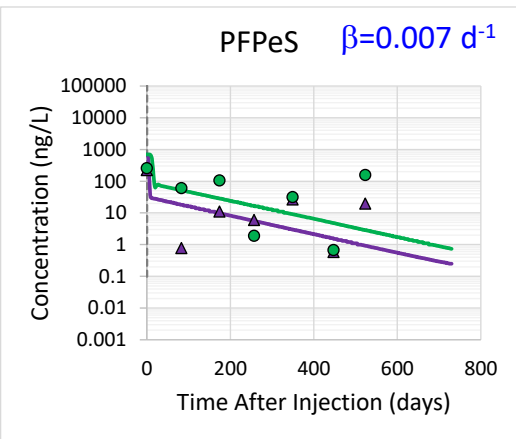
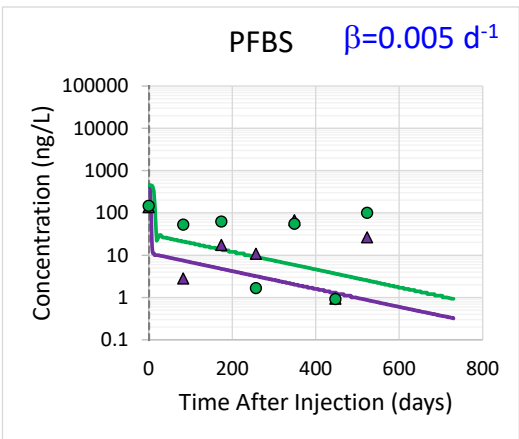
$$C_{max} = 7 \mu\text{g/L}$$

5 ft

# Kinetic Desorption Using ISR-MT3DMS

$$\rho_b \frac{dS}{dt} = \rho_b \beta (S_e - S)$$

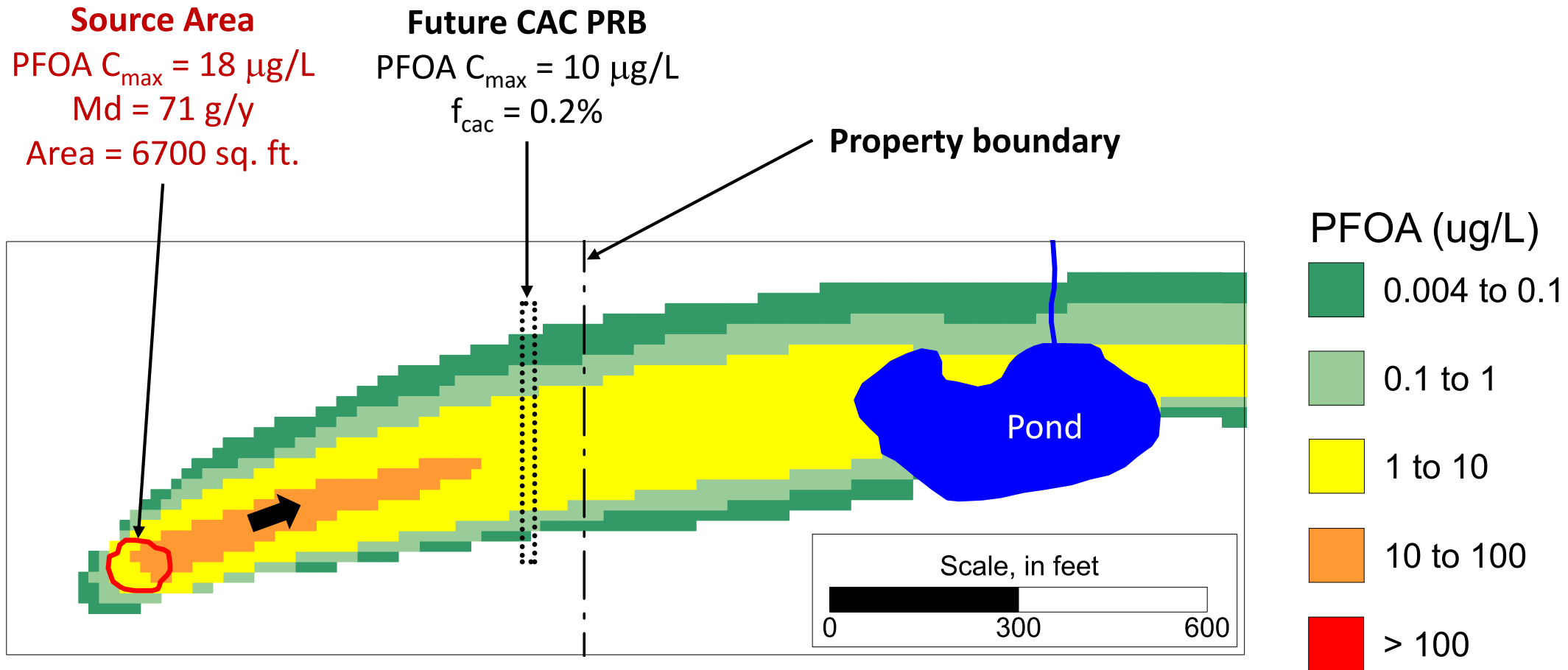
$\beta$  = first-order rate ( $d^{-1}$ )



# Long-Term Remediation Strategies

## Section 3

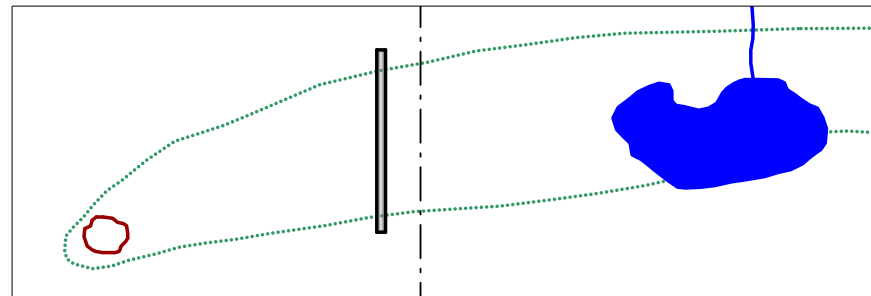
# Integrated Remedy Analysis



- Velocity = 200 ft/year,  $f_{\text{oc}} = 0.1\%$
- 50% source mass discharge from vadose zone

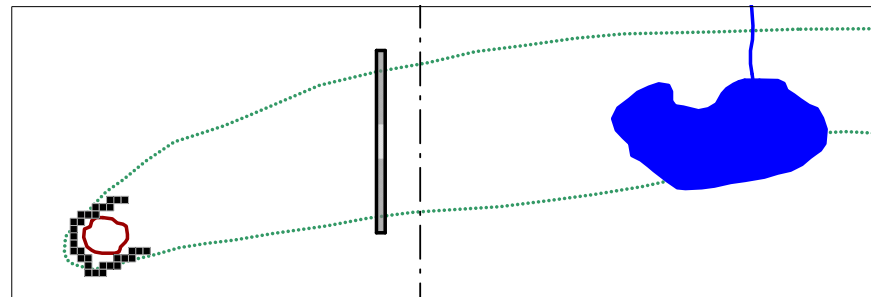
# Simulated Remedial Alternatives

Alternative No. 1  
**CAC PRB**



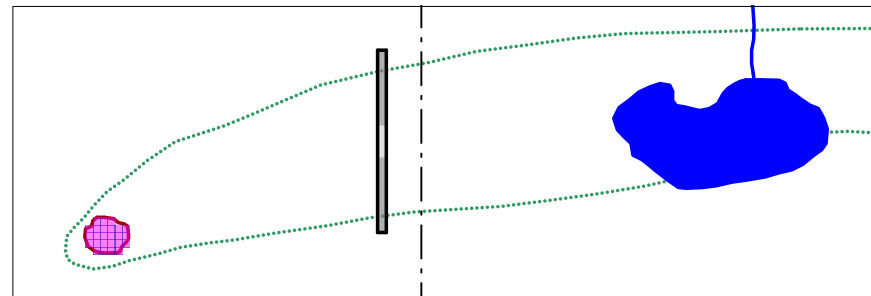
Pre-remediation plume outline

Alternative No. 2  
**CAC PRB + Partial Wall**

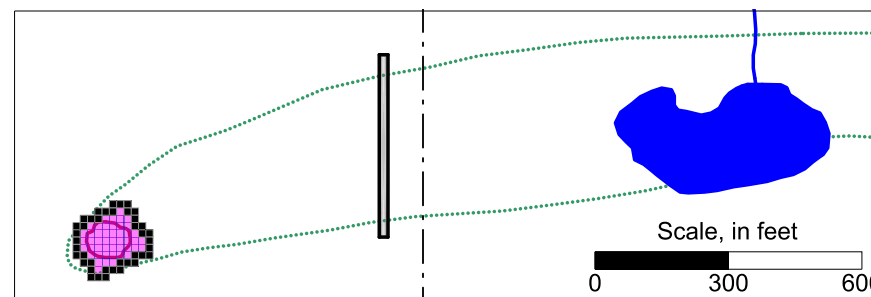


Source mass discharge declines with half-life of 30 years (Carey et al., 2019)

Alternative No. 4  
**CAC PRB + Cover**



Alternative No. 4  
**CAC PRB + Full Wall + Cover**

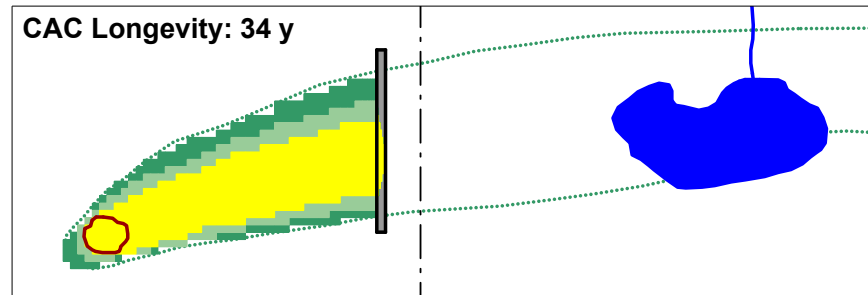


# Modeled PFOA Plumes 30 years Post-Injection

## Alternative No. 1

### **CAC PRB**

Source Md = 36 g/y

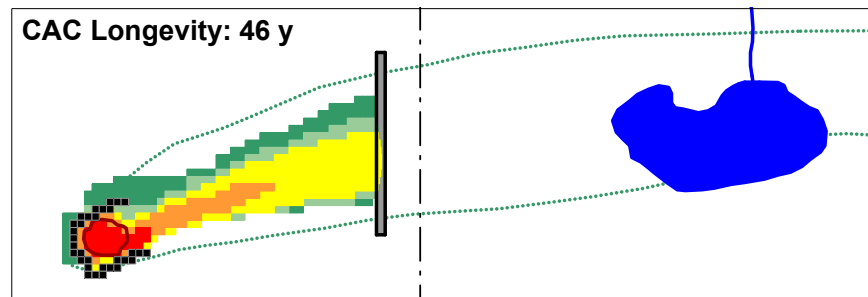


Pre-remediation plume outline

## Alternative No. 2

### **CAC PRB + Partial Wall**

Source Md = 35 g/y



PFOA (ug/L)

0.004 to 0.1

0.1 to 1

1 to 10

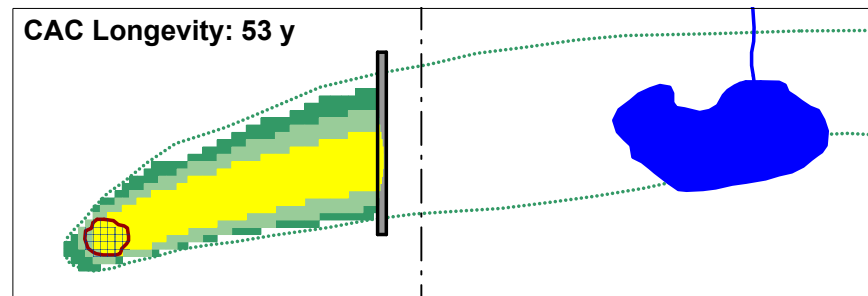
10 to 100

> 100

## Alternative No. 4

### **CAC PRB + Cover**

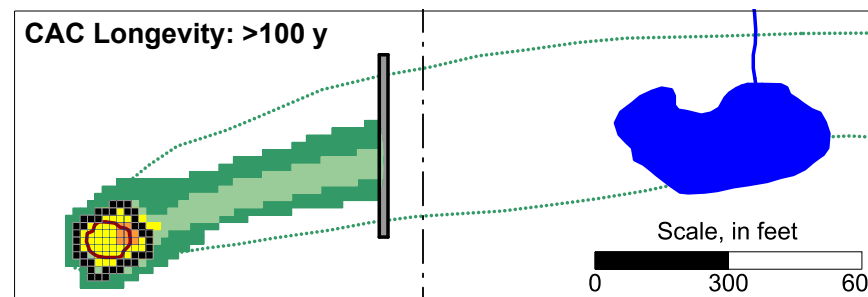
Source Md = 18 g/y



## Alternative No. 4

### **CAC PRB + Full Wall + Cover**

Source Md < 1



*CAC: colloidal activated carbon*  
*PRB: permeable reactive barrier*  
*Md: Mass discharge*

# New EPA PFAS MCLs (April 2024)

PFAS  
of Concern

EPA Final MCL (µg/L)				
PFOS	PFOA	PFHxS	PFNA	HFPO-DA
0.004	0.004	0.010	0.010	0.010

## Hazard Index (HI) MCL for PFAS Mixtures

$$\text{Hazard Index (HI) MCL} = \left( \frac{\text{PFNA}}{0.01 \mu\text{g/L}} \right) + \left( \frac{\text{PFHxS}}{0.01 \mu\text{g/L}} \right) + \left( \frac{\text{PFBS}}{2 \mu\text{g/L}} \right) + \left( \frac{\text{HFPO - DA}}{0.01 \mu\text{g/L}} \right) = 1$$

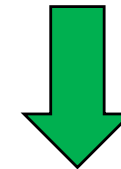
- Mixtures of **two or more** of these PFAS are not to exceed HI of 1
- PFHxS and PFNA adsorb well in CAC PRBs
- PFBS is not of concern on its own
- Establishing site background will be critical

# CAC Long-Term Remediation Strategies

## Downgradient PRBs

- Greater longevity
- Faster goal attainment at downgradient receptors

**Short-Term Goal:** PFAS mass discharge



**Longer Term Goal:** Cleanup criteria attainment

- Attenuation between compliance bdy and receptor?



# 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 10-20 years, we may have technologies to treat PFAS-laden CAC in-situ (e.g., thermal)

**SERDP ESTCP**

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**savoron**  
smoldering solutions  
savoronsolutions.com

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

ER22-7470

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

**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.

**PRODUCTS**  
Webinar  
Advances in PFAS Destructive Technologies  
5/2/2024

Conceptual Diagram of In Situ Treatment of PFAS

The diagram illustrates the process of in-situ treatment of PFAS. It shows a cross-section of the ground with various layers and components. On the surface, there is a yellow excavator, a CAC/EVO unit, an Air Treatment unit, and a Savoron mobile unit. Below the surface, there is a layer of Clean Fill, a Vapor Extraction Point, and a Former Fine Tracking Pit. The ground is contaminated with PFAS, and the process involves Mixing Soil with GAC, Soil Mixed with GAC, and Mixed Soil being Smoldered. A Heater is used to smolder the soil, and a Well Screen is installed. The final state is Clean Soil with No GAC and No PFAS. Thermocouples are used to monitor the temperature of the soil.

# Questions?

**Grant R. Carey, Ph.D.**

Porewater Solutions  
[gcarey@porewater.com](mailto:gcarey@porewater.com)  
Phone: 613-890-2286



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