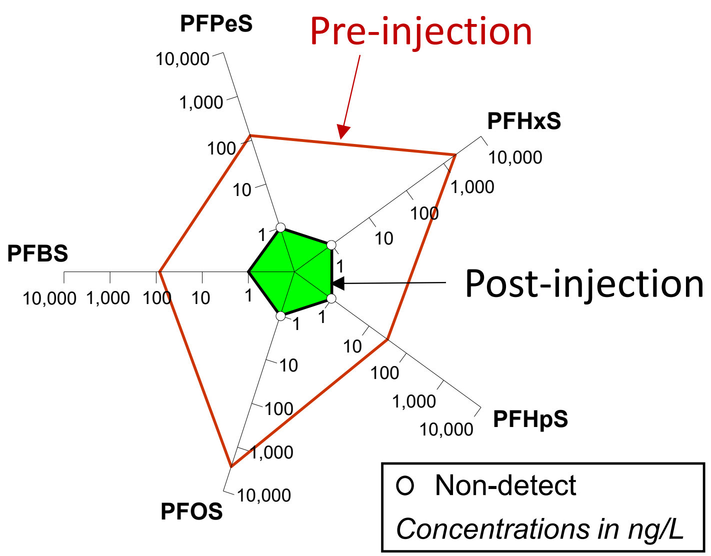
Case Studies and Long-Term Strategies for PFAS Remediation Using CAC



Presented By

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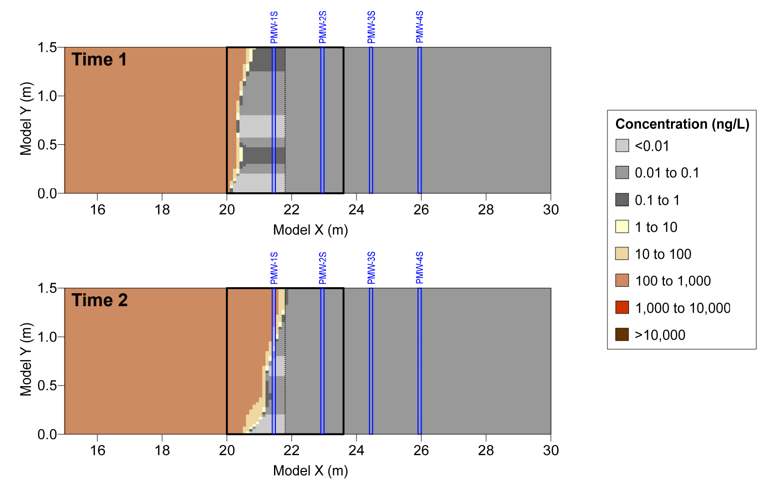


June 2 to 6, 2024

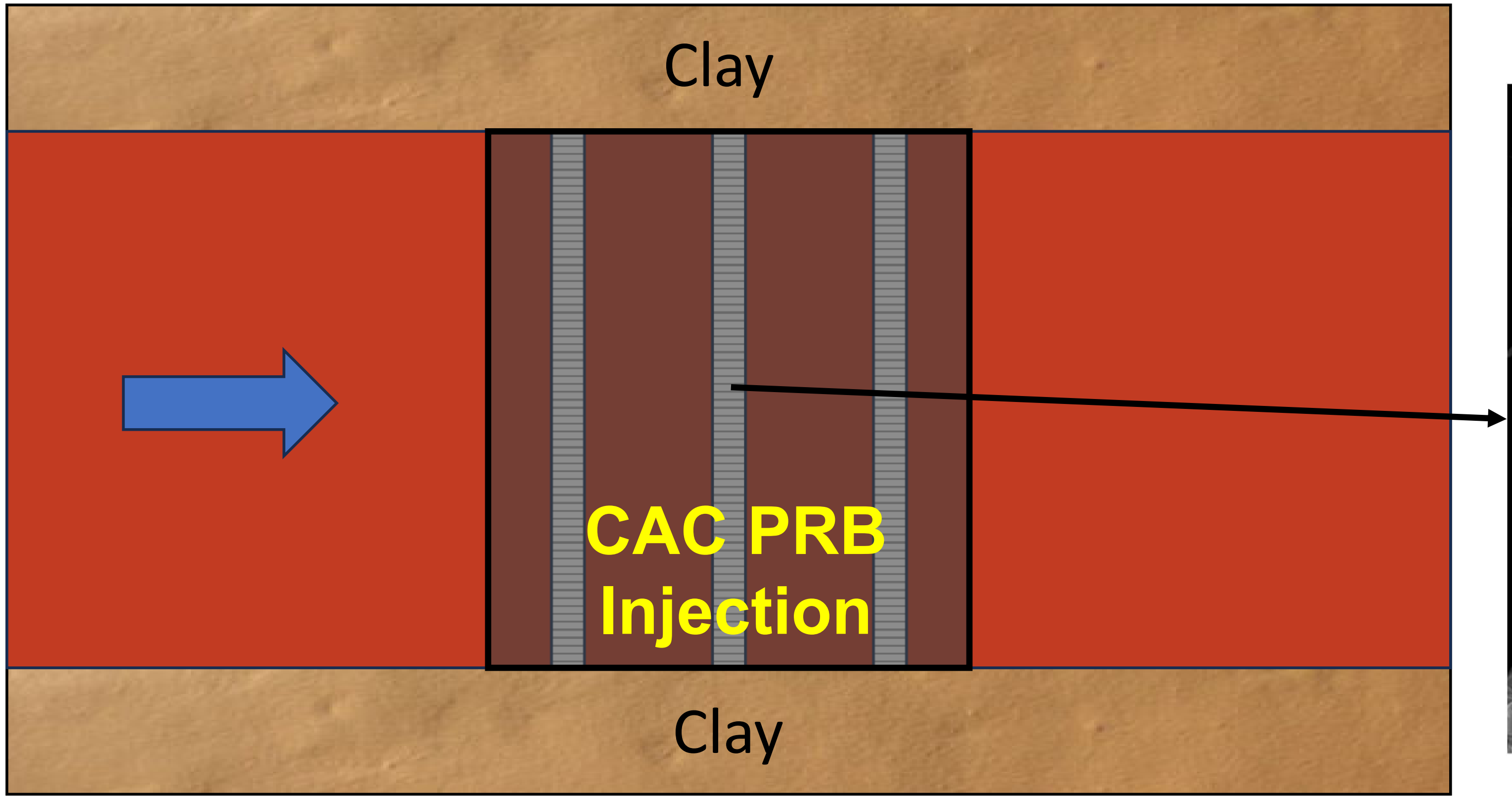
POREWATER SOLUTIONS

Expertise • Experience • Innovation

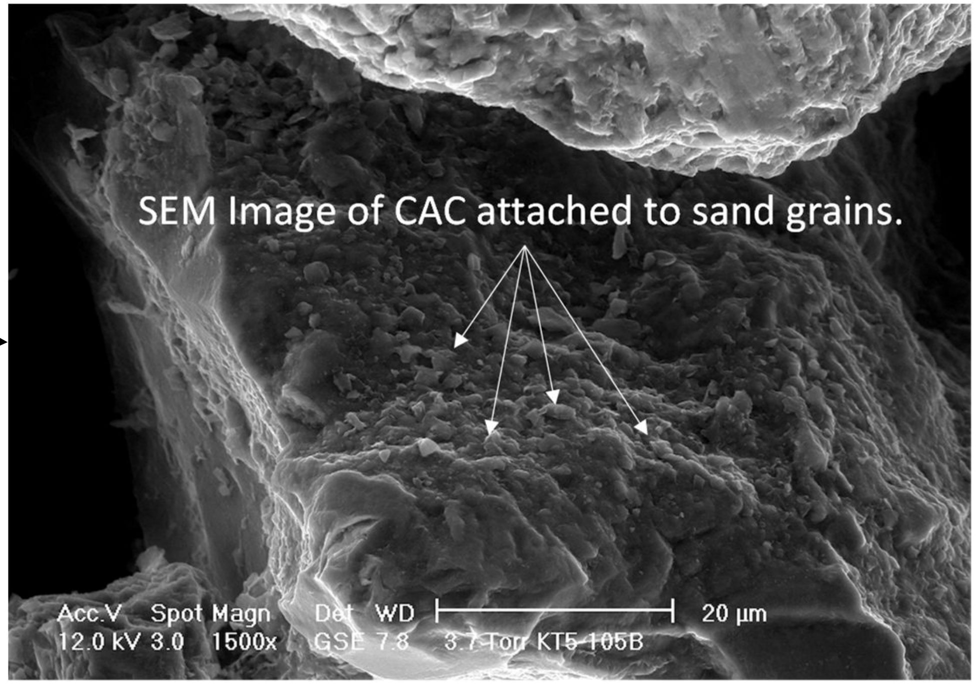
Remediating PFAS With Colloidal Activated Carbon (CAC)

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

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

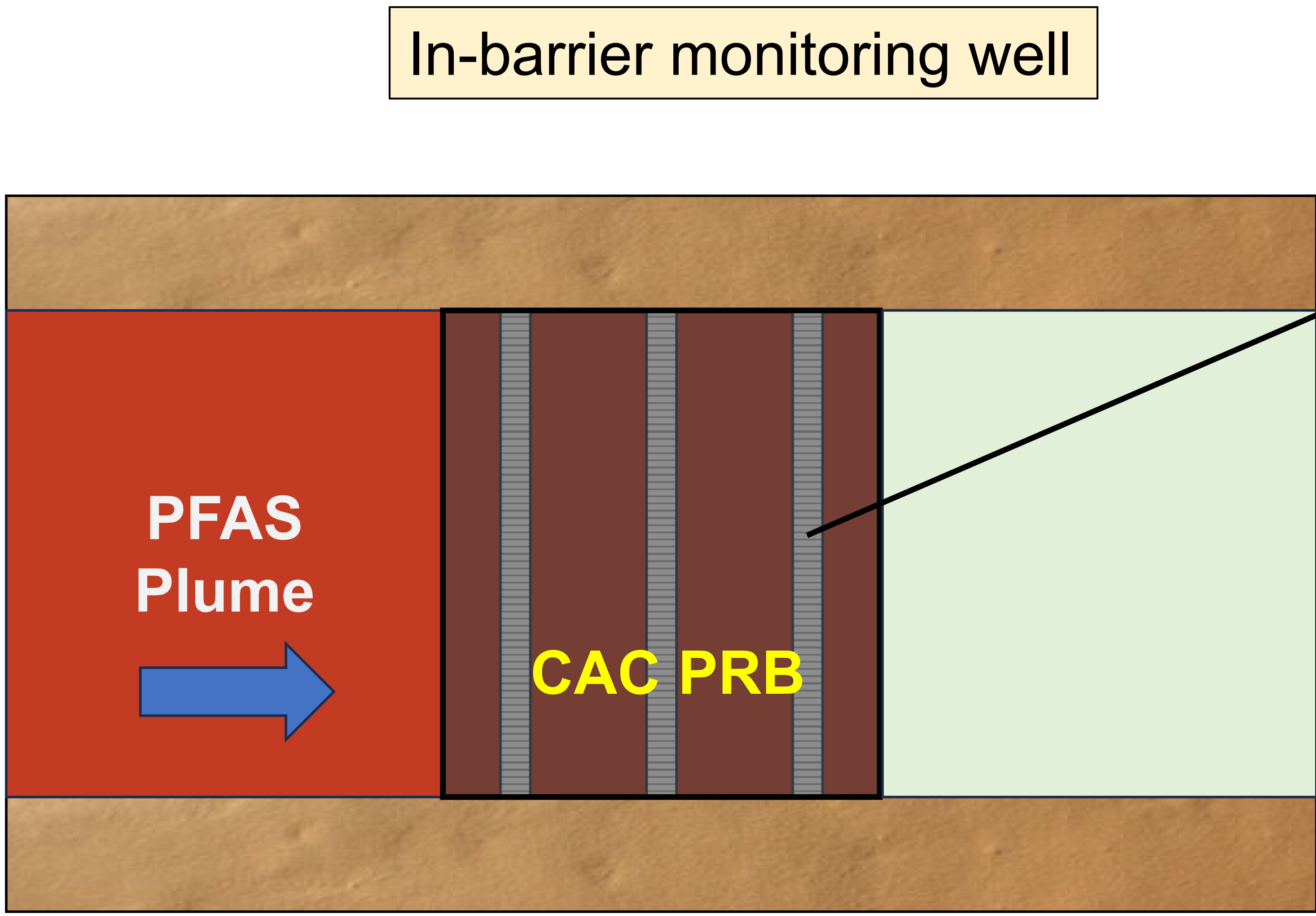


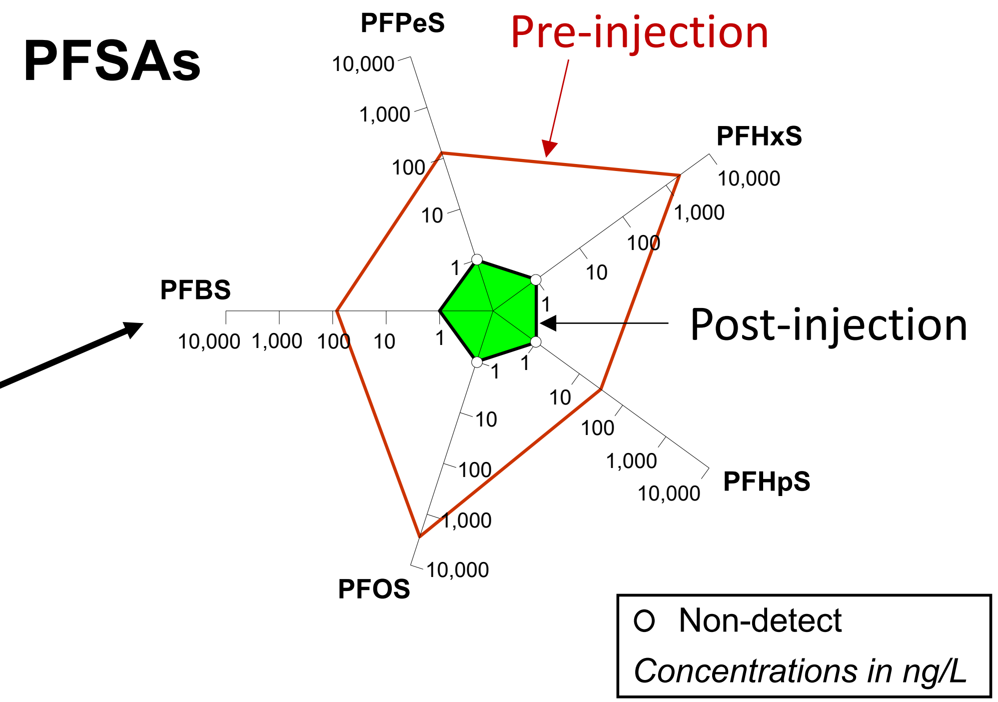
PRB: Permeable Reactive Barrier



Courtesy of REGENESIS

Remediating PFAS With Colloidal Activated Carbon (CAC)

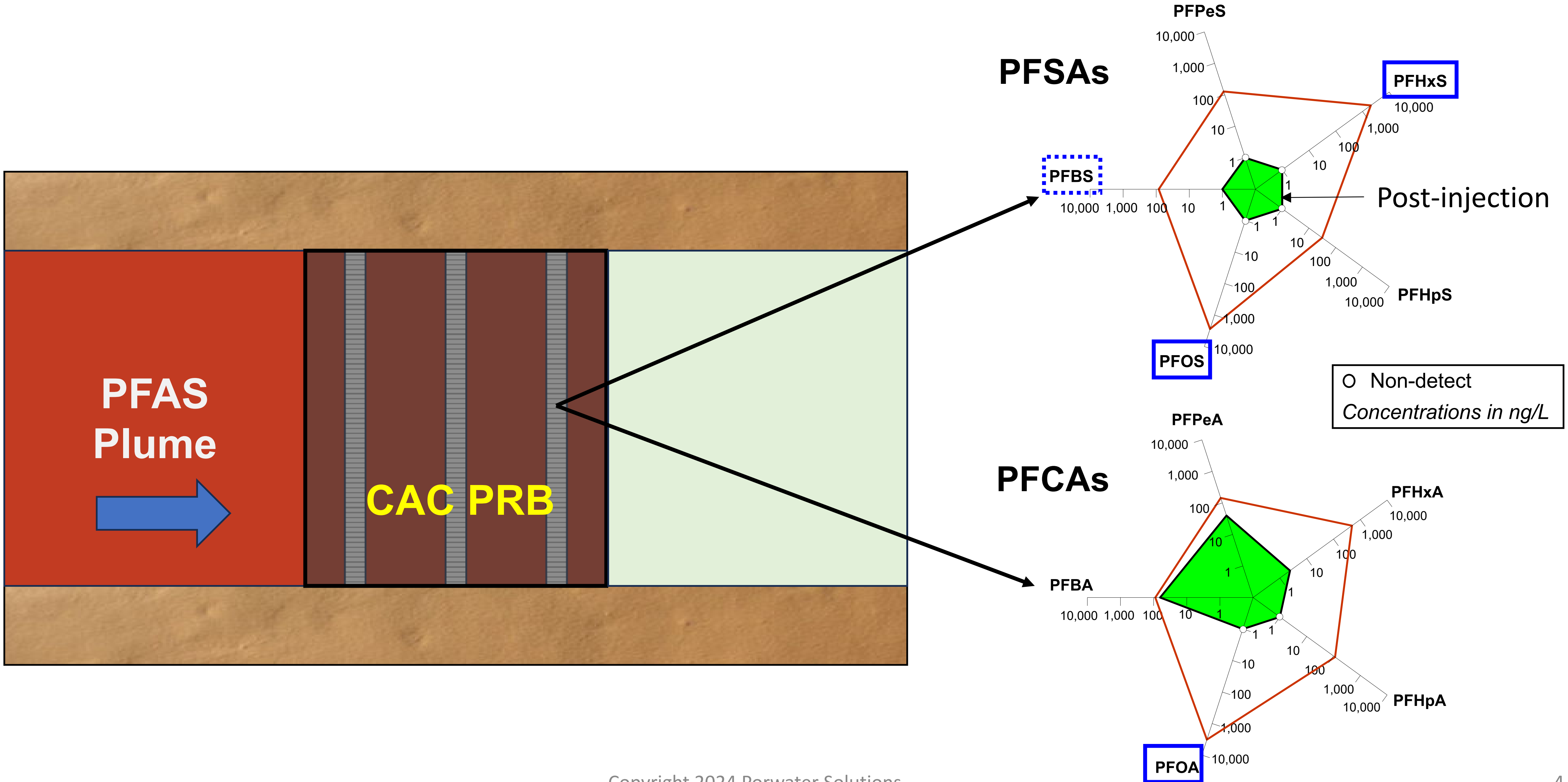




Note: Radial diagram illustrated using Visual CHEM which was developed by Porewater Solutions.

More info: www.porewater.com/PFAS.html

Remediating PFAS With Colloidal Activated Carbon (CAC)



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

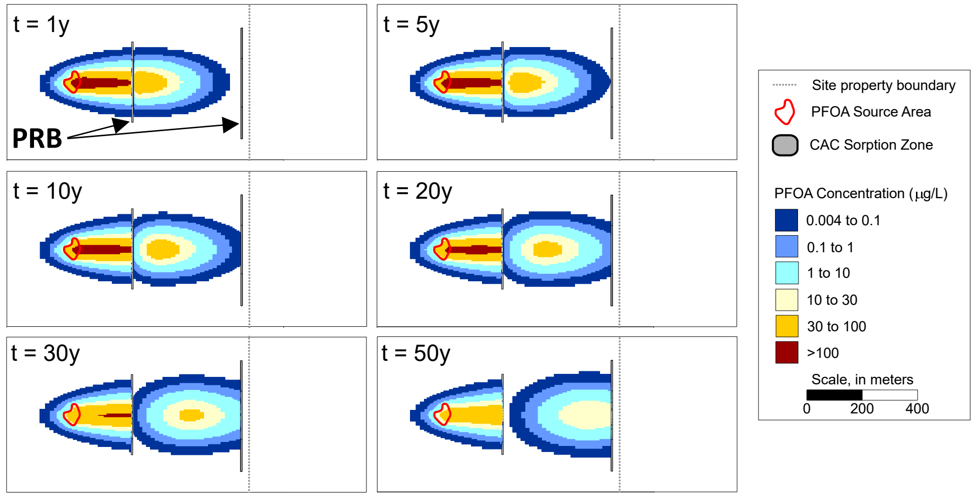
The In-Situ Remediation Model (ISR-MT3DMS)

- Originally developed in 1998 as BioRedox-MT3DMS
- Used to support SERDP-ESTCP projects
- PFAS-related functionality
  - ✓ PFAS re-equilibration after CAC injection
  - ✓ Kinetic sorption
  - ✓ Competitive adsorption
  - ✓ Colloidal transport
  - ✓ CAC aging

  (Competitive adsorption, Colloidal transport, CAC aging: In progress)

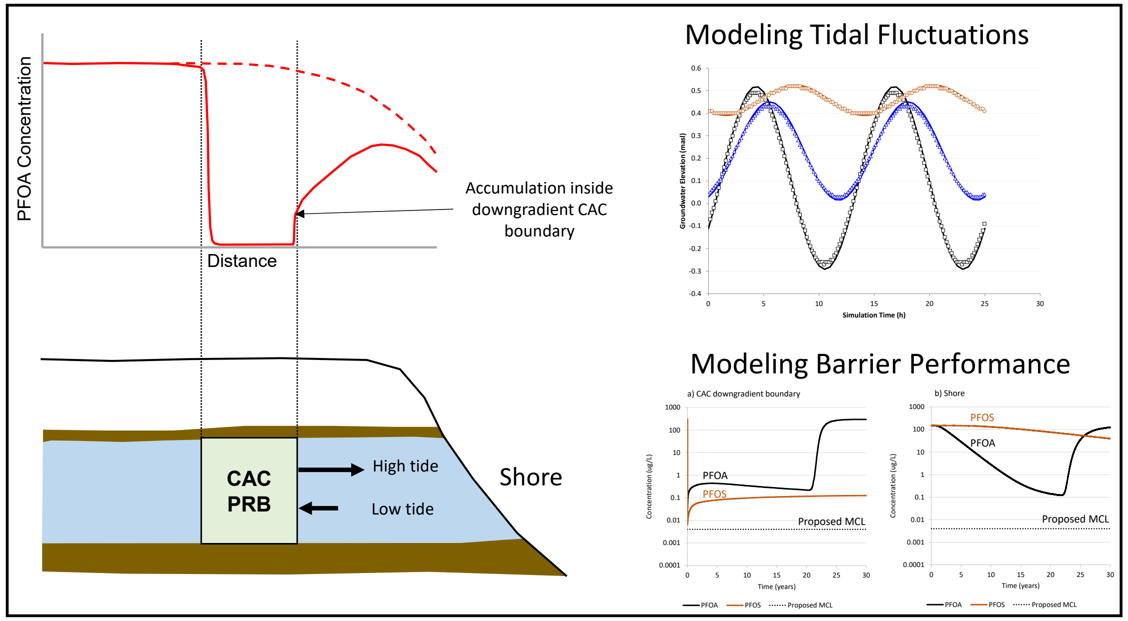
South Dakota Air Force Base

Carey et al. (2023)



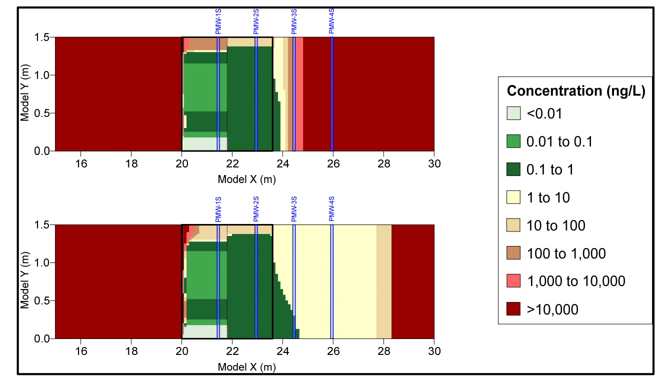
Navy Coastal Site

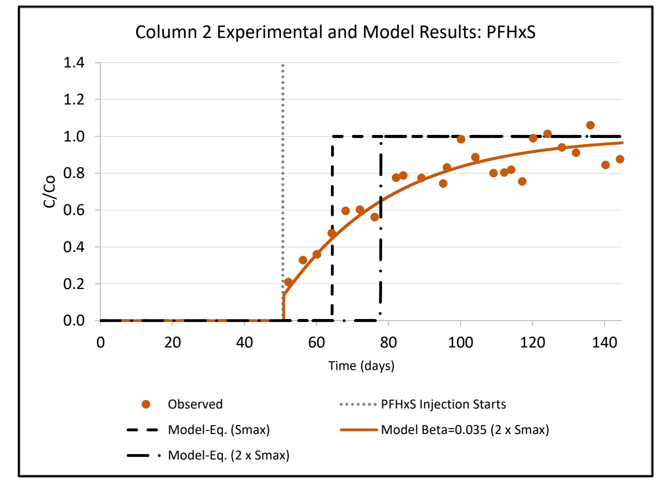
Carey et al. (2024)



Recent ISR-MT3DMS Publications

Two papers in progress





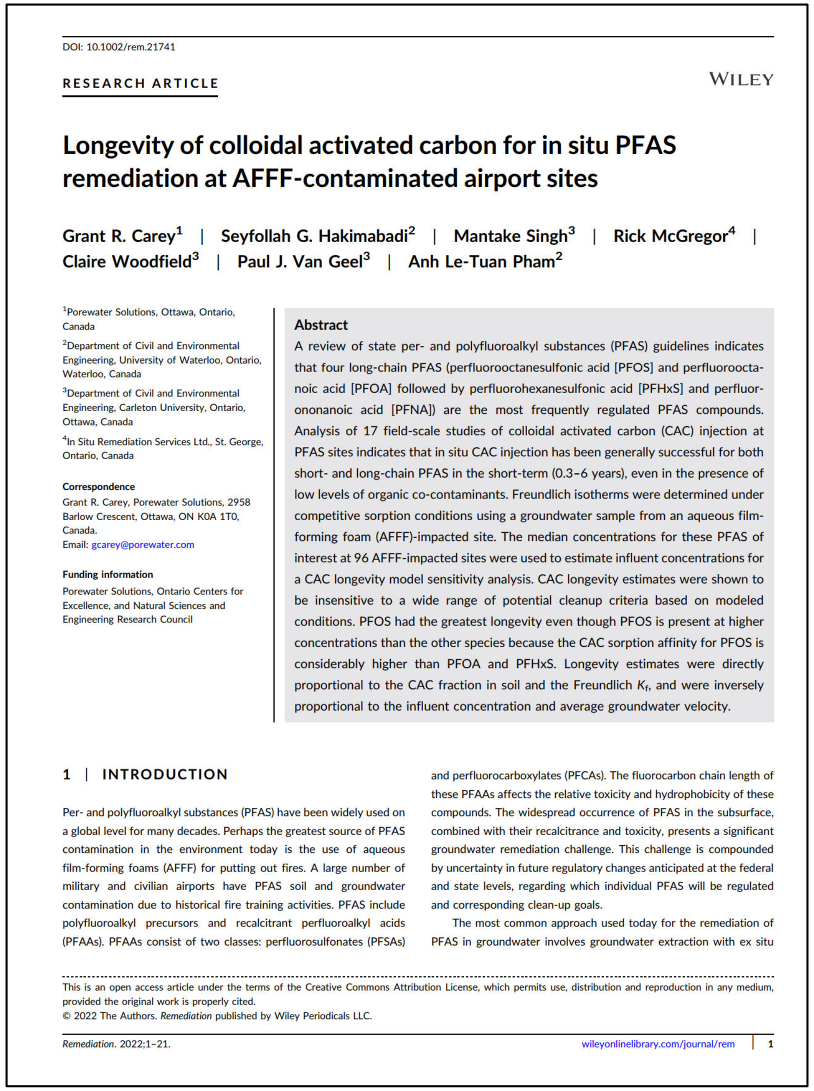
Outline

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

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Funding information
Porewater Solutions, Ontario Centers for Excellence, and Natural Sciences and Engineering Research Council

Abstract

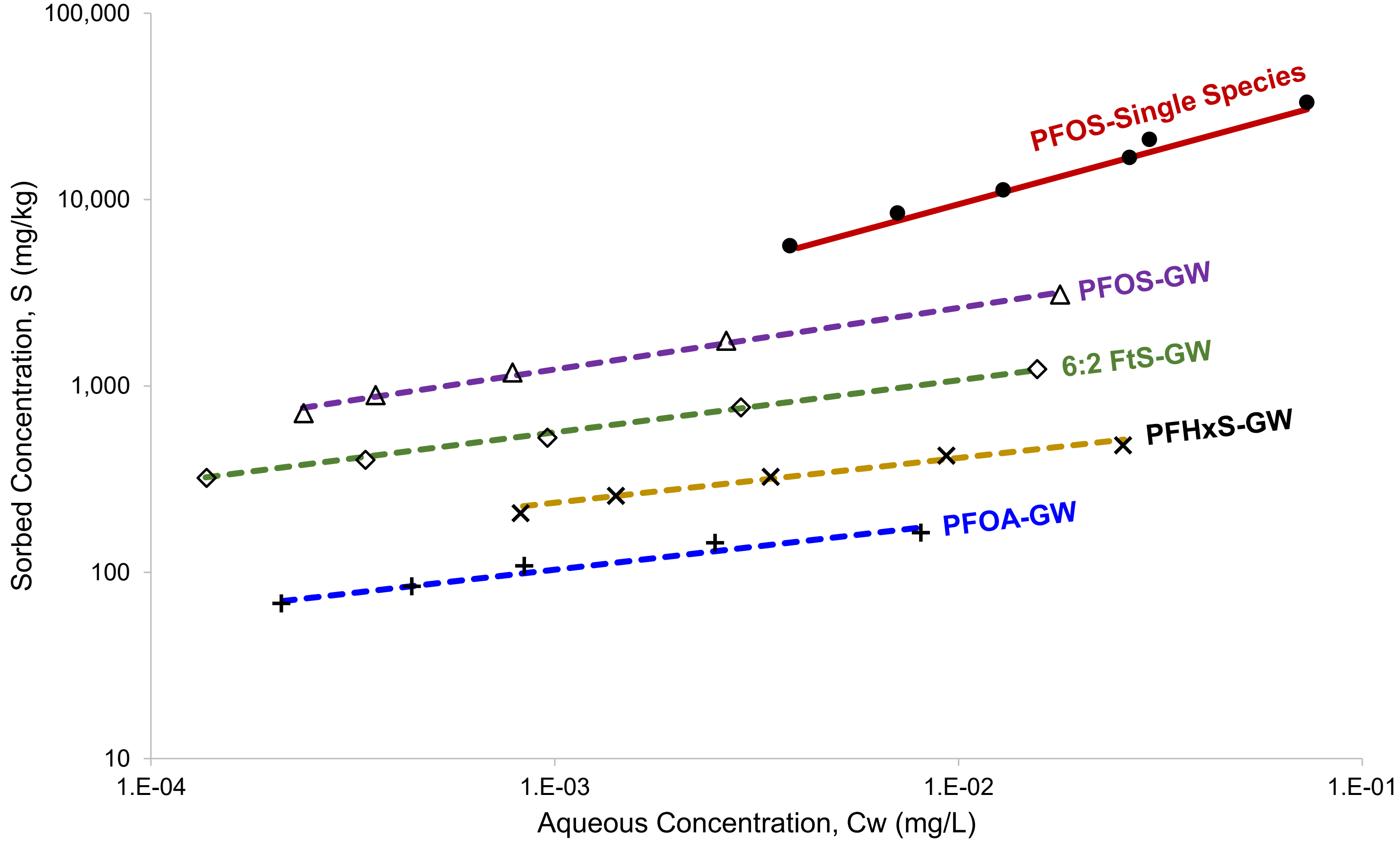
A review of state per- and polyfluoroalkyl substances (PFAS) guidelines indicates that four long-chain PFAS (perfluorooctanesulfonic acid [PFOS] and perfluorooctanoic acid [PFOA] followed by perfluorohexanesulfonic acid [PFHxS] and perfluorononanoic acid [PFNA]) are the most frequently regulated PFAS 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

Single Species and Groundwater Sample Isotherms (Freundlich)



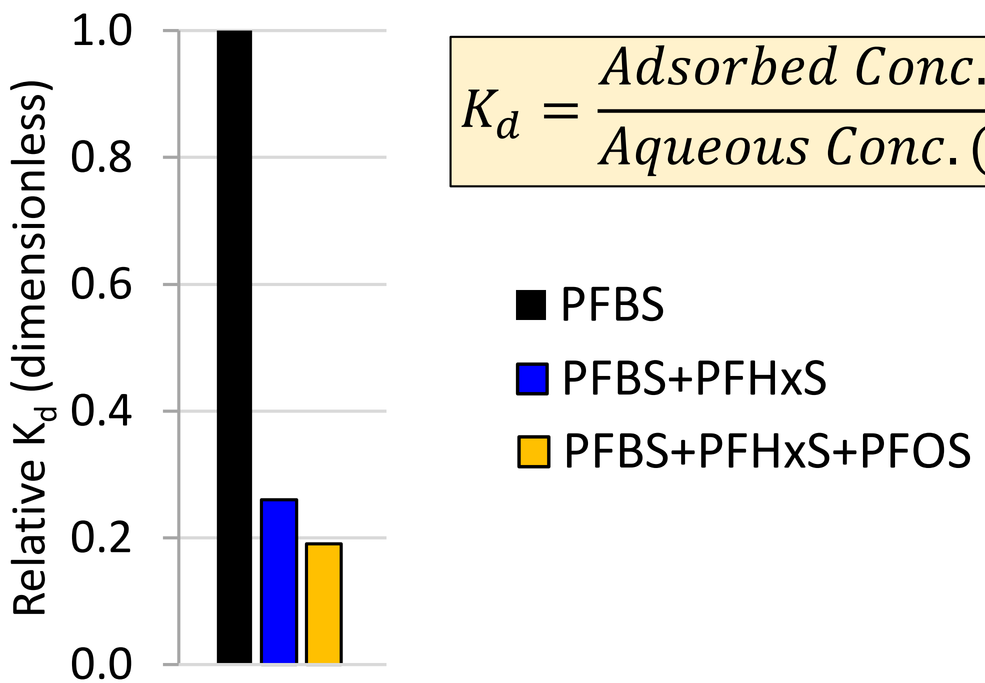
UNIVERSITY OF WATERLOO

Dr. Anh Pham

Seyfollah Gilak Hakimabadi

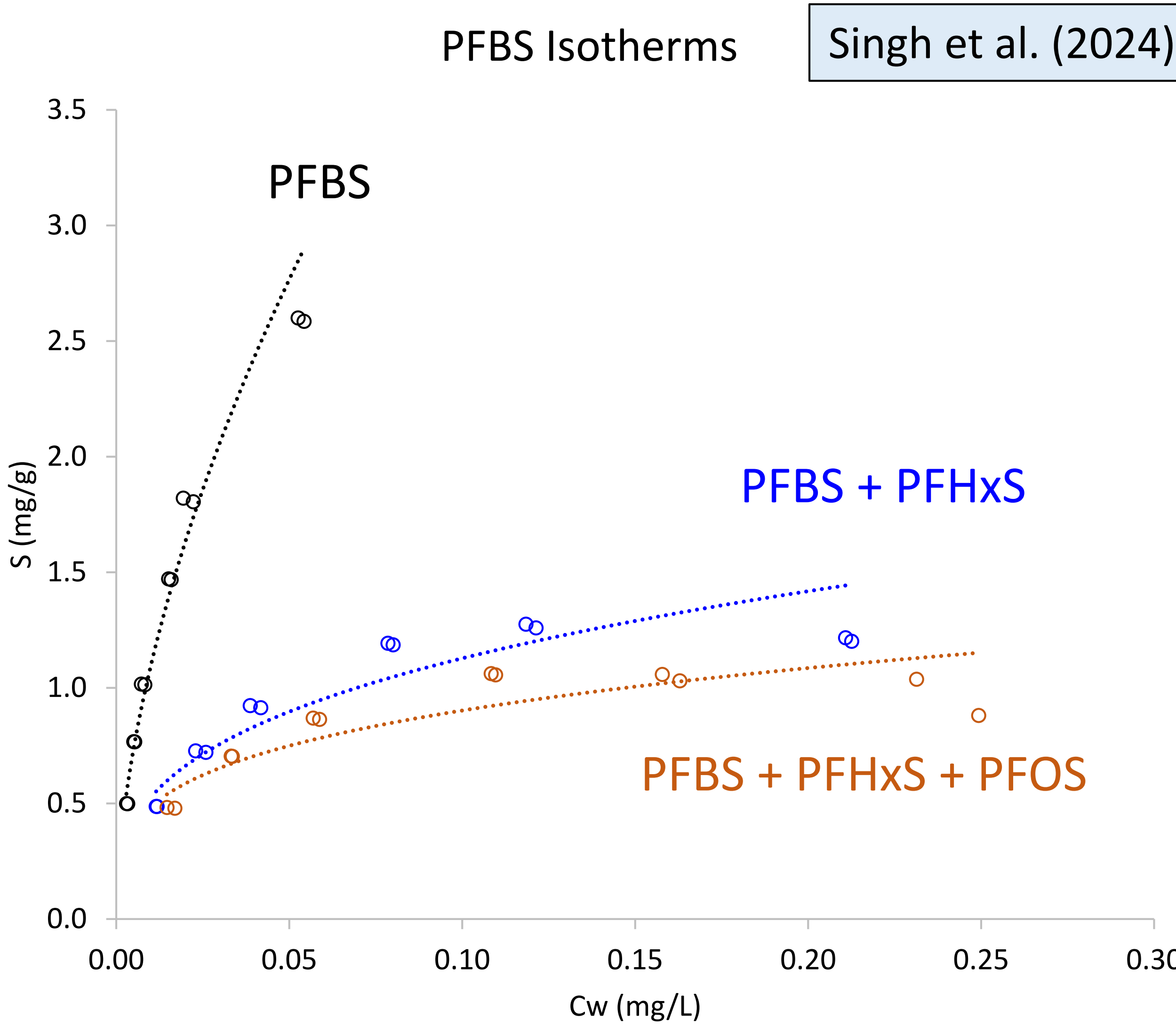
17 Field case studies generated CAC effectiveness, even in the presence of low levels of organic co-contaminants.

Influence of Competition on Relative K_d



$$K_d = \frac{Adsorbed\ Conc.\,(S)}{Aqueous\ Conc.\,(C_w)}$$

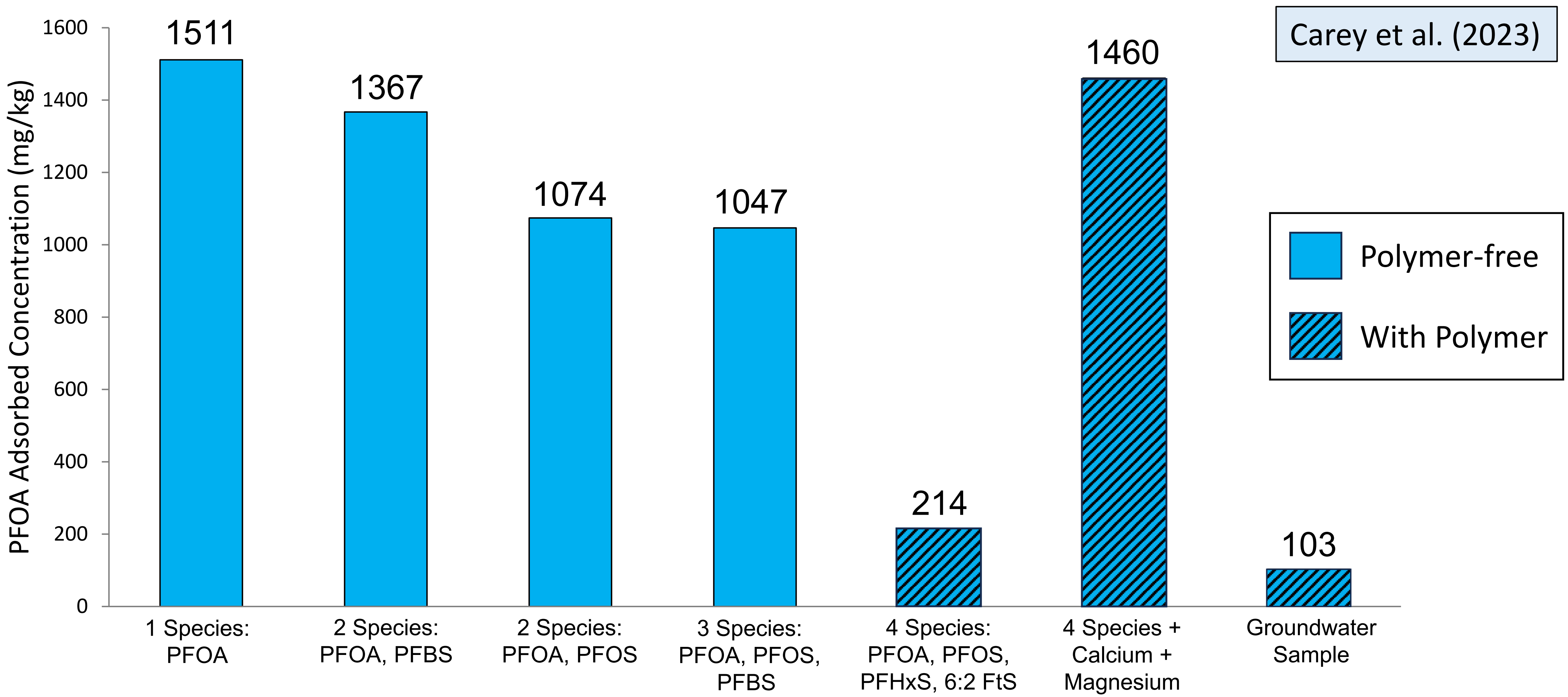
Singh et al. (2024)



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?

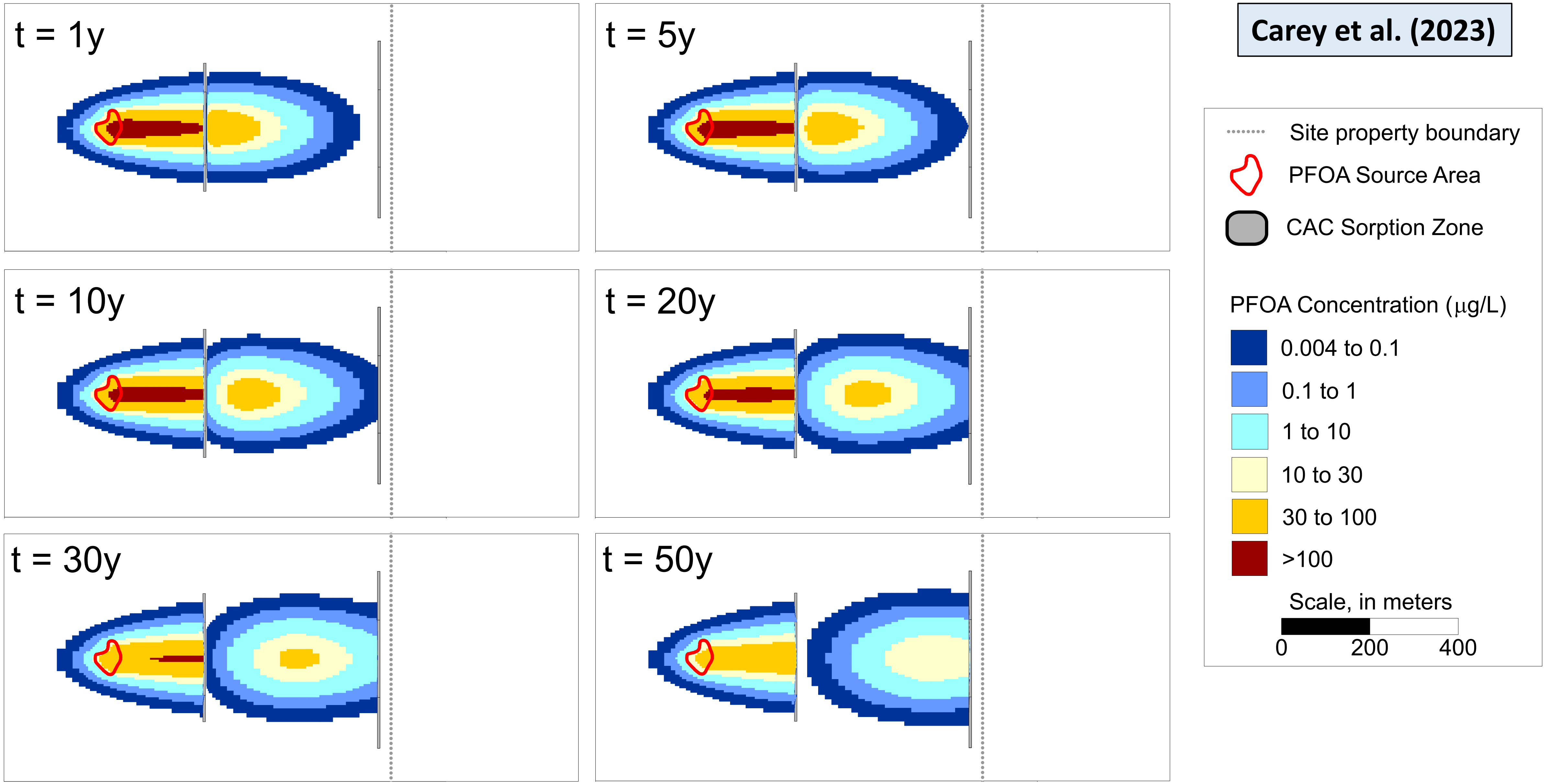
Co-contaminants: No

DOC: Yes, at a landfill

Case Studies of PFAS Remediating Using CAC

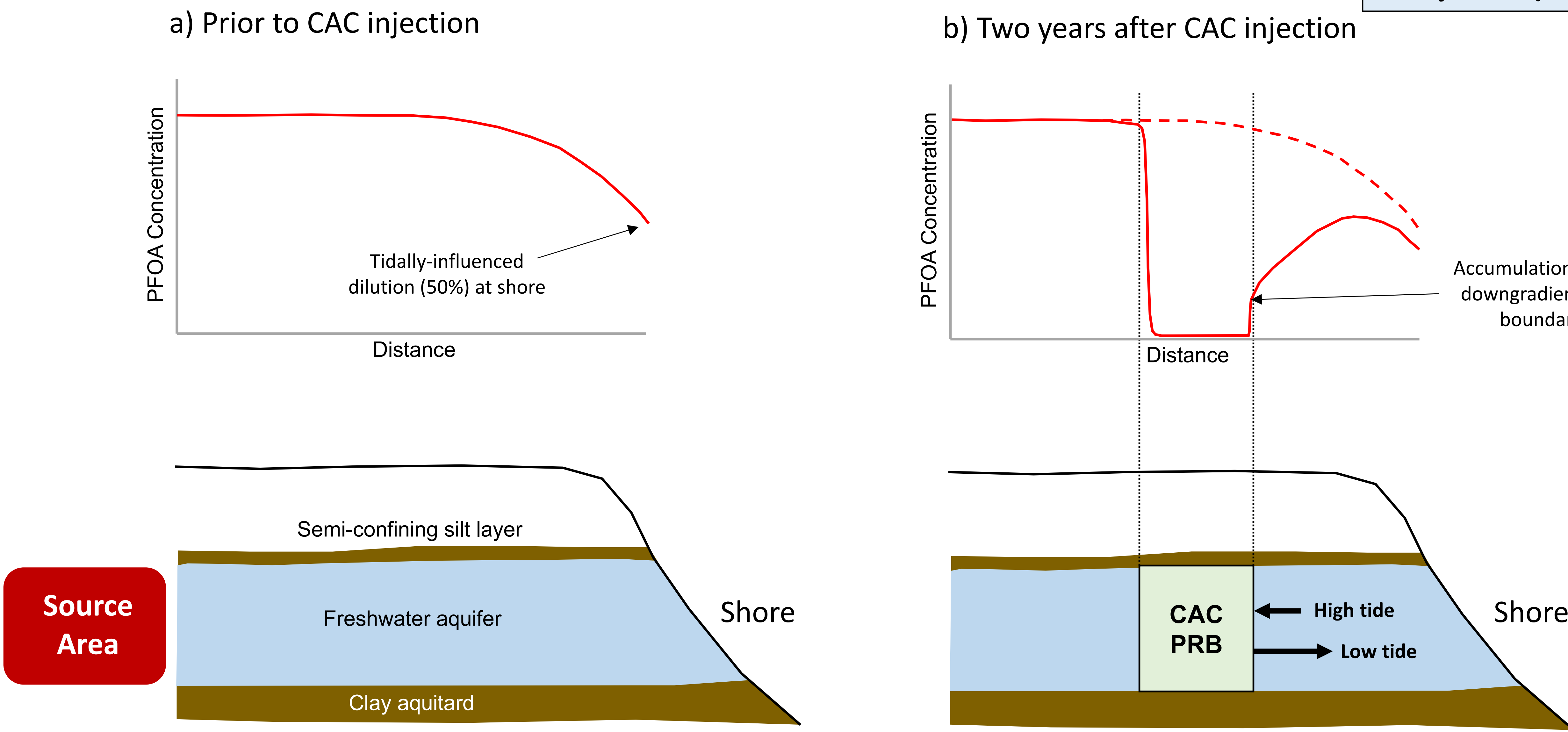
Section 2

South Dakota Site: Integrated PRB Alternative

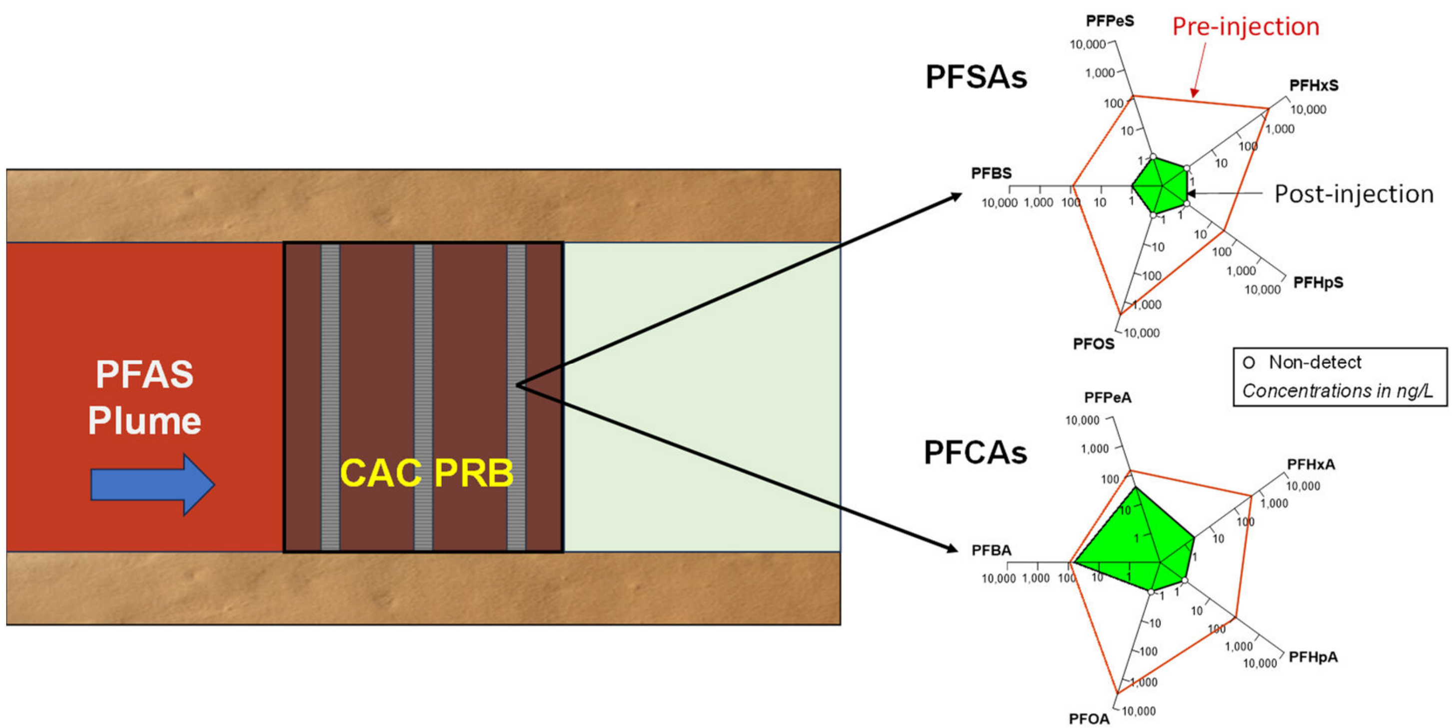


Coastal Site Conceptual Model

Carey et al. (2024)

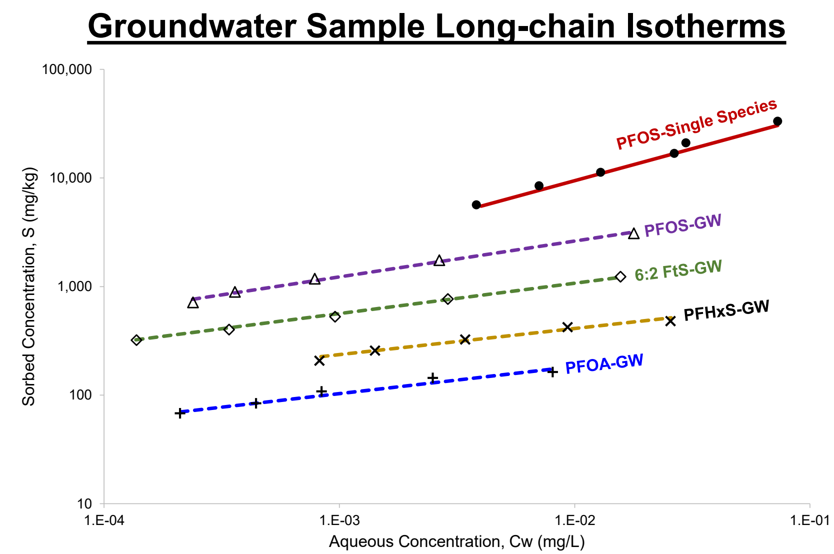


Model Calibration of CAC Performance at A Field Site

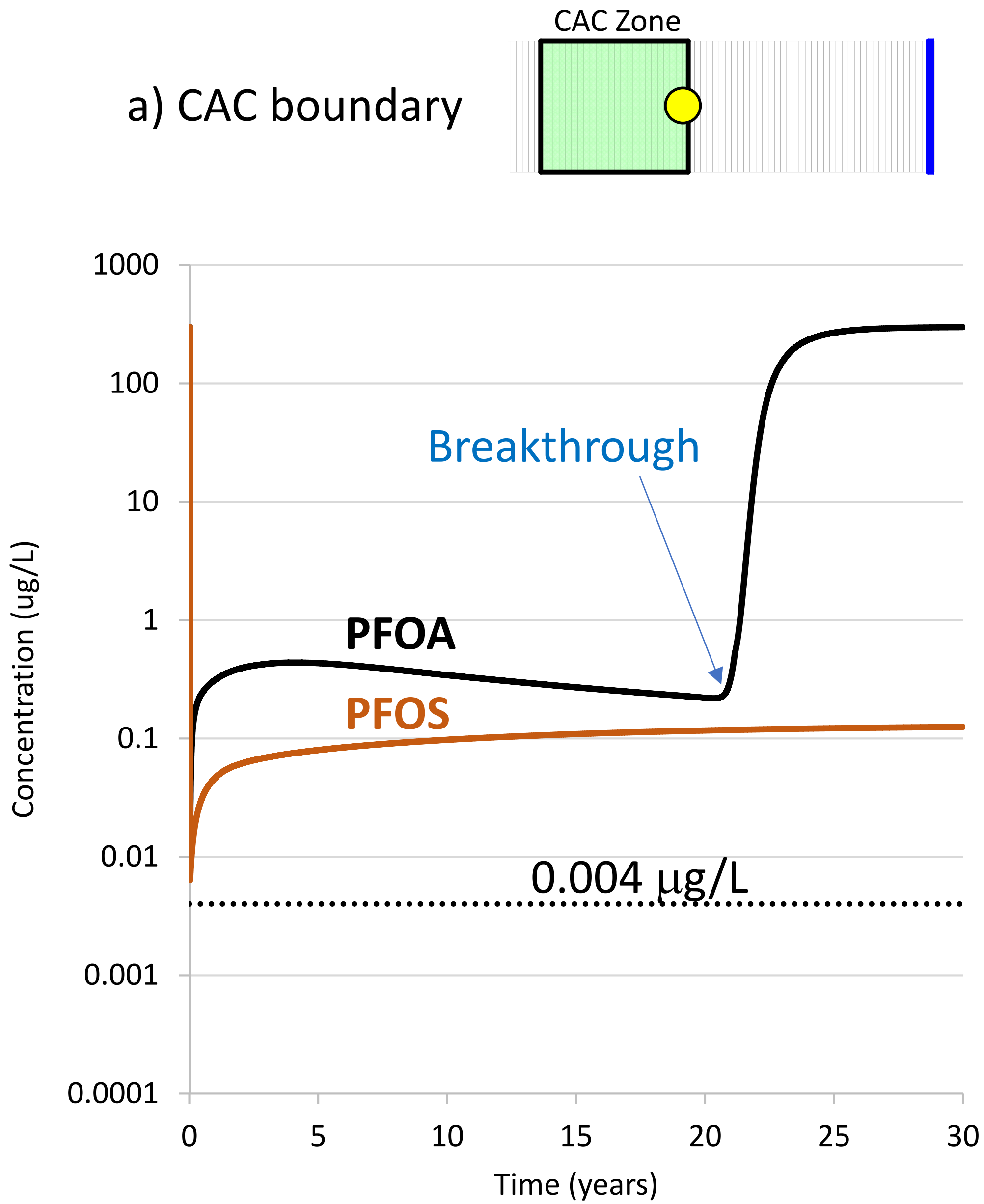


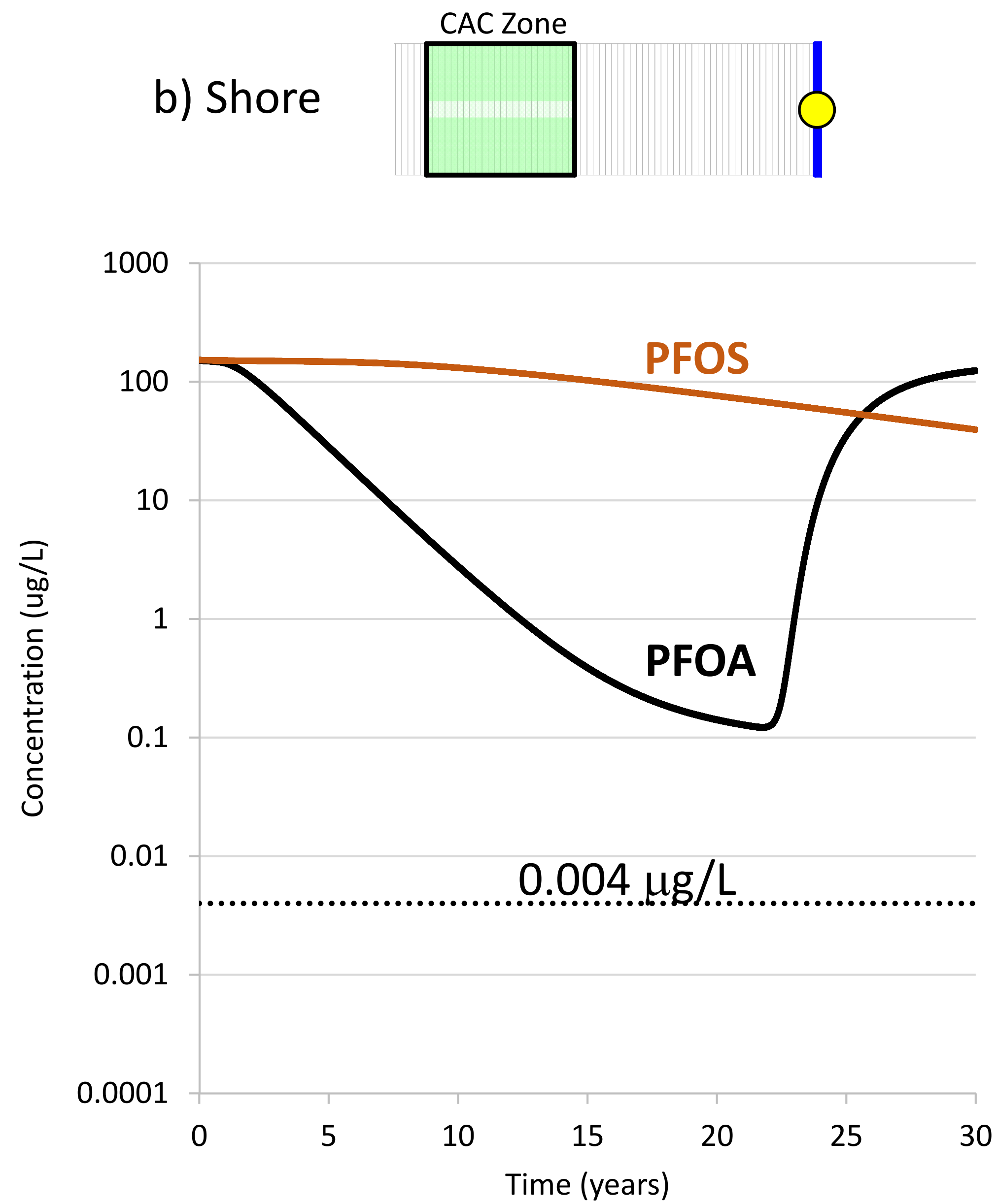
Modeling Objectives

- 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

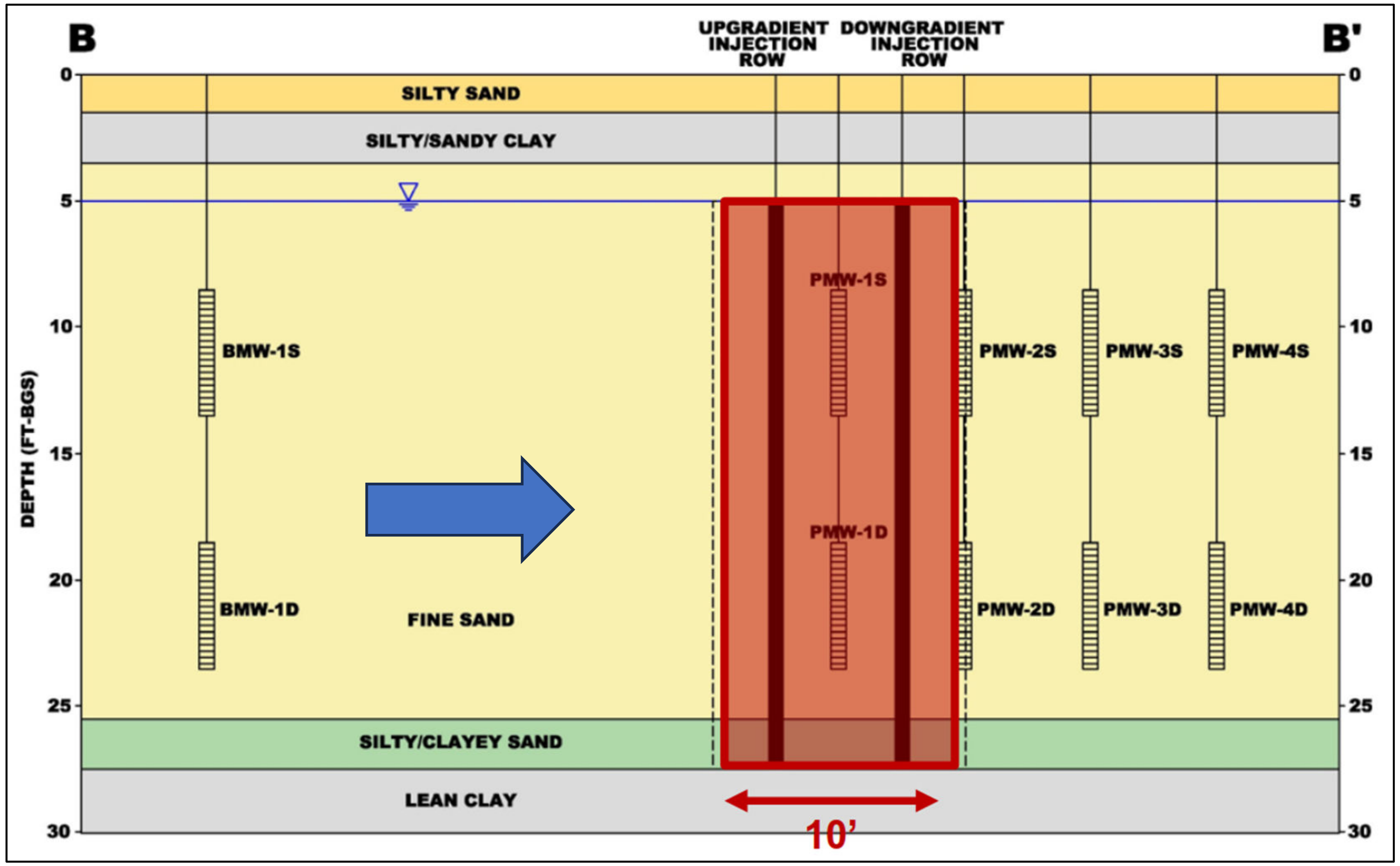


PFOA vs PFOS Trends





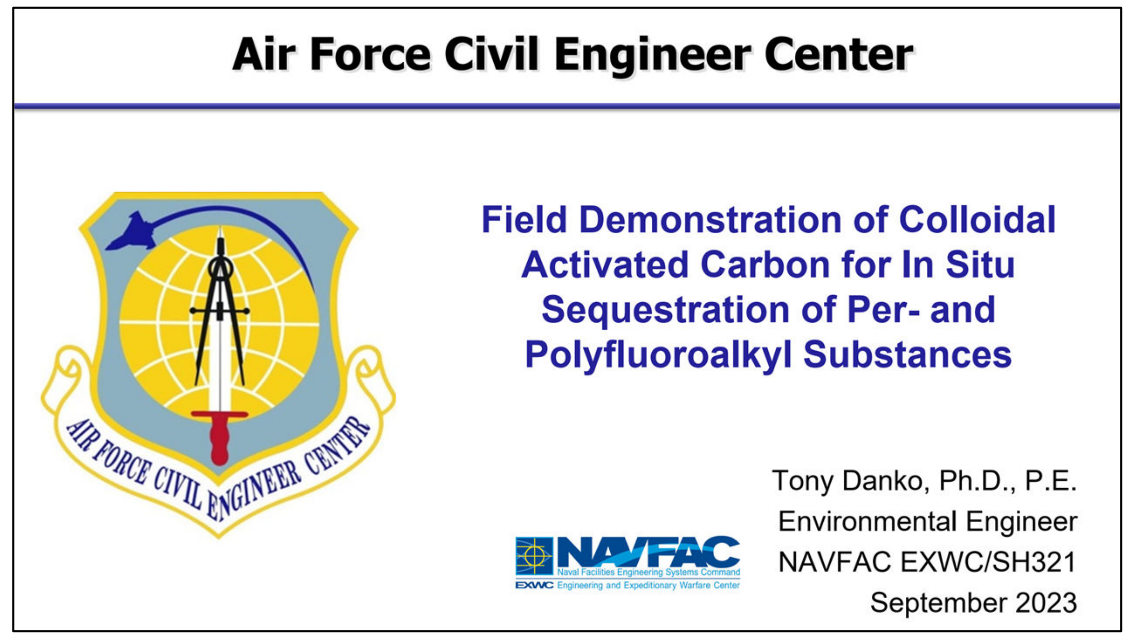
Eastern U.S. Site CAC Permeable Reactive Barrier



Carey et al. (2024) – in progress

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

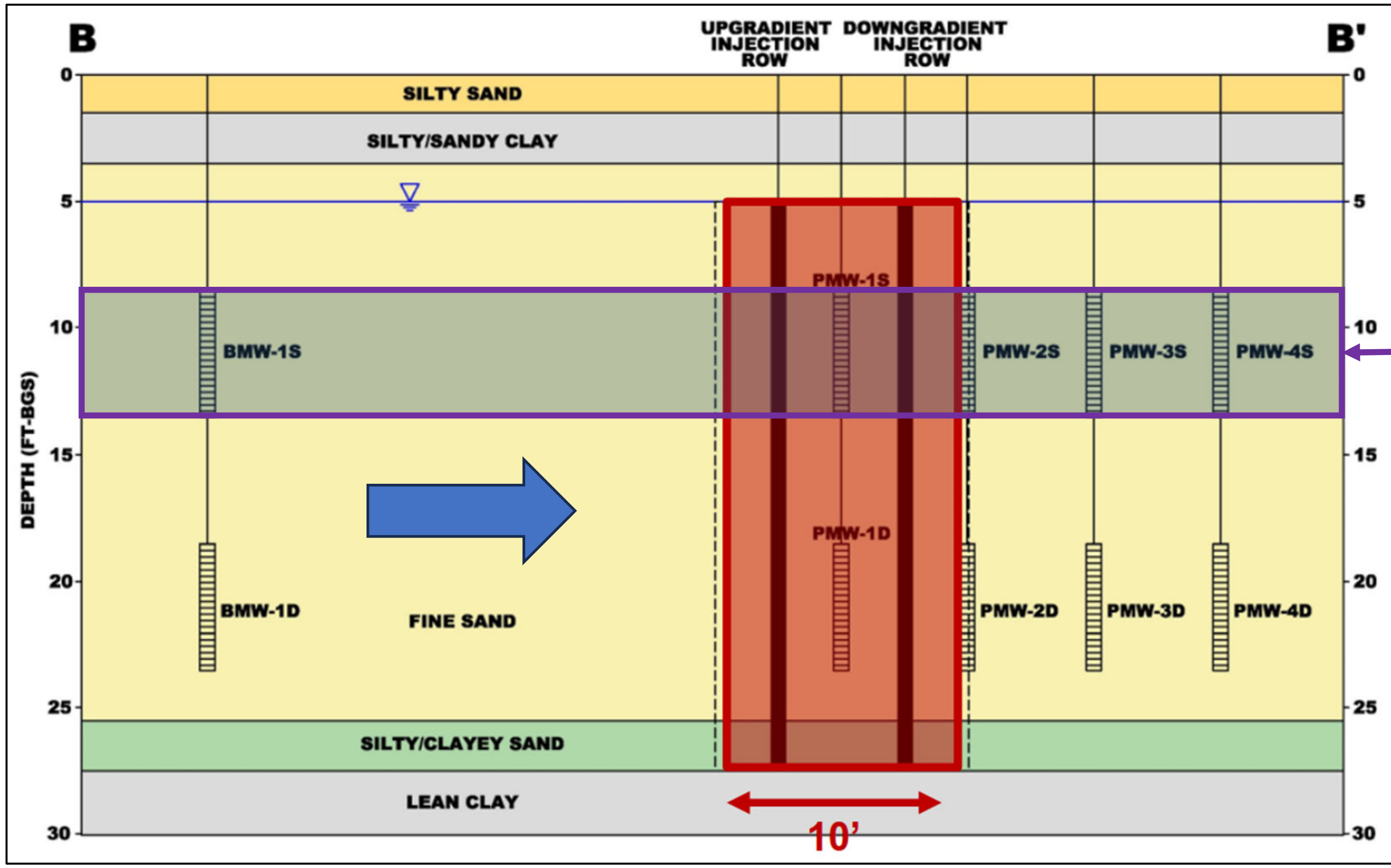
Navy
Dr. Tony Danko


Air Force Civil Engineer Center

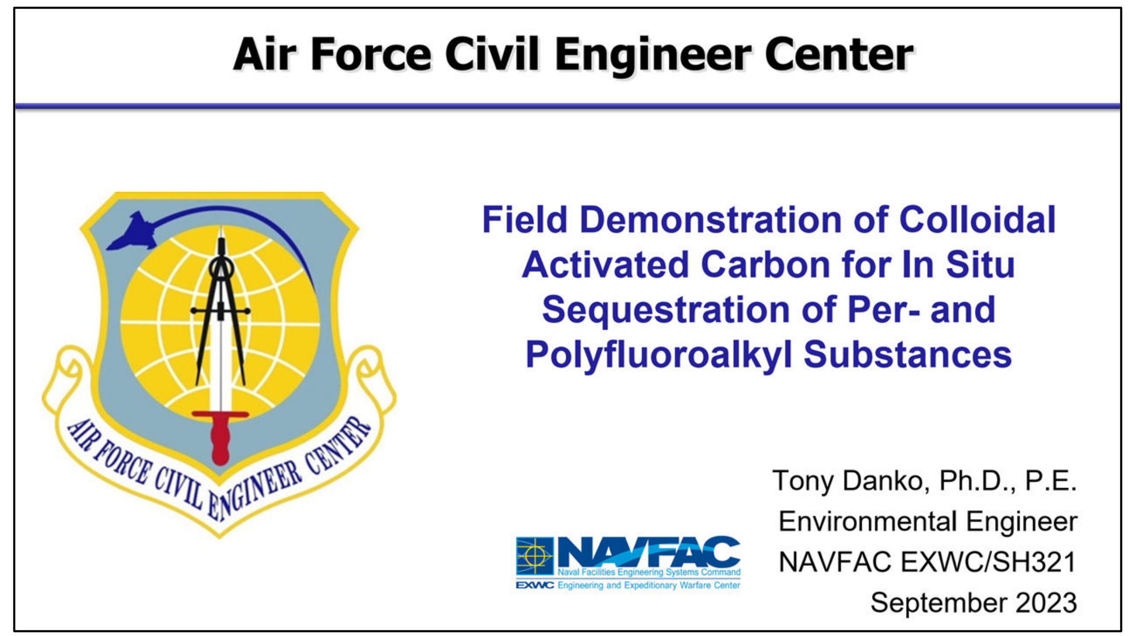
Field Demonstration of Colloidal Activated Carbon for In Situ Sequestration of Per- and Polyfluoroalkyl Substances

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

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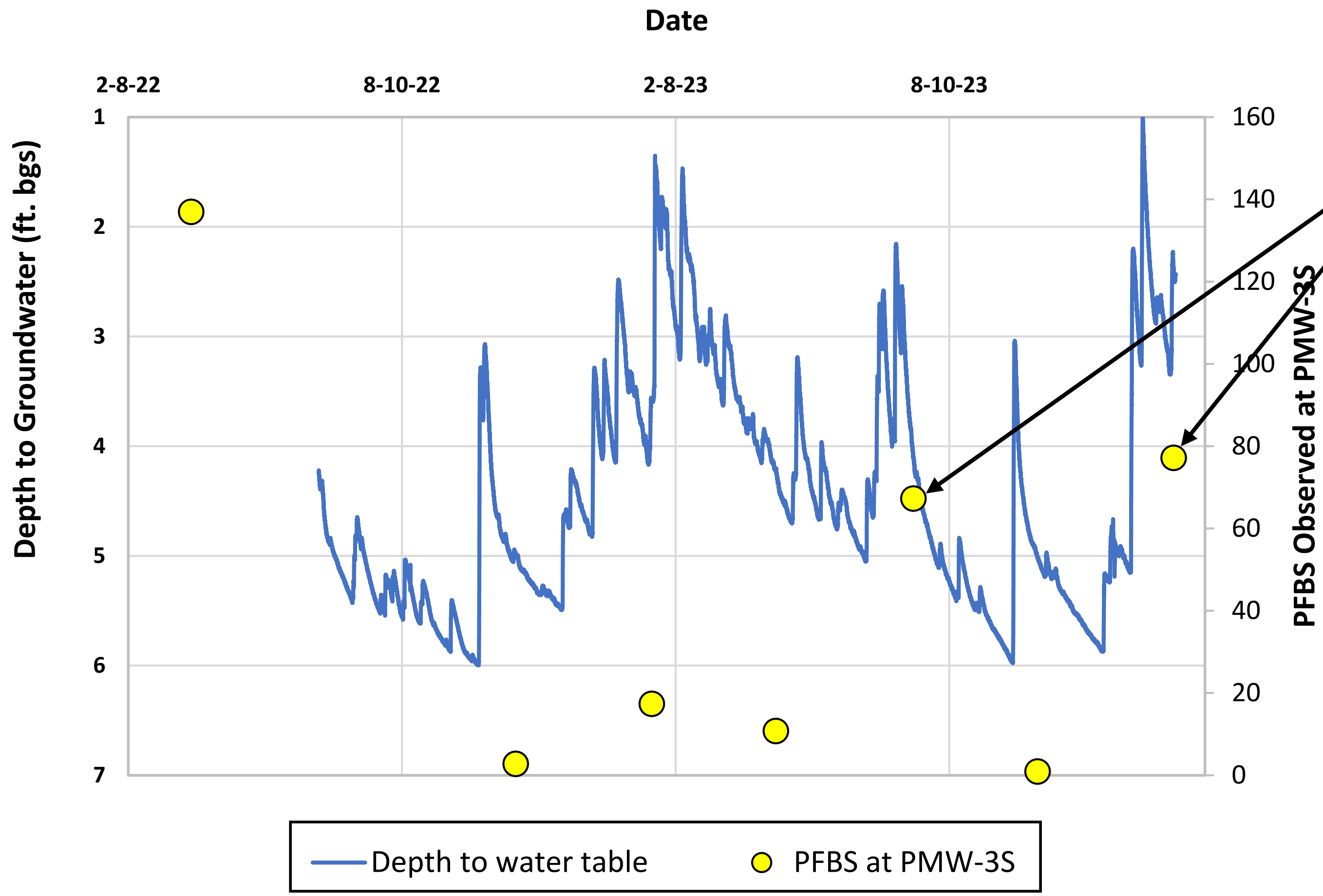
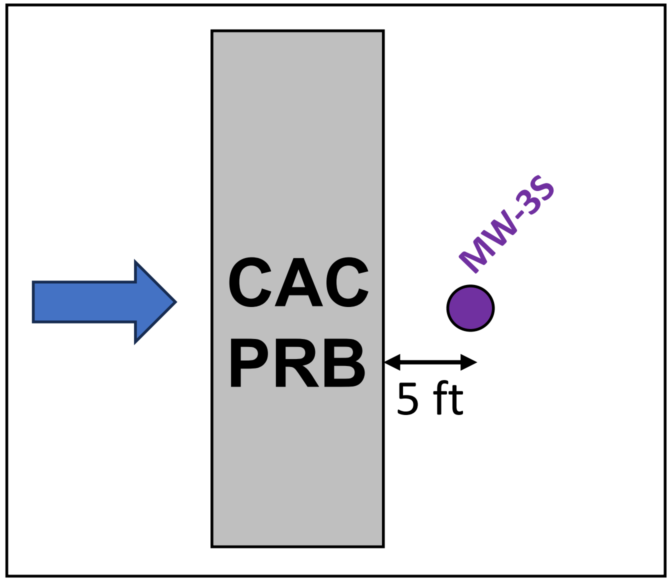
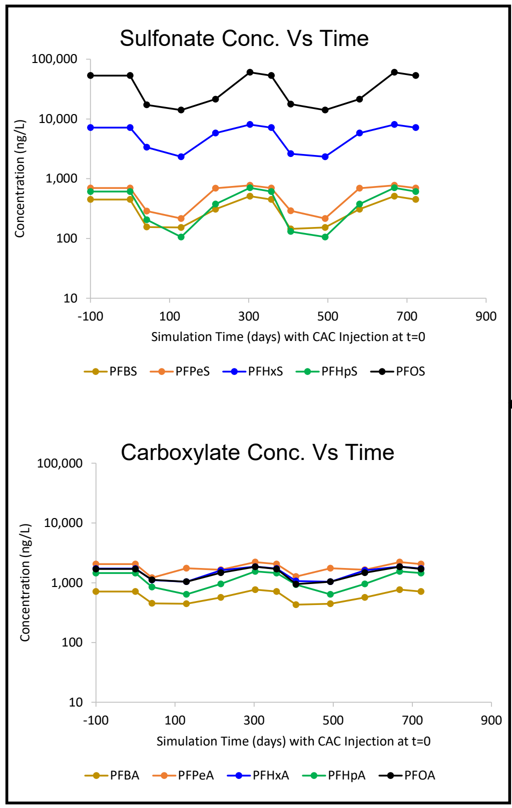
Downgradient Wells Influenced by Water Table



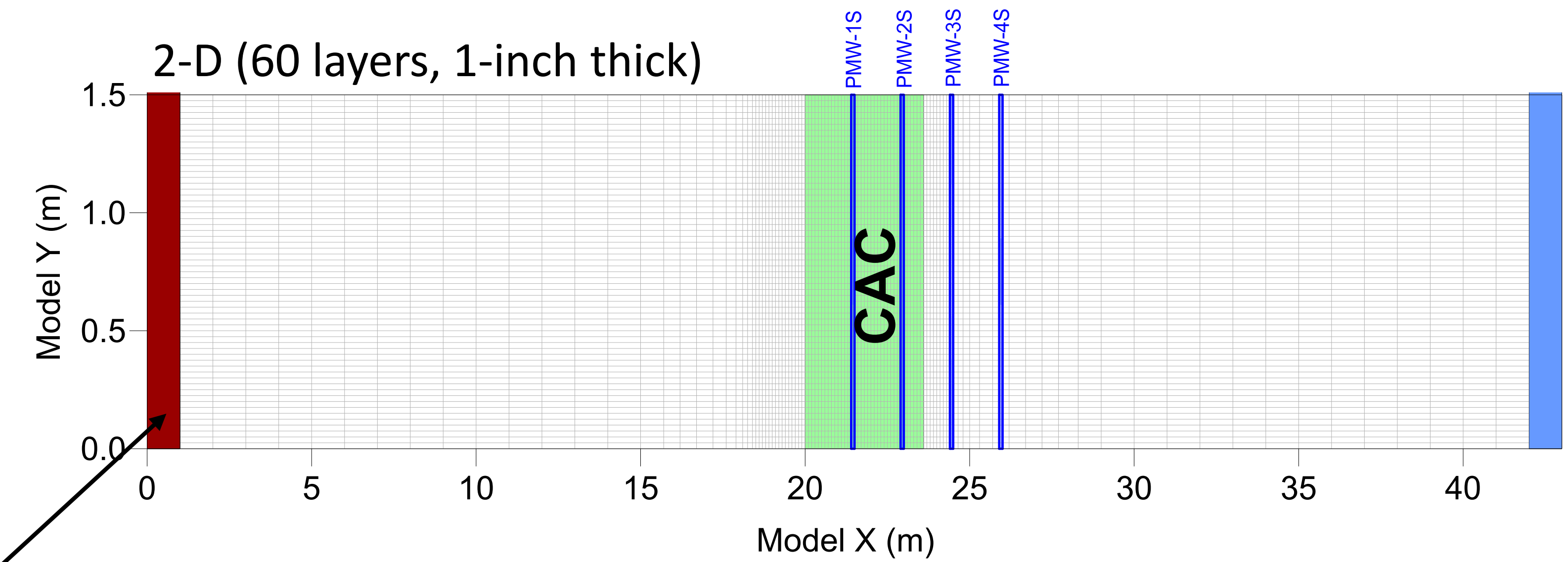
Spikes in PFBS downgradient from PRB after 2-3 ft rise and fall in water table.



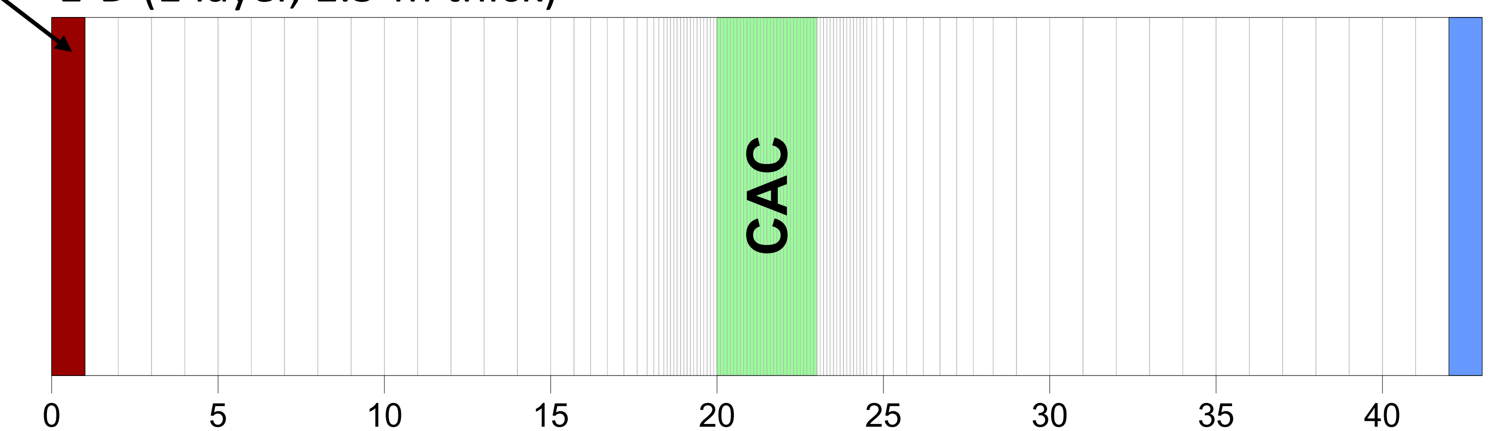
Model Domain and Boundary Conditions



2-D (60 layers, 1-inch thick)



1-D (1 layer, 1.5-m thick)



Carey et al. (2015)

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

α_z = 0.3 m

Note: K in m/s

K = 150 ft/y

i = 0.001 ft/ft

v = 220 ft/y

f_{oc} = 0.2%

θ_e = 0.25

ρ_b = 1.6 kg/L

α_x = 0.03 m

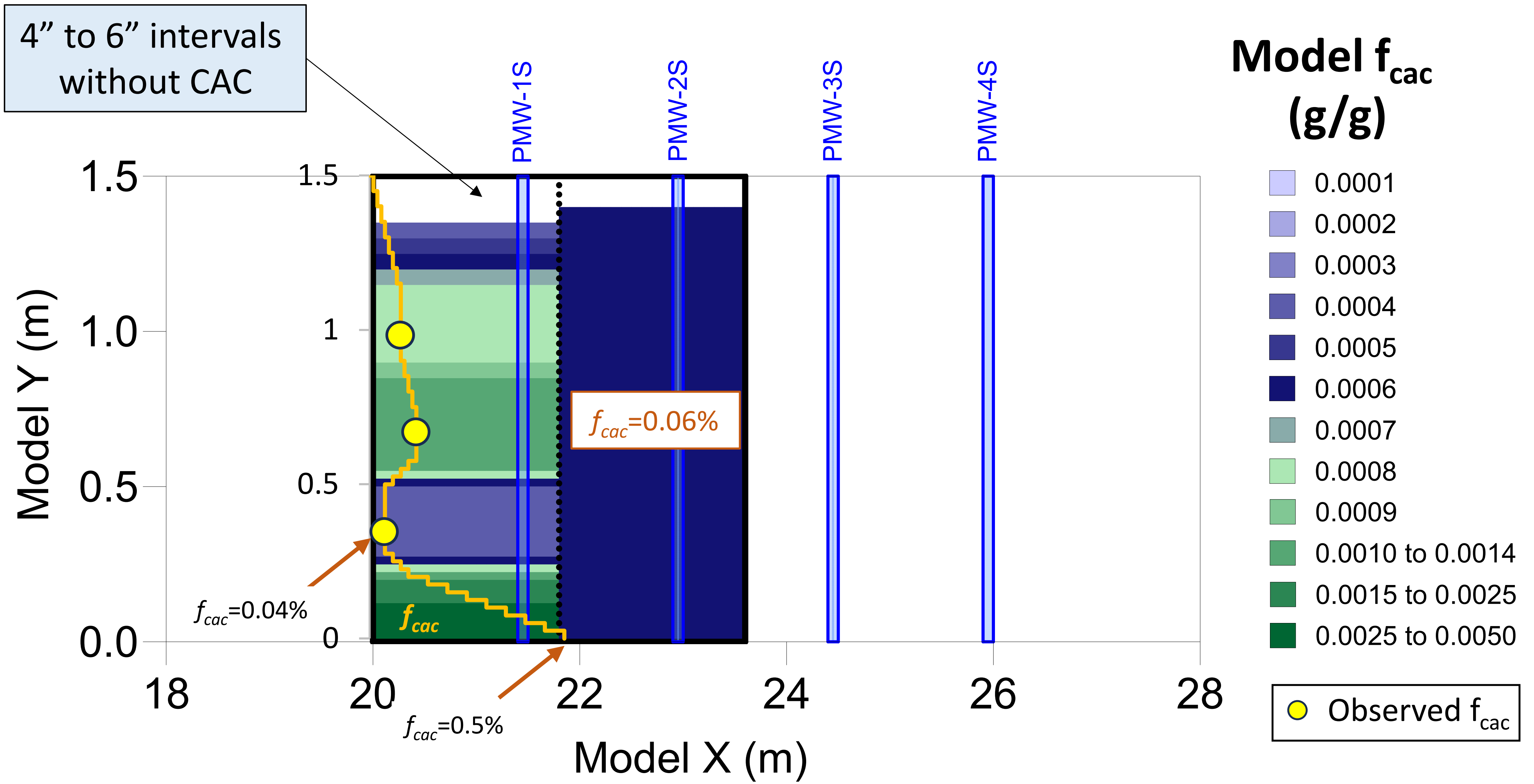
10 PFAS Solutes Modeled

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.

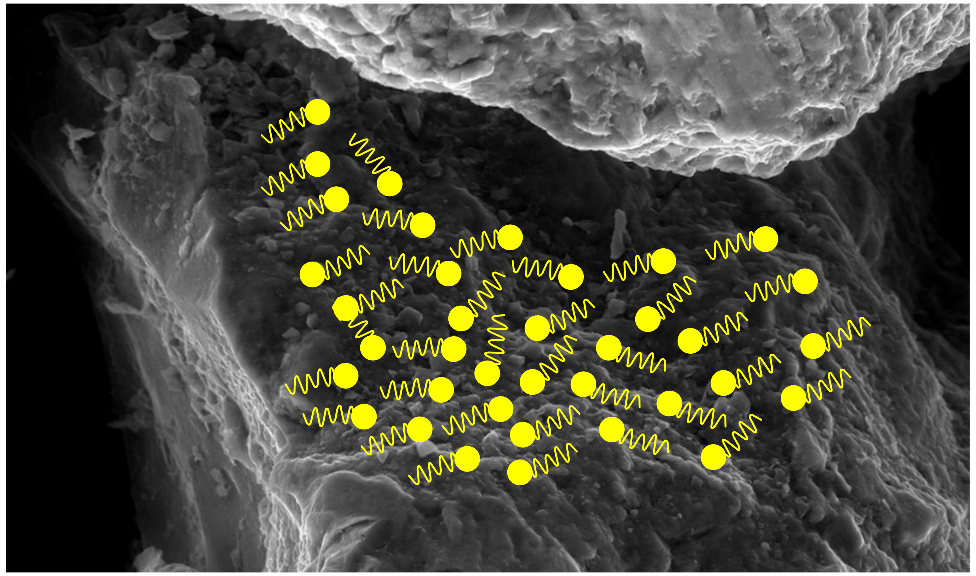
Modeled CAC Distribution

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

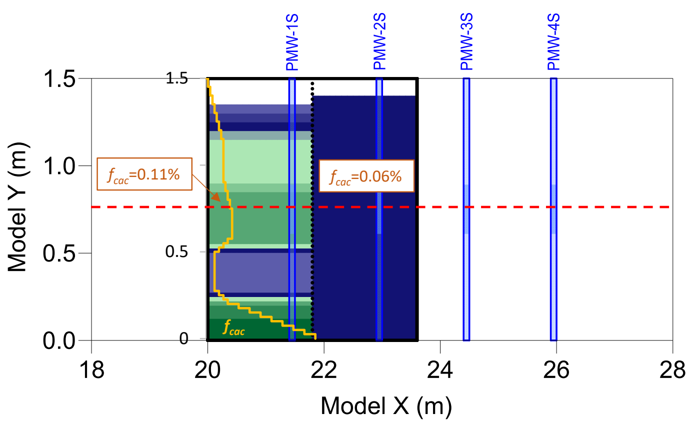


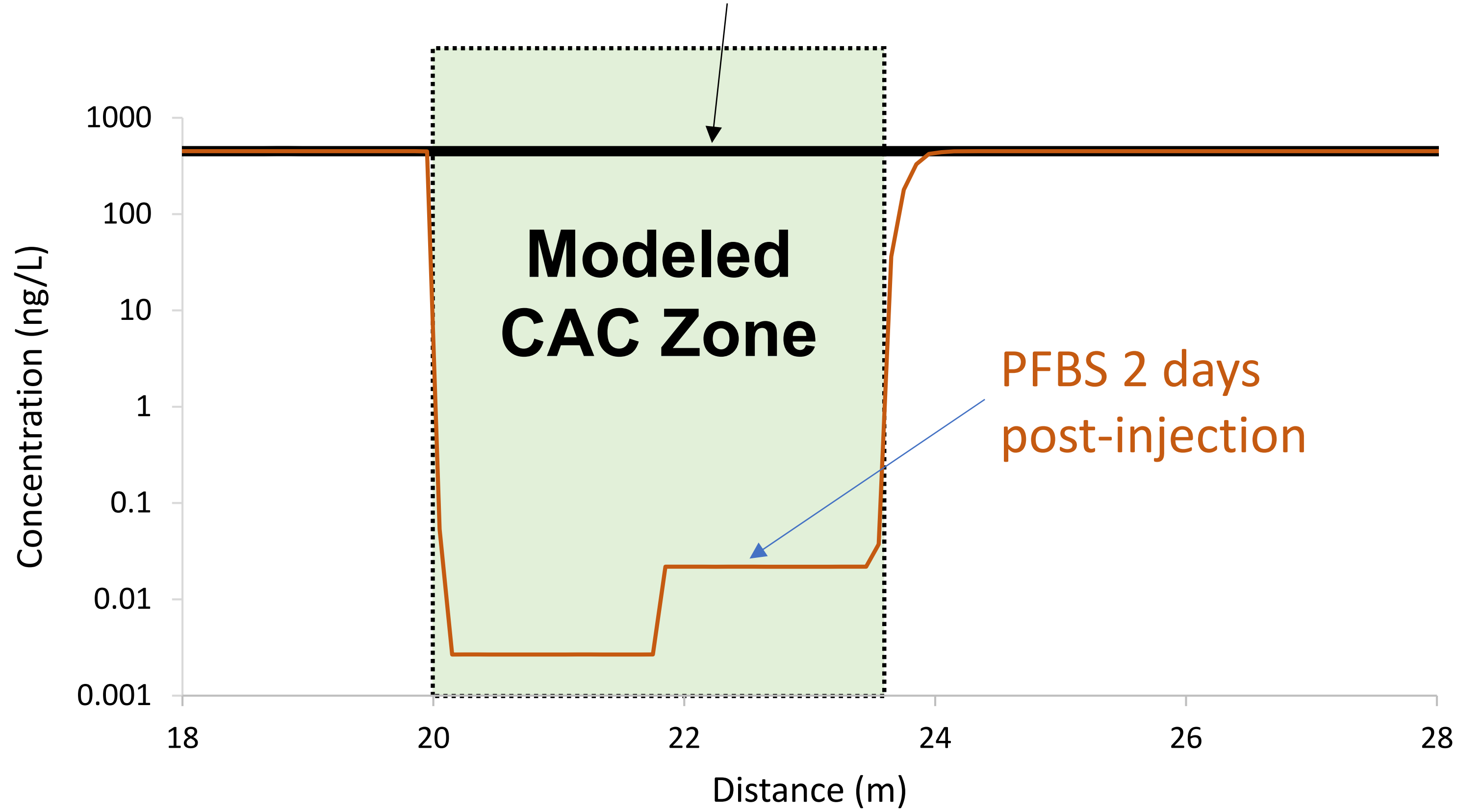
Modeling CAC Injection: PFAS Concentration

PFAS adsorbed to CAC particles



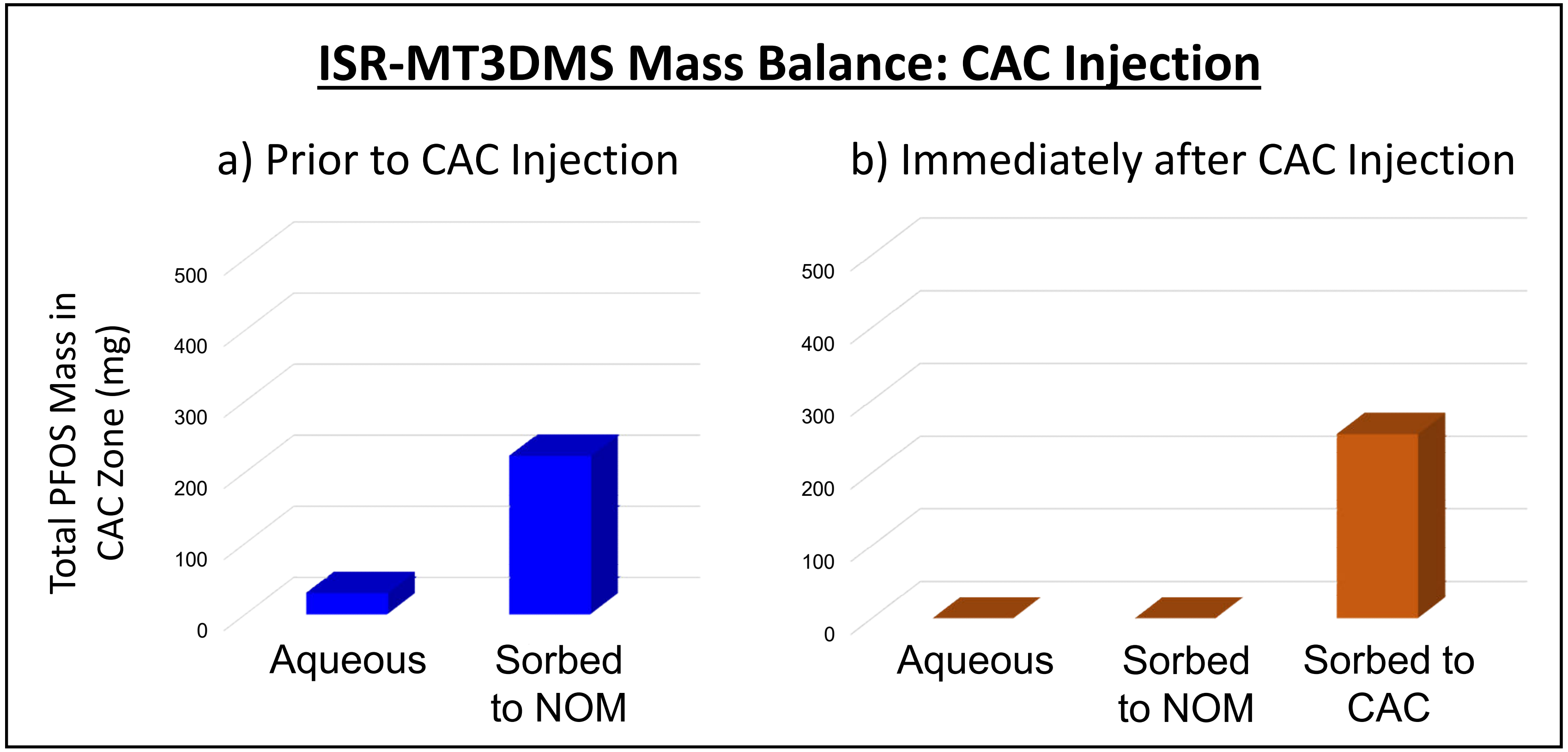
Not to scale – Conceptual illustration only





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

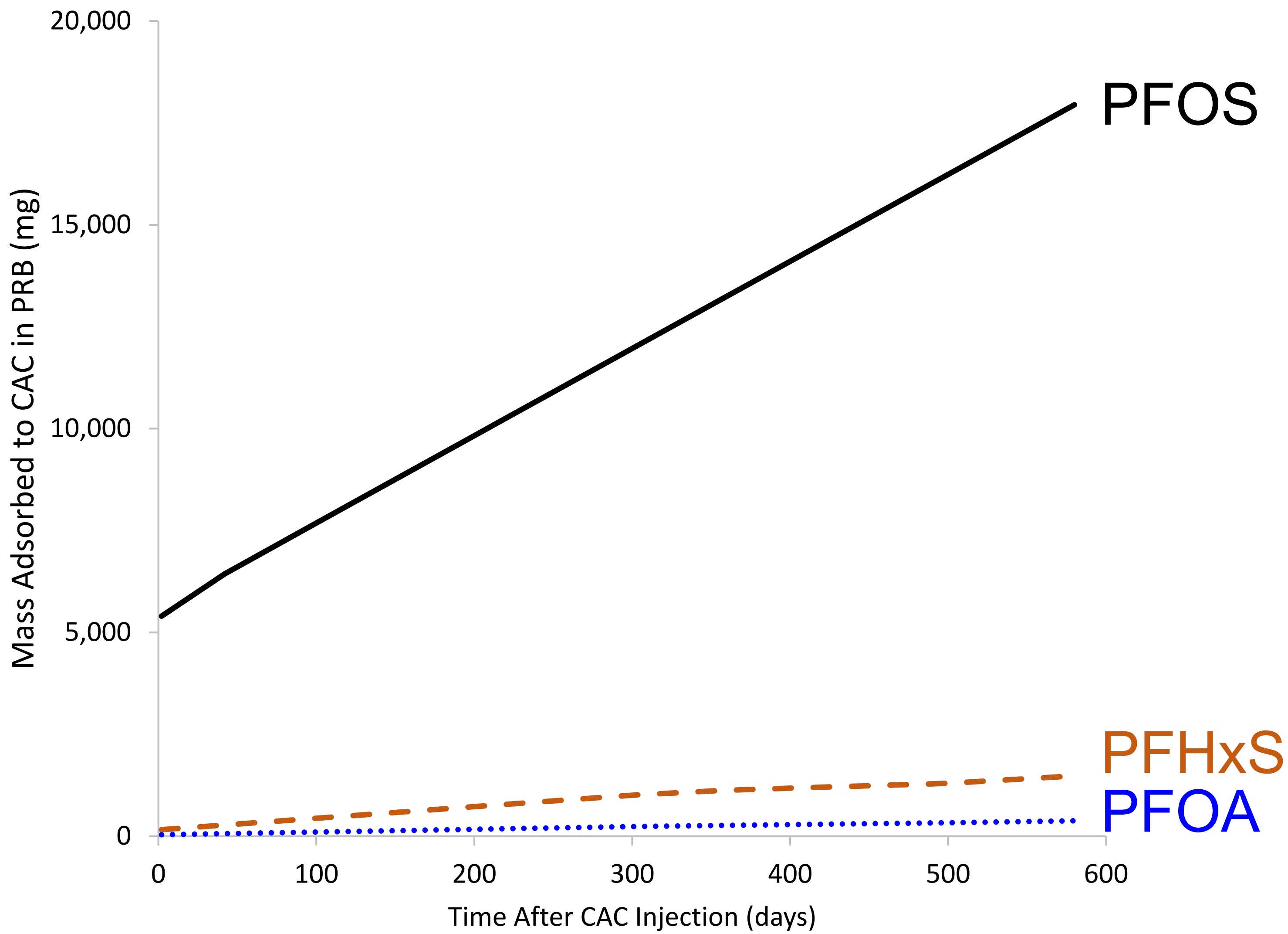
Post-injection C depends on:

- 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.

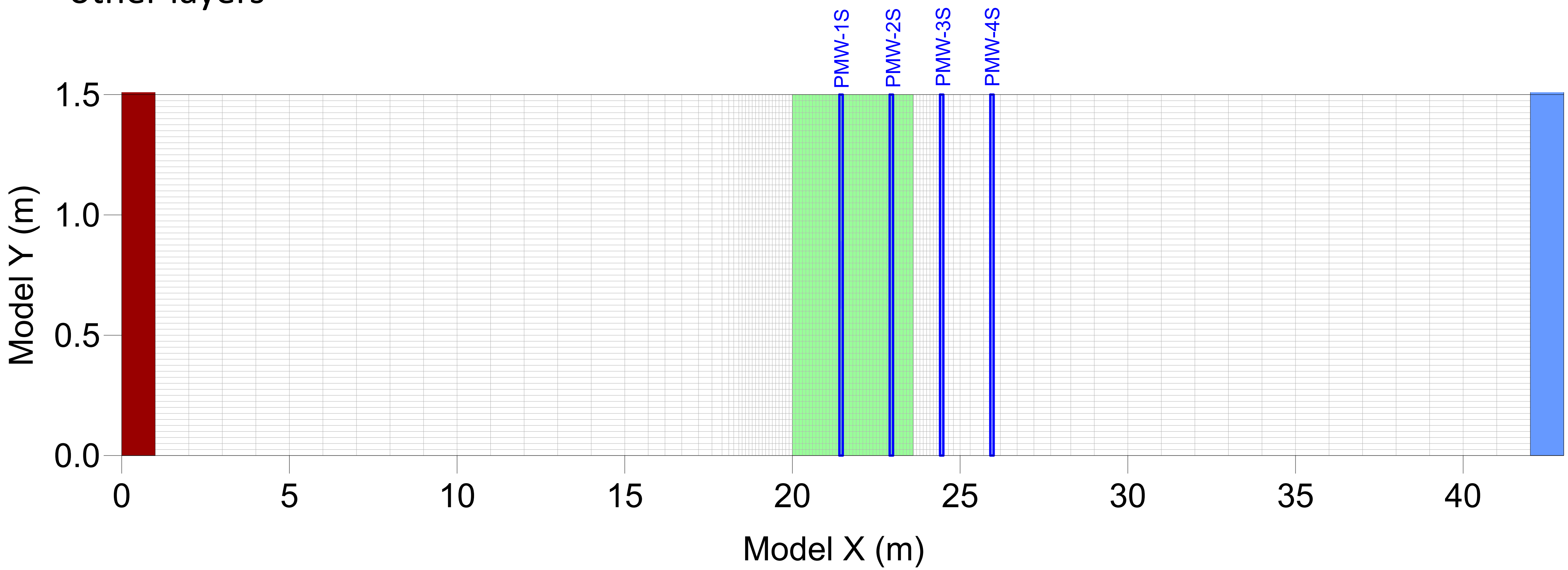
Model Mass Balance

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

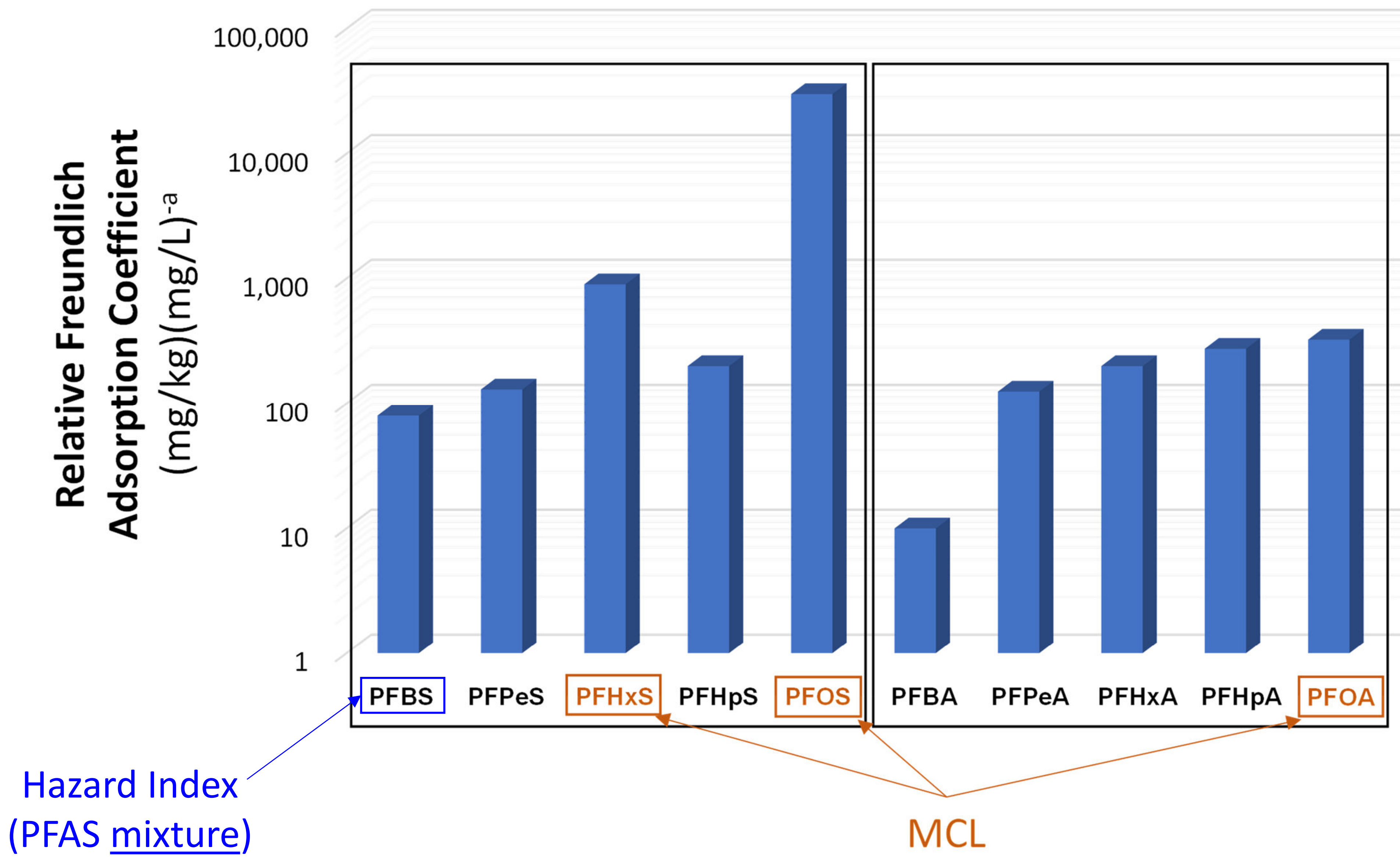


Multi-Layer Monitoring Wells in ISR-MT3DMS

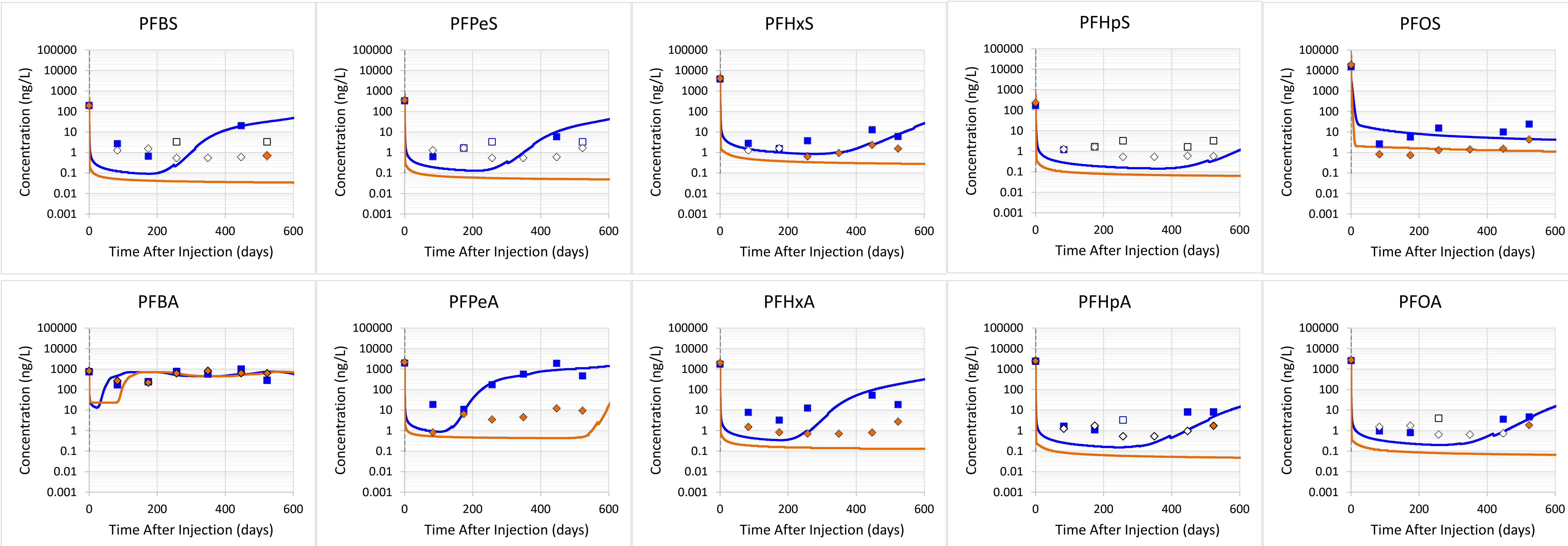
- Monitoring wells screened over 60 layers
- ISR-MT3DMS calculates transmissivity-weighted average concentration over all screened model layers
- Breakthrough in some layers with lower fcac will be diluted in the well with clean water from other layers



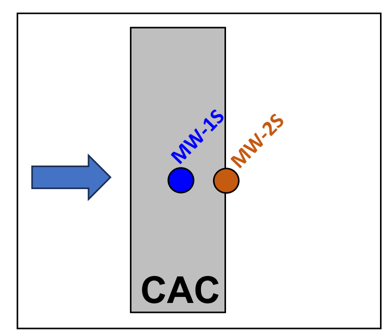
Eastern US Site: Calibrated PFAS Adsorption Isotherms



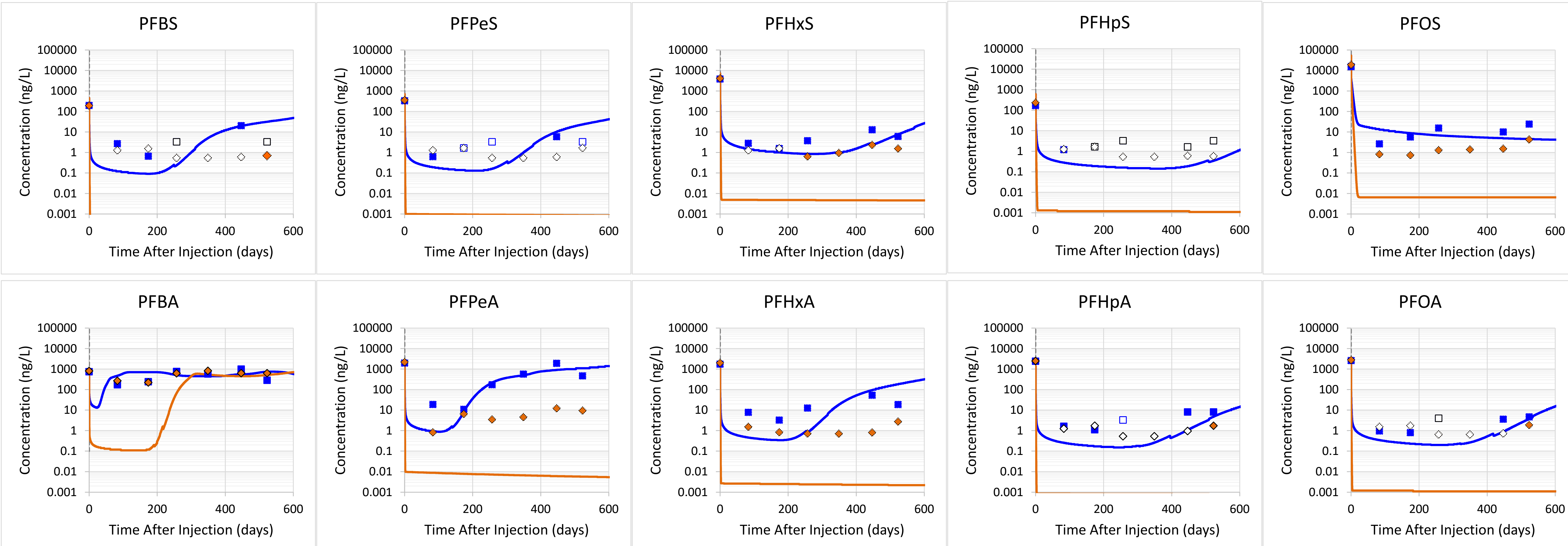
Modeled PFAS Trends at In-Barrier Monitoring Wells



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%



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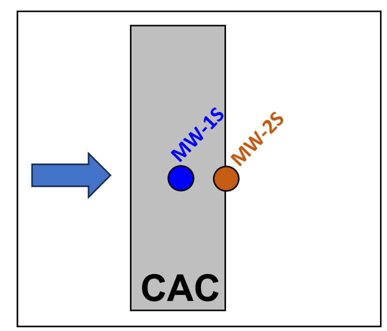
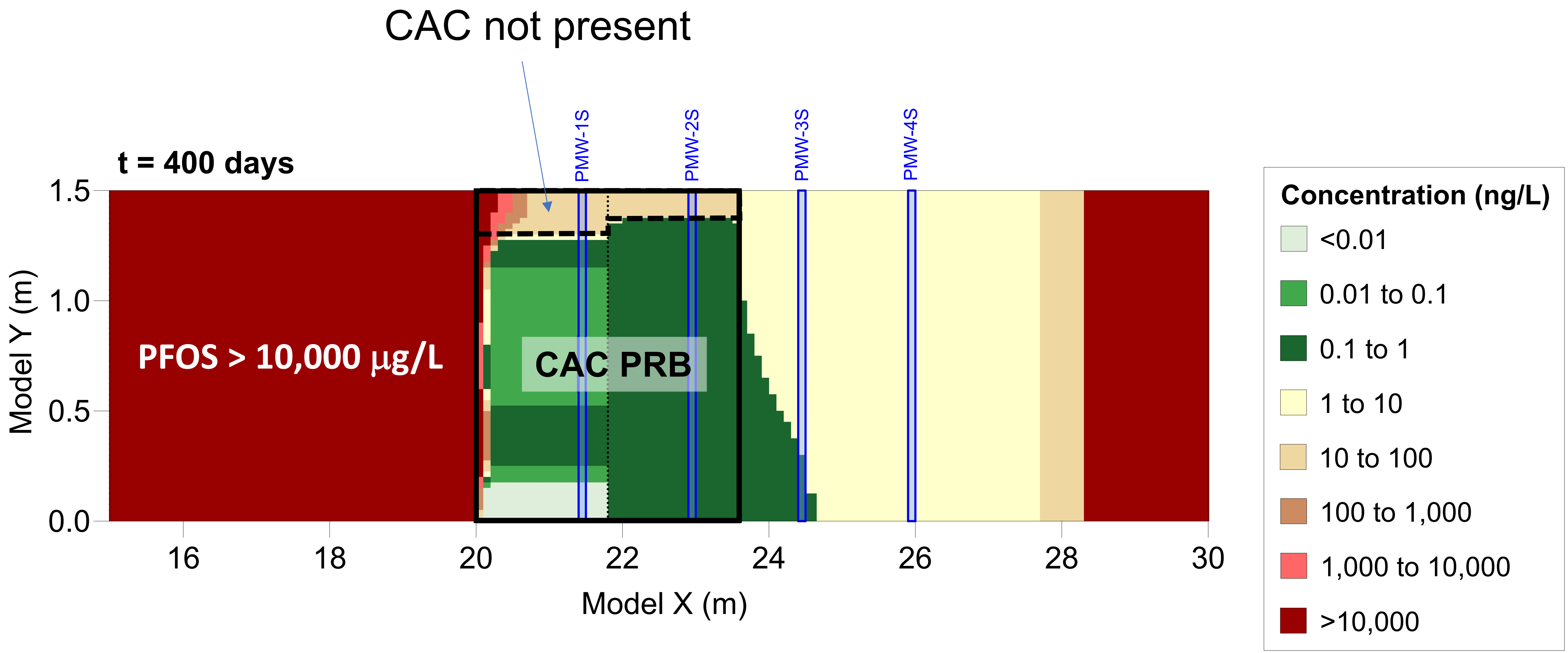
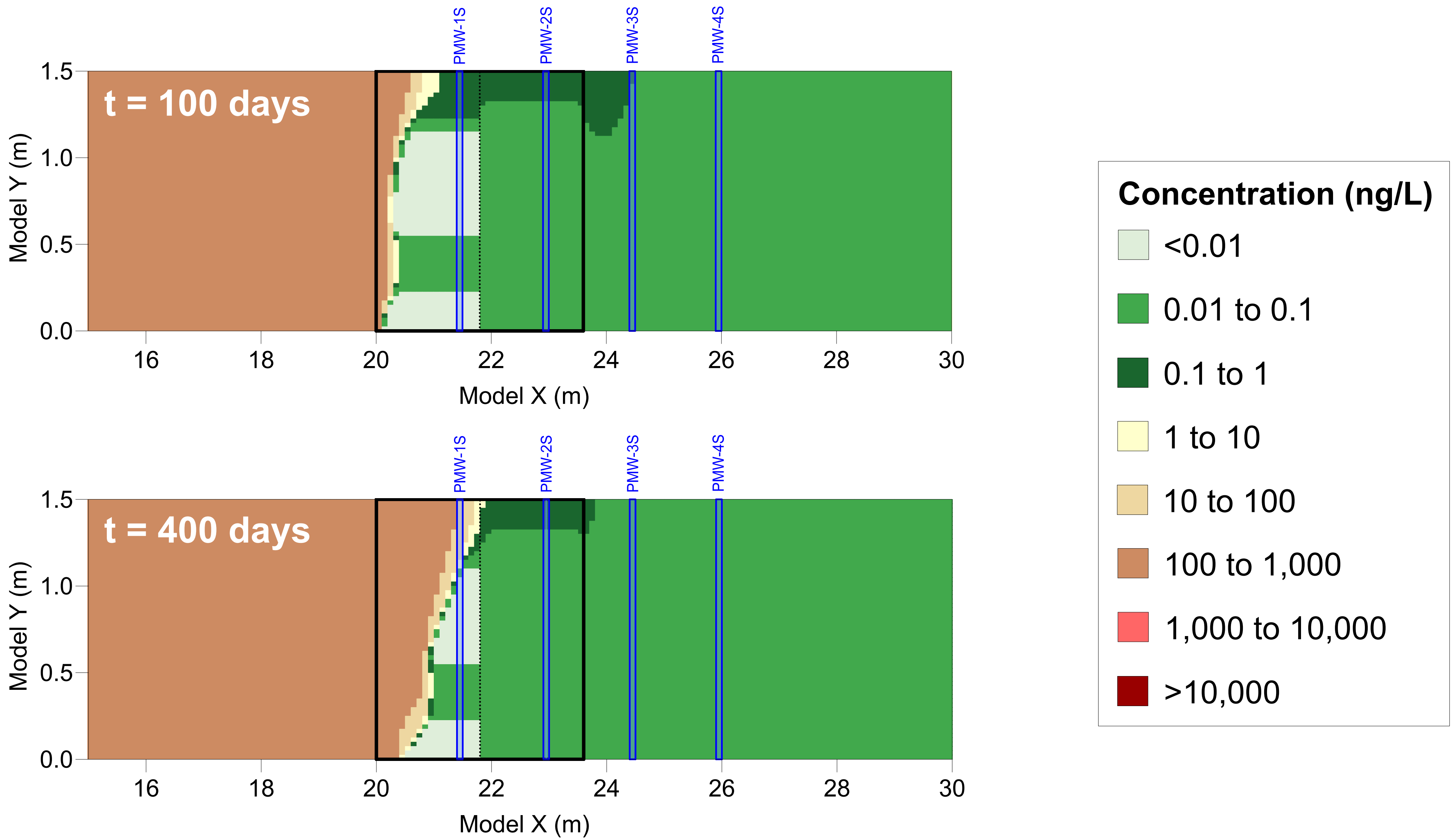


Modeled PFOS Concentrations in Cross-Section

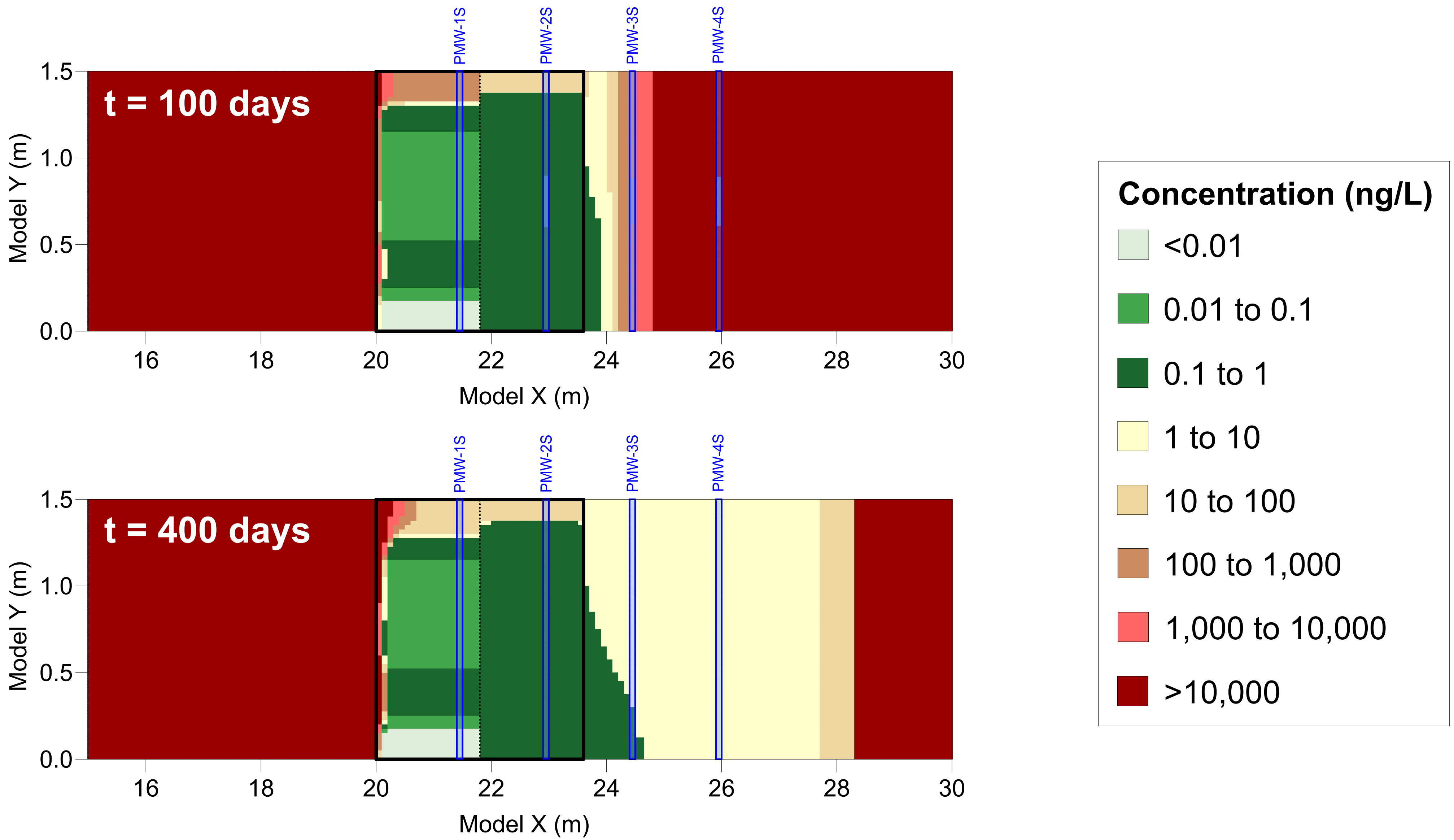


ISR-MT3DMS calculates the transmissivity-weighted average of PFAS concentrations in multi-layer well screens.

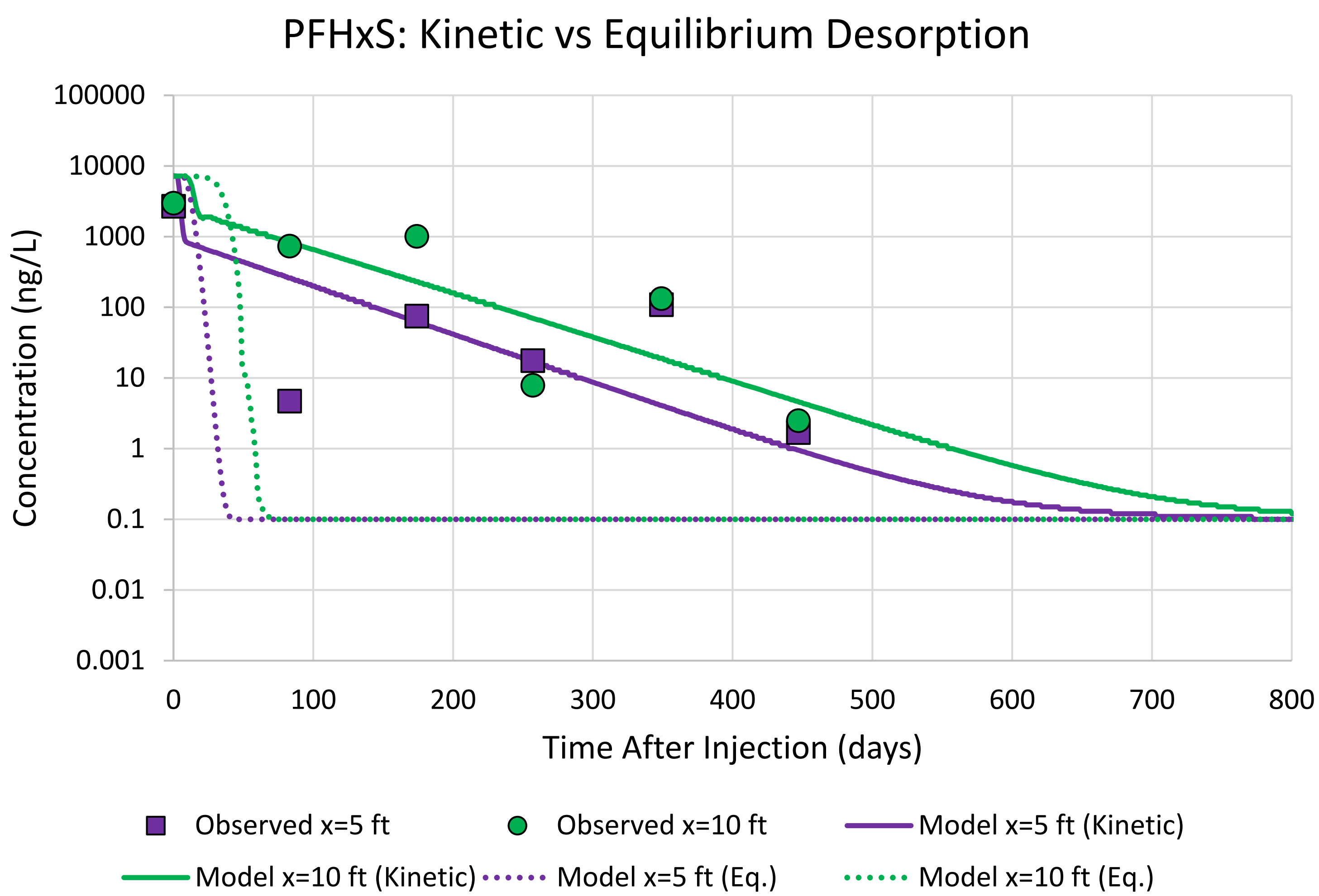
Modeled PFBS Concentrations in Cross-Section

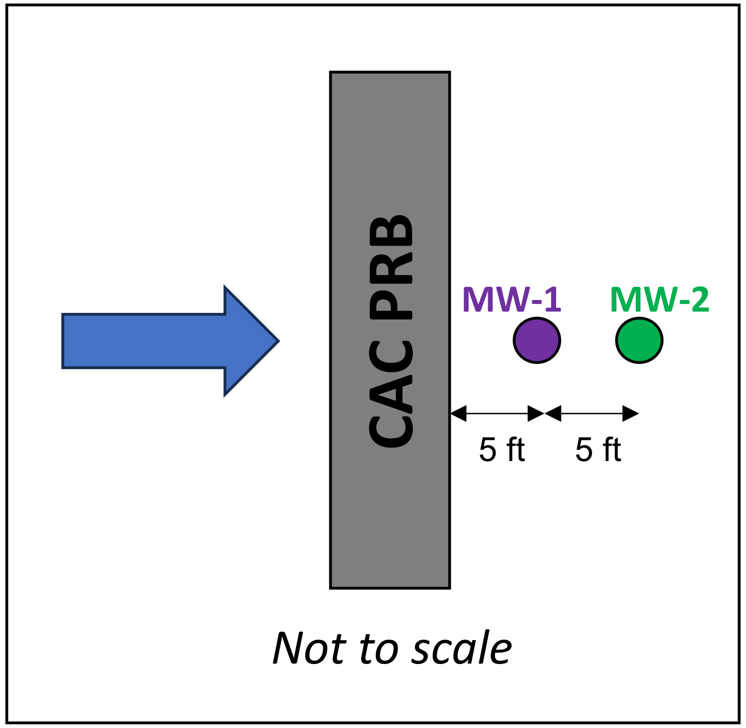


Modeled PFOS Concentrations in Cross-Section



East US Site: PFAS Desorption Downgradient of PRB





v = 200 ft/y

f_{oc} = 0.2%

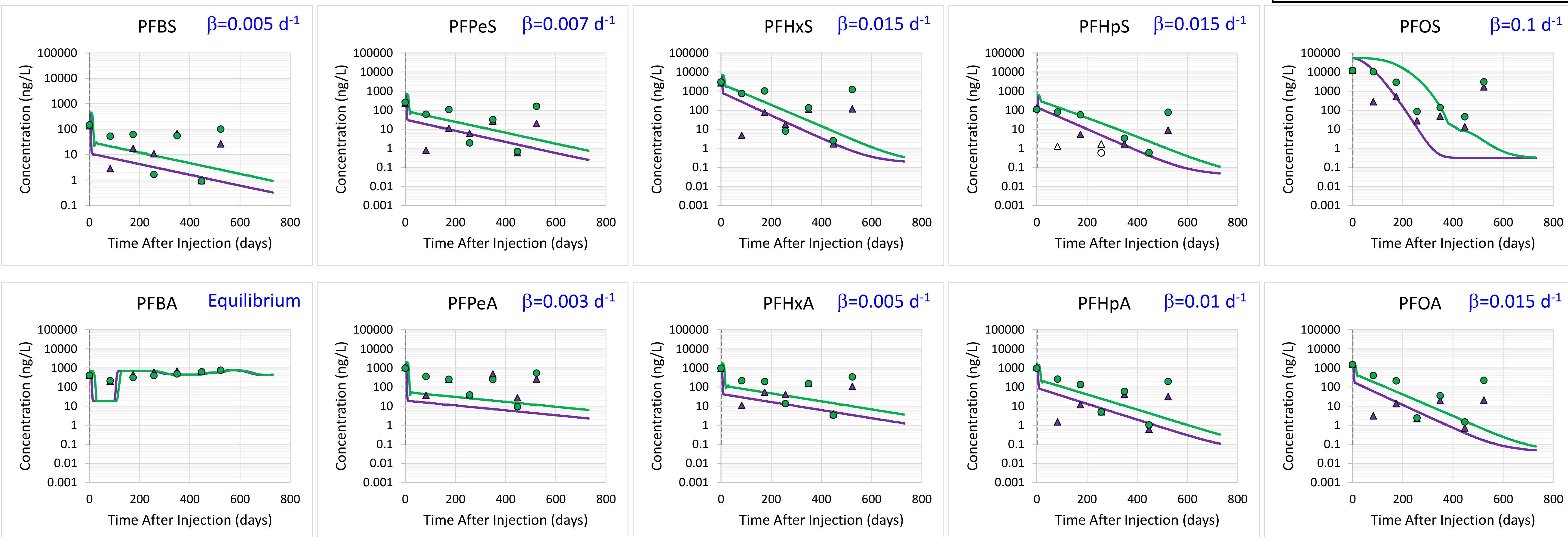
C_{max} = 7 μg/L

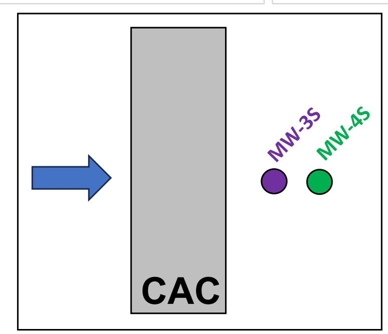
5 ft

Kinetic Desorption Using ISR-MT3DMS

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

β = first-order rate (d^{-1})

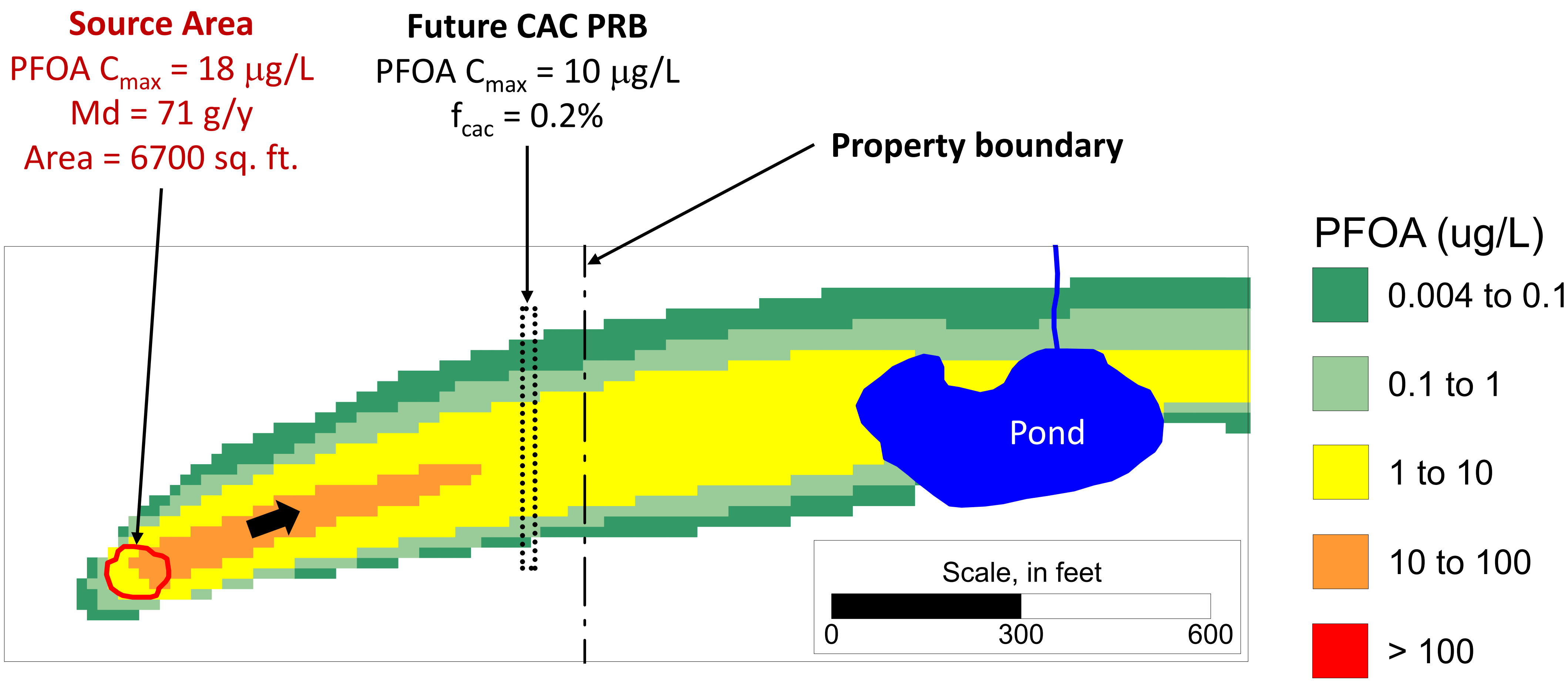




Long-Term Remediation Strategies

Section 3

Integrated Remedy Analysis



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

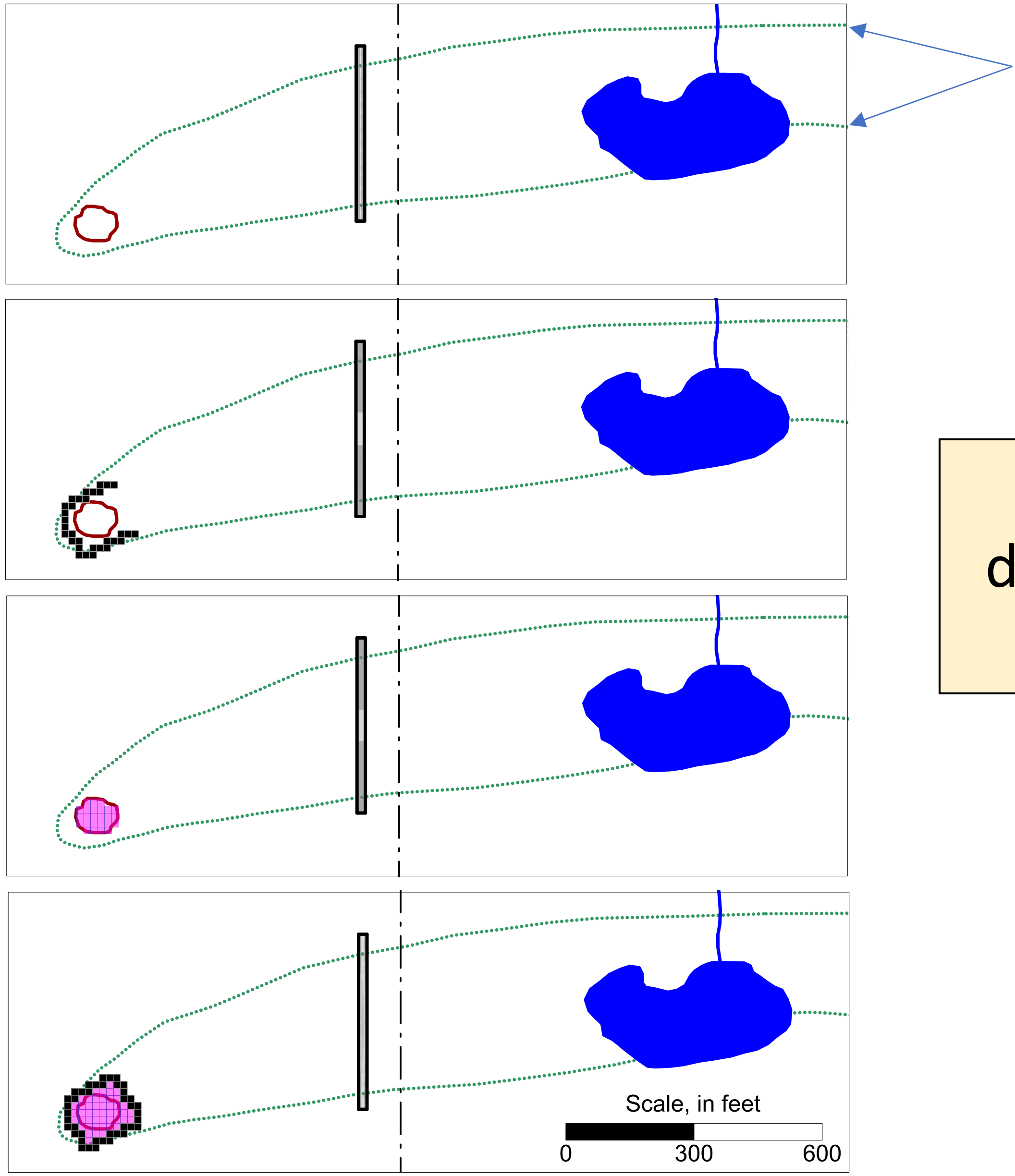
Simulated Remedial Alternatives

<u>Alternative No. 1</u>
CAC PRB

<u>Alternative No. 2</u>
CAC PRB + Partial Wall

<u>Alternative No. 4</u>
CAC PRB + Cover

<u>Alternative No. 4</u>
CAC PRB + Full Wall + Cover



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

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

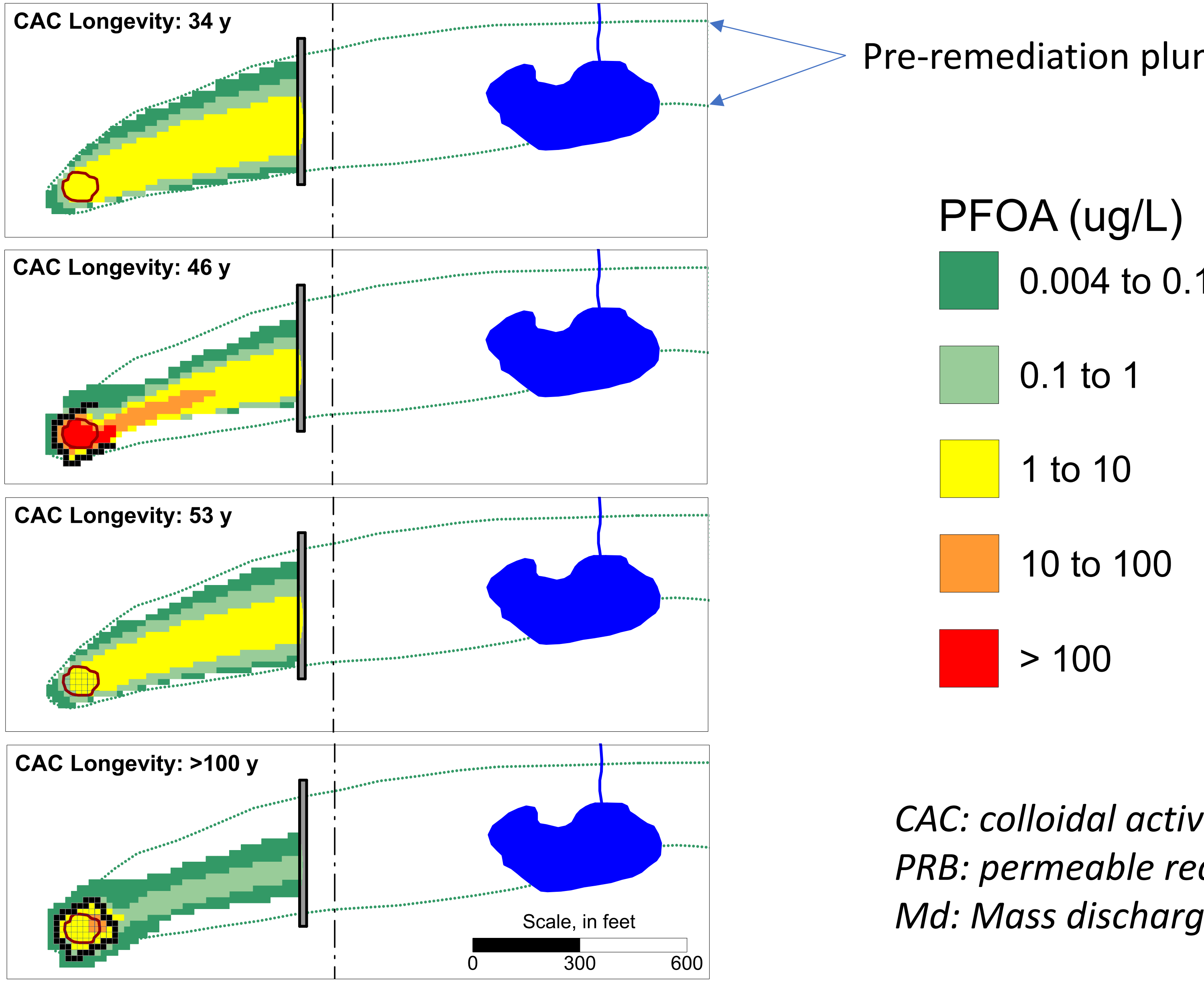
Modeled PFOA Plumes 30 years Post-Injection

<u>Alternative No. 1</u>
CAC PRB
Source Md = 36 g/y

<u>Alternative No. 2</u>
CAC PRB + Partial Wall
Source Md = 35 g/y

<u>Alternative No. 4</u>
CAC PRB + Cover
Source Md = 18 g/y

<u>Alternative No. 4</u>
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**

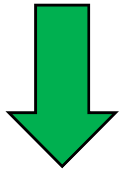
$$\text{Hazard Index (HI) MCL} = \left(\frac{\text{PFNA}}{0.01\ \mu\text{g/L}}\right) + \left(\frac{\text{PFHxS}}{0.01\ \mu\text{g/L}}\right) + \left(\frac{\text{PFBS}}{2\ \mu\text{g/L}}\right) + \left(\frac{\text{HFPO}-\text{DA}}{0.01\ \mu\text{g/L}}\right) = 1$$

- 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

<u>Downgradient PRBs</u>

- Greater longevity
- Faster goal attainment at downgradient receptors

Short-Term Goal: PFAS mass discharge 

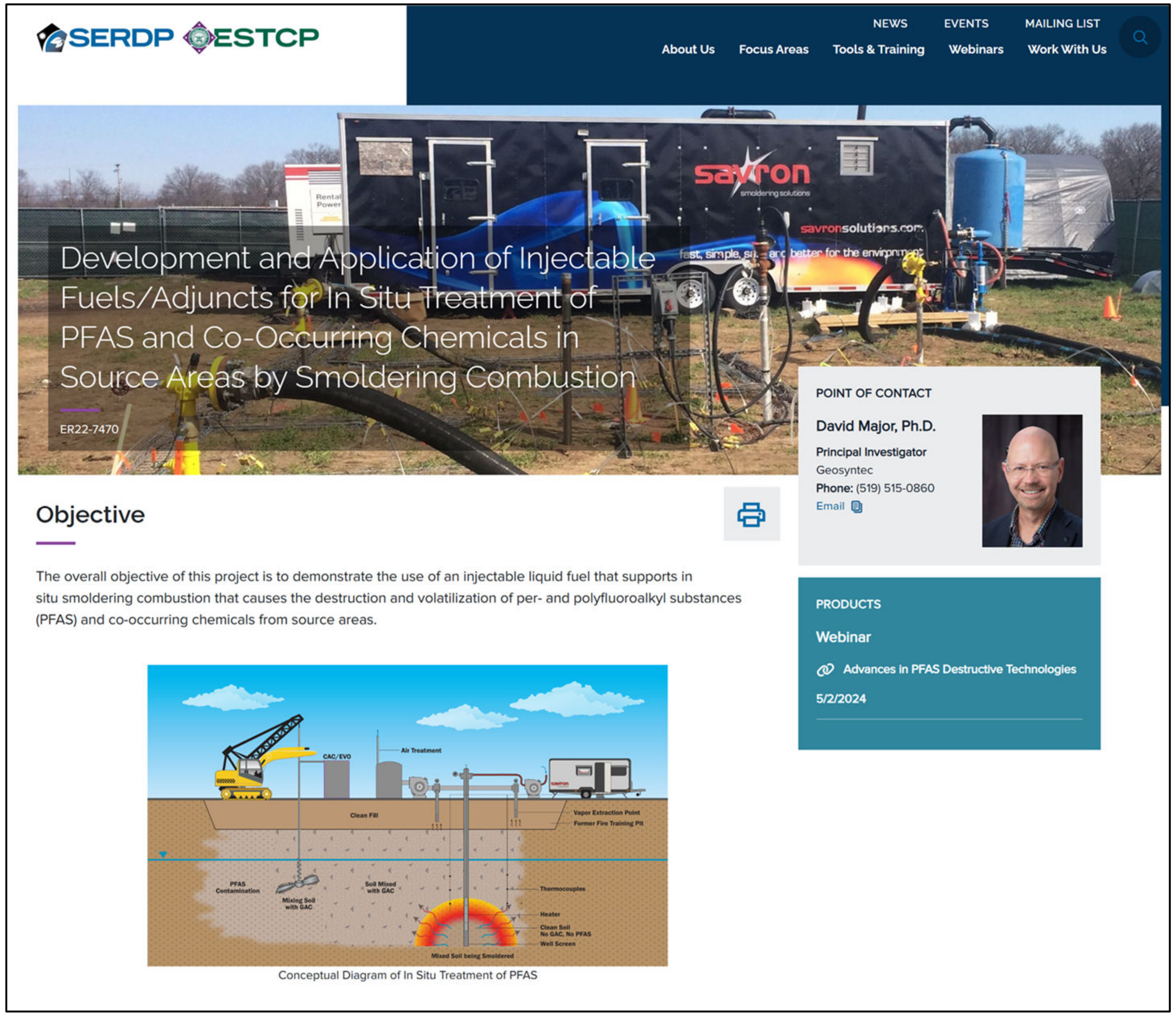
Longer Term Goal: Cleanup criteria attainment

- 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)



Questions?

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