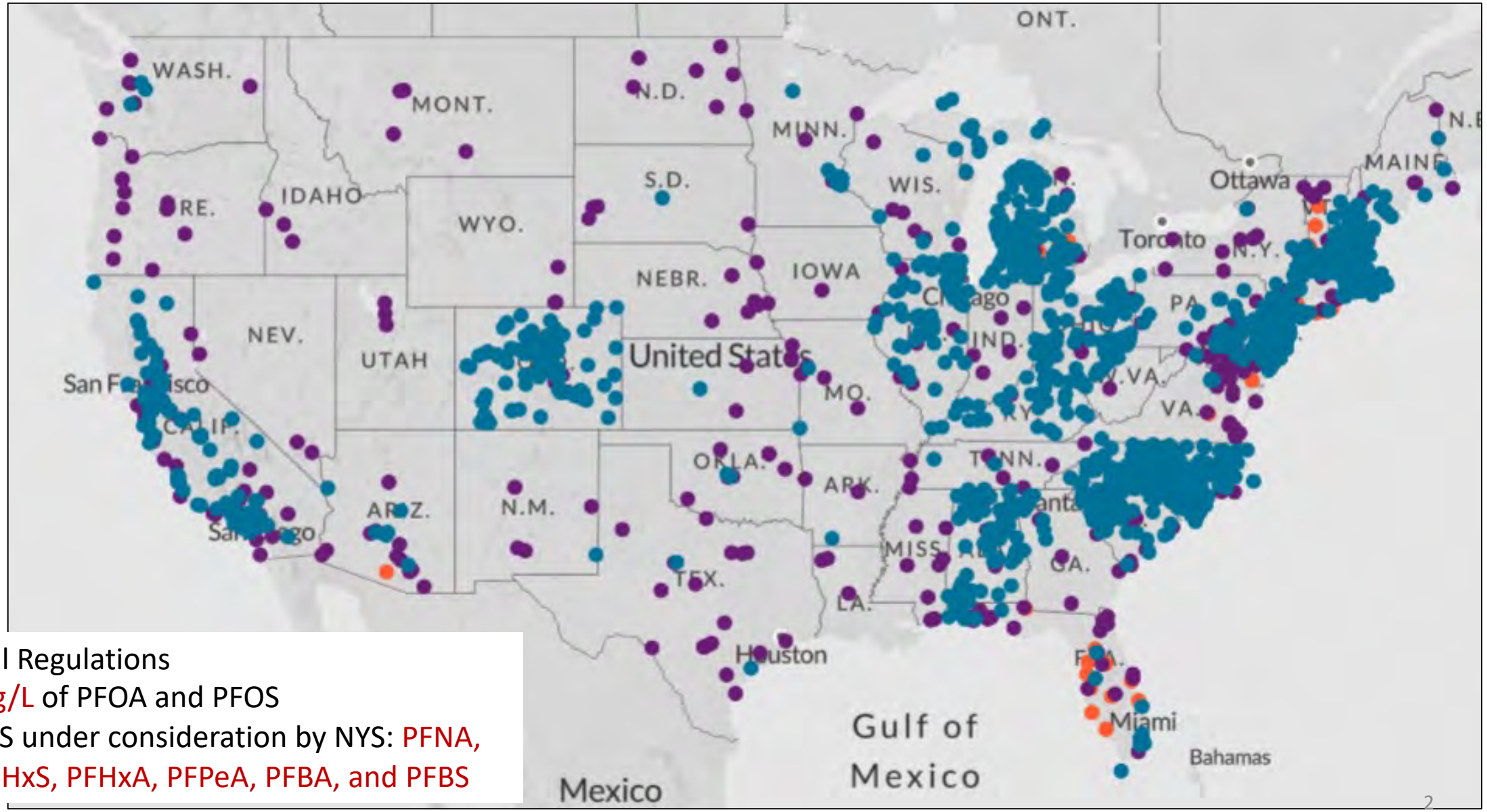
Understanding the competitive sorption between short-chain and long-chain PFAS during granular activated carbon treatment

Yi Zhang[1], Cheng-Shiuan Lee[1], Onur Apul[2], Arjun Venkatesan[1]

[1] Stony Brook University
[2] University of Maine

Widespread PFAS Occurrence in U.S.



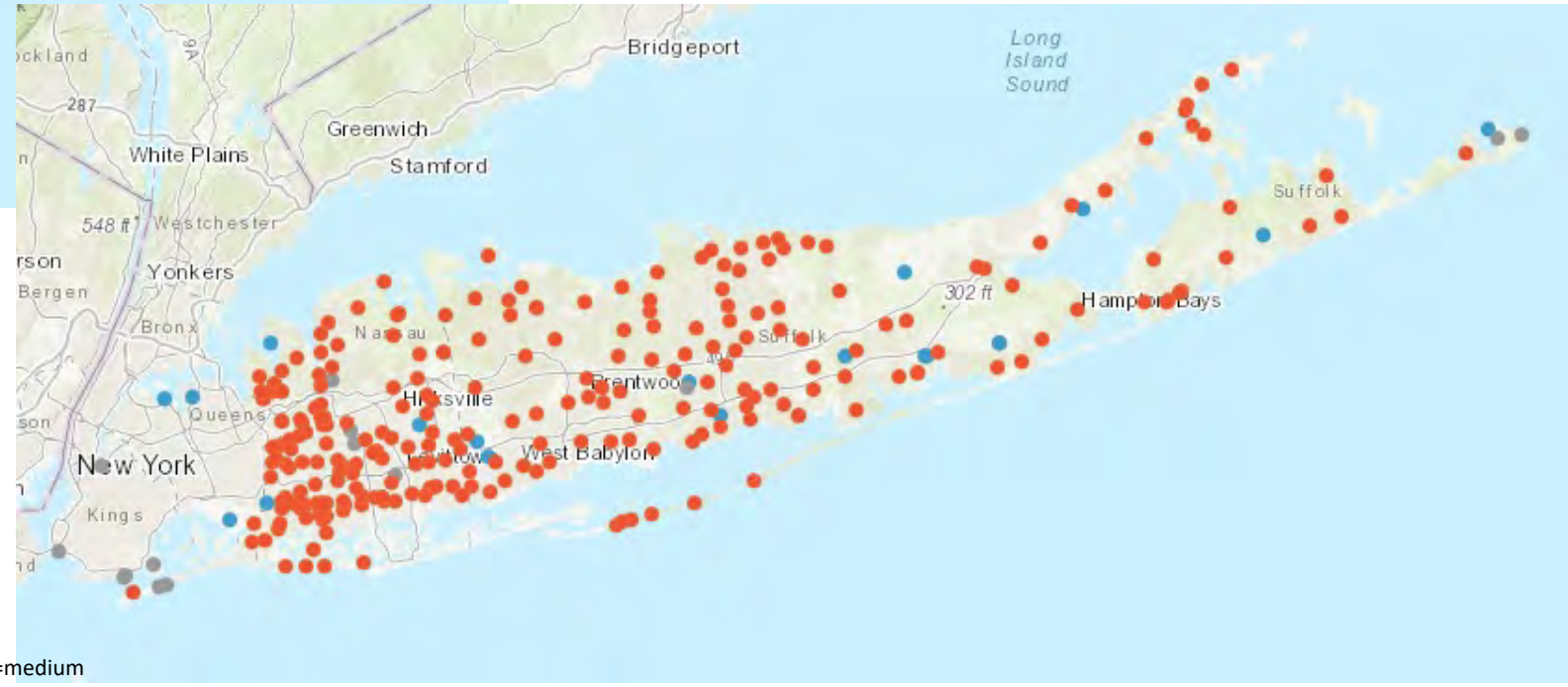
No Federal Regulations
NYS: 10 ng/L of PFOA and PFOS
Other PFAS under consideration by NYS: PFNA, PFHpA, PFHxS, PFHxA, PFPeA, PFBA, and PFBS

Source: https://www.ewg.org/interactive-maps/pfas_contamination/map/

PFAS in Long Island, NY

Detections in public water supply

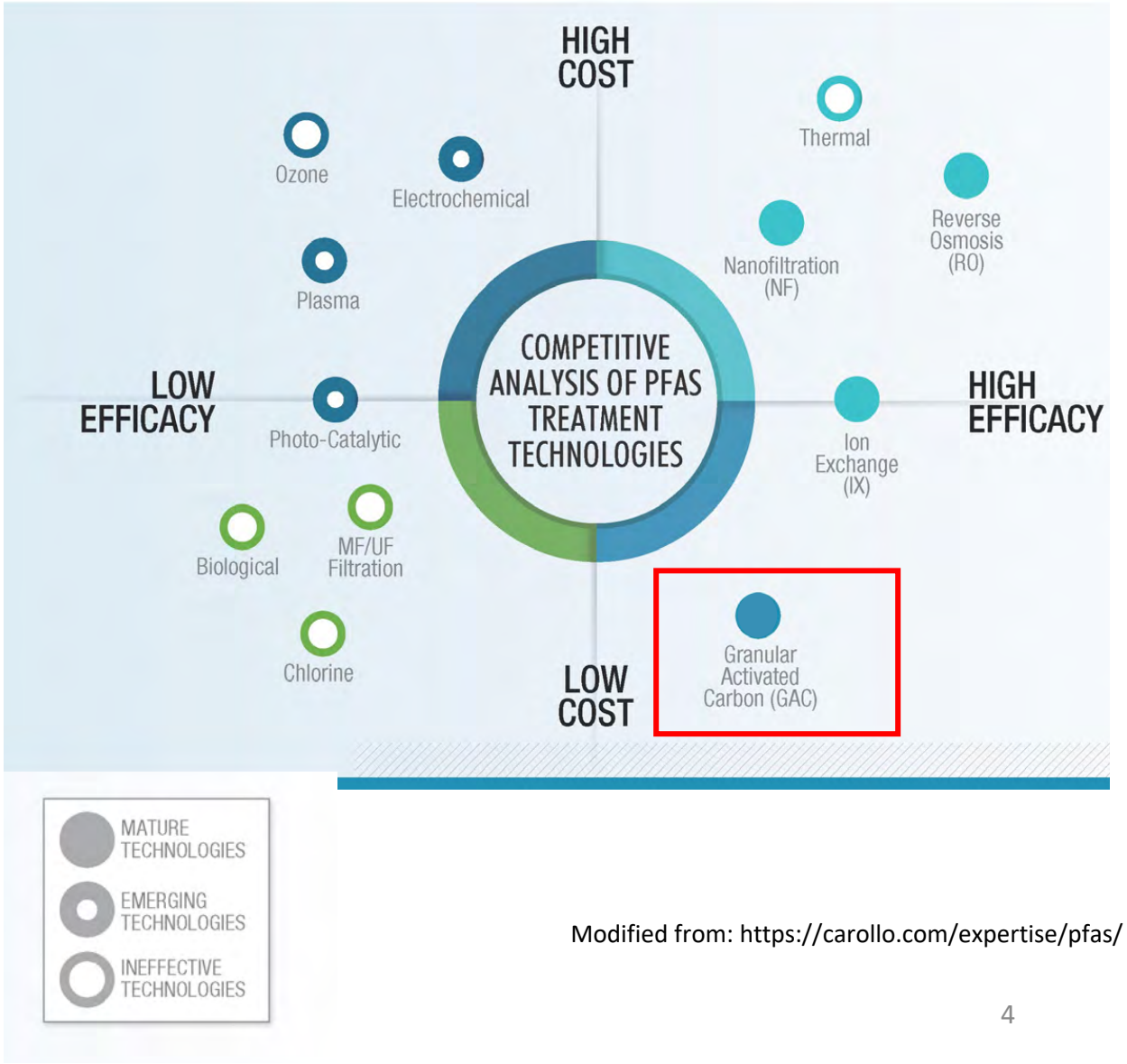
Potential sources



https://storymaps.arcgis.com/stories/3d1343836d71453faf1590e6ae81f4f5?play=true&speed=medium

PFAS treatment technologies: a summary

Treatment Type	Technology Category	Technology
Sequestration Technologies	Sorption	Activated Carbon Anion Exchange Resin Biochar Zeolites/clay minerals
	Membrane Filtration	Reverse Osmosis Nanofiltration
	Coagulation	Specialty Coagulants
Transformation or destruction technologies	Redox treatment	Electrochemical Electron beam Ozone Plasma
	Other	Sonochemical Thermal Biological



Modified from: https://carollo.com/expertise/pfas/

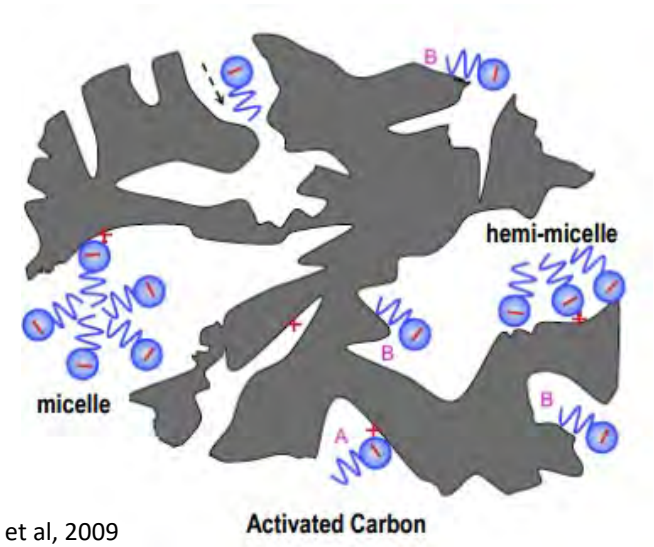
Removal by Granular Activated Carbon (GAC)

Most common approach for PFAS treatment

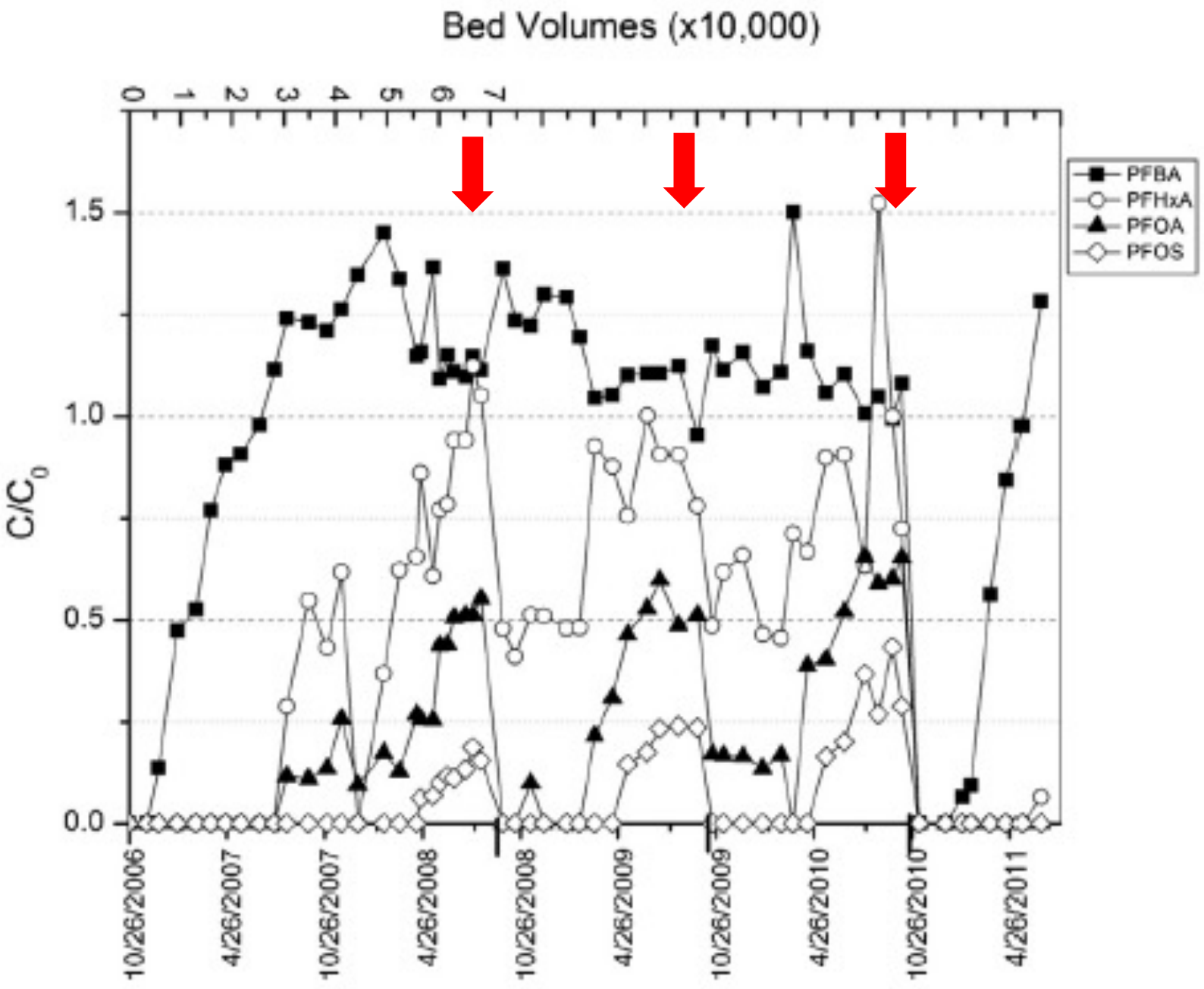
Sorption Mechanism:

- Hydrophobic interactions - dominant mechanism
- Long-chain PFAS with higher hydrophobicity show better removal compared to short-chain PFAS
- Electrostatic interactions – minor but important for short-chain PFAS

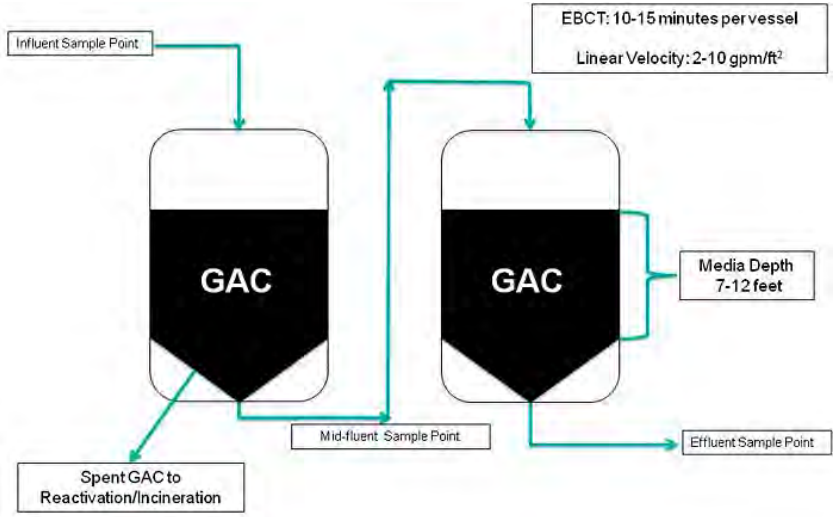
Granular mean particle diameter (1mm)
Powdered mean particle diameter (0.043 mm)



Yu et al, 2009



Appleman et al., 2014. Water Res 51: 246-255

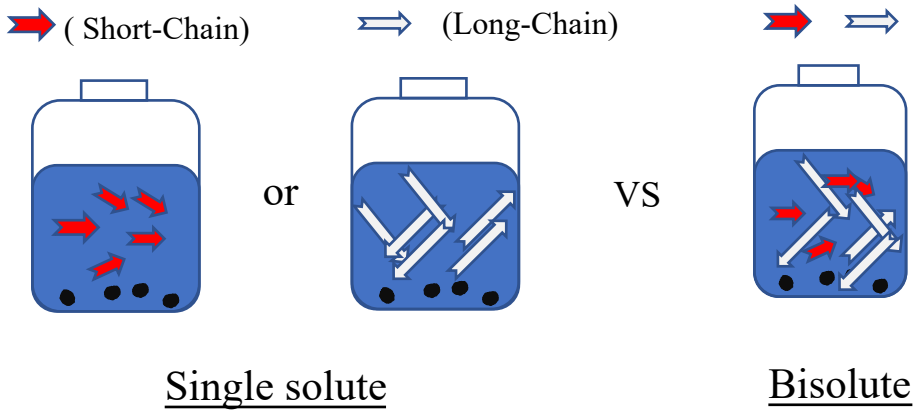


- PFBA breakthrough occurred within 2 months
  - C/C_0 >1 –accumulated PFBA being replaced by other competing species (long-chain PFAS)
- Lead vessel breakthrough –
  - PFHxA/PFOA ~10 months
  - PFOS ~ 18 months

Research Objectives

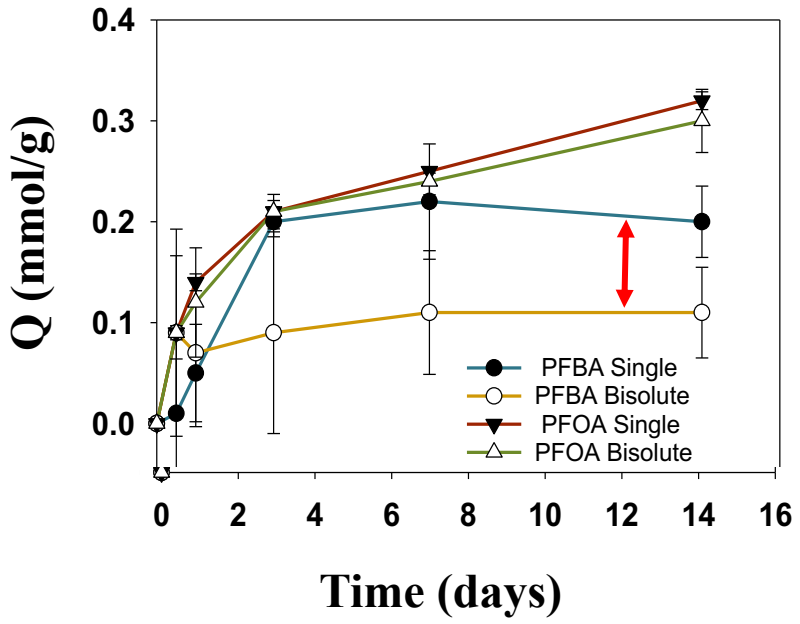
- Understand competition between short-chain and long-chain PFAS using controlled batch experiments
- Influence of cations on PFAS sorption
- Improve short-chain PFAS removal by GAC (ongoing)

Bisolute Competition

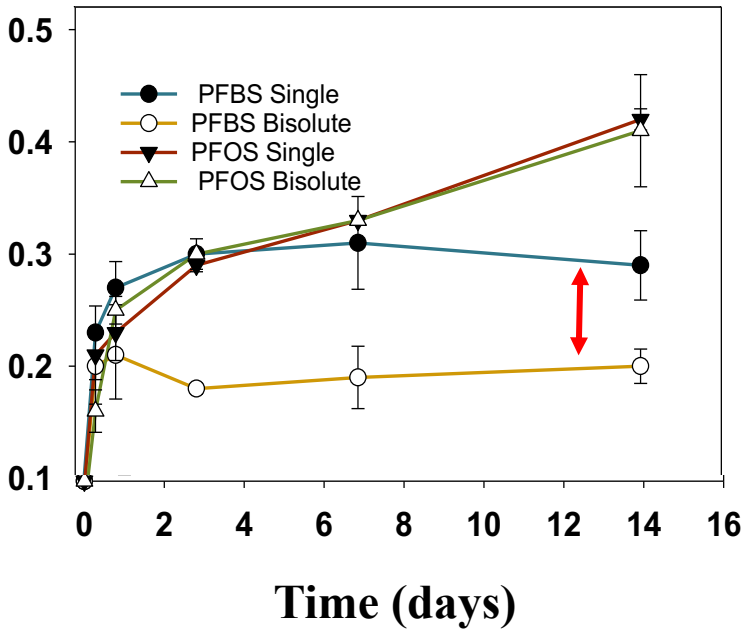


Experimental conditions: 4 mg/L GAC in 250 mL deionized water for 14 days mixing

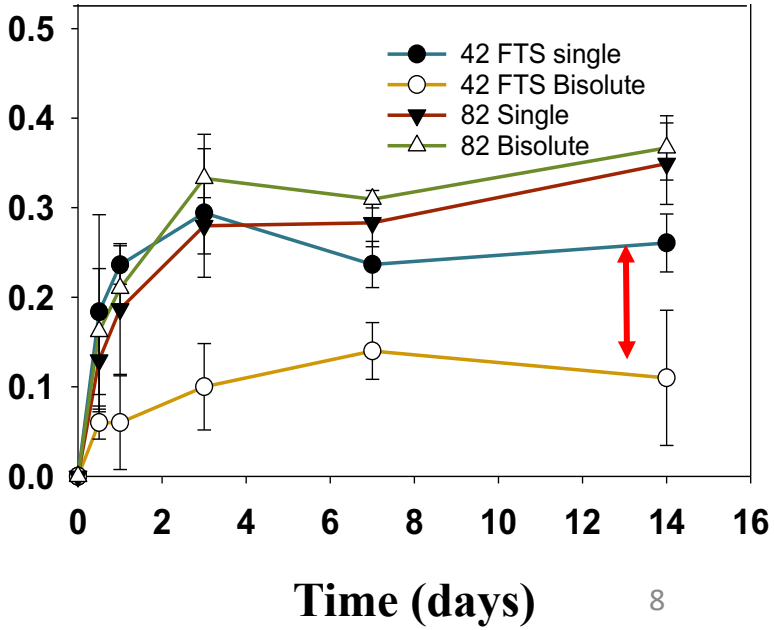
Carboxylic acids



Sulfonic acids

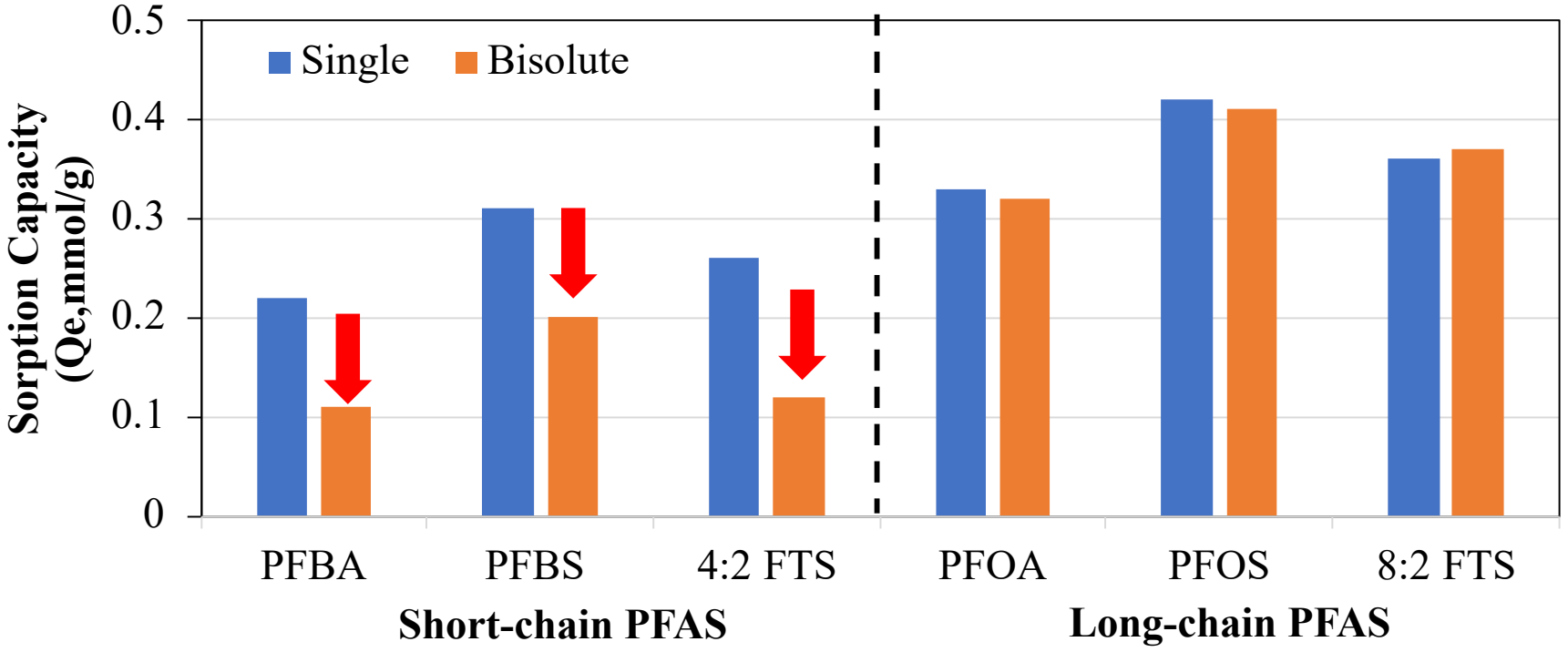


Fluorotelomer sulfonates

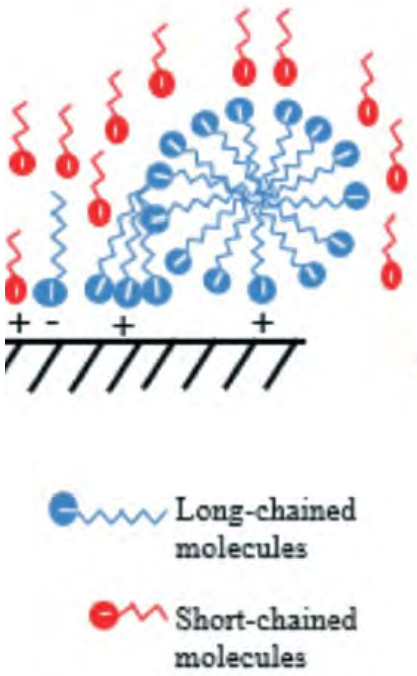


Results – Bisolute Competition

- Kinetics fitting– sorption capacity (Qe) fitted from pseudo-second-order model

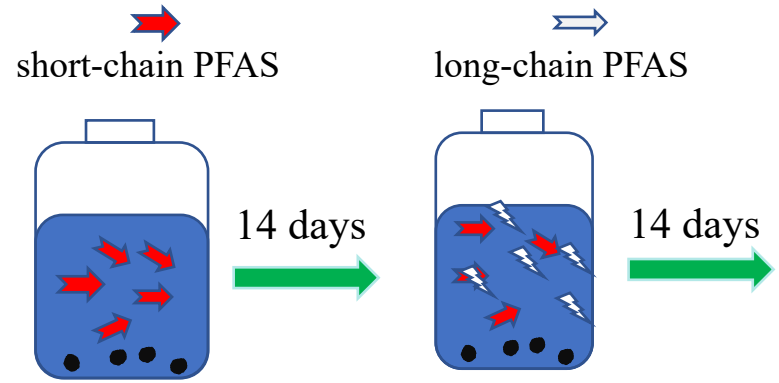


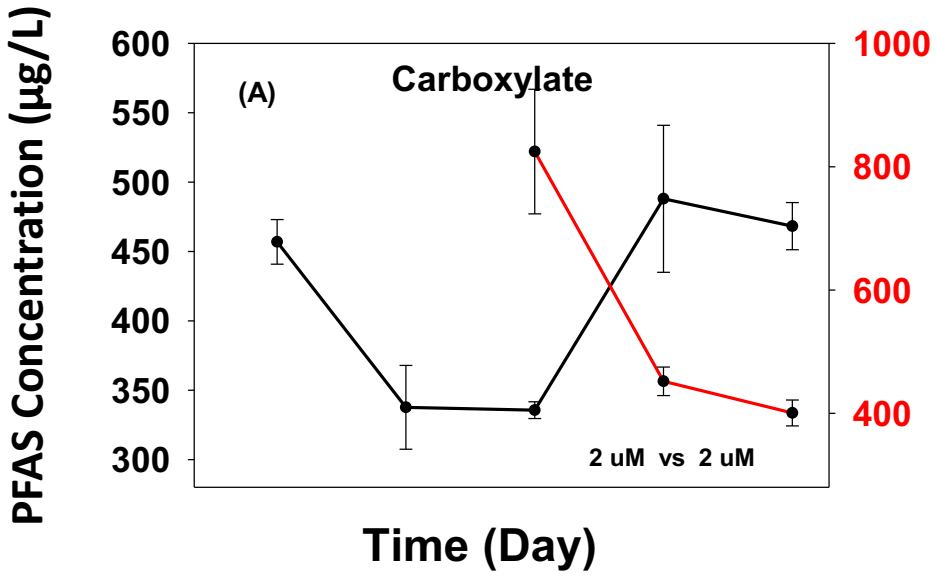
Competition/blockage of adsorption site by long-chain PFAS

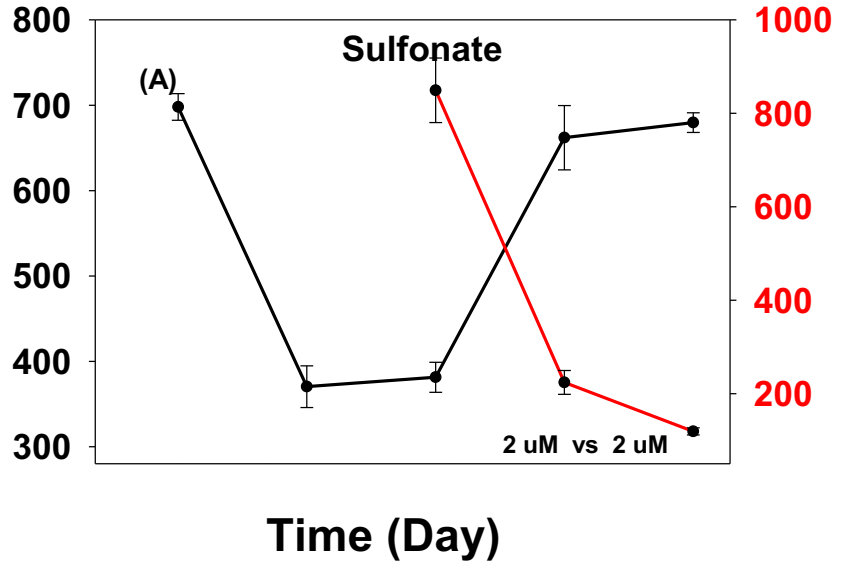


Desorption of Short-chain PFAS

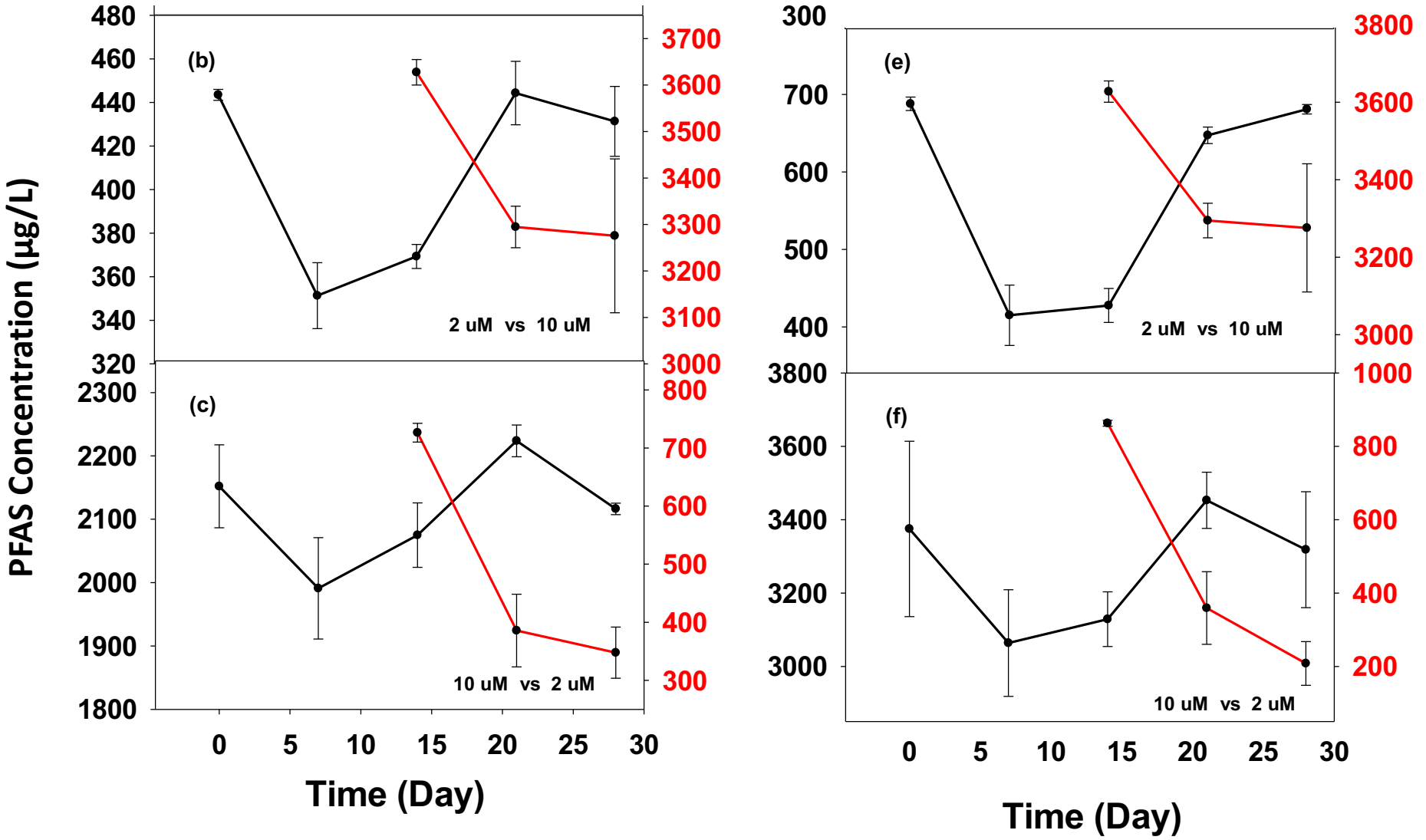
- Pre-loaded (equilibrated) short-chain PFAS on GAC (14 days); long-chain PFAS was added on day 14

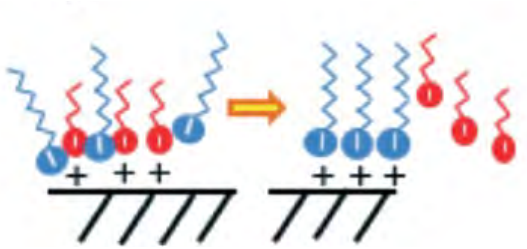






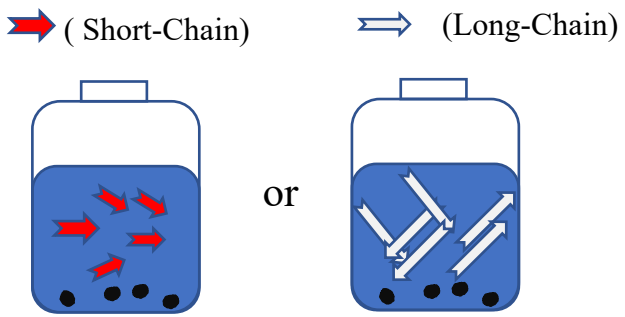
Desorption happens irrespective of molar ratio





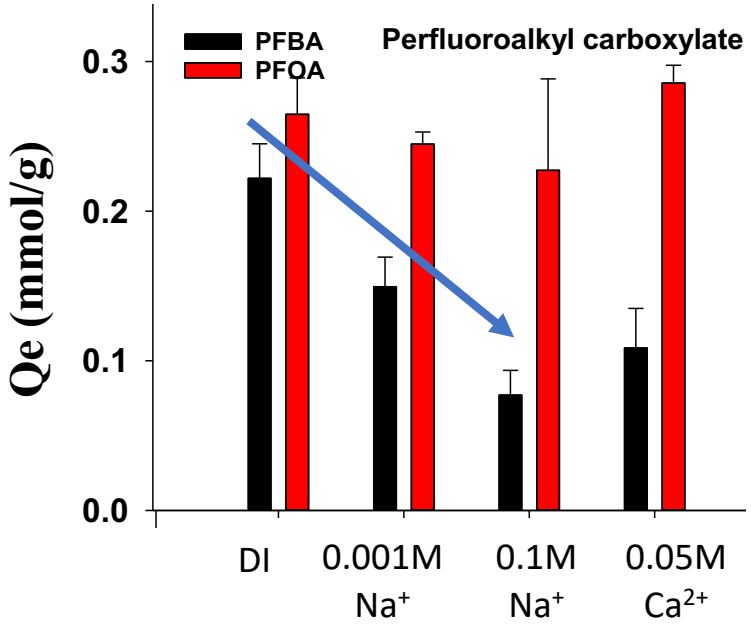
Displacement of short-chain by long-chain PFAS

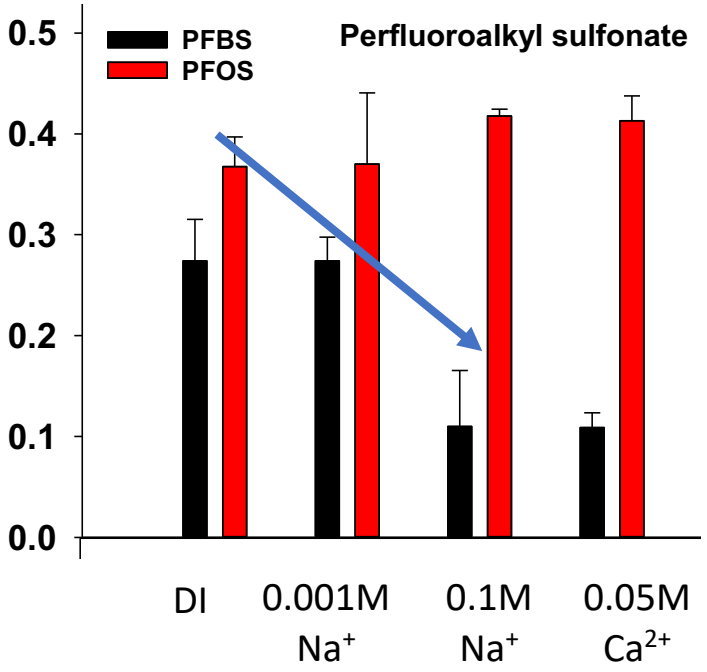
Impact of cations on short-chain PFAS sorption

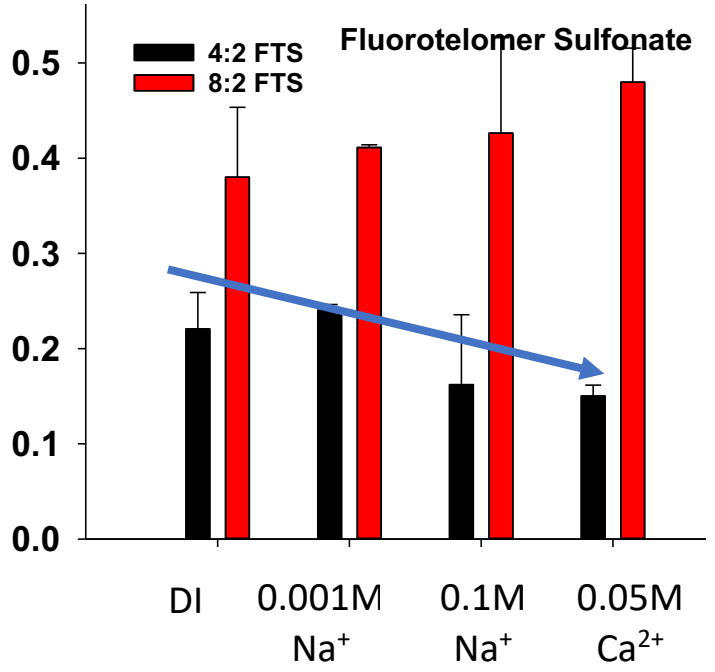


Single solute + salt

Conc. (M)		Ionic Strength (M)
Na^+	0.001	0.005
Na^+	0.1	0.1
Ca^{2+}	0.05	0.1

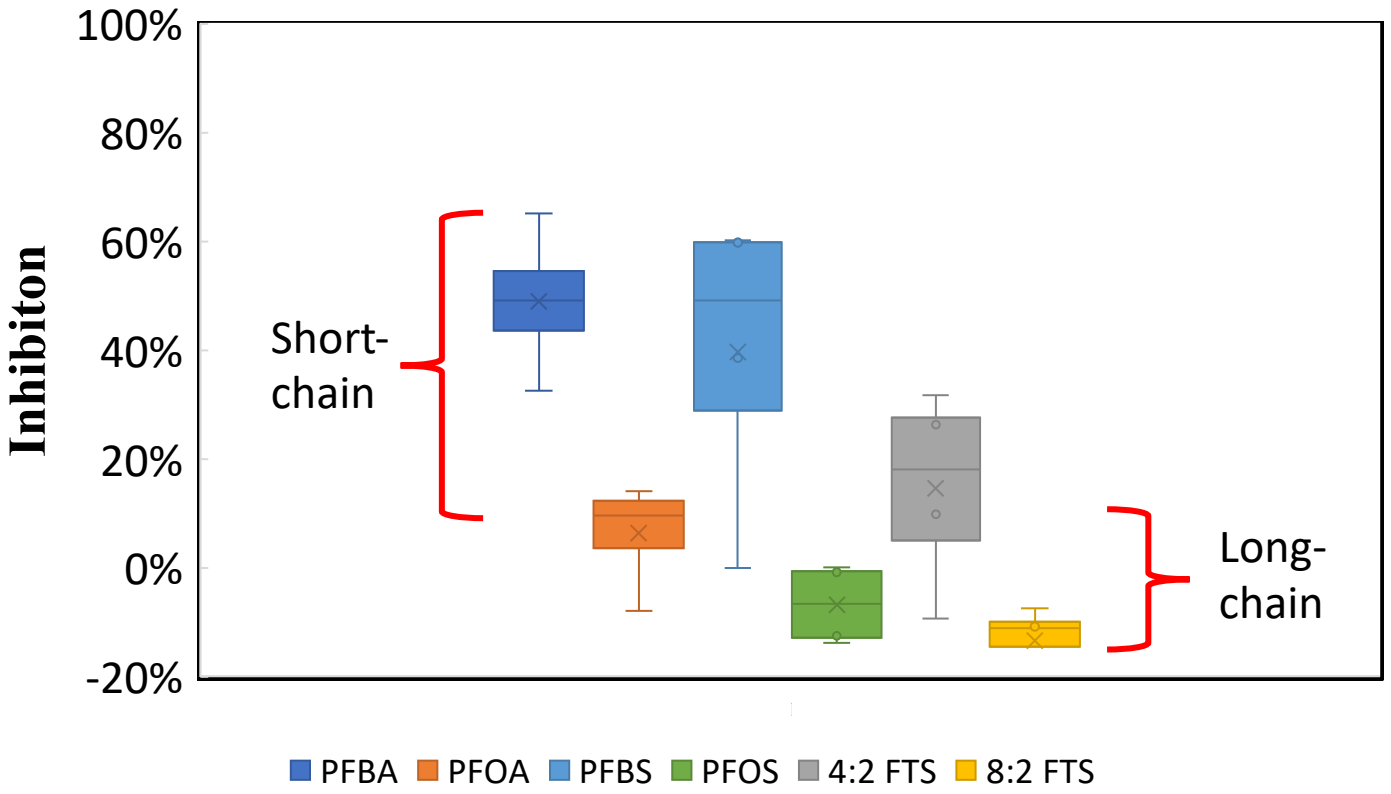


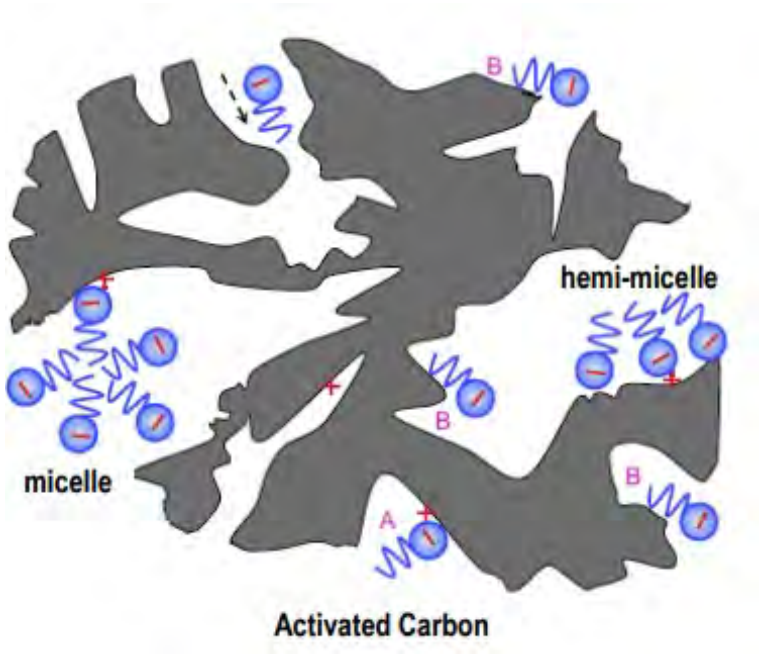




Impact of cations on short-chain PFAS sorption

- Removal = $(1-C_t/C_0)*100\%$
- Cation inhibition % = (1- removal in matrix/removal in D.I.) * 100





Yu et al, 2009

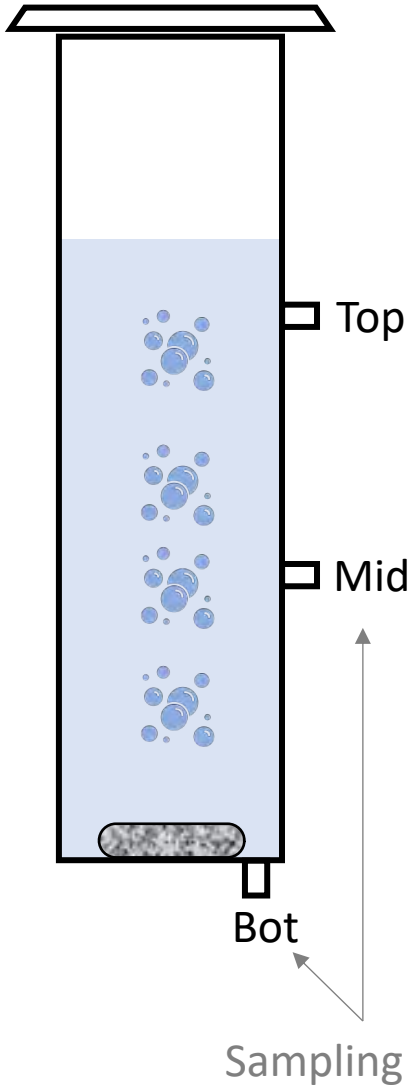
Summary

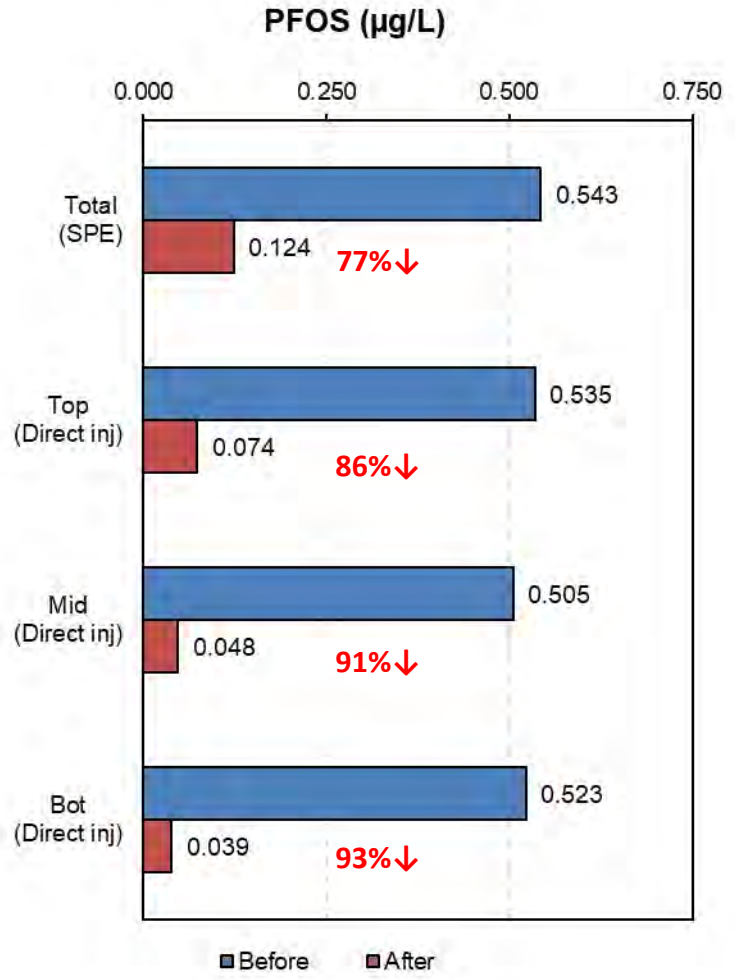
- Short-chain PFAS was suppressed in the presence of long-chain PFAS: while long-chain PFAS was not impacted by the presence of short-chain PFAS
- Long-chain PFAS replaced short-chain PFAS on adsorbed GAC surface at various molar ratios
- Presence of inorganic cation suppressed the short-chain PFAS sorption, while having little effect on long-chain PFAS sorption

Ongoing Work

- Developing approaches to minimize competition between short-chain vs. long-chain PFAS: (i) additives; (ii) combination of technologies
- Rapid Small Scale Column Testing (RSSCT) vs. pilot systems
- Combination of technologies: GAC + ion exchange

Air-bubbling to remove PFAS

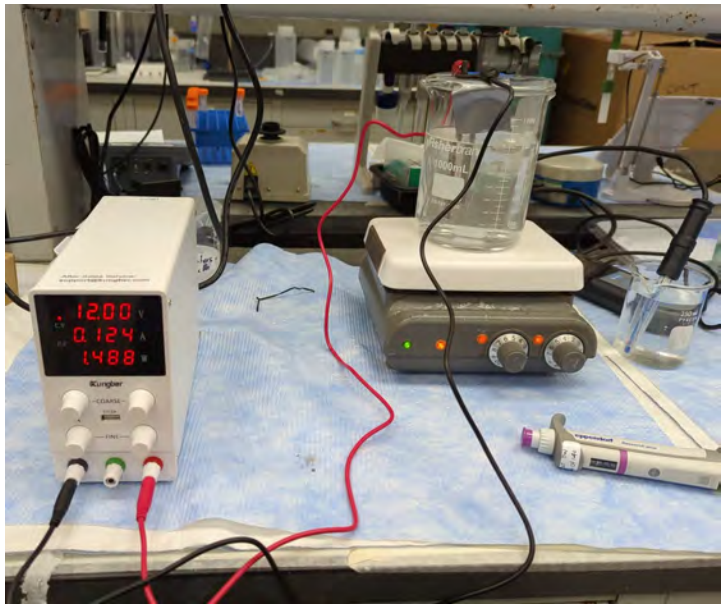




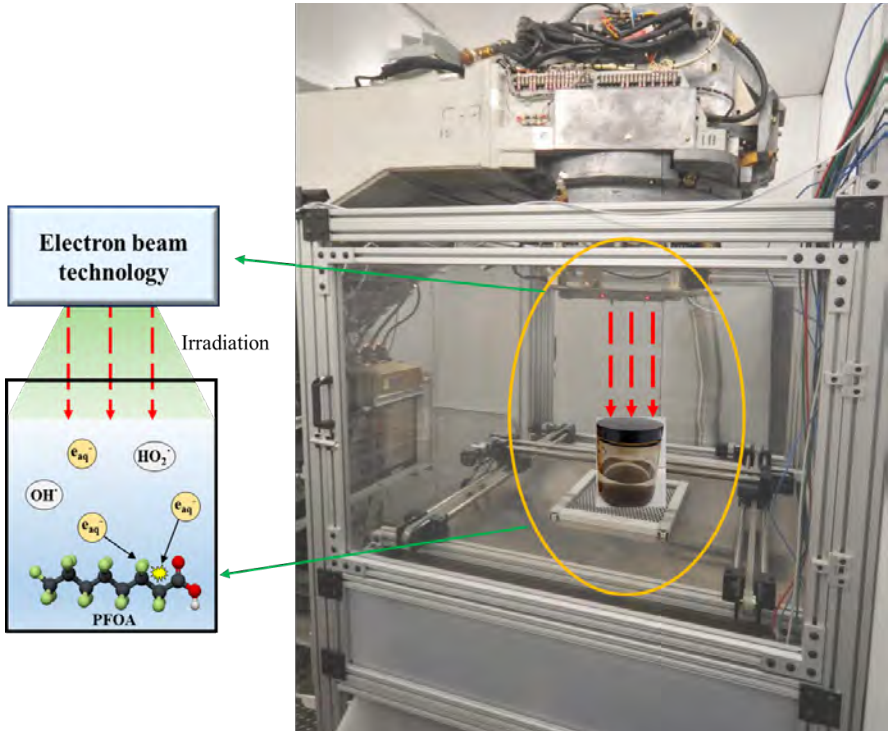
DI water matrix

Destructive Technologies for PFAS

Electrochemical Oxidation

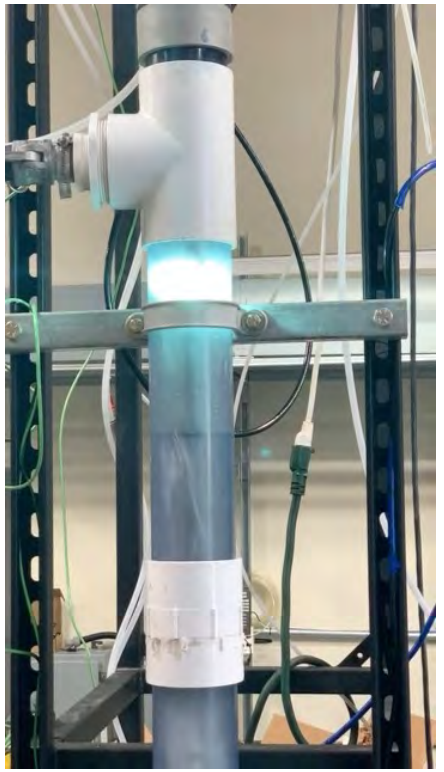


Electron Beam



In collaboration with Fermi Accelerator National Laboratory

Non-thermal Plasma



In collaboration with Brookhaven National Lab

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Contact: Arjun.Venkatesan@stonybrook.edu

Twitter: @nysccwt; @arjun_water

https://www.stonybrook.edu/cleanwater/

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ccwt@stonybrook.edu