# Enhancing PFAS Treatment in Water: Insights from Bench-Scale Treatability Studies using Traditional and Novel Adsorbents

2024 NEWEA Annual Conference

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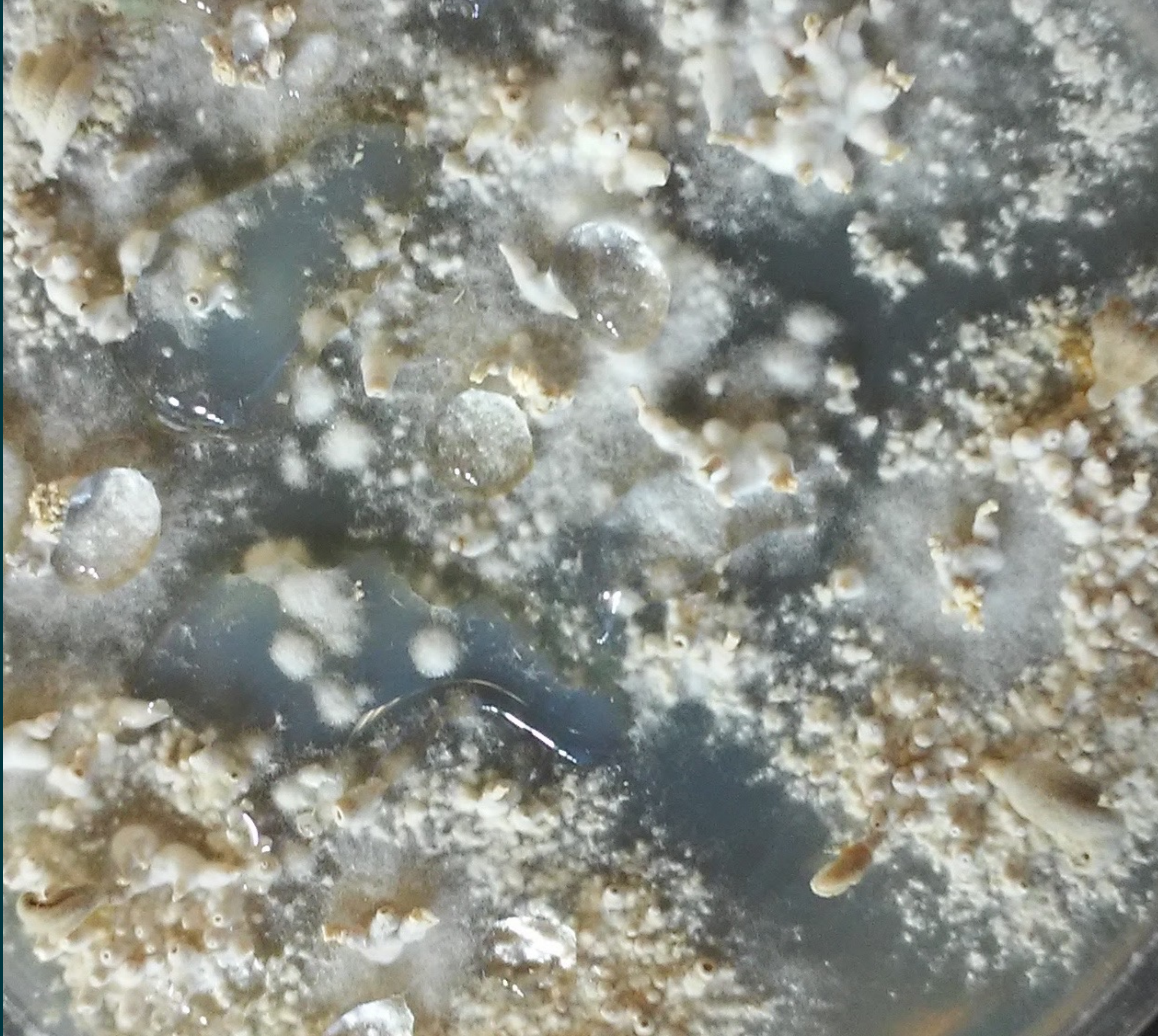
AECOM

## Agenda

PFAS Treatability

Case Studies

Take Home Message



# PFAS Treatability

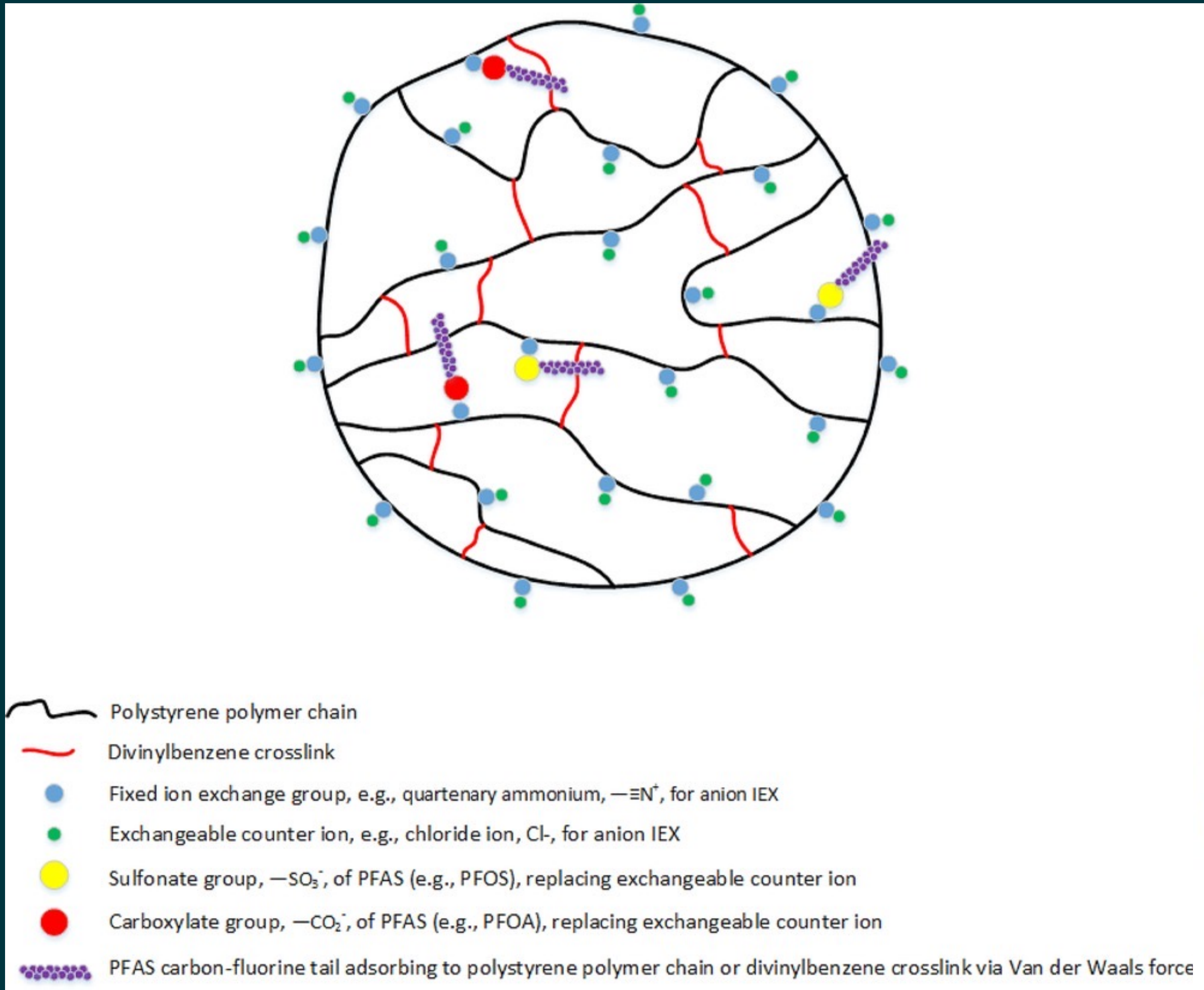
# PFAS Treatability – Adsorptive Technologies

Adsorption

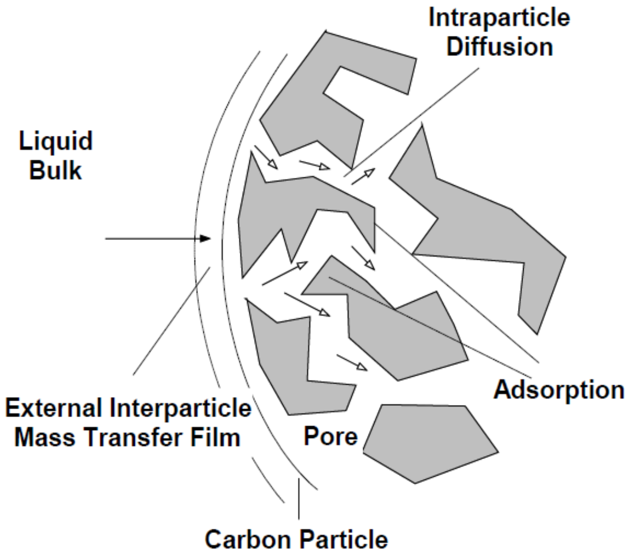
- Various mechanisms
  - Hydrophobic
  - Electrostatic
  - Molecular entanglement
- Material types
  - Activated Carbon
  - Ion exchange resins
  - Bentonites
  - Cyclodextrins

| Treatment Technology (Separation) | Maturity |
|---|---|
| Sorption - GAC | Mature and established |
| Sorption - IX | Mature and established |
| Reverse Osmosis | Mature and established |
| In situ colloidal activated carbon | Limited application |
| Precipitation/Flocculation/ Coagulation | Limited application |
| Surface Activation Foam Fractionation | Limited application |

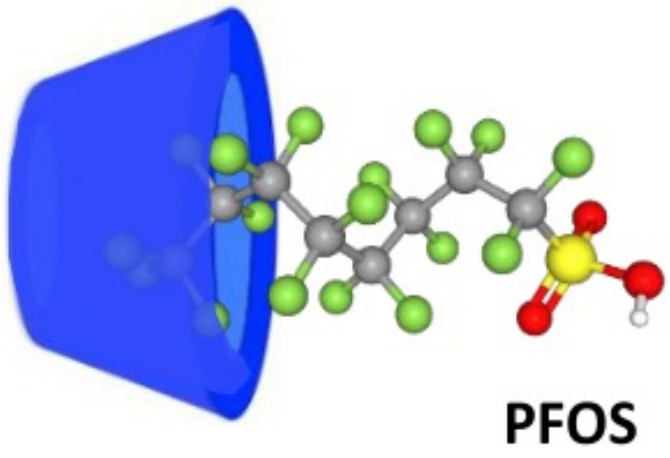
# PFAS Treatability – Adsorptive Technologies




**Ion Exchange Adsorption**
Woodard et al. (2017)

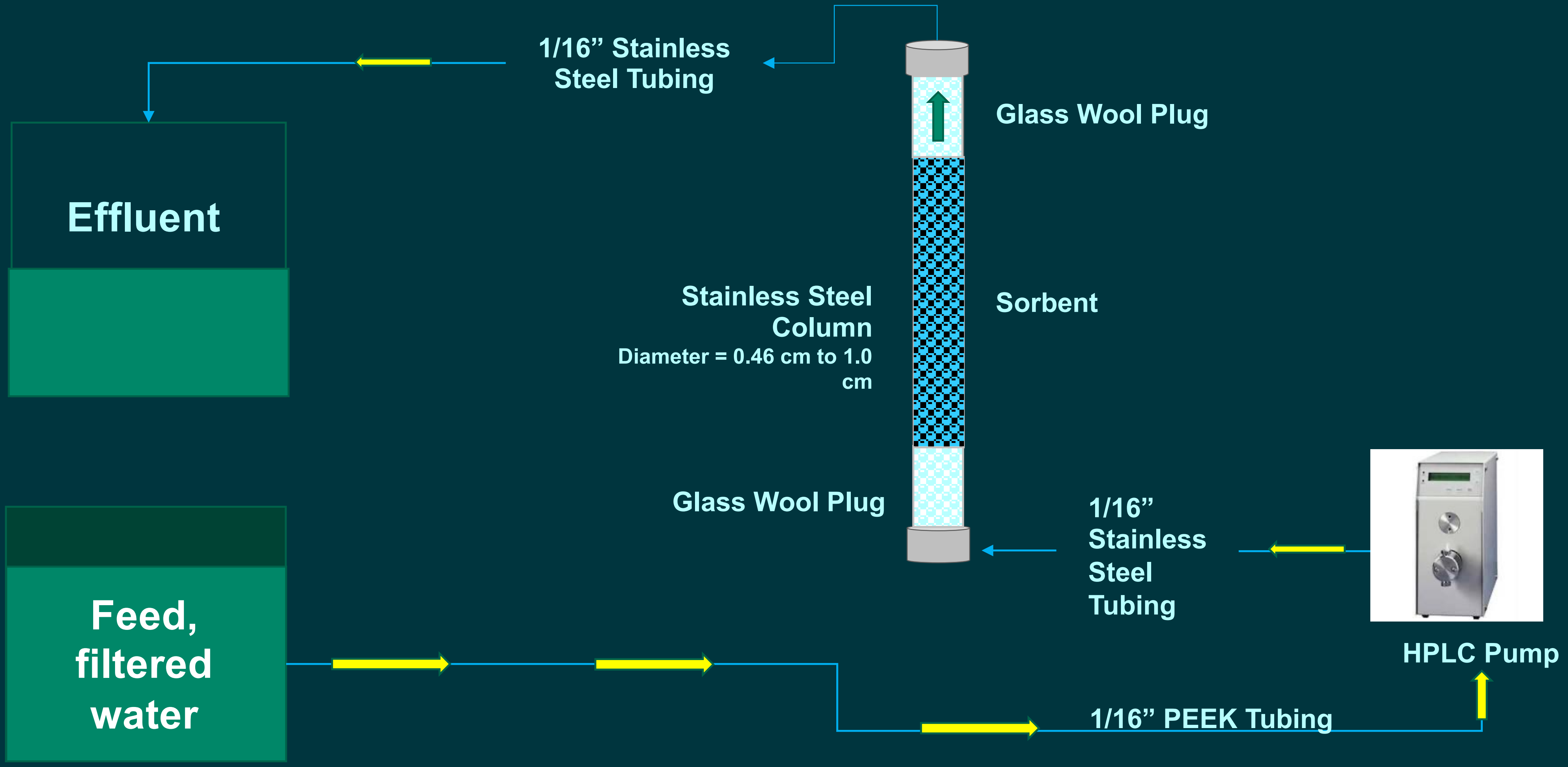



**GAC Adsorption**
Armenante (1991)

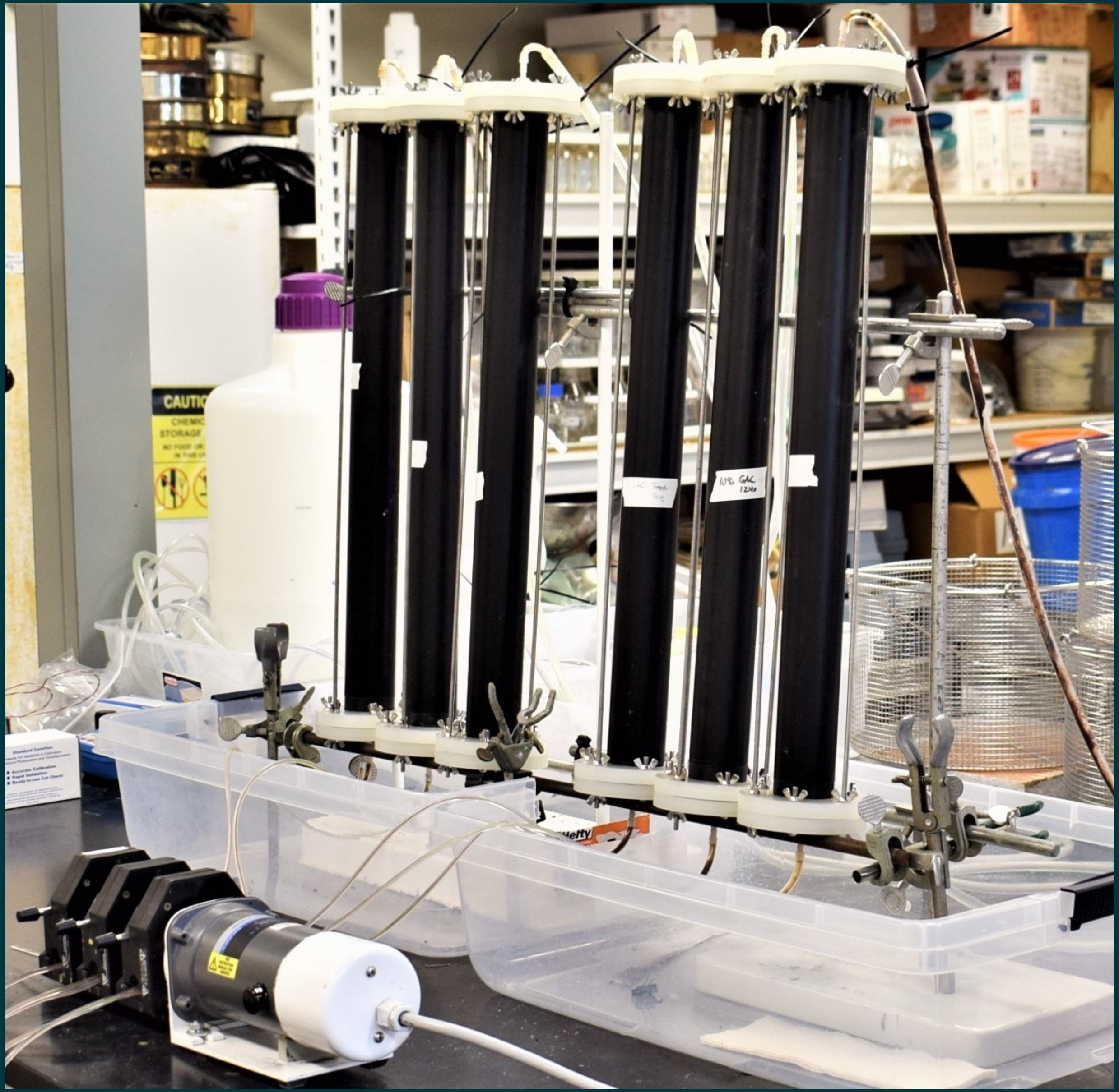



**Cyclodextrin Adsorption**
Ling (2021)

# RSSCT Flow Schematic



## Large Columns



## RSSCTs

# Case Studies

# PFAS Treatability Case Studies

| Case Study # | Site/Source | PFAS Concentration Range (µg/L) | Media Tested | Column Scale |
|---|---|---|---|---|
| 1 | Landfill Groundwater | 300 – 1,000 | Mixed (GAC, biochar, soil, sand) | 2.5 cm ID x 61 cm |
| 2 | Drinking Water Well Groundwater | 0.02 – 0.03 | GAC | 0.46 cm ID x 3 cm |
| 3 | Drinking Water Surface Water | 0.02 – 0.03 | GAC | 0.46 cm ID x 3 cm |
| 4 | Drinking Water Well Groundwater | 0.035 – 0.045 | GAC and IX | 0.46 cm ID x 3 cm |
| 5 | Industrial Site Groundwater | 12,000 – 19,000 | GACs, IX, novel adsorbents | 0.46 cm ID x 5 cm |
| 6 | Landfill Leachate | 10,000 – 11,000 | Novel adsorbents | 0.46 cm ID x 3 cm, 2.5 cm ID x 30 cm |
| 7 | Municipal WW | 0.50 | Novel cyclodextrin | 0.46 cm ID x 3 cm |

# Case Study 1A – PFAS Removals by Biochar

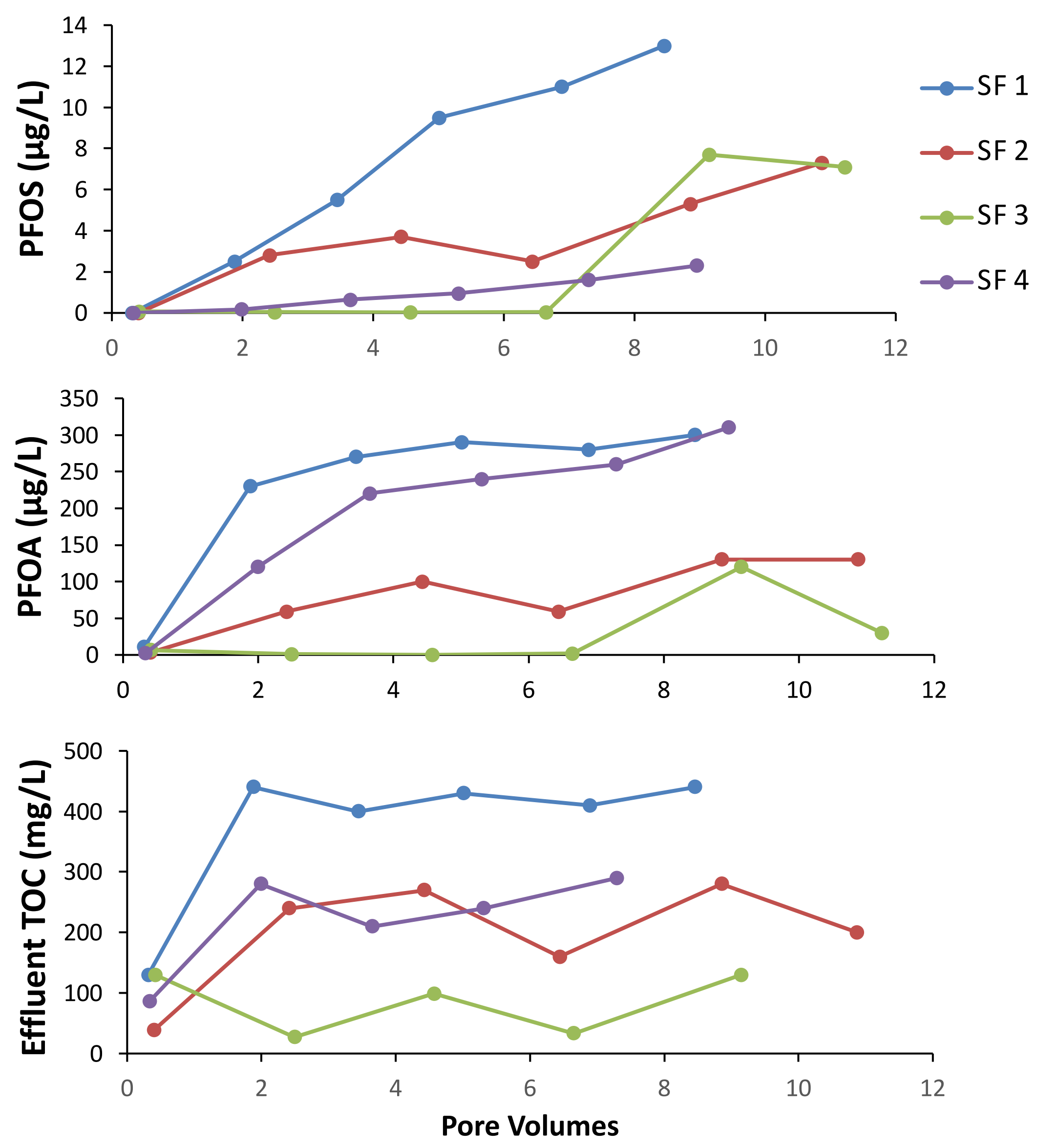
Groundwater impacted by landfill leachate

Biochar derived from forest debris (wood)

High TOC → 300-350 mg/L

Biochar in mixed media
- Improves PFAS retention vs woodchips
- Improves TOC removal vs woodchips

| Label | Media Content |
| --- | --- |
| SF1 | 1% Biochar, 14 % Wood |
| SF2 | 5% Biochar, 10% Wood |
| **SF3** | **5% Biochar, 0% Wood** |
| SF4 | 0% Biochar, 0% Wood |

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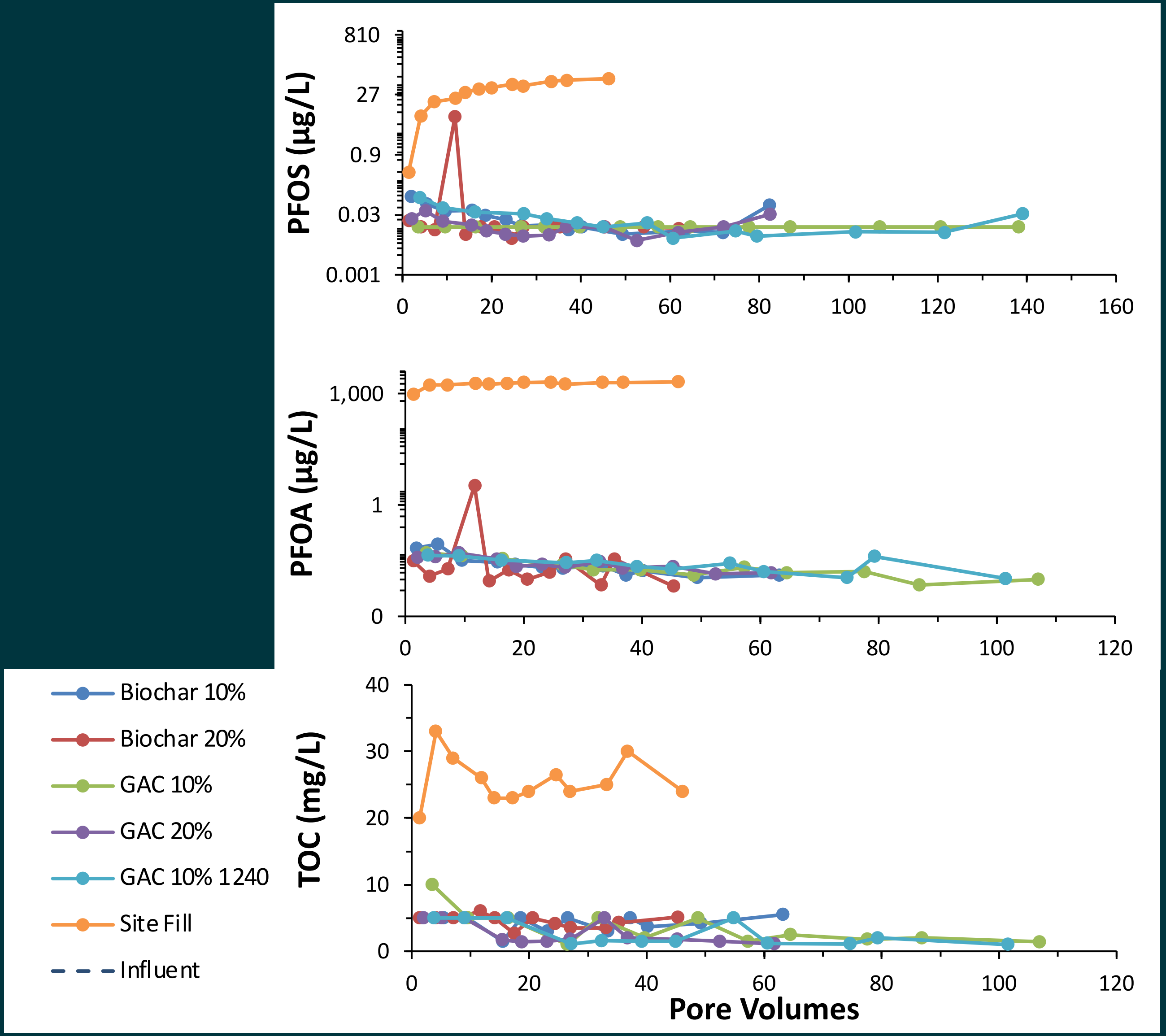
# Case Study 1B – PFAS Removals Biochar vs GAC

Groundwater impacted by landfill leachate

Biochar/sand mix vs GAC/sand mix

– Both amendments showed no breakthrough of PFAS
– Breakthrough at >100 vs <10 pore volumes from previous test due to:
  - Higher biochar or GAC content in sand: 10% and 20% wt/wt
  - TOC in influent → 30 mg/L; 10X lower than in previous water sample



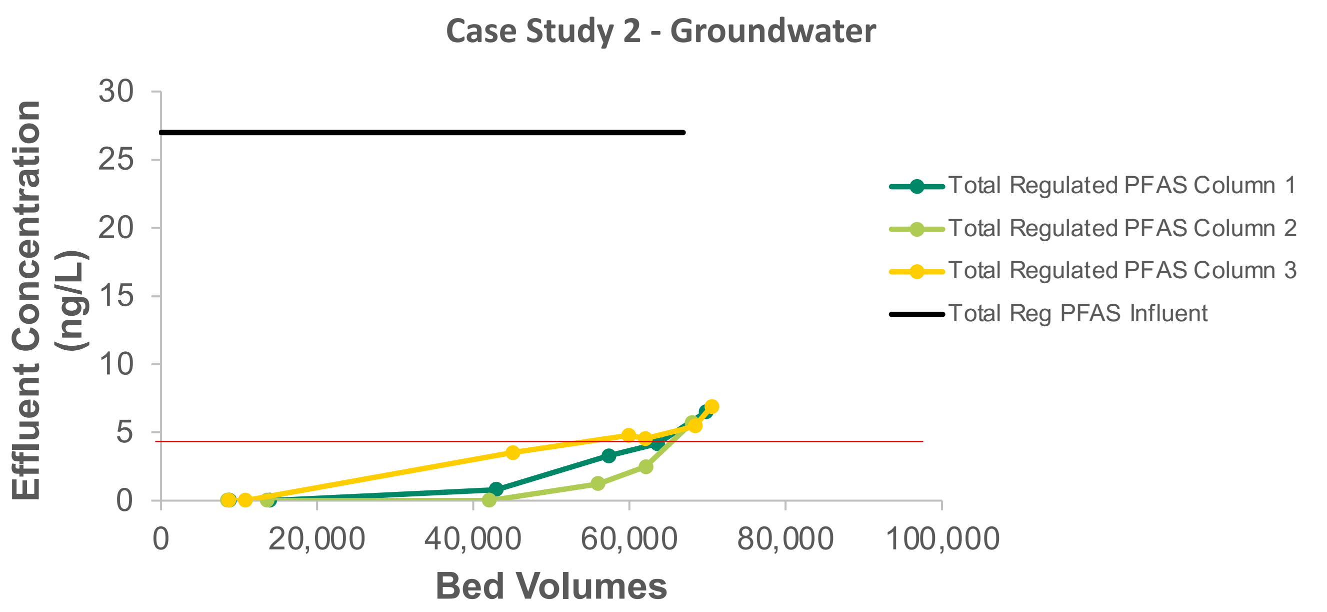
# Case Studies 2 and 3 – PFAS Removals with GAC

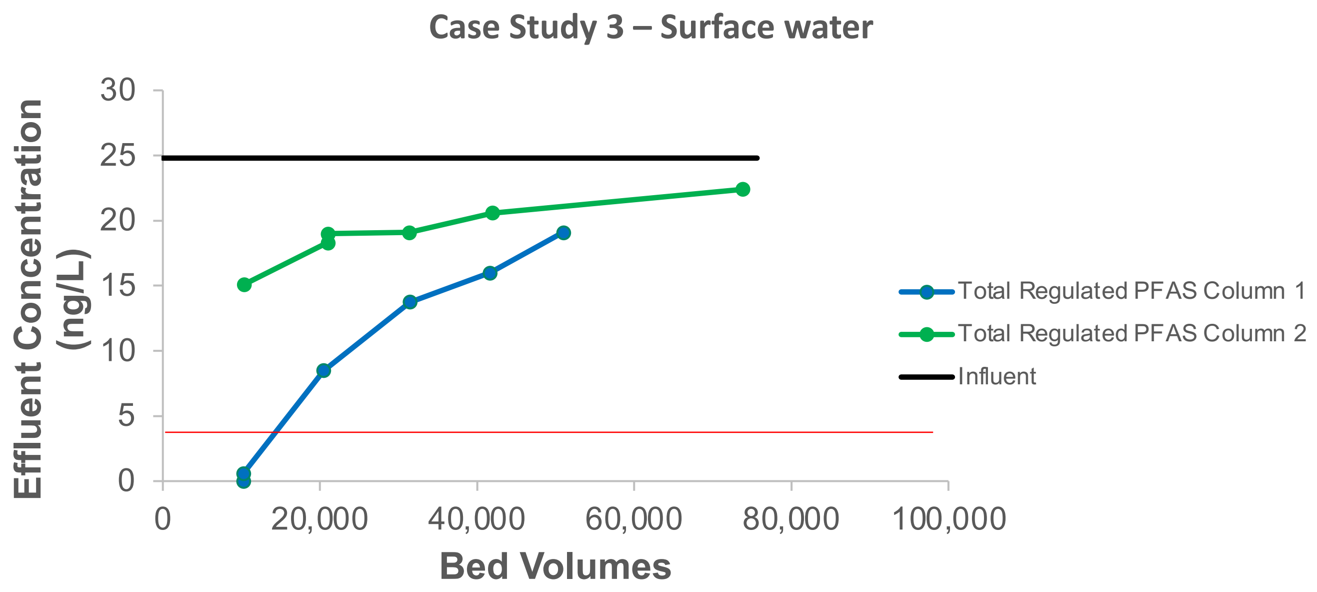
**Case Study 2**: groundwater as drinking water source

**Case Study 3**: surface water as drinking water source

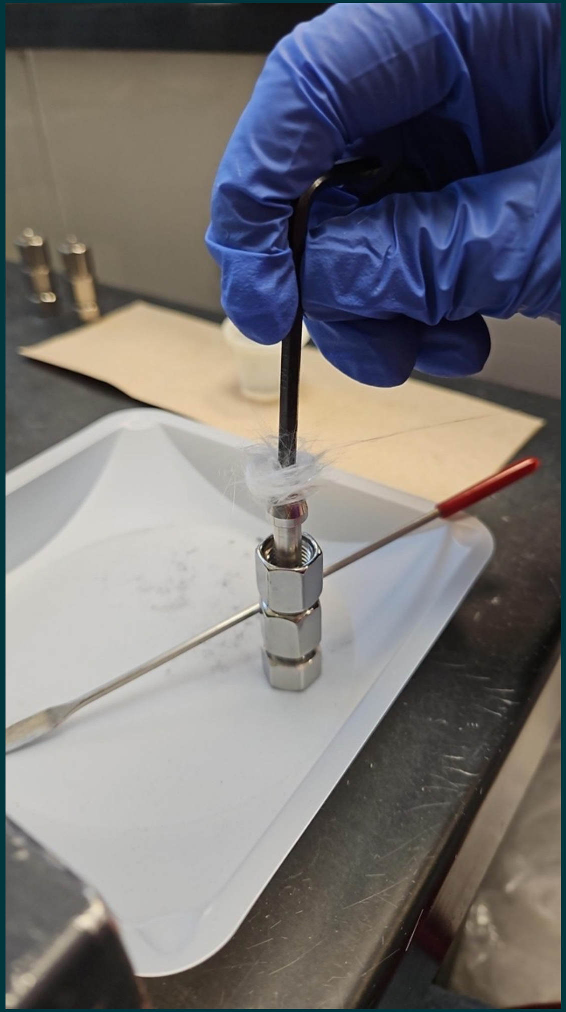
Observations from RSSCTs

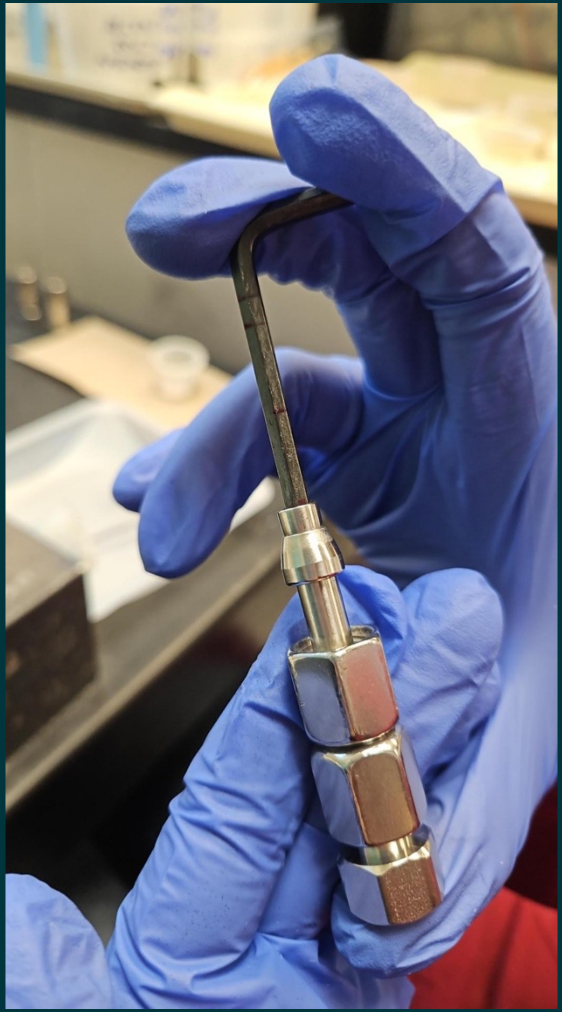
- Performance is highly affected by TOC
- Breakthrough at 4 ng/L:
  - Groundwater ~ 65 K bed volumes
  - Surface water ~12 K bed volumes
- In most cases, different GAC products perform similarly

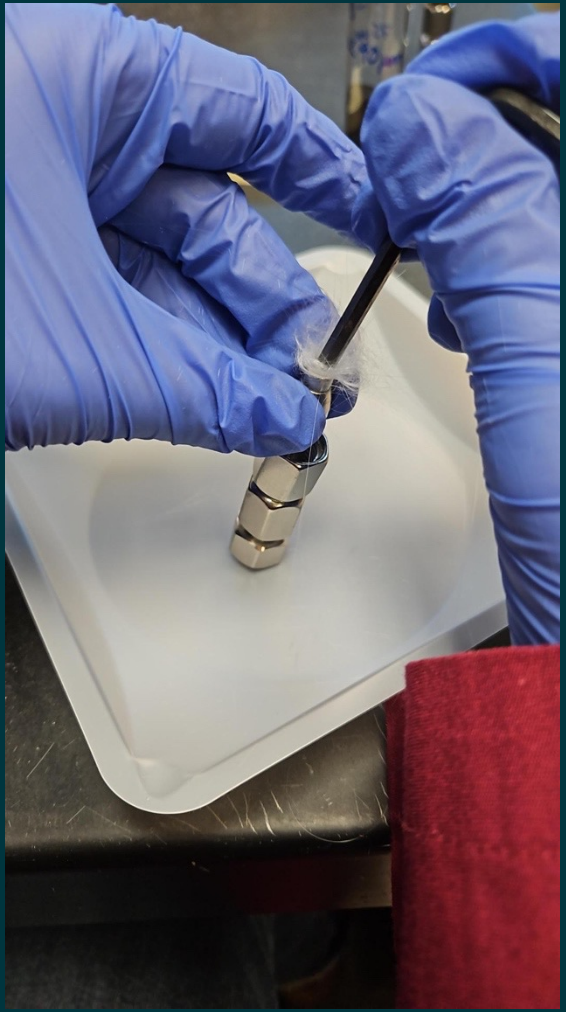


# RSSCT – Packing the Columns



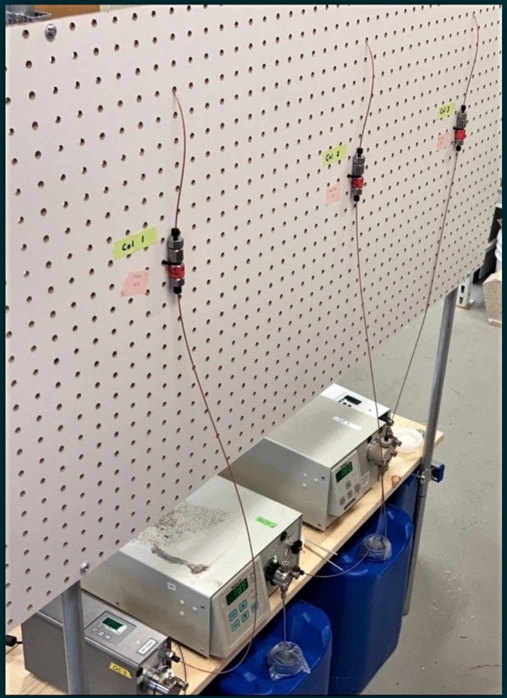


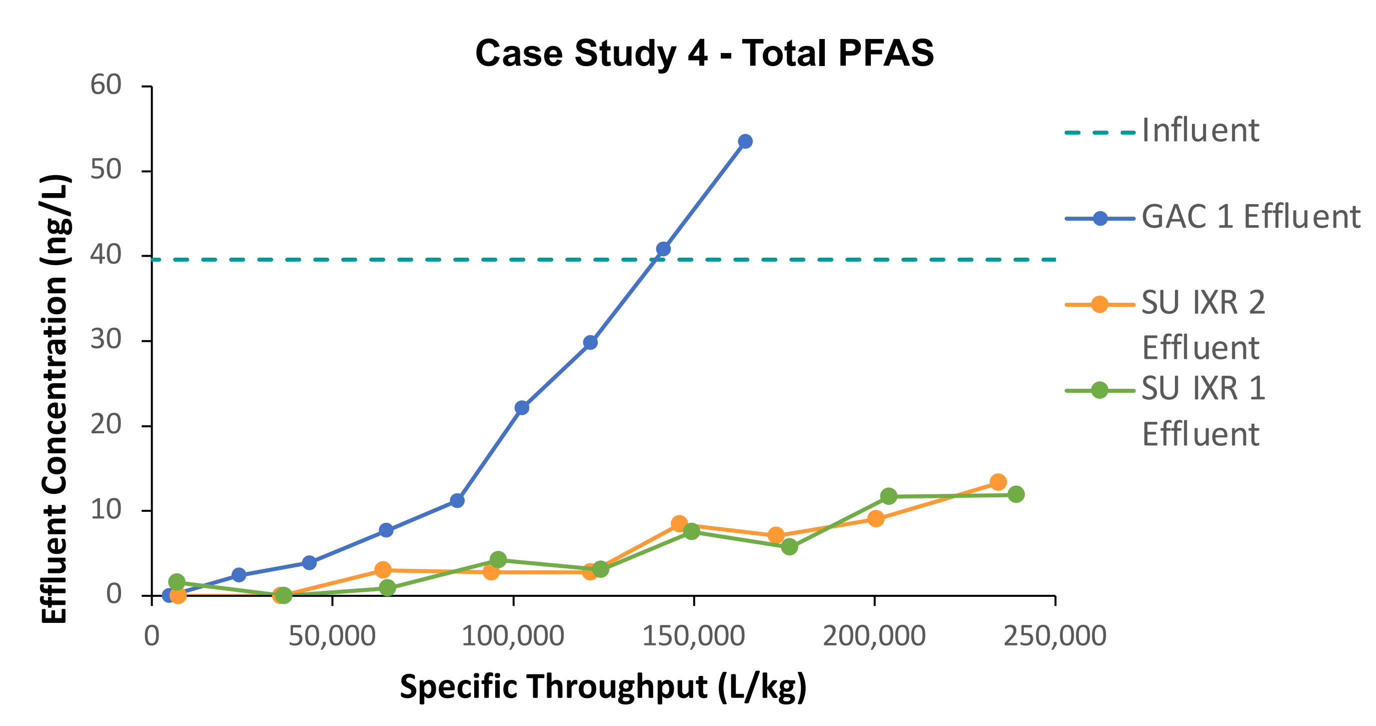


# Case Study 4 - PFAS Removals by IXRs and GAC

Case Study 4: Groundwater for drinking water, impacted with TCE

- Long specific throughputs for IXRs
- IXRs breakthrough > GAC breakthrough



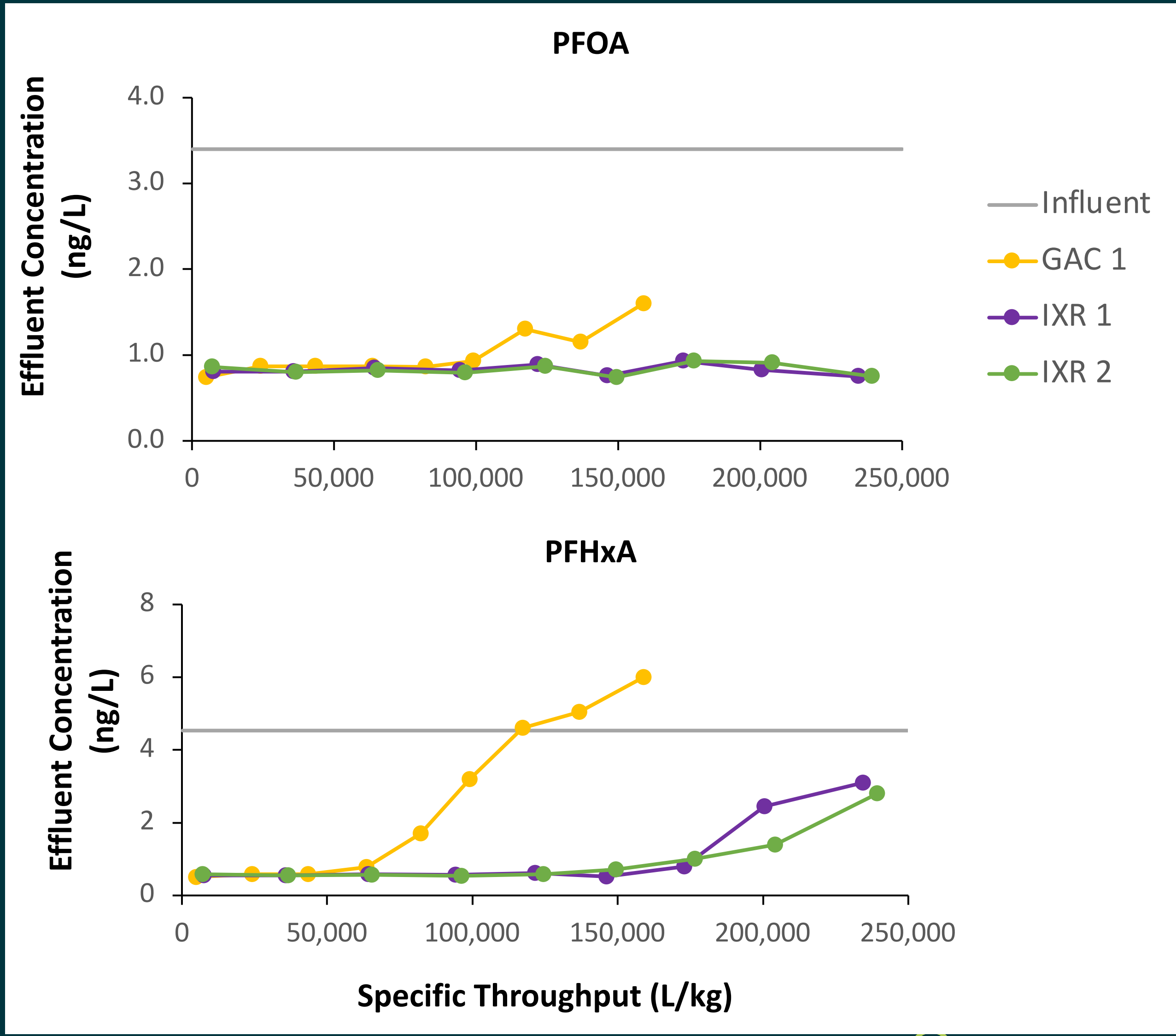



| | |
|---|---|
| NS | Novel Sorbent, Cyclodextrin |
| GAC | Granular Activated Carbon |
| SU IXR | Single Use Ion Exchange Resin |

# Case Study 4 – PFAS Removals, GAC vs Other Media

Groundwater as drinking water, impacted with TCE

- GAC outperformed by IXRs
- Differences in PFAS retention is greater for short chain PFAS molecules
- No breakthrough for PFOA by IXRs
- PFOA breakthroughs (based on detection)
  - GAC ~ 100,000 L/kg
  - IXR 1 and IXR 2 > 245,000 L/kg
- PFHxA breakthroughs (based on detection)
  - GAC ~ 65,000 L/kg
  - IXR 1 and IXR 2 ~ 200,000 L/kg

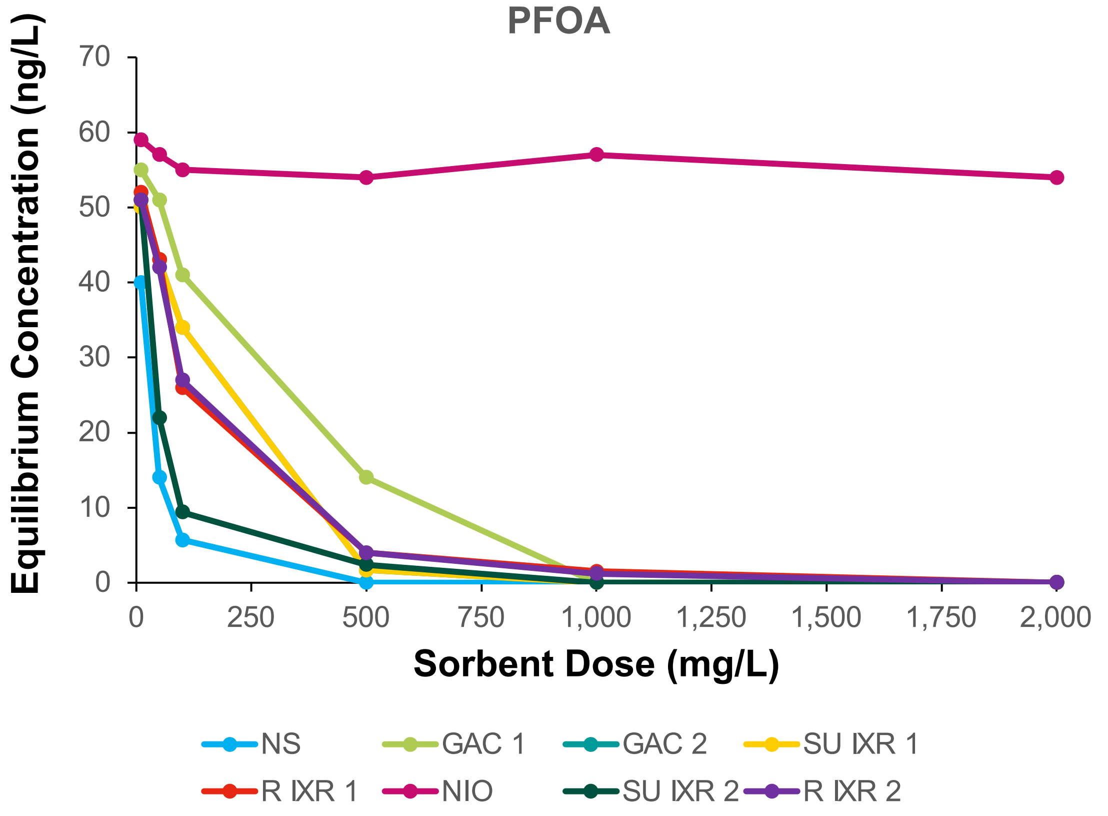


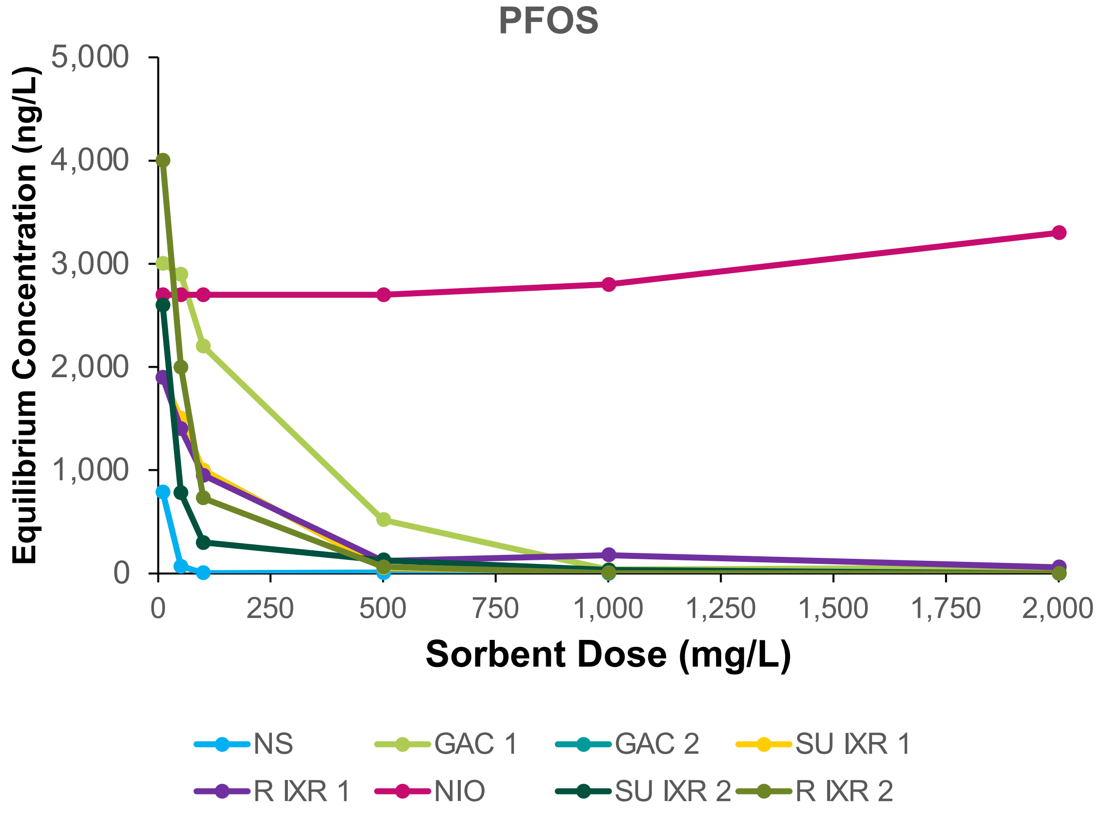
# Case Study 5 – PFAS Removals, GAC vs Other Media

Groundwater seeped into an industrial building basement

- Batch experiments show similar results across PFAS compounds

| | |
|---|---|
| NS | Novel Sorbent, Cyclodextrin |
| NIO | Nanoscale Iron Oxide |
| SU IXR | Single Use Ion Exchange Resin |
| R IXR | Regenerable Ion Exchange Resin |

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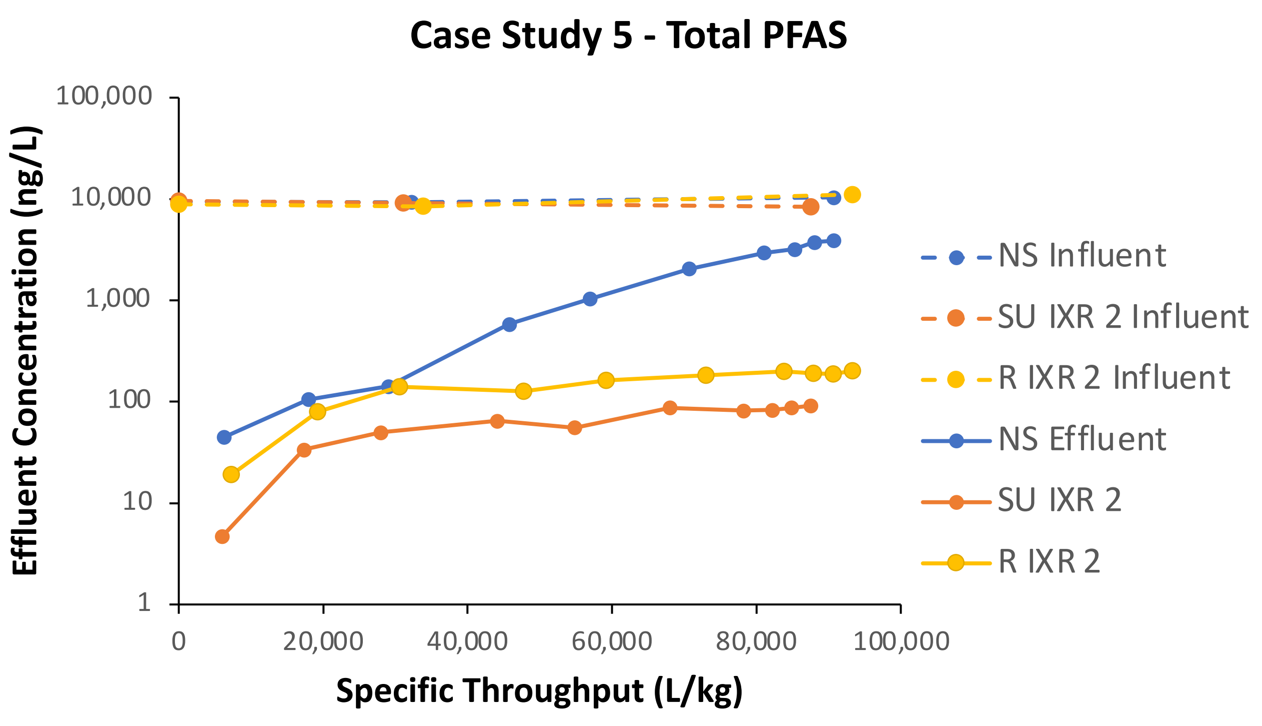
# Case Study 5 – PFAS Removals by IXR and GAC

- Single Use IXRs = Regenerable IXRs
- Project required short EBCT = 5 min
- Lower footprint for site system
- IXRs breakthrough > GAC breakthrough
- Single Use IXR breakthrough > Regenerable IXR breakthrough
- All media capable of treating 10,000 gallons for site treatment, including cyclodextrin (novel sorbent)




| | |
|---|---|
| NS | Novel Sorbent, Cyclodextrin |
| NIO | Nanoscale Iron Oxide |
| SU IXR | Single Use Ion Exchange Resin |
| R IXR | Regenerable Ion Exchange Resin |

# Case Study 6 – PFAS Removals in Landfill Leachate by Novel Adsorbents

Case Study 6: Raw landfill leachate

RSSCT evaluated novel adsorbents

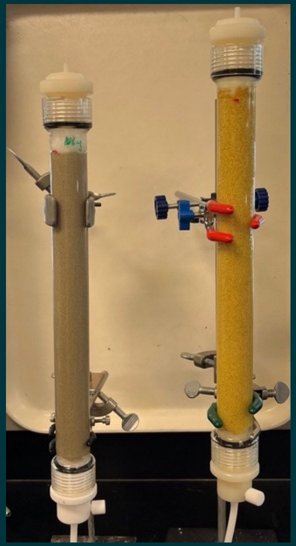
- Cyclodextrin
- Modified bentonite clay

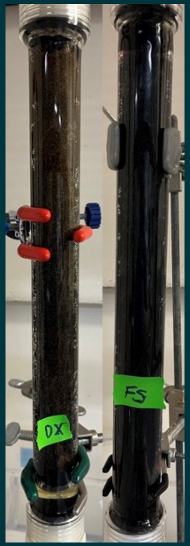
Results

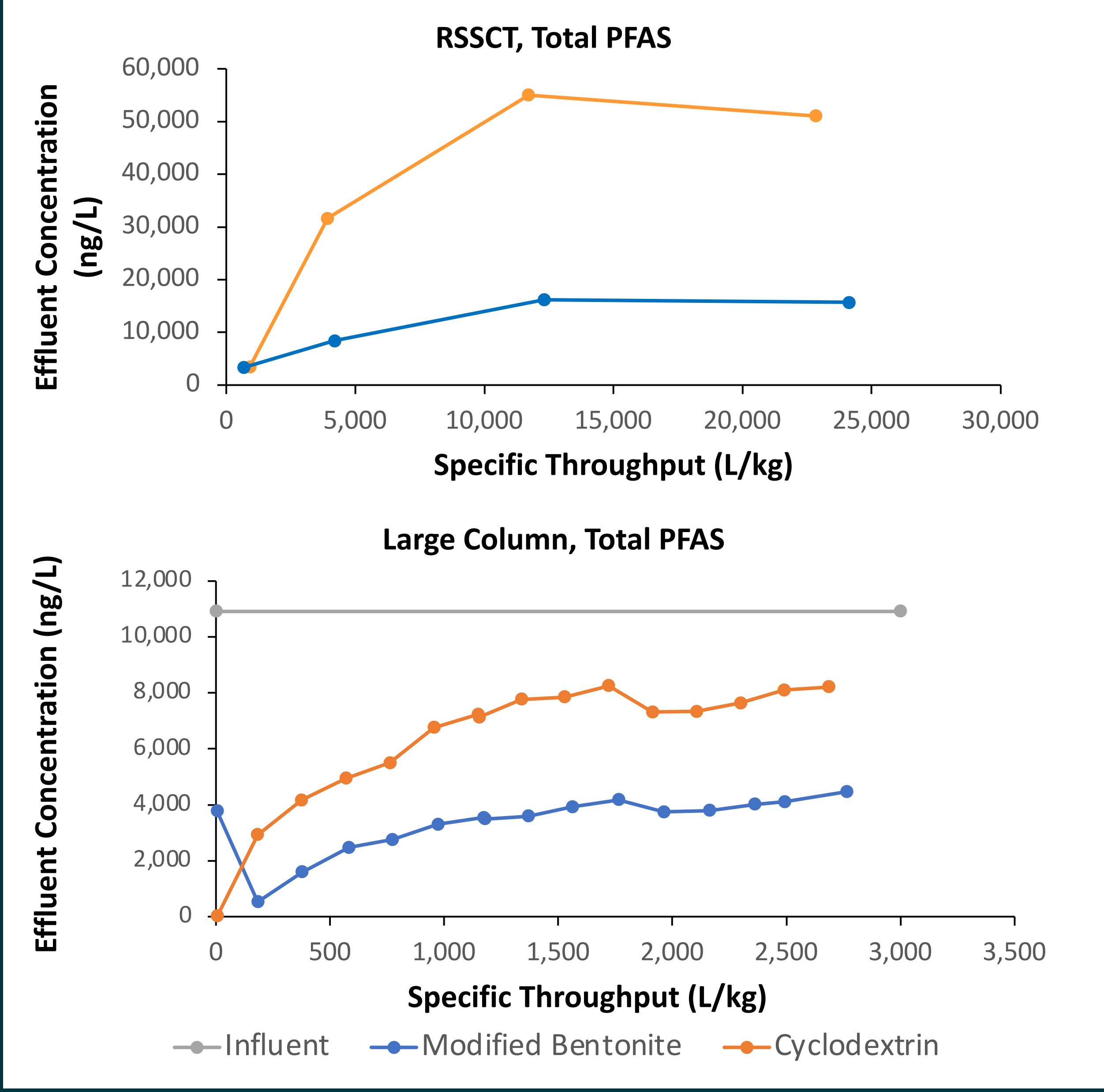
- Higher PFAS retention with modified bentonite

Large Glass Column Test

- Same sorbents, same outcome
- Clogging issues with modified bentonite

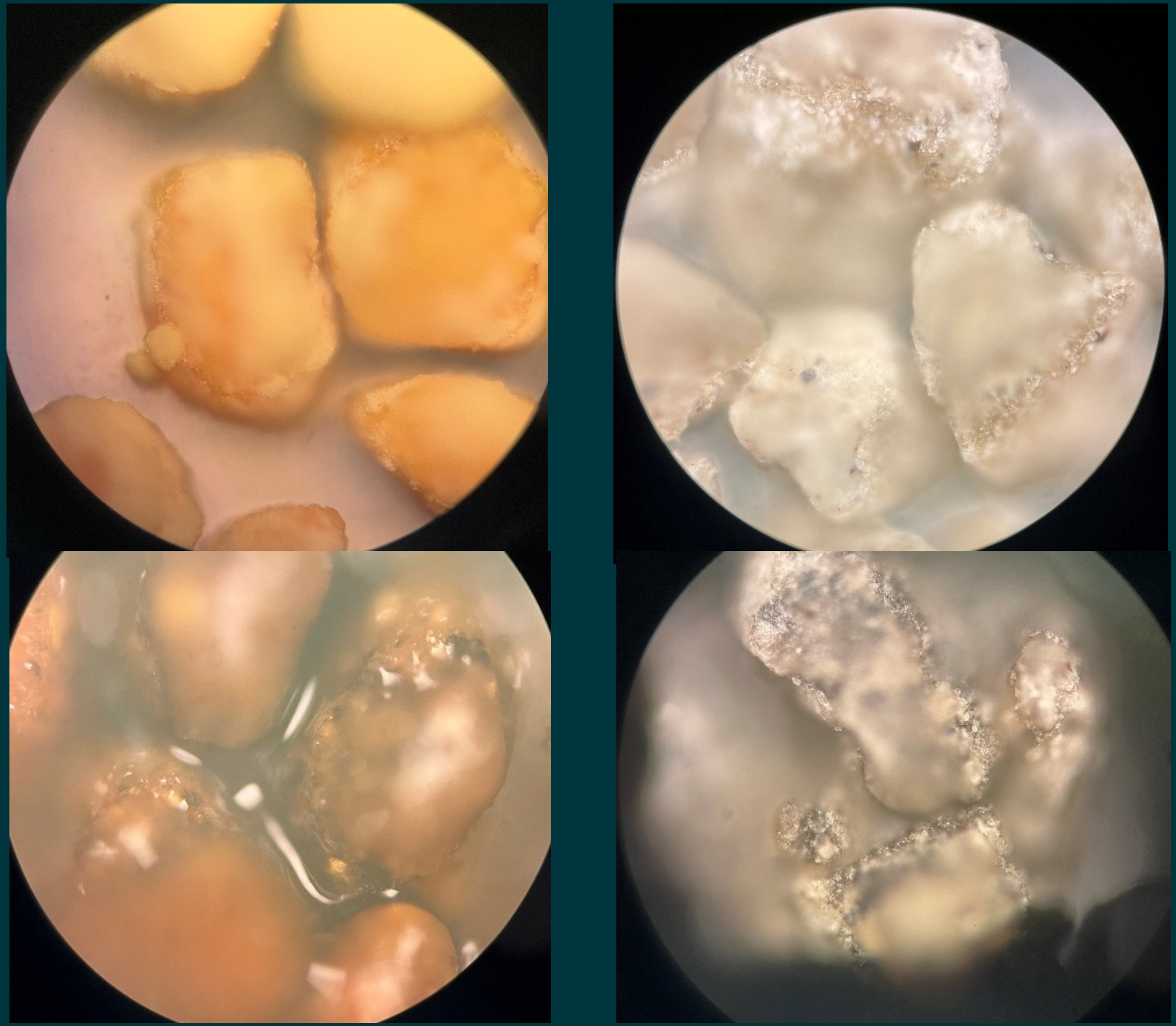




# Case Study 6 – PFAS Removals in Landfill Leachate by Novel Adsorbents


Cyclodextrin | Bentonite Clay



Clean

Spent

# Case Study 7 – PFAS Removals by Novel Cyclodextrin

## Case Study 7: Municipal Wastewater

- US-Israel Collaboration Water-Energy Research Center (CoWERC)
- Cationic, styrene-linked beta-cyclodextrin
- Spiked PFAS and trace organics at 500 ng/L
    - PFOA, PFHxA, PFOS, PFHxS
    - Sucralose, caffeine
    - Diclofenac, metformin, among others
- **300 – 400 mg/L of TOC!**

Environmental Science & Technology
pubs.acs.org/est
Article

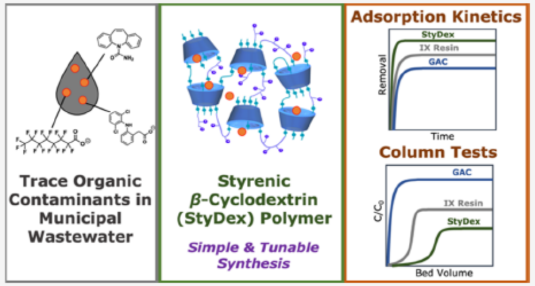
### Trace Organic Contaminant Removal from Municipal Wastewater by Styrenic $\beta$-Cyclodextrin Polymers

Zhi-Wei Lin, Emma F. Shapiro, Francisco J. Barajas-Rodriguez, Arsen Gaisin, Mohamed Ateia, John Currie, Damian E. Helbling, Rosa Gwinn, Aaron I. Packman, and William R. Dichtel*

Cite This: https://doi.org/10.1021/acs.est.3c04233
Read Online



ABSTRACT: Trace organic contaminants (TrOCs) present major removal challenges for wastewater treatment. TrOCs, such as perfluoroalkyl and polyfluoroalkyl substances (PFAS), are associated with chronic toxicity at ng $L^{-1}$ exposure levels and should be removed from wastewater to enable safe reuse and release of treated effluents. Established adsorbents, such as granular activated carbon (GAC), exhibit variable TrOC removal and fouling by wastewater constituents. These shortcomings motivate the development of selective novel adsorbents that also maintain robust performance in wastewater. Cross-linked $\beta$-cyclodextrin ($\beta$-CD) polymers are promising adsorbents with demonstrated TrOC removal efficacy. Here, we report a simplified and potentially scalable synthesis of a porous polymer composed of styrene-linked $\beta$-CD and cationic ammonium groups. Batch adsorption experiments demonstrate that the polymer is a selective adsorbent exhibiting complete removal for six out of 13 contaminants with less adsorption inhibition than GAC in wastewater. The polymer also exhibits faster adsorption kinetics than GAC and ion exchange (IX) resin, higher adsorption affinity for PFAS than GAC, and is regenerable by solvent wash. Rapid small-scale column tests show that the polymer exhibits later breakthrough times compared to GAC and IX resin. These results demonstrate the potential for $\beta$-CD polymers to remediate TrOCs from complex water matrices.




KEYWORDS: *PFAS, cyclodextrin polymer, wastewater, adsorption, RSSCT, organic contaminants*

https://doi.org/10.1021/acs.est.3c04233
*Environ. Sci. Technol.* XXXX, XXX, XXX–XXX

# Case Study 7 – PFAS Removals by Novel Cyclodextrin

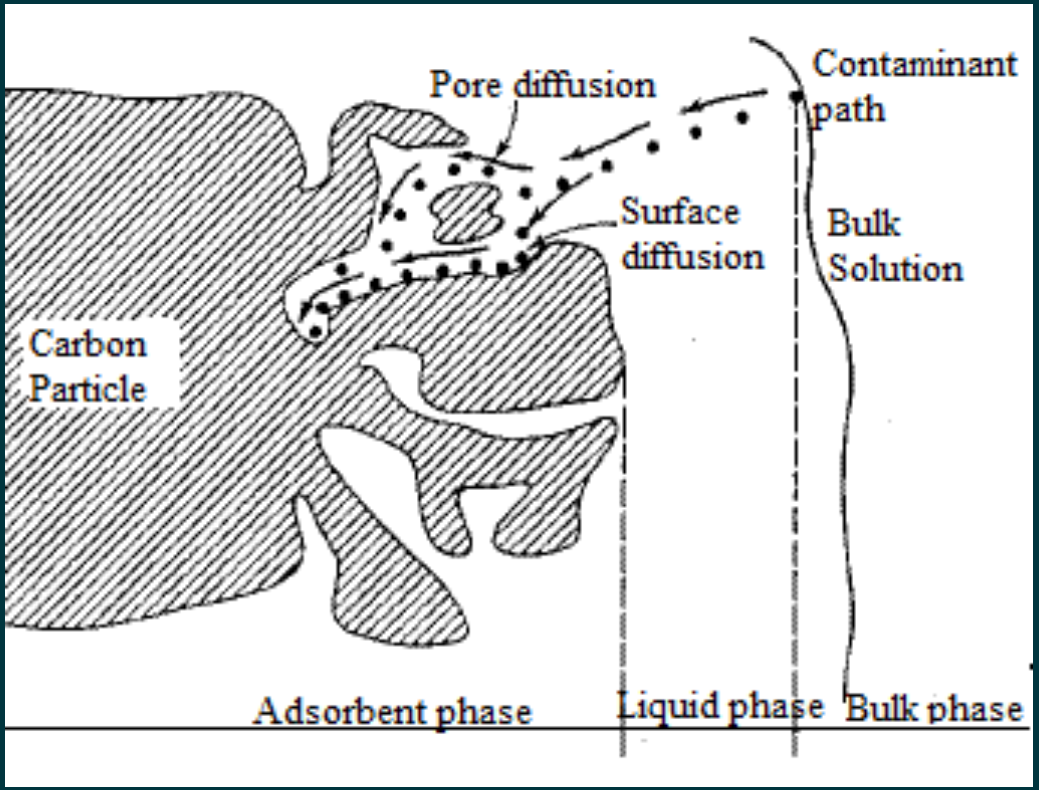
Case Study 7: Municipal Wastewater

RSSCTs scaling model approaches:

- Proportional diffusivity (PD) – dependent on particle radius
- Constant diffusivity (CD) – independent on particle radius

$$\frac{EBCT_{sc}}{EBCT_{lc}} = \left(\frac{R_{sc}}{R_{lc}}\right)^{2-x}$$

EBCT = empty bed contact time
sc = small column
lc = large column
R = sorbent particle radius or diameter
x = 1 for PD
x = 0 for CD



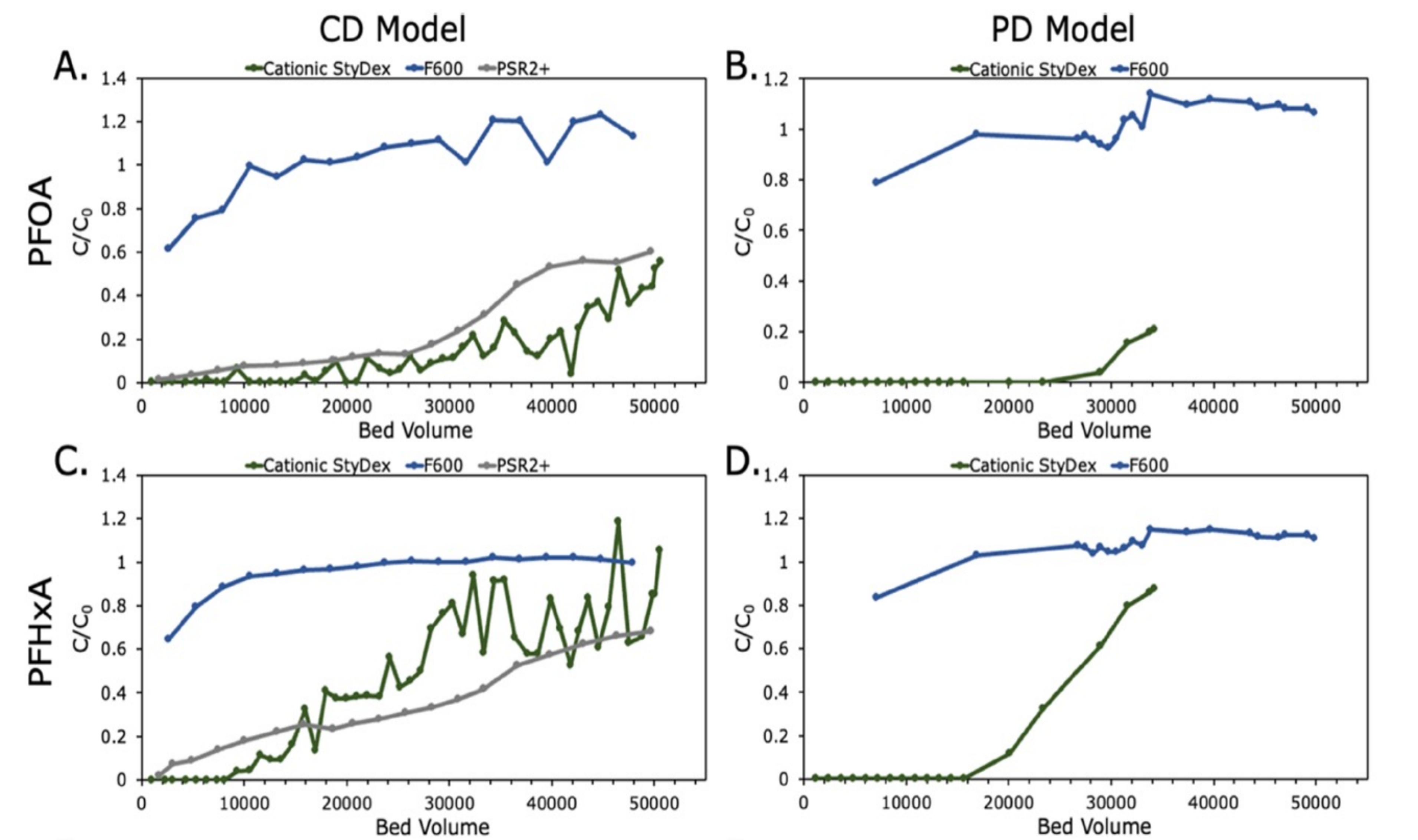

**GAC Particle and Contaminant Adsorption**
Hand et al. (1983)

# Case Study 7 – PFAS Removals by Novel Cyclodextrin

RSSCT Models:

PD = proportional diffusivity

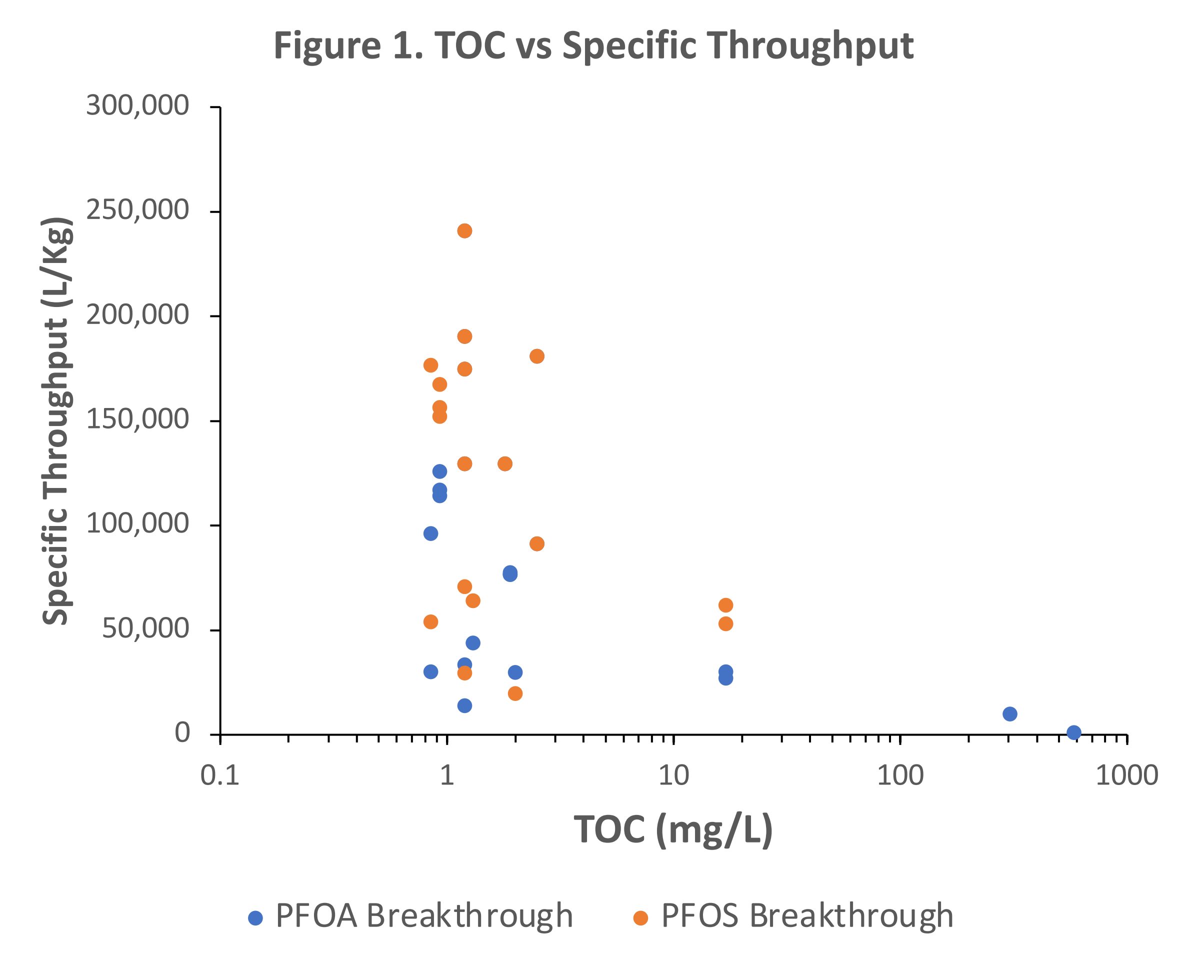
CD = constant diffusivity

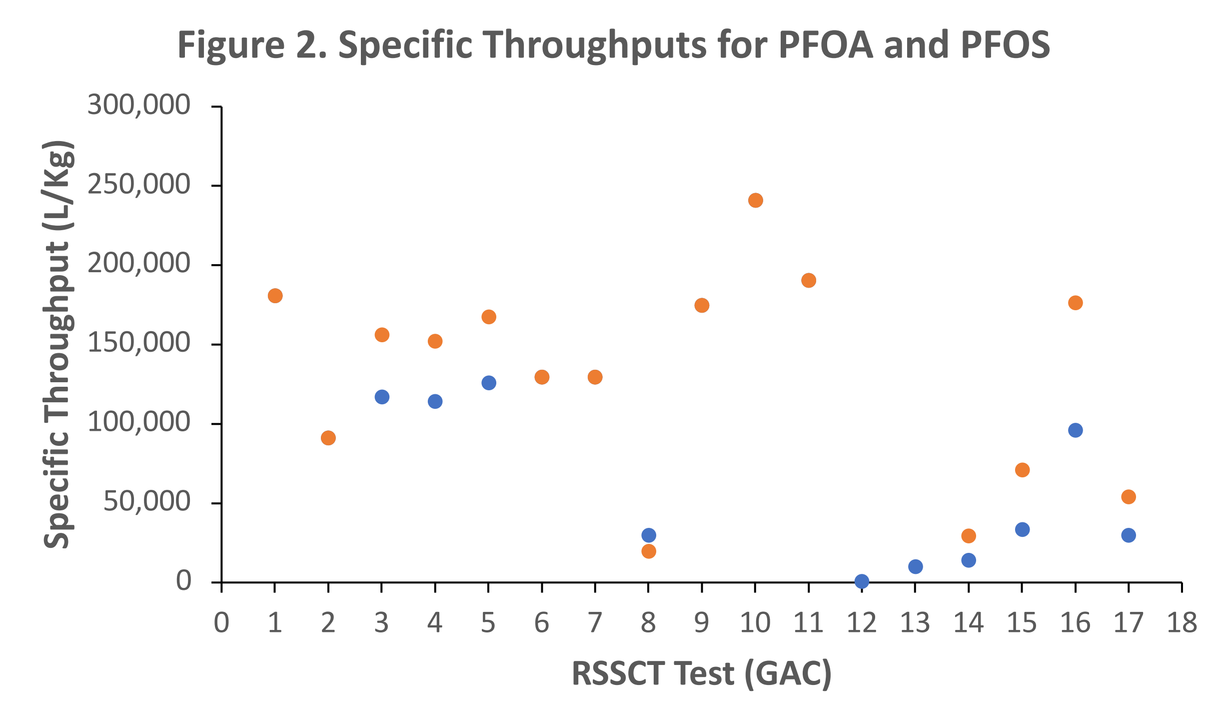



https://doi.org/10.1021/acs.est.3c04233
*Environ. Sci. Technol.* XXXX, XXX, XXX–XXX

# Findings – PFAS Removal by GAC

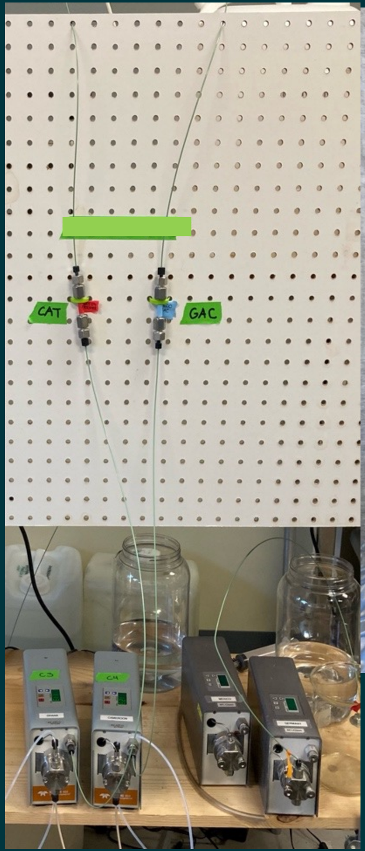
– GAC adsorption trends
  - Higher TOC usually results in lower specific throughputs
  - PFOS shows higher specific throughputs than PFOA
  - Not controlled for water quality or influent concentrations



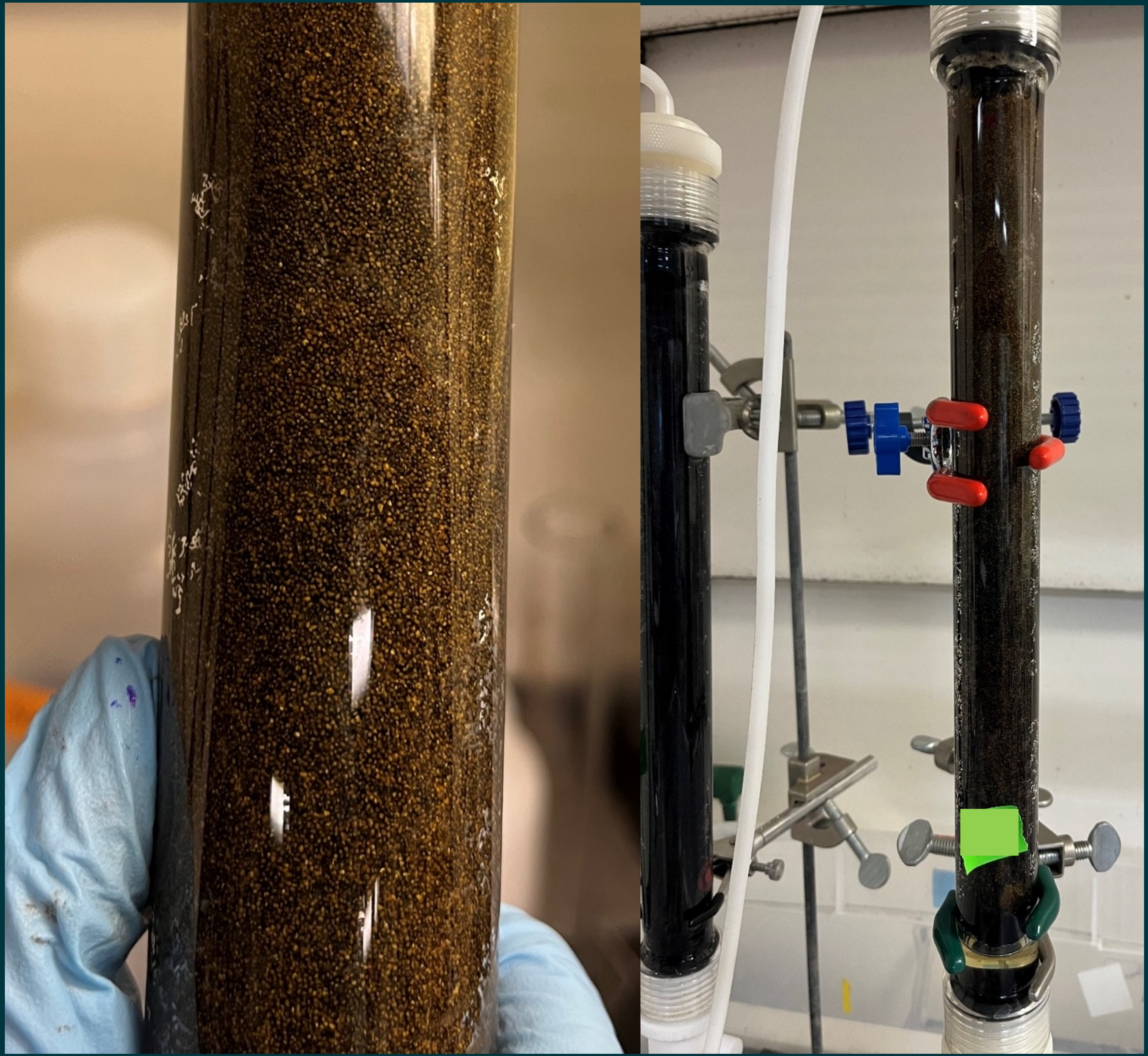
# Considerations

- Scalability of RSSCTs with IXRs and novel adsorbents is still being explored
- Bigger columns offer better breakthrough resolution, but cost more, and take significantly more time




RSSCT disassembled

RSSCT in operation



Glass column (1 inch ID)

# Take Home Messages

# PFAS Treatability via Adsorption

Sorbent performance is highly specific to water matrix properties → **bench-scale tests are important**

- Influent concentrations of PFAS and co-contaminants
- TOC concentration

Other factors to consider

- Particle size of media
- Total suspended solids --> pre-filtration requirements

GAC performs better with clean, low TOC, water matrices

Novel Adsorbents are more selective than GAC and IXRs

- Modified bentonite clays → high adsorption capacity, susceptible to clogging
- Cyclodextrin → high adsorption capacity, long contact time

## Future Work for PFAS Treatability

Beyond relative performance evaluation

- Are RSSCTs scalable for IXRs and Novel Adsorbents?
- Currently deploying pilot tests for remediation and drinking water
- Compare specific throughputs for those waters that were tested under RSSCT and pilot conditions
- Compile more data on effect of TOC and other water constituents

# References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# Thank you.

Any questions?

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