Adsorbents Treatability Evaluation for PFAS Removal from Groundwater Infiltrating into a Chrome-Plating Facility Basement

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Agenda

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02 Study Objectives
03 Technical Approach
04 Results
05 Conclusions and Next Steps

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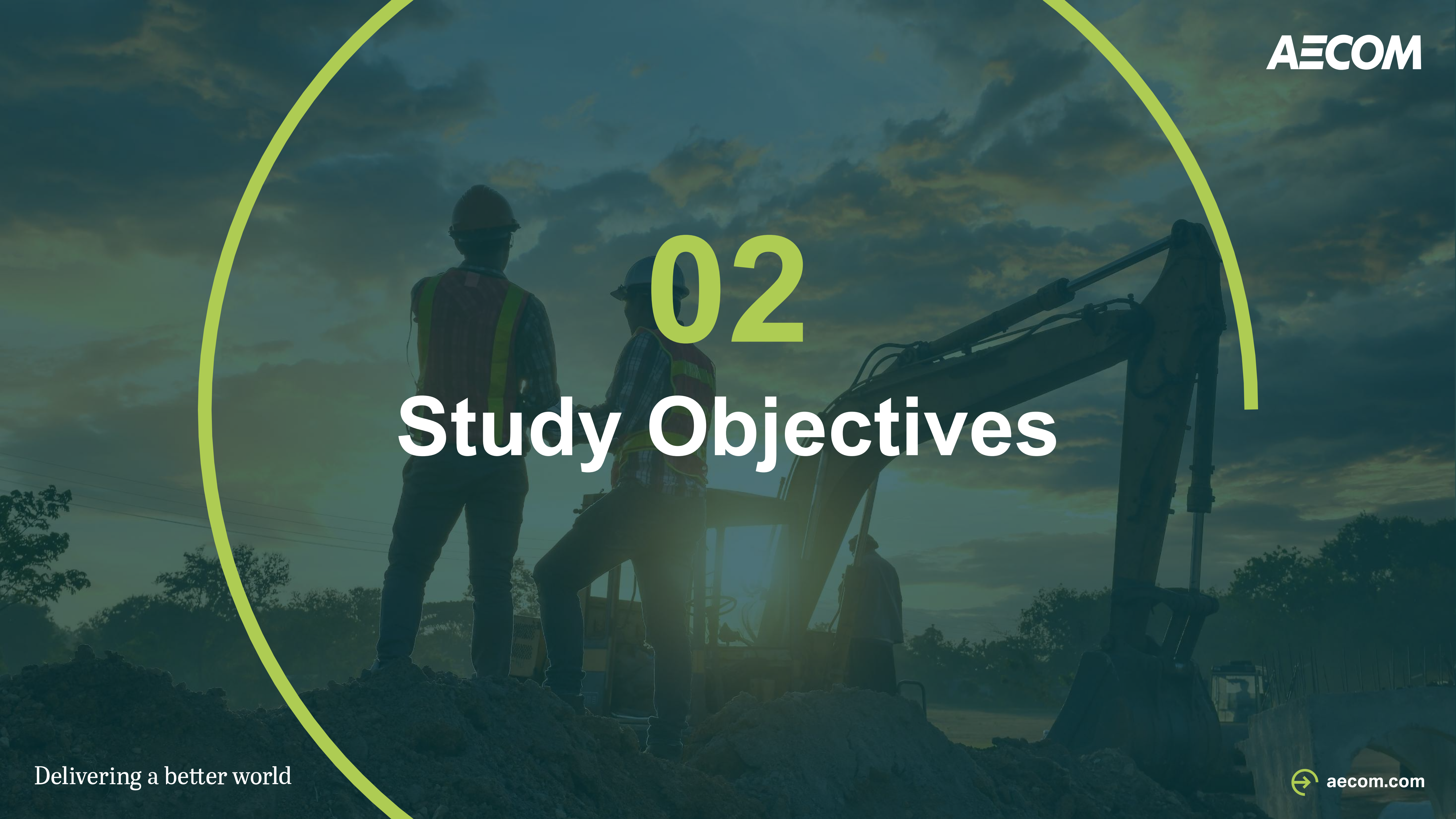
Introduction

Introduction – Site Background

- Site is an old plating facility that operated from the 1930s to 2007
- Waste containers containing cyanide, zinc cyanide, nickel chloride and other chemicals found in 2015
  - Followed by a time-sensitive removal strategy
- Chlorinated solvents and PFAS detected at the site
- Groundwater is infiltrating into a basement
  - 1,4-dioxane, chlorinated solvents, metals, and PFAS
- Focus of this study was on PFAS treatment



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Study Objectives

Study Objectives

General Objective: Evaluate efficacy of sorbent treatment technologies for PFAS-laden basement water from a metal plating manufacturing site.

Specific Objectives:

- Screen for various adsorbent products that may remove PFAS from the water matrix
- Further evaluate the effectiveness of select adsorbents that show the highest potential for PFAS removal under flow-through conditions

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Technical Approach

Overview of General Approach

Batch Isotherms

Six Doses / Sorbent

Cyclodextrin
GAC 1
GAC 2
Single Use IXR 1
Regenerable IXR 1
Nano Iron Oxide
Single Use IXR 2
Regenerable IXR 2

Column Tests

1. Cyclodextrin
2. Single Use IXR 1
3. Regenerable IXR 1

Regeneration

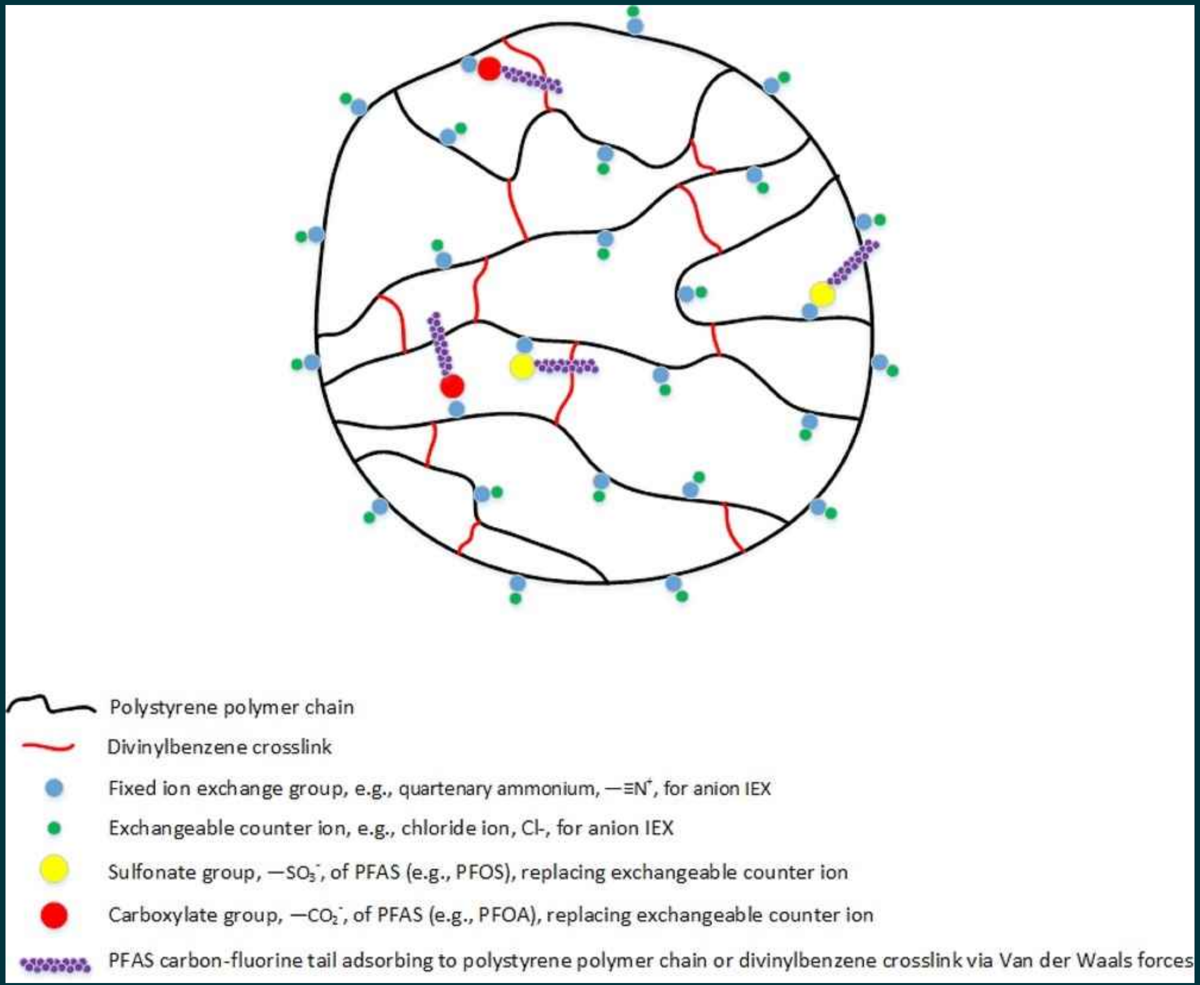
- Spent sorbents
- Cyclodextrin
- Regenerable IXR 1

Destruction vs Disposal

Overview – Adsorbent Media Studied

Ion Exchange Resins (IXRs)

- Single Use IXR 1
  - Polystyrene crosslinked with divinylbenzene
  - Complex amino functional group
- Single Use IXR 2
  - Tributylamine functionalized chloromethylated copolymer of polystyrene in the chloride form
- Regenerable IXR 1
  - Polyvinyl benzyl triethyl ammonium chloride
  - Regenerable via methanol extraction
- Regenerable IXR 2
  - Quaternary amine divinylbenzene/styrene copolymer, chloride ion form
  - Regenerable via methanol extraction



Ion Exchange Adsorption
Woodard et al. (2017)

IXR: ion exchange resin

Overview – Adsorbent Media Studied

Granular Activated Carbon (GAC)

- Two commercial GAC products: GAC 1 and GAC 2
- Both are bituminous coal-based

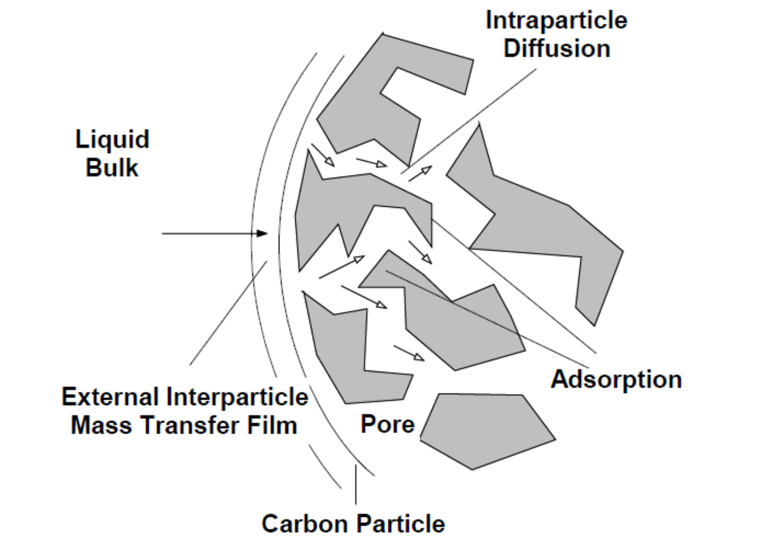
Cyclodextrin

- Cross-linked cyclodextrin polymer
- Cellulose acetate
- Regenerable with ethanol-based solvent extraction

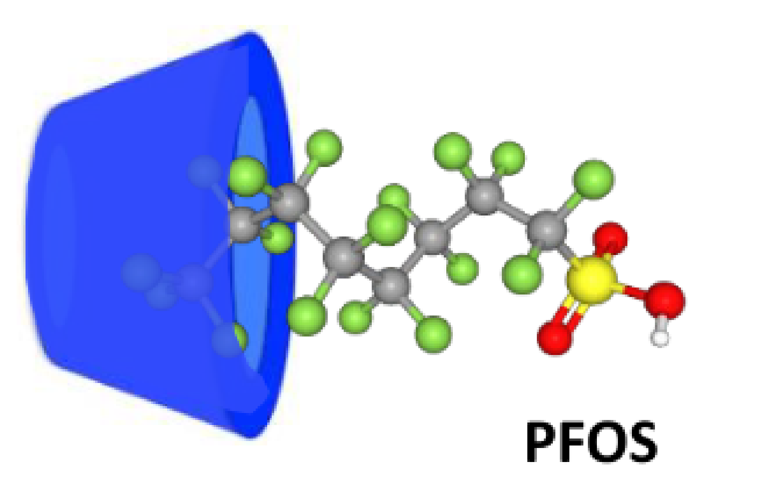
Nano Iron Oxide

- Nanoporous Fe_2O_3
- Used to remove phosphate and heavy metals
- Dual function: absorption and adsorption

GAC: granular activated carbon



GAC Adsorption
Armenante (1991)



Cyclodextrin Adsorption
Ling (2021)

Phase 1 – Batch Isotherms

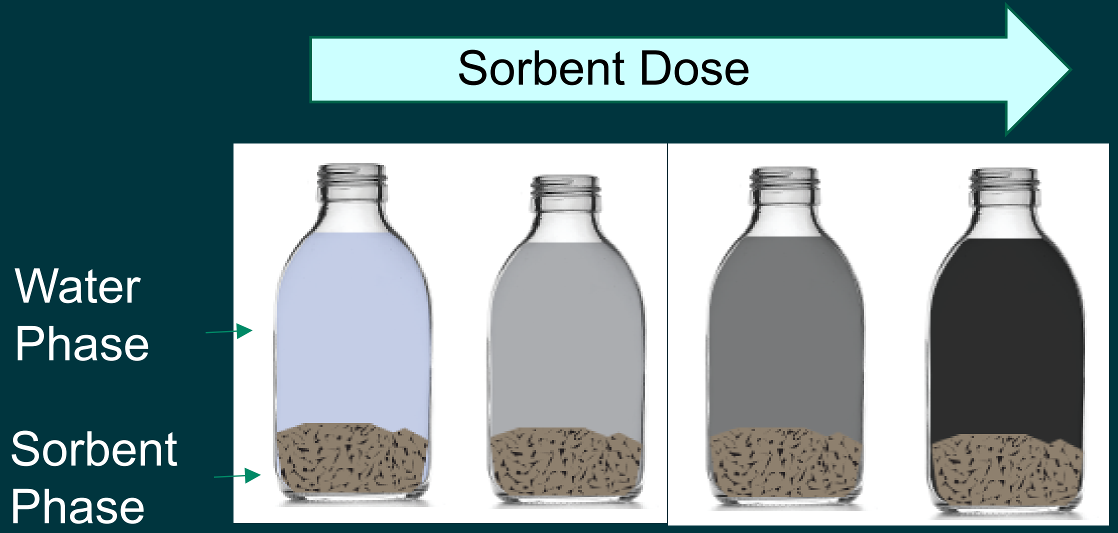
Screened various sorbent media

- Three regenerable sorbents
  - Cyclodextrin
  - Regen IXR 1
  - Regen IXR 2
- Five single-use sorbents
  - GAC 1
  - GAC 2
  - Single Use IXR 1
  - Single Use IXR 2
  - Nano Iron Oxide

Tested six sorbent doses to equilibrium

- 10 to 2,000 mg/L

Determined adsorption capacity, *q*



$$q = \frac{M_{PFAS,S}}{M_S} = \frac{V_W(C_{W,0} - C_{W,E})}{M_S}$$

$M_{PFAS,S}$ = Mass of PFAS sorbed

M_S = Mass of sorbent

V_W = Volume of water

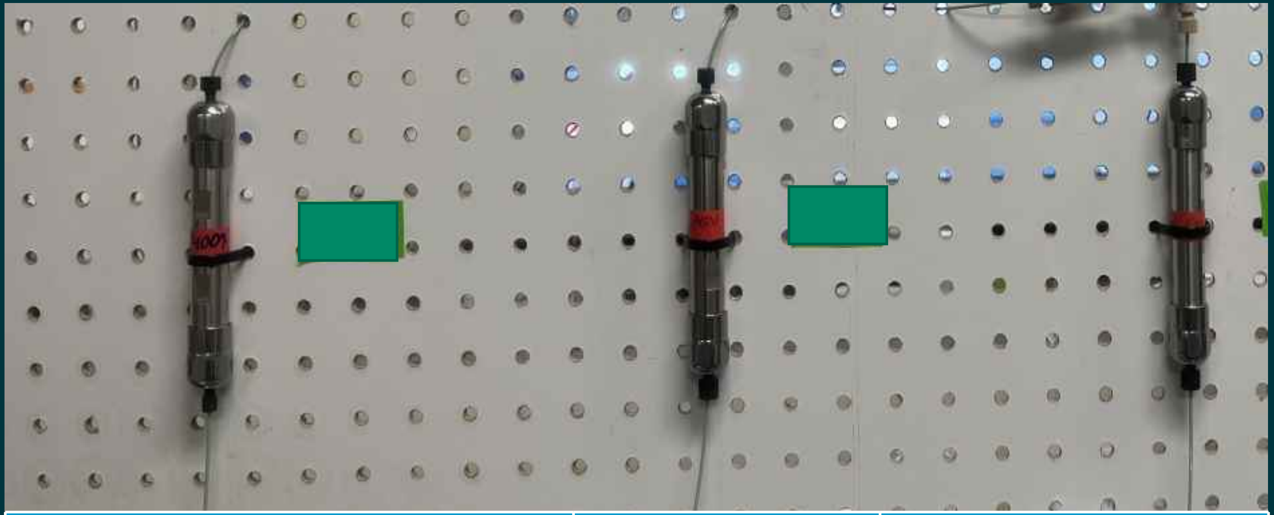
$C_{W,0}$ = Initial PFAS concentration in water

$C_{W,E}$ = Equilibrium PFAS concentration in water

GAC: granular activated carbon
IXR: ion exchange resin

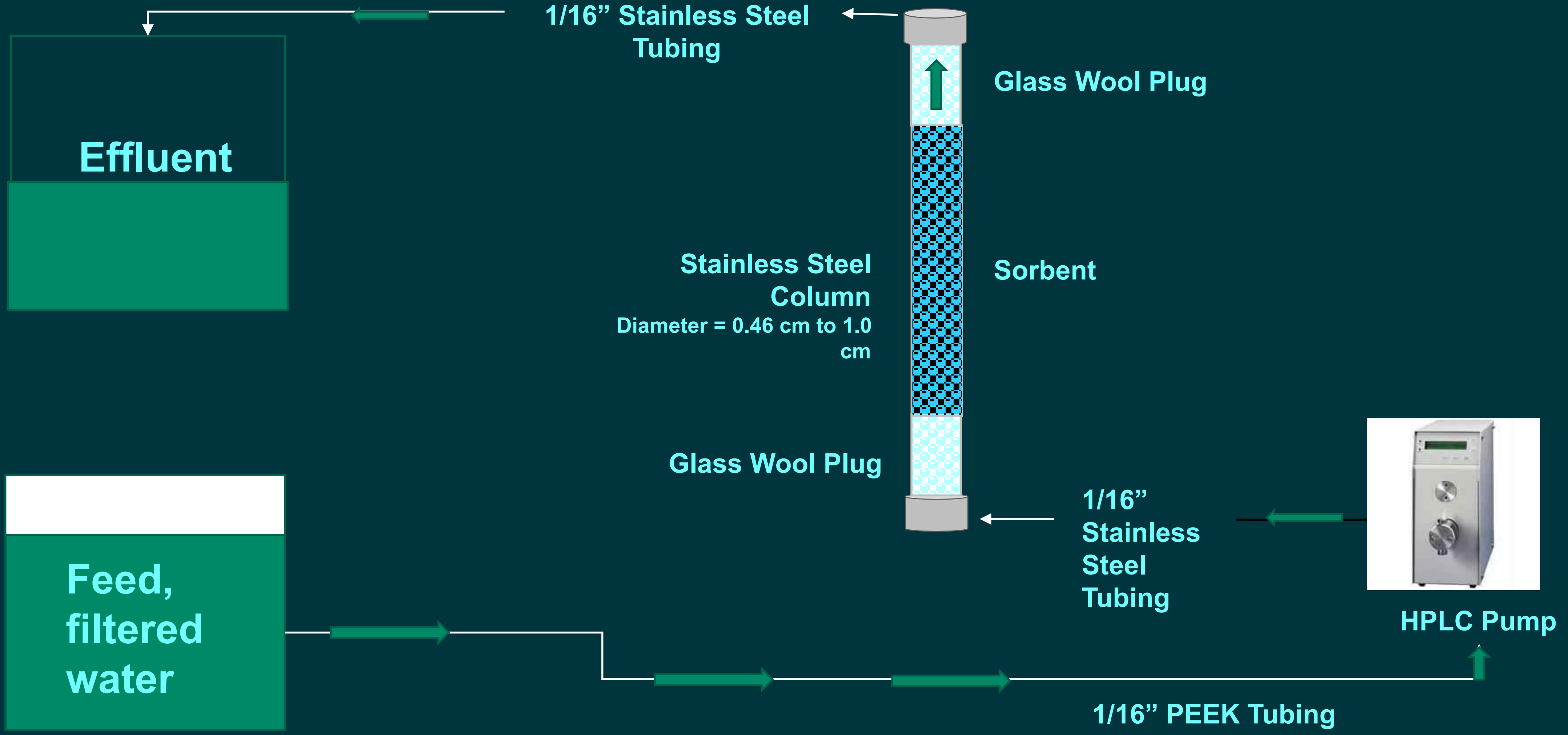
Phase 2 – Rapid Small Scale Column Tests (RSSCTs)

- Media selected based on batch testing results from Phase 1 and consultation with client
- Design based on empty bed contact time (**EBCT**)
  - Desire for low footprint treatment system = short EBCT
  - Assumed 5 minutes of EBCT for adsorbents tested
- Volume of water to test = ~10 gal/column = ~50,000 bed volumes
- Three RSSCT columns



Sorbent	Influent Samples	Effluent Samples
Cyclodextrin	3	10
Single Use IXR 2	3	10
Regen IXR 2	3	10

Phase 2 – Rapid Small Scale Column Tests (RSSCTs)



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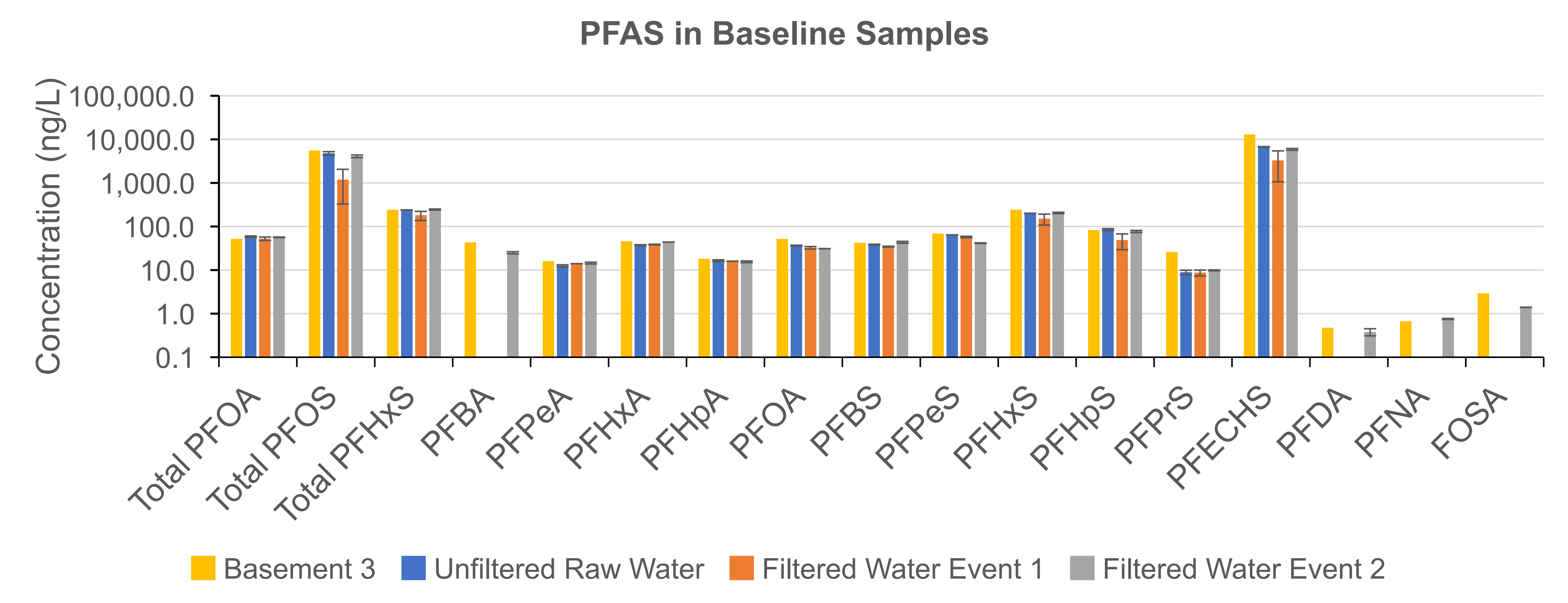
Results

Results – Baseline Characterization

- PFAS dominated by perfluorooctanoic sulfonate (PFOS) and perfluoroethyl cyclohexane (PFECHS)
- Water samples analyzed: basement water (field-collected), raw water (as-received), filtered water (two sampling events)
- Total PFAS: 15,123 ng/L to 19,430 ng/L

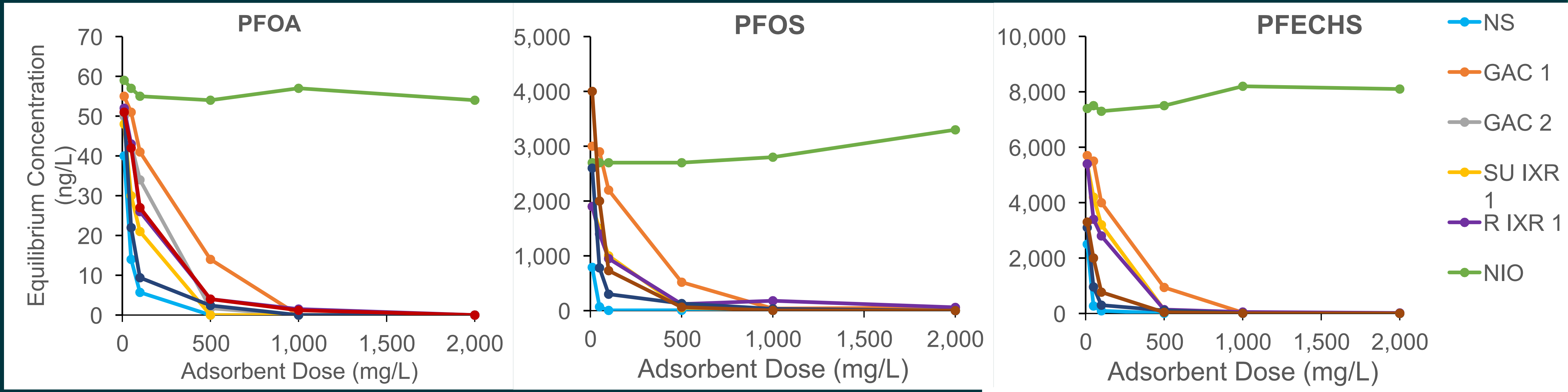


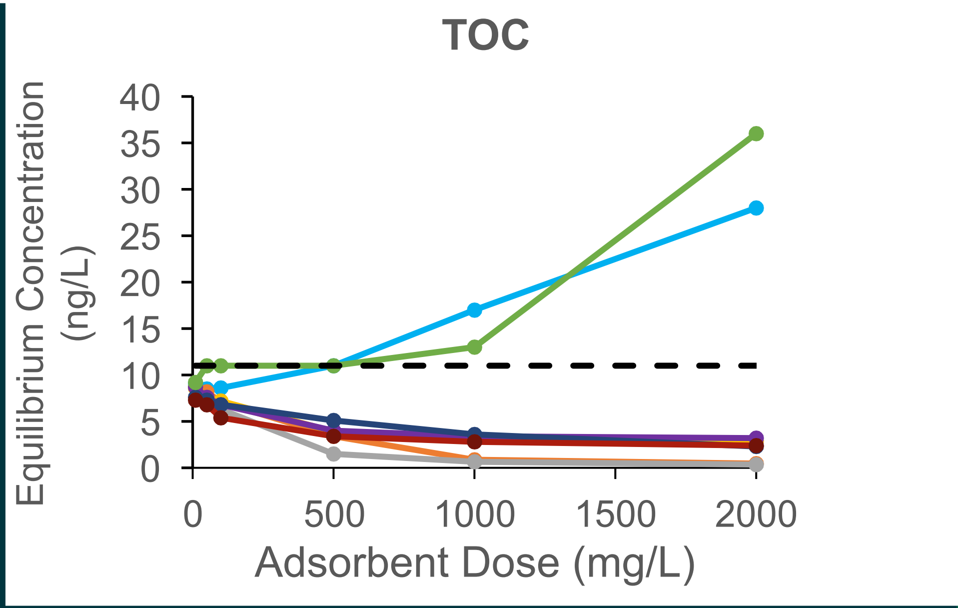
Results – Baseline Characterization

- Branched and linear isomers analyzed for PFOA, PFOS, and PFECHs
- Distribution changed between raw and filtered water for PFOS only
- Total organic carbon (TOC) = 11 mg/L
- Volatile organic compounds (VOCs) detected
  - cis-1,2-dichloroethane = 305 µg/L
  - 1,1-dichloroehene = 295 µg/L
  - 1,1,1-trichloroethane = 135 µg/L

Compound	Unfiltered Raw Water	Filtered Water Event 1	Filtered Water Event 2
PFOA	36.8%	38.1%	45.1%
PFOS	93.9%	57.8%	57.1%
PFHxS	18.6%	20.0%	16.9%

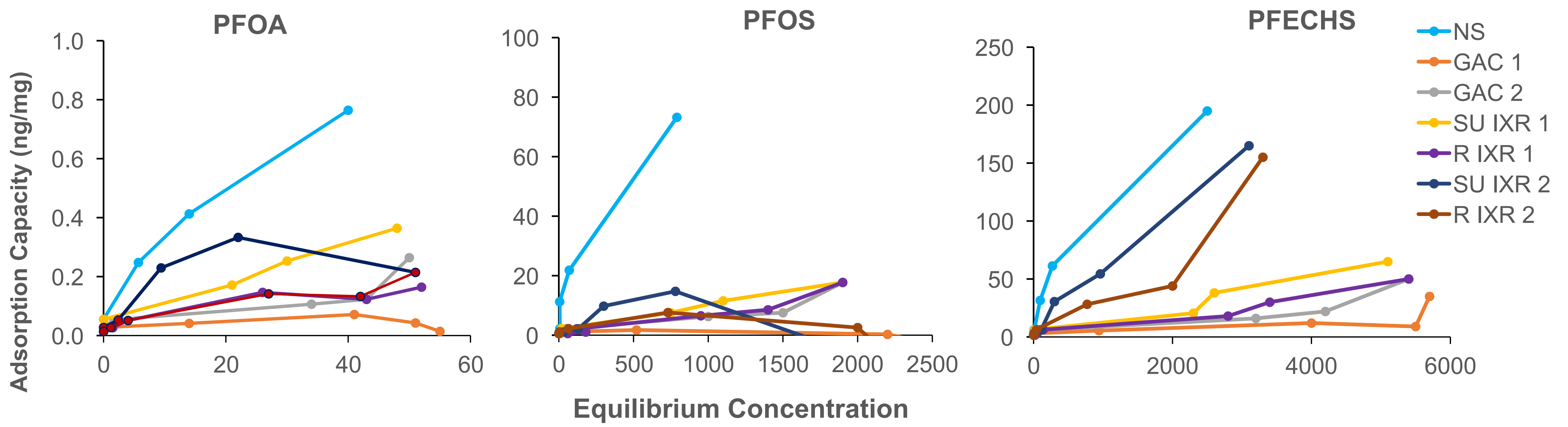
Results - Isotherms





GAC: granular activated carbon
IXR: ion exchange resin
NIO: nano iron oxide
NS: novel adsorbent, cyclodextrin
PFOA: perfluorooctanoic acid
PFOS: perfluorooctanoic sulfonate
PFECHS: perfluoroethylcyclohexane sulfonate

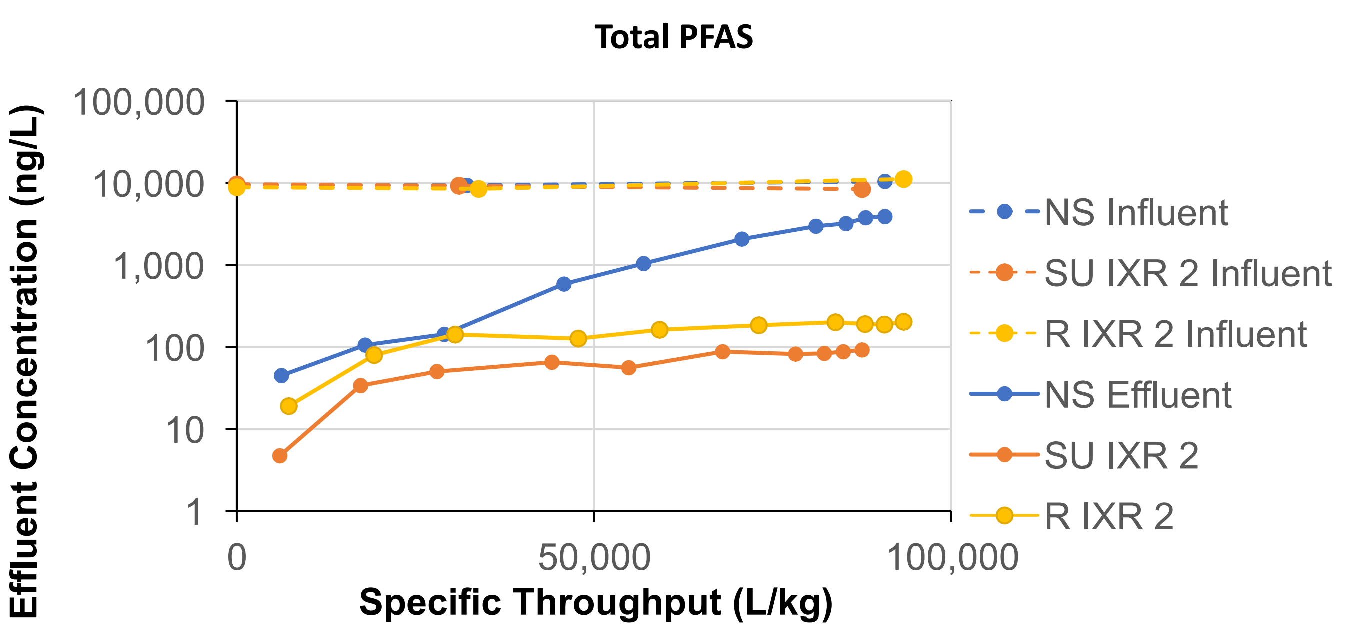
Results - Isotherms

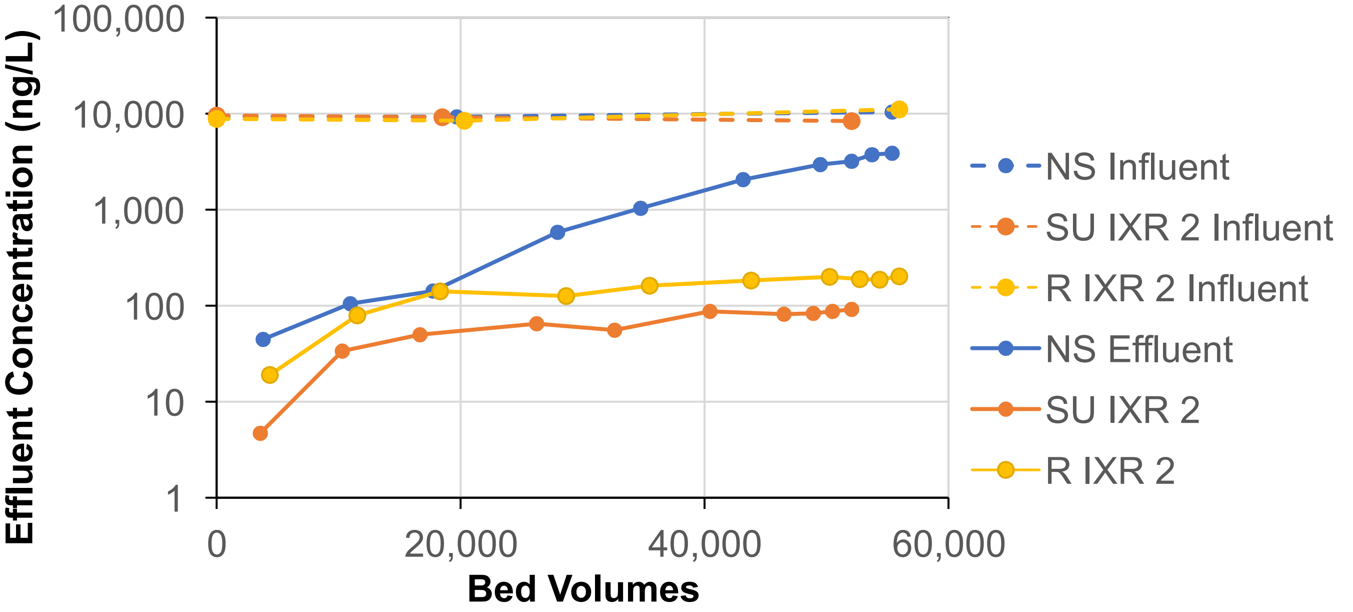


Ranking	Sorbent	PFOA (ng/mg)	PFOS (ng/mg)	PFECHS (ng/mg)
1	Cyclodextrin	0.76	85.9	195
2	Single Use IXR 1	0.33	17.3	165
3	Regen IXR 1	0.21	8.9	155
4	Single Use IXR 2	0.36	30.4	65
5	GAC 2	0.26	30.4	50
6	Regen IXR 2	0.16	30.4	50
7	GAC 1	0.07	2.0	35
8	NIO	0	0	0

Results - RSSCT

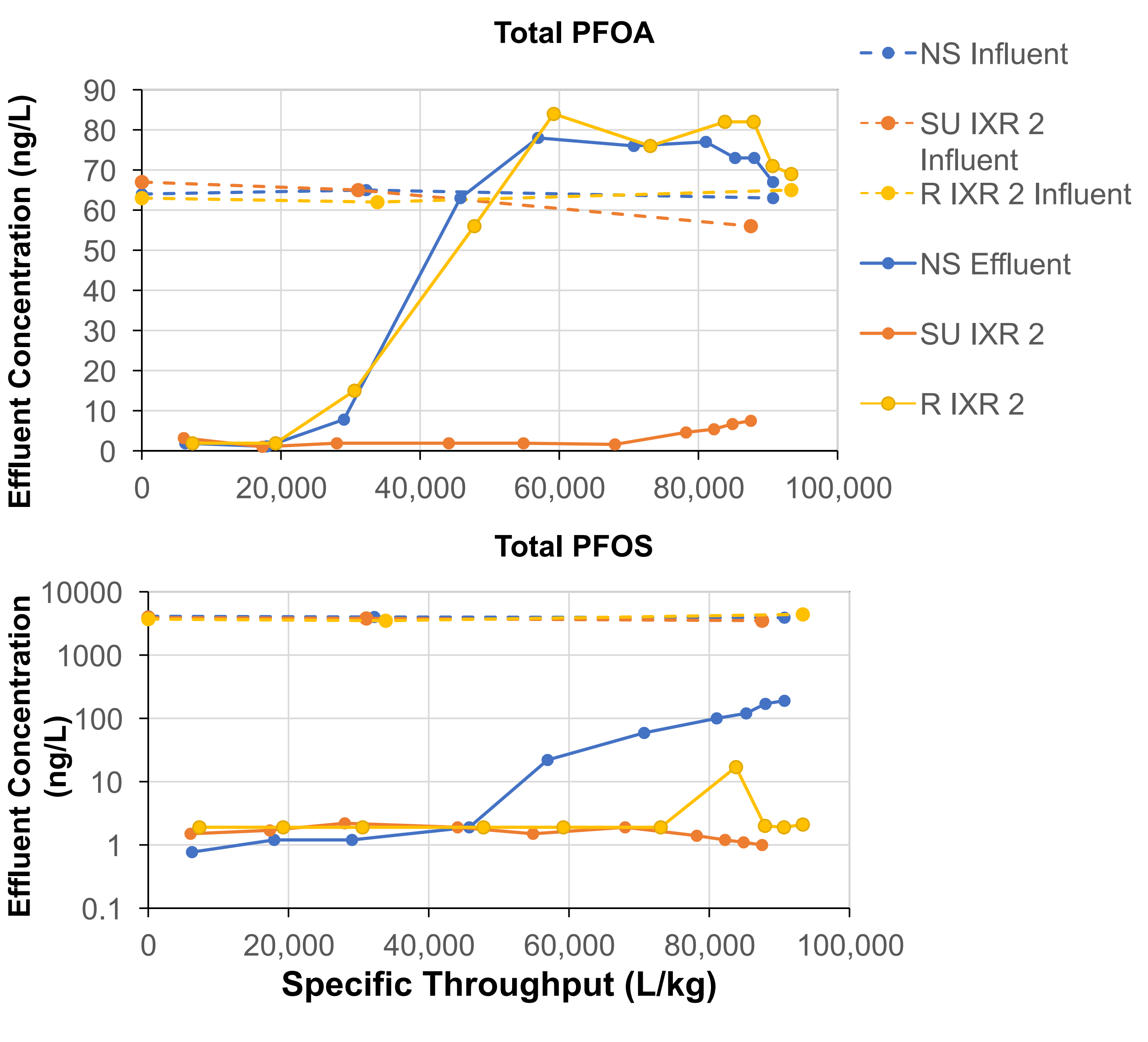
- All columns showed breakthrough of total PFAS concentrations
- Influent concentrations were variable, but within 20% of the average
- The cyclodextrin column showed higher effluent concentrations





Results - RSSCT

- Retention of PFOA by the cyclodextrin and Regen IXR 2 was similar
- Retention of PFOS by the two IXRs was similar
- Removal of PFAS by the cyclodextrin was limited by the short EBCT



Results - RSSCT

		At 5% of influent, Total PFAS			At 8 ng/L of PFOA		
Metric	Unit	Cyclodextrin	Single Use IXR 2	Regen IXR 2	Cyclodextrin	Single Use IXR 2	Regen IXR 2
Bed Life	days	4,661	9,948	9,842	2,689	9,938	3,077
Water Treated	L	9.5	20.3	20.5	5.5	20.2	6.4
Bed Volumes	-	26,000	52,051	55,966	15,000	52,000	17,500
Specific Throughput	L/Kg	42,000	87,523	93,343	24,500	87,500	29,000
Sorbent Usage Rate	Kg/L	2.38E-05	1.14E-05	1.07E-05	4.08E-05	1.14E-05	3.45E-05

– Performance metrics on effluent Total PFAS
– Criteria: 8 ng/L of PFOA vs. 5% of influent concentration (~500 ng/L)
– PFOA might be the limiting factor due to its lowest threshold concentration
– The single-use and regenerable IXR had long breakthrough values
– The cyclodextrin has a higher selectivity and capacity for PFAS adsorption, but it was limited by the short EBCT in RSSCT

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Conclusions and Next Steps

Conclusions

From Isotherms

- Up to 99.97% removal of most PFAS → PFOA, PFOS, and PFECHS.
- Removal efficiencies at 10 mg/L of adsorbent from 3.4% for GAC 1 to 58% for the Cyclodextrin.
- Adsorption capacity: cyclodextrin > Single Use IXR 2 > Regen IXR 2
- NIO not effective for PFAS removal.
- No TOC removal by the cyclodextrin → high selectivity towards PFAS.
- TOC was removed by GACs, and partially removed by ion exchange resins.

Conclusions

From RSSCTs

- Performance Single Use IXR 2 > Regen IXR 2 > Cyclodextrin
  - The EBCT of 5 min was not enough to maximize the cyclodextrin's adsorption capacity.
- Short-chain PFAS such as PFBA and PFPeA showed poor retention times.
- PFECHS and PFOS → no breakthrough in IXR columns.
- PFOA was the first compound to breakthrough, despite an influent concentration two orders of magnitude lower than PFOS and PFECHS.
- TOC was poorly removed by the three adsorbents.
- All adsorbents, including the cyclodextrin, exhibited sufficient specific throughput to treat 10,000 gallons of basement water.

Next Steps

Considerations for regenerable media

- Ethanol (Cylodextrin) and Methanol (Regen IXR 1).
- Reliability/feasibility of media regeneration

Scaleup, cost, and other practical considerations

- Treatment goals, as these could be evolving quickly
- TOC and co-contaminants treatment
- Media Costs: Single Use IXR 1 = Cyclodextrin
- Disposal vs regeneration

Potential Pilot-Scale Test

- Cyclodextrin and/or Single Use IXR
- Volume = 10,000 gallons of basement water to treat
- Flowrate = 1 – 2 gallons per minute


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