A Case Study:

Optimizing an Existing Treatment System to Address PFAS

BATTELLE CHLORINATED CONFERENCE 2024, DENVER, CO

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Sustainability is our business

1. Background
2. Factors leading to PFAS study and data
3. Optimization efforts & considerations
4. Lessons learned

Background

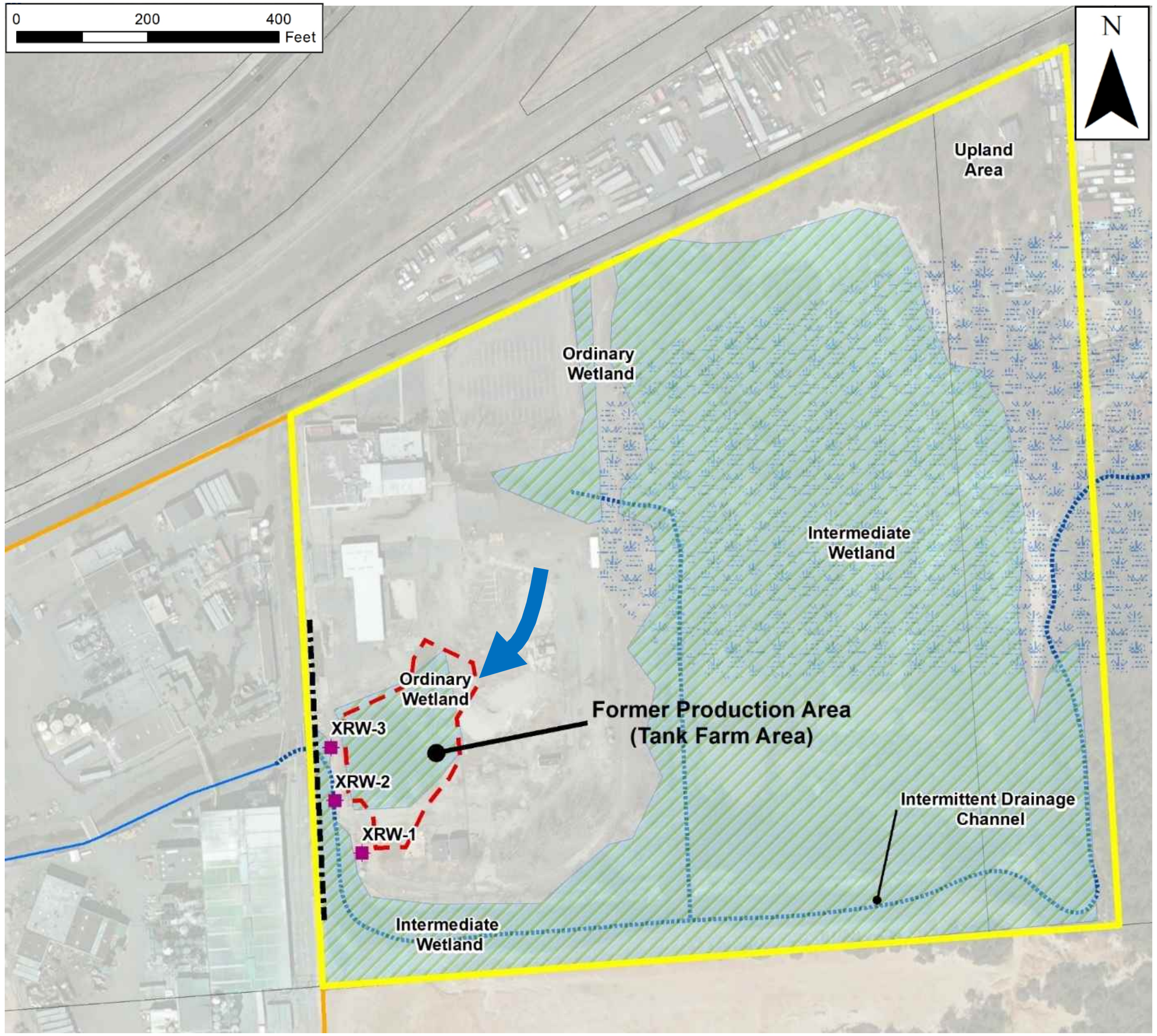
Site Location and History

- 30-acre parcel, 6.7 acres developed for plant
- History of various chemical processing, manufacturing and storage dating back to late 1960s
  - Solvent recovery and refining
  - Organic chemicals to produce water treatment chemicals, lubricants, oilfield chemicals, anti-corrosive agents and various solvents
- Groundwater impacts identified ~1980; NPL listing in 1983; initial groundwater P&T installed in 1991
  - Groundwater P&T system converted into an IRM pending source area remedy
- Plant ceased operations in 2001, by 2005, all structures (tank farm and production equipment) were demolished
- Record of Decision (ROD) issued in 2019
  - Selected remedy includes in-situ chemical oxidation (ISCO)

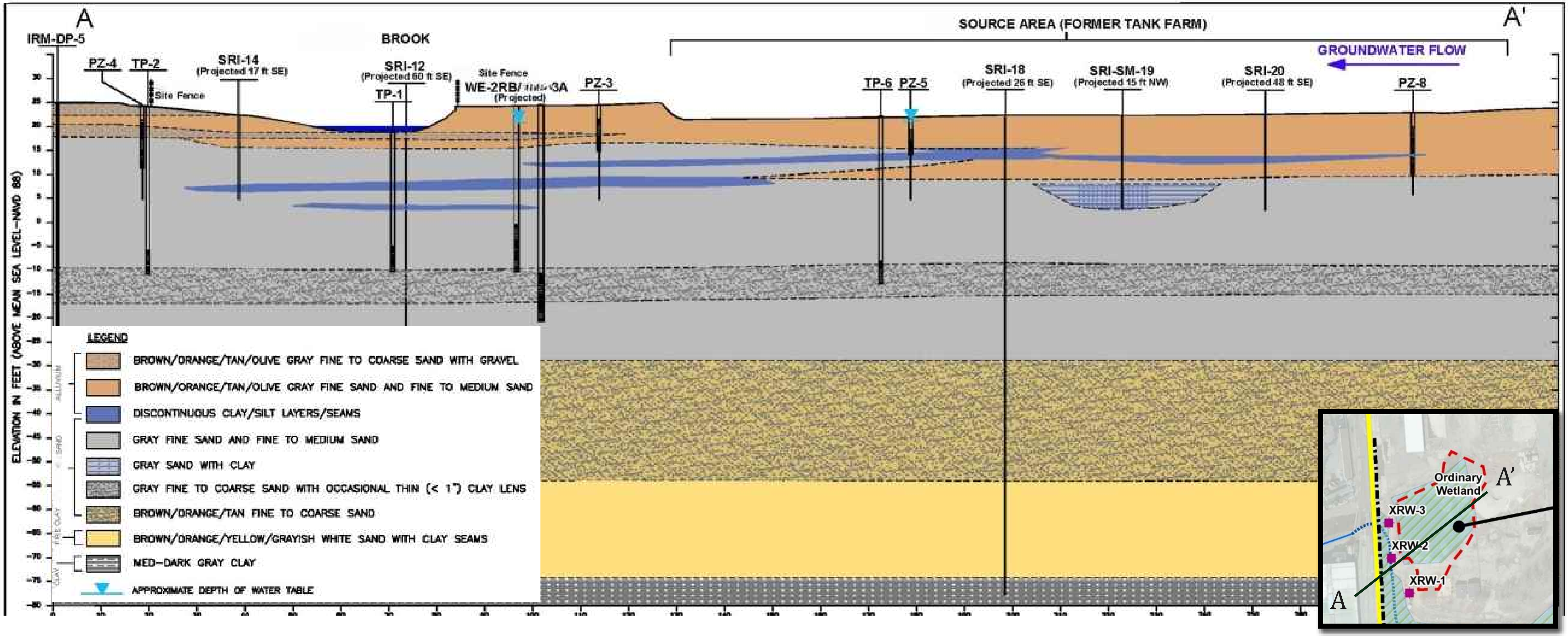
Interim Remedial Measure

Groundwater pump and treat system

- Recovery Wells: Three wells in operation, screened 15 to 35 feet below ground surface
- Flow Rate: Combined rate of ~30 gallons per minute
- VOC treatment: air stripping and granular activated carbon (GAC)
- Discharge: Permitted discharge of treated water to a Brook
- Groundwater Conditions:
  - Shallow water table (~3 ft bgs), flow toward southwest, and impacts to ~35 ft bgs near source
  - Frequently exposed in wetland that formed in footprint of former tank farm (primary COC source area)
  - Wetland also collects surface water runoff from on- and off-site properties, which mixes with groundwater
- COCs: Chlorobenzenes, chlorinated ethenes, chlorinated ethanes, BTEX

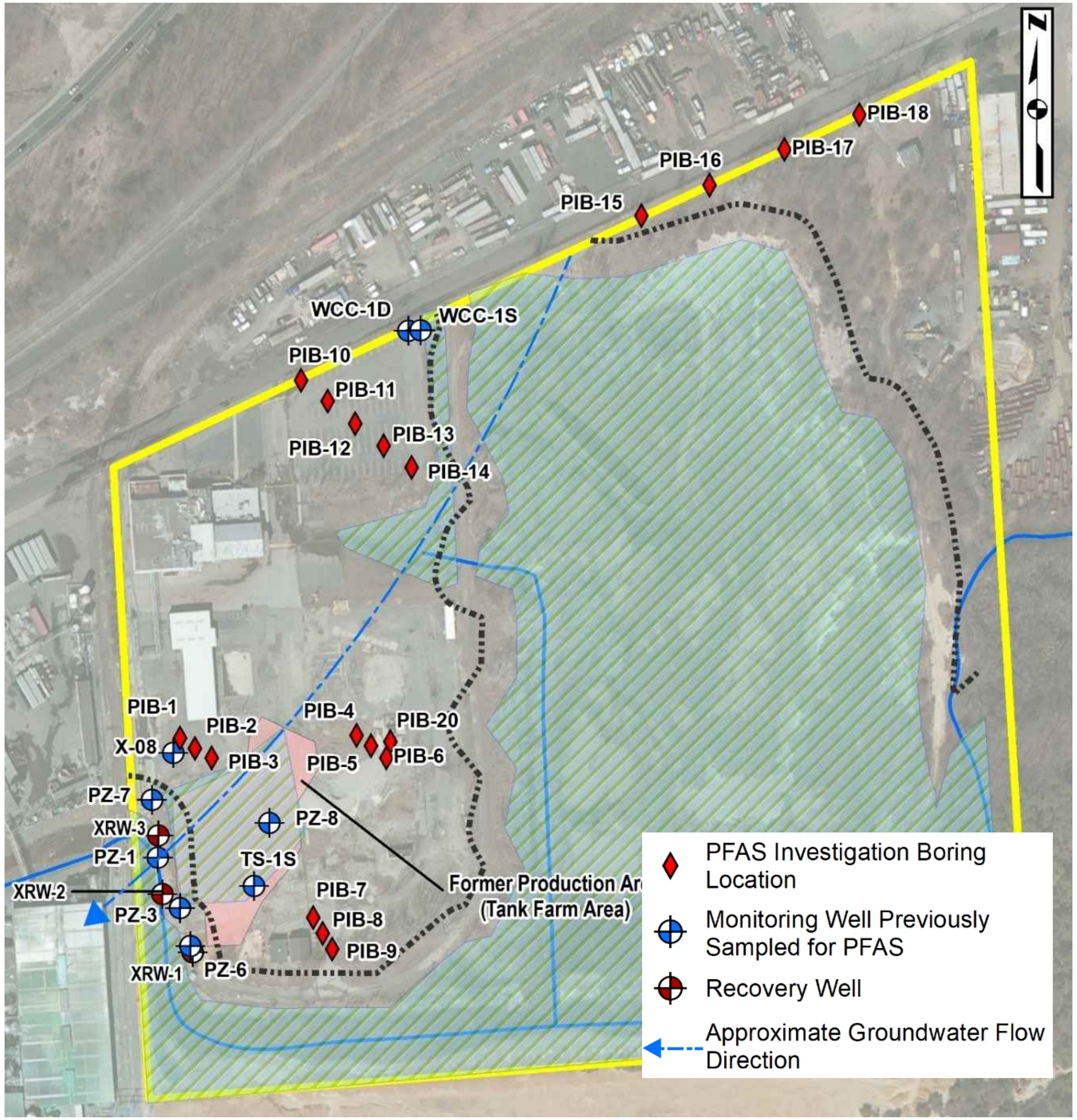


Geology and Hydrogeology



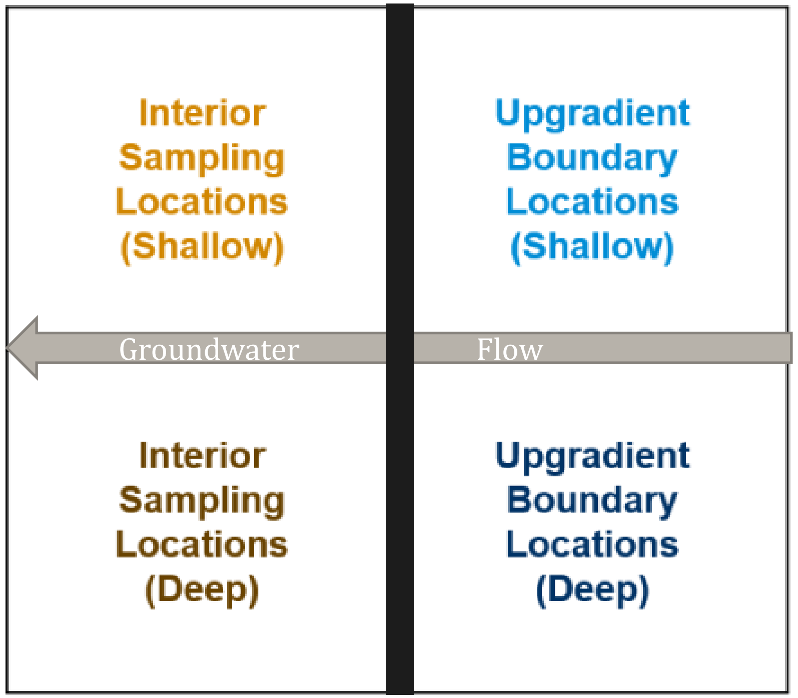
Factors Leading to PFAS Study

- ISCO can degrade precursor PFAS to regulated PFAAs if precursors present; Total Oxidizable Precursors (TOP) assay analysis of Site samples performed
  - Initial PFAS sampling (Nov. 2021 – Feb. 2022):
    - 9 onsite monitoring wells and 3 IRM P&T recovery wells
    - Regulated PFAS (i.e., PFOA, PFOS and PFNA) and others detected in groundwater
  - Additional groundwater sampling (Sept. 2022):
    - 18 temporary borings at shallow (water table) and deep (approx. 25 feet) depth intervals along the upgradient site boundary and within the site interior.
- Data sets were compared in combination to evaluate concentrations of PFAS coming onto the site and potential onsite contributions.

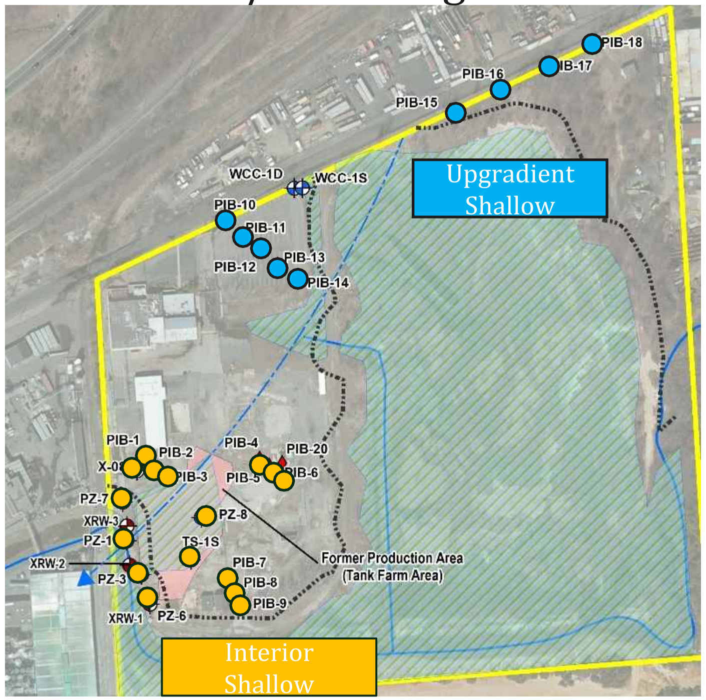


Conceptual Visualization of Sampling Classifications

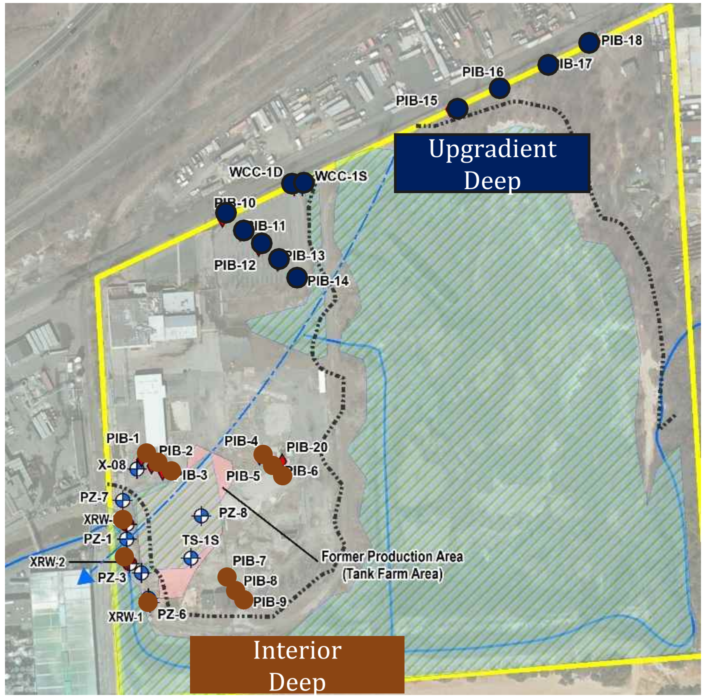
- The PFAS data were classified into four groups based on their sampling locations



Shallow Samples (<15 ft bgs)
MWs/PZs and grabs

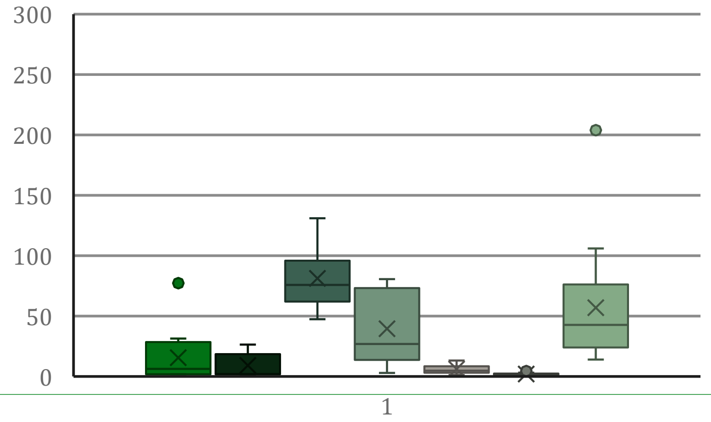
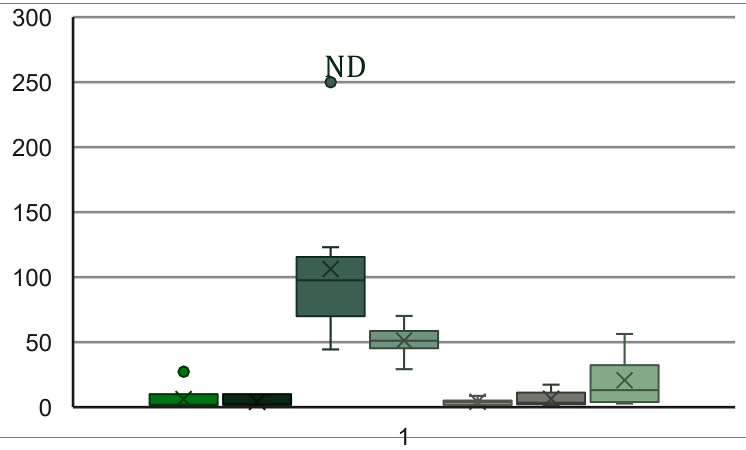
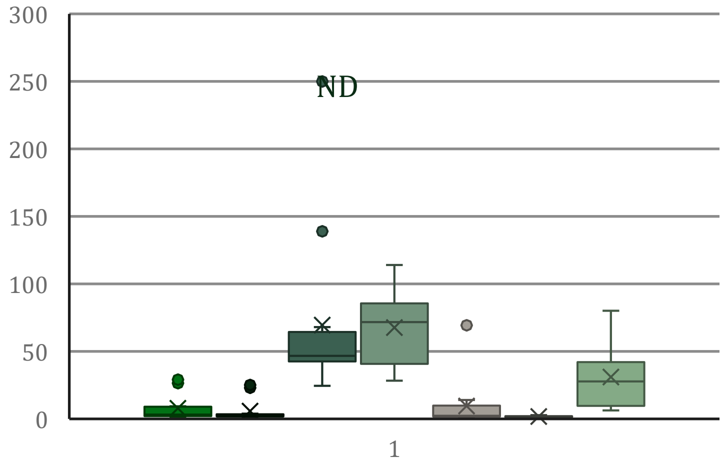
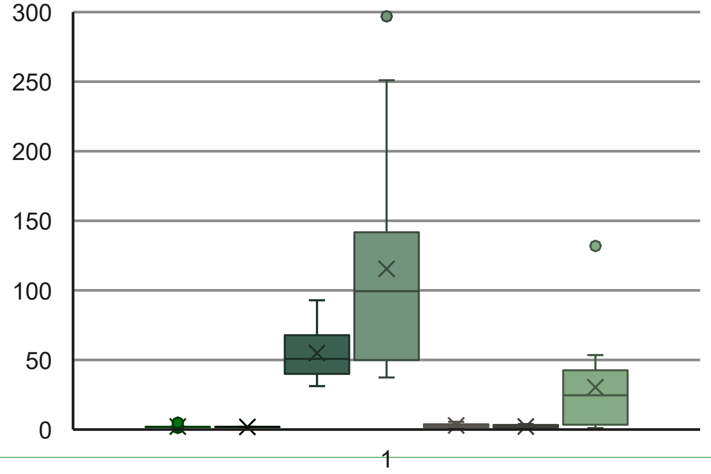


Deep Samples (>15 ft bgs)
RWs/MWs and grabs



PFAS Detections

- PFAS detected upgradient and onsite, generally at similar concentrations

	Interior Samples	Upgradient Samples
Shallow (<15 bgs)		
Deep (>15 bgs)		

- 6:2-FtS
- 8:2-FtS
- HFPO-DA
- PFOA
- PFNA
- PFBS
- PFOS

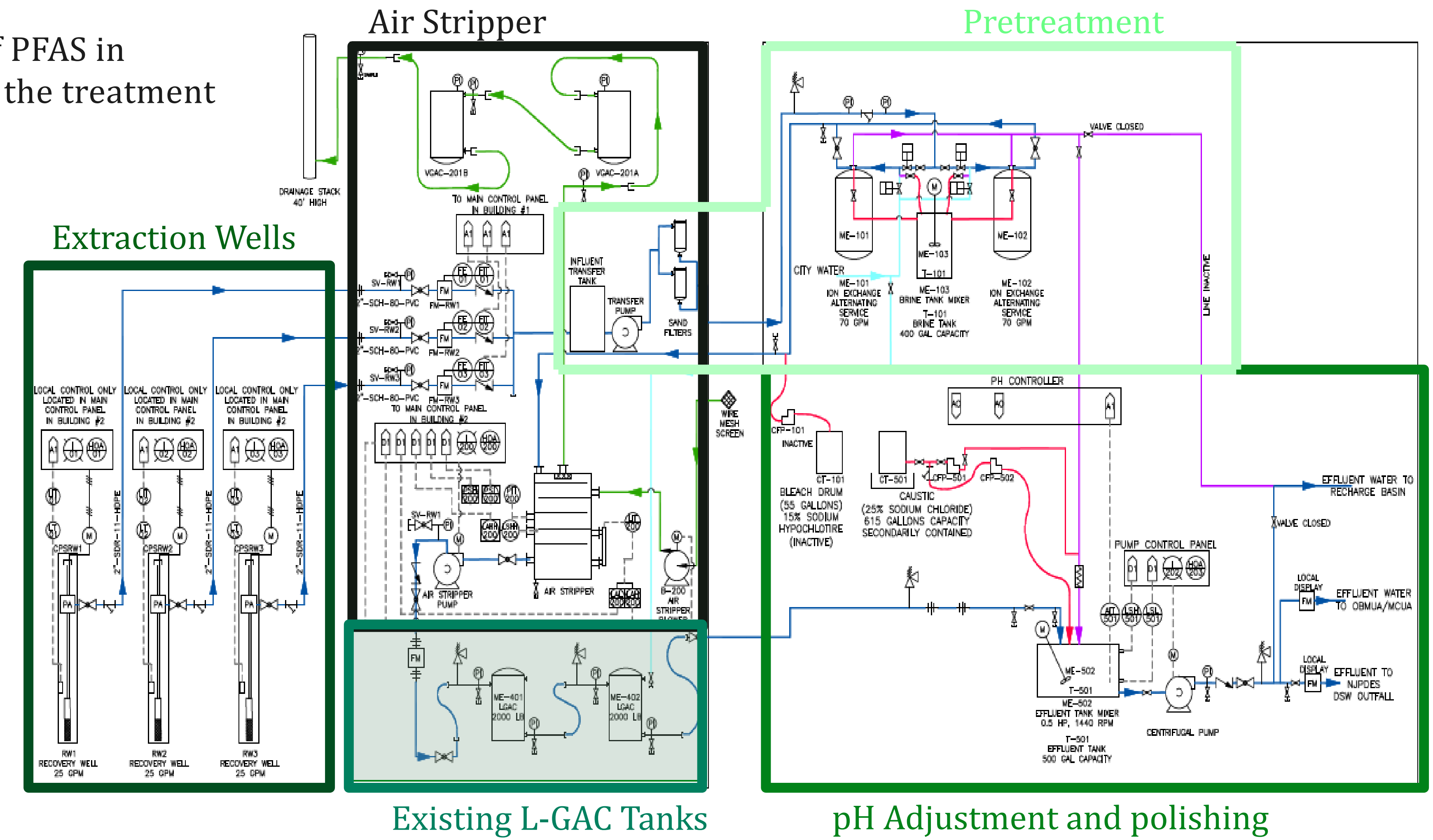
Regulated PFAS

Existing Treatment System of the IRM P&T

- Treatment system intended to address VOCs
- Upon confirming the presence of PFAS in groundwater, efforts to optimize the treatment system were initiated.

Average PFAS influent conc

- PFOS: ~30 ng/L
- PFOA: ~75 ng/L
- PFNA: ~3 ng/L



Design considerations for PFAS treatment

- The treatment objective was set to meet the regulatory standards for PFOA (14 ppt), PFOS (13 ppt), and PFNA (13 ppt); HFPO-DA standard promulgated recently

- To optimize the existing GAC system for PFAS removal the following parameters needed to be optimized:
  - GAC consumption rate (determines the breakthrough time, and in turn the changeout frequency)
  - Empty Bed Contact Time / residence time

- Geochemistry and competition can impact both the GAC consumption and the required contact time

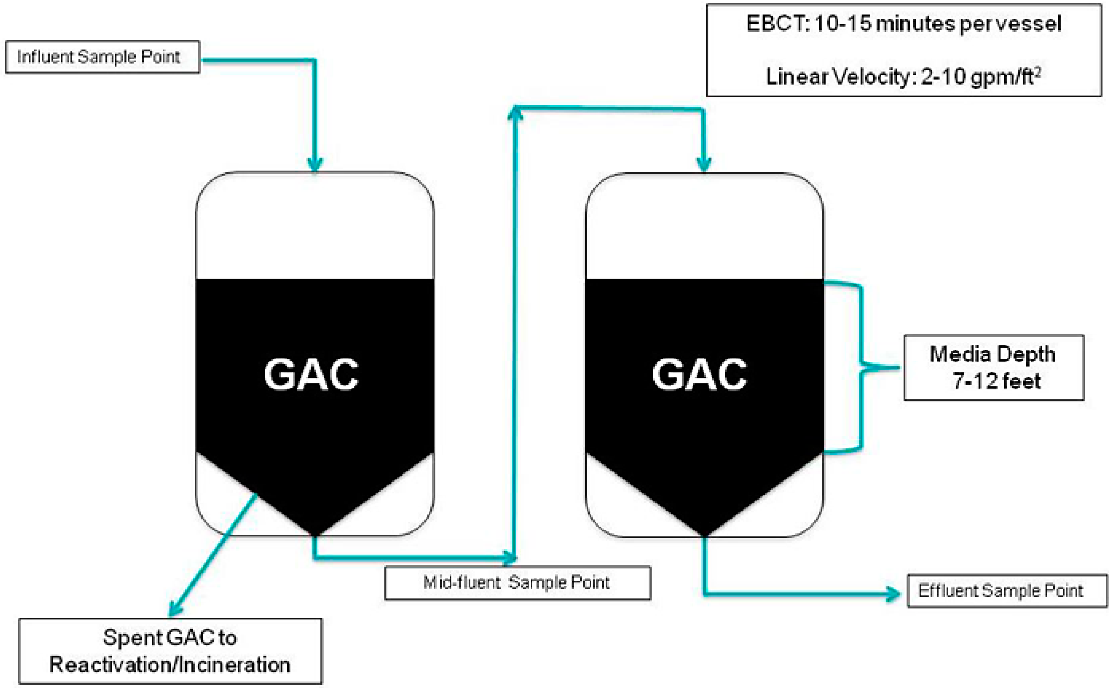
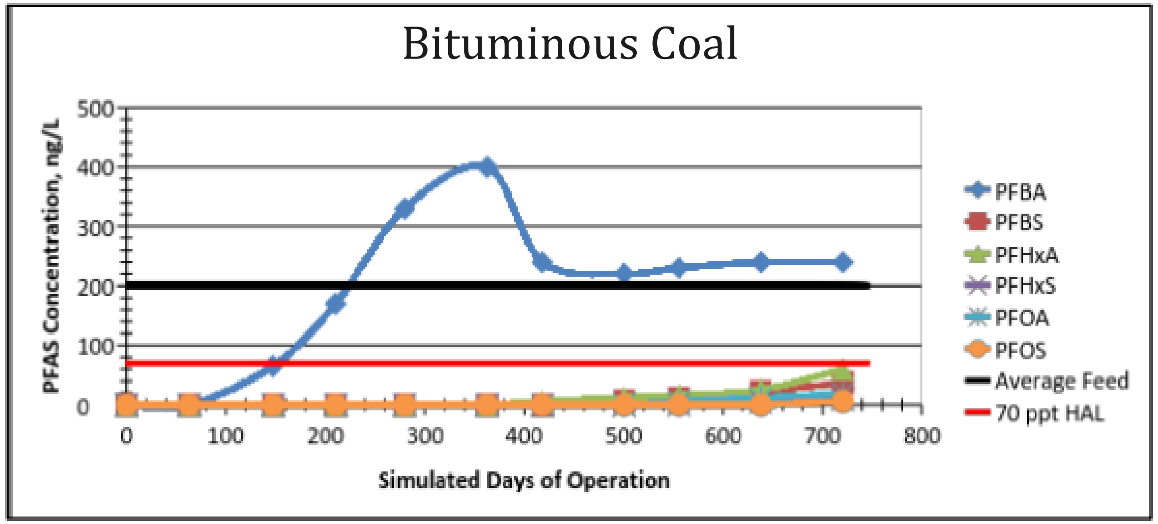
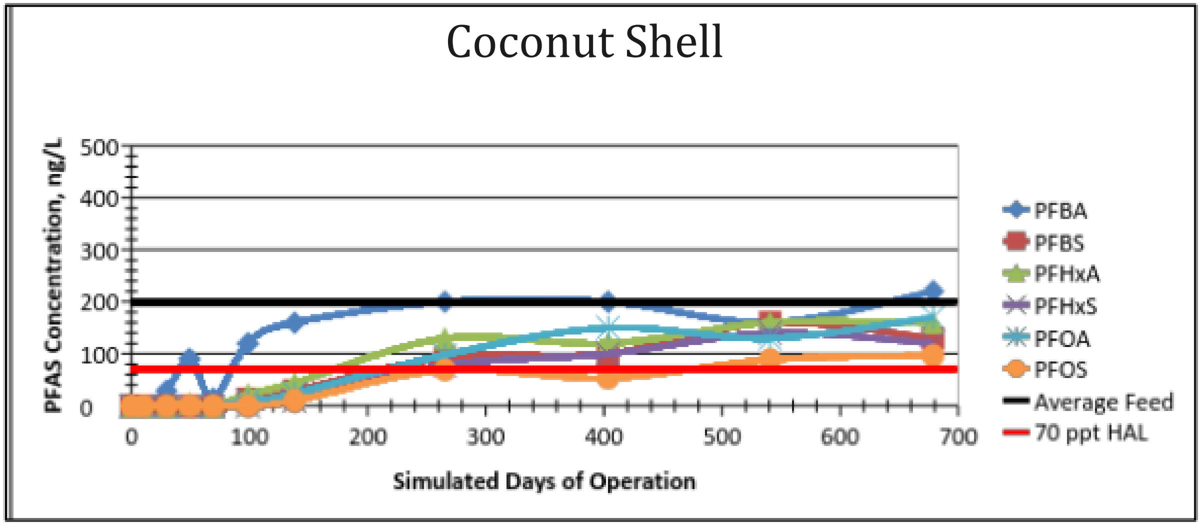


Figure from Calgon Carbon Corporation, adapted from ITRC (2023)

Activated Carbon Selection

- The existing system used a coconut shell GAC for VOC removal
- Multiple studies indicate that bituminous coal has superior performance for the removal of most PFAS (e.g., McNamara et al., 2018; Westreich et al., 2018, as cited in ITRC, 2023)
- Results demonstrated that bituminous coal-based carbons provide considerably greater removal capacity of the targeted compounds compared with the coconut-based direct activated carbon, resulting in a later breakthrough in a similarly sized GAC system





Figures adapted from Calgon Carbon Corporation column study report (Calgon, 2017)

Optimization Activities

GAC Optimization

- Switched from coconut shell to bituminous GAC for better PFAS removal effectiveness
- Increased vessel size from 1,100 lb to 2,000 lb tanks in Feb 2024 (increased contact time from 17 minutes to 30 minutes)

Performance Evaluation

- Routine sampling of influent, mid-fluent, and effluent water for a suite of PFAS compounds
- Ongoing evaluation of larger (2,000 lb) vessels
- Assessment of geochemistry and TOC

Monitoring and Reporting

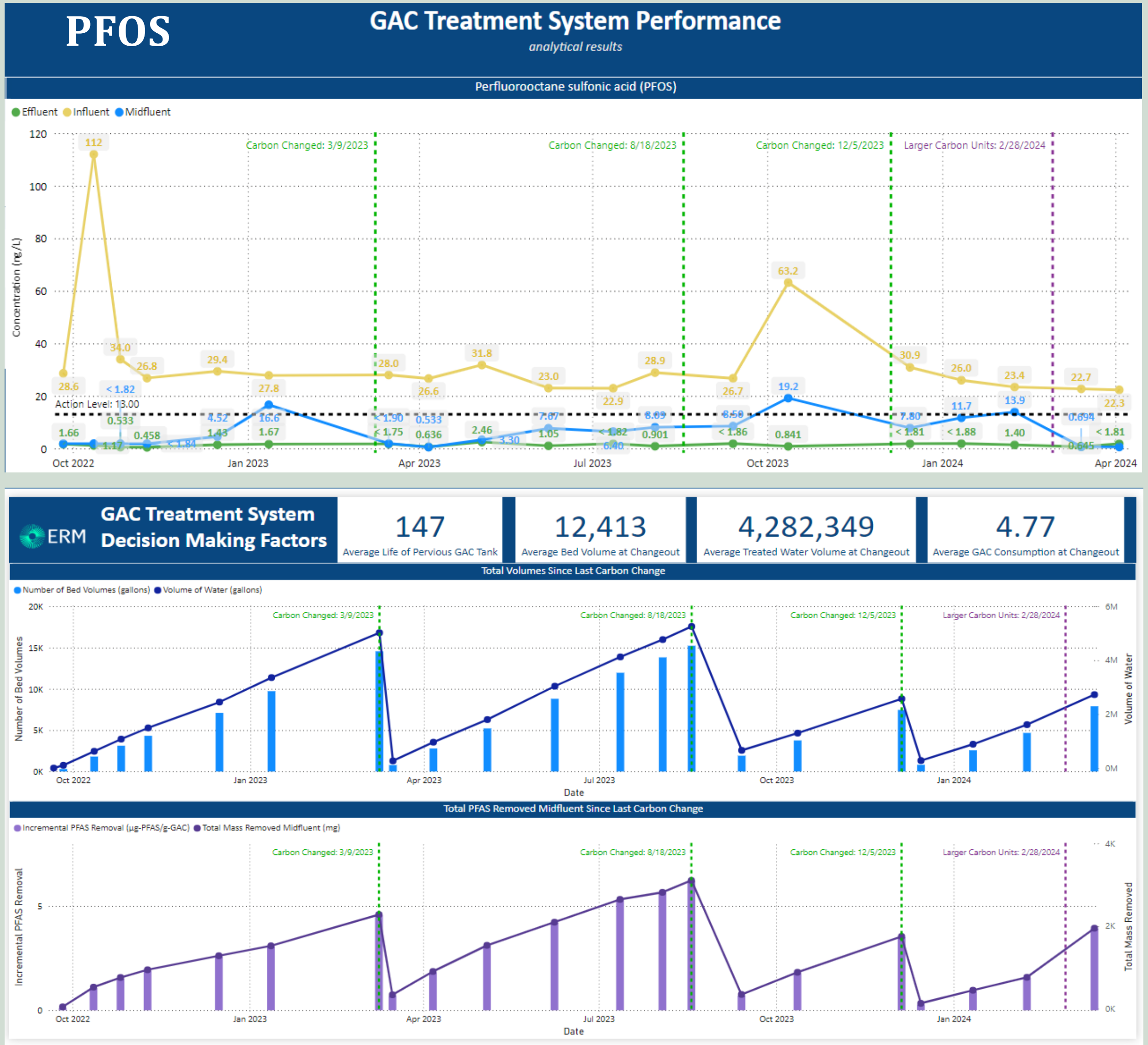
- Developed a GAC performance tracking tool for real-time updates and to mitigate reporting delays

Additional Measures Under Consideration

- Detected total organic carbon (TOC) concentrations > 2 ppm, potentially decreasing PFAS removal efficiency
  - Pretreatment using a “cheaper” GAC to reduce TOC
- Desktop study for ion exchange resins for PFAS treatment

GAC Performance Tracking Tool

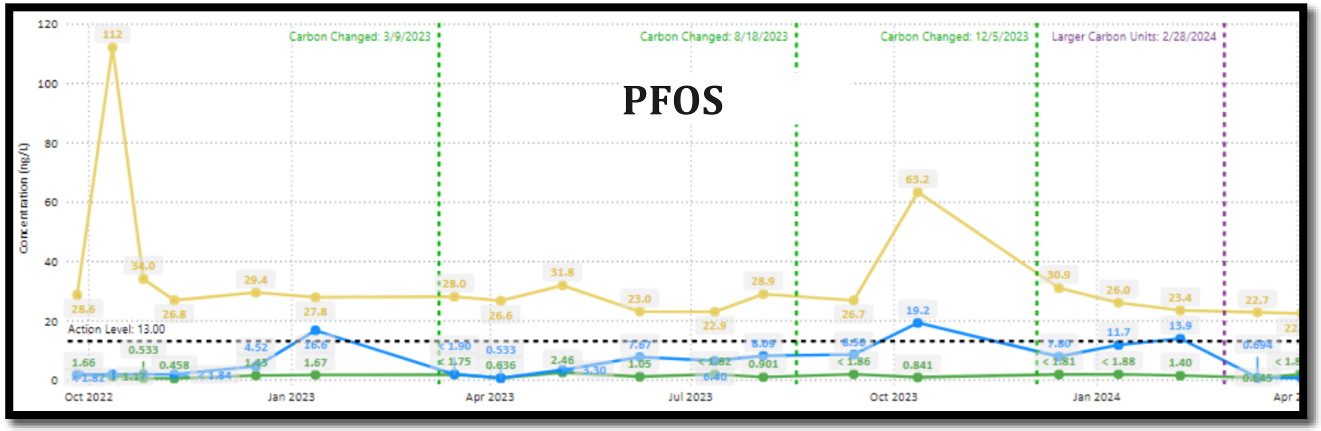
- System required close monitoring due to temporal variations in performance
- Online data sharing and visualization tool was developed for site owners, consultants, and operators to track GAC performance and optimize response times
- The tool estimates the expected GAC change-out time using the moving average of GAC consumption, influent concentrations, and flow parameters
- The tool flags unexpected breakthroughs and issues alerts, allowing for early identification of PFAS breakthrough
- The tool has identified unexpected breakthroughs at the midpoint. Interim response actions included collecting confirmation samples and performing early carbon change-outs. As a result, no action level exceedance occurred at the effluent point

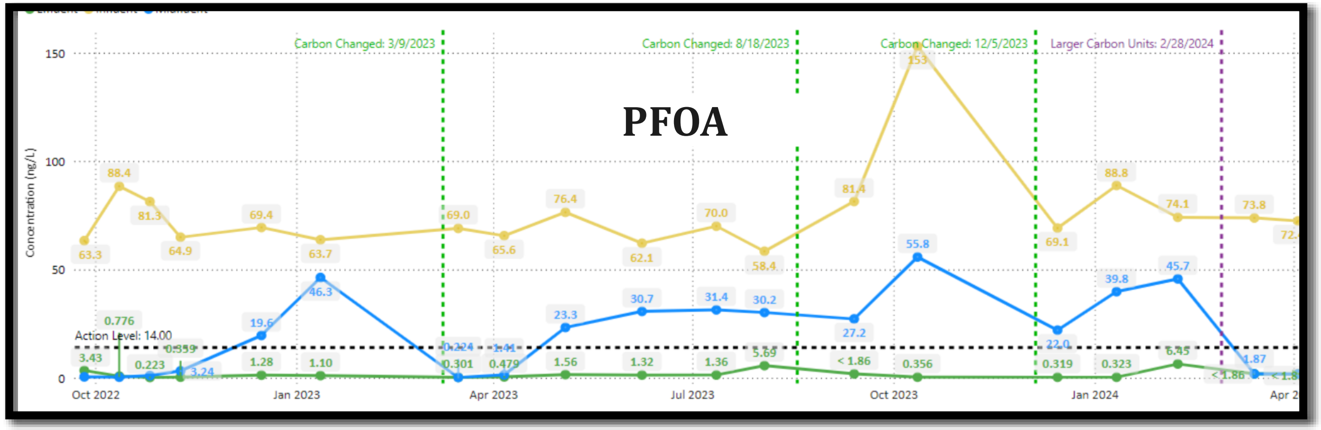


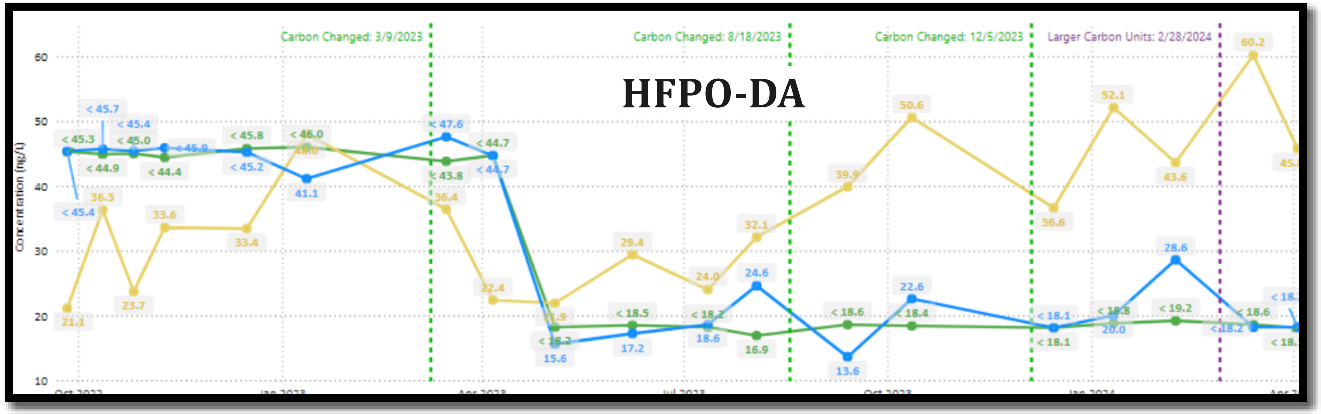
Results & Observations

- The system effectively removed PFOA and PFOS to below regulatory standards (PFNA below standards in influent)
- GAC is not as effective for removing HFPO-DA from water; HFPO-DA standard promulgated recently after the initial system optimization

Carbon Type	Coconut-based	Bituminous-based
Average time between changeouts (days)	~28	~120







Additional Considerations

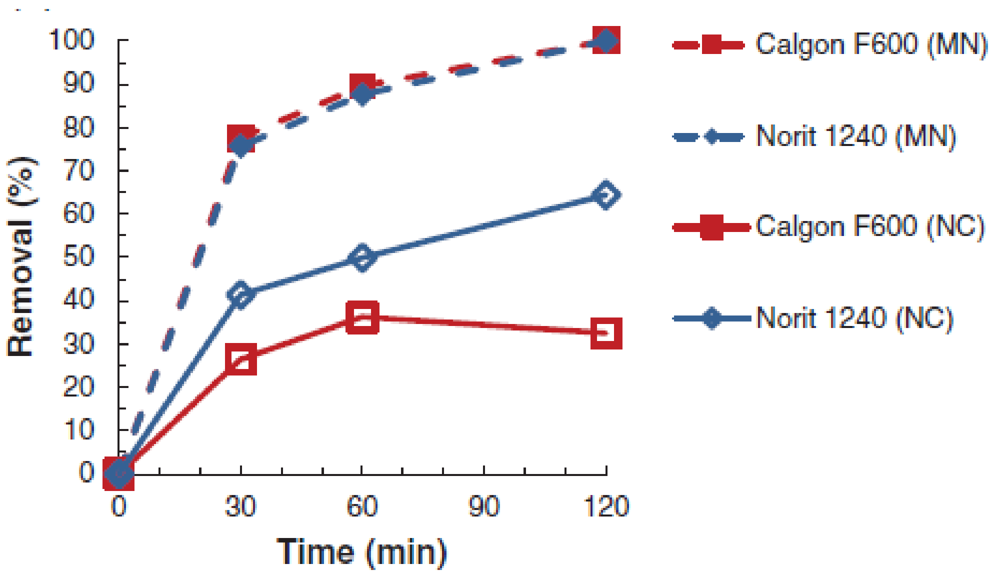
Potential TOC Pretreatment:

- Influent water has ~2.5 mg/L of TOC
- TOC > 1.0 mg/L adversely impacts GAC performance
- PFOS removal significantly impacted by TOC presences (Kempisty et al. 2022)
  - Considering TOC pretreatment using a cheaper GAC

Considering Other Treatments

- Desktop evaluation for ion (anionic) exchange resins completed and benchtop and/or field pilot under consideration
- Effects of salts from ISCO (e.g., anions after sodium persulfate addition) on the efficiency of ion exchange resins

PFOS Removal



TOC in NC samples 2.7 (mg/L)
TOC in MN samples 0.7 (mg/L)

Bituminous Coal
Coconut Shell

Figures adapted from Kempisty et al. (2022)

Lessons Learned

Assess for PFAS before significant remedial activities, e.g., ISCO

- ISCO can transform precursor PFAS to regulated PFAAs

Implement routine monitoring program and real-time evaluation tools

- Collect a comprehensive data set upfront to facilitate future design improvements

Use treatment objectives and Site data for a tailored optimization

- Bituminous GAC more effective than coconut shell GAC for most common PFAS
- Optimize operating parameters (e.g., tank size/contact time)
- Consider addressing geochemistry and competing demands through pretreatment (cost-benefit of pretreatment vs GAC changeout costs)
- Consider anionic ion exchange for PFAS treatment

Adapt solutions to keep pace with evolving regulations and action levels

- Consider additional PFAS compounds that may be regulated in near future (e.g., HFPO-DA)
- Design P&T systems with room for expansion to address current unknowns
- Balance between temporary fixes versus long-term system overhaul

Thank you

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