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Cottage Grove Pilot Study Final Report

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STANTEC INSTITUTE FOR
WATER TECHNOLOGY & POLICY

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Executive Summary

A pilot-scale study was carried out to test five different treatment column configurations for treatment of PFAS contaminated groundwater at Cottage Grove Well #3 in the East Metro of Minneapolis-St. Paul, MN. One column evaluated the ability of a granular activated carbon (GAC) media to treat raw water, two columns evaluated the ability of ion exchange (IX) resins to treat raw water, and two columns evaluated the ability of the same IX resins to treat GAC column effluent. The purpose of these final two columns was to investigate the potential for GAC-IX mixed media treatment.

The pilot study found that significant fouling occurred in the IX columns treating raw water within weeks of startup; however, these results are complicated by potential fouling acceleration from water contact with the atmosphere prior to treatment. The GAC column was affected to a lesser degree by this fouling, while the IX columns treating GAC effluent did not exhibit any noticeable fouling. Iron and manganese pretreatment using manganese dioxide media was added to the pilot scope to reduce influent water iron and manganese concentrations.

Although the pilot was run for approximately a year and a half, the use of sample ports placed along the media column allowed for observation of accelerated treatment to imitate a much longer treatment runtime. The results of this pilot showed significant advantages to IX treatment compared to GAC treatment for perfluorosulfonic acids, such as PFBS, PFHxS, and PFOS, which comprise the majority of the health index value for the pilot source water and several other water sources in the East Metro. Neither GAC nor IX treatment showed significant treatment capacity for short-chain perfluorocarboxylic acids, such as PFBA, and they showed similar mid-level treatment capacity for long-chain perfluorocarboxylic acids, such as PFOA. The breakthrough of various PFAS compounds were used to calculate the breakthrough of the overall Health Index to predict approximate media life.

20-year net present value estimates for facilities of 1.0 MGD, 4.5 MGD, and 10 MGD flow rates were calculated taking into account building capital costs and facility operation and maintenance costs. These estimates included media costs, chemical costs, and in-facility pumping costs. High-level cost estimates reviewed each of the treatments evaluated: GAC treatment with lead-lag vessels, IX treatment with lead-lag vessels, and GAC-IX treatment with a lead GAC vessel and a polishing IX vessel.

Estimated 20-year net present values

	GAC Lead-Lag	Purolite Resin Lead-Lag	Dow/Evoqua Resin Lead-Lag	GAC and Purolite Resin	GAC and Evoqua/Dow Resin
1.0 MGD	$7.3M	$5.8M	$5.9M	$7.1M	$7.2M
4.5 MGD	$23.1M	$17.8M	$18.3M	$22.2M	$22.7M
10 MGD	$42.9M	$32.2M	$33.2M	$41.1M	$42.0M

Abbreviations

DNR	Department of Natural Resources
DP	differential pressure
EBCT	empty bed contact time
EPA	Environmental Protection Agency
GAC	granular activated carbon
gpm	gallons per minute
HI	health index
IX	ion exchange
L	liter
MDH	Minnesota Department of Health
μg	microgram
MGD	million gallons per day
μm	micrometer
MPCA	Minnesota Pollution Control Agency
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanioc acid
PFBS	perfluorobutane sulfonate
PFCAs	perfluorocarboxylic acids
PFEtS	perfluoroethane sulfonate
PFHpA	perfluoroheptanioc acid
PFHpS	perfluoroheptane sulfonate
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFPeA	perfluoropentanioc acid
PFPeS	perfluoropentane sulfonate
PFPrA	perfluoropropanoic acid
PFPrS	perfluoropropane sulfonate
PFSAs	perfluorosulfonic acids

1.0 BACKGROUND AND OBJECTIVES

1.1 BACKGROUND

Per- and polyfluoroalkyl substances (PFAS) encompass a large family of anthropogenic chemicals that are environmentally pervasive and not readily destructible. Certain PFAS compounds can bioaccumulate and can be toxic above the permissible dose, causing adverse health effects in humans and wildlife. The carbon fluorine bond is one of the strongest single bonds, making PFAS extremely durable and widely employed in many commercial and industrial applications. However, their stability inhibits natural breakdown, making them very difficult to destroy and resulting in their nickname “forever chemicals.”

Several communities across the Twin Cities south-east metropolitan region are served by groundwater where PFAS contamination exceeds the Minnesota Department of Health (MDH) Health Index (HI) resulting from prior industrial manufacturing activities at a 3M Company facility. Several Cities, including the City of Cottage Grove, the City of Oakdale, and the City of St. Paul Park have installed interim granular activated carbon (GAC) treatment systems, but significant investment will be required to install permanent treatment facilities or expand water supply in all impacted communities.

Federal and state regulators are working to incorporate PFAS contaminants into health and environmental programs. Health-based drinking water guidance values have been issued by MDH, a list of which are shown in Table 1-1 and are accurate as of the publication of this report. MDH combines these health-based values into the HI, an additive risk assessment to track co-contamination of multiple PFAS, based on the below calculation, where the bracketed PFAS are the concentrations of those PFAS in µg/L. An HI value greater than 1.0 indicates that the water supply does not pass the requirement for safe drinking water as determined by MDH. The average raw water PFAS concentrations for Well #3 and the resulting HI are also shown in Table 1-1.

Table 1-1: Drinking Water Guidance Values for PFAS

	PFAS Monitored in Minnesota						
	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS	HI
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	-
Drinking Water Guidance Value[1]	7.000	2.000	0.200	0.047	0.035	0.015	-
Well #3 Raw Water	0.896	0.127	0.043	0.074	0.014	0.001	2.45

[1] For a detailed description of the Health Risk Index model see MDH’s website: https://www.health.state.mn.us/communities/environment/risk/guidance/gw/additivity.html

$$\mathrm{HI} = \frac{[\mathrm{PFBA}]}{7} + \frac{[\mathrm{PFBS}]}{2} + \frac{[\mathrm{PFHxA}]}{0.200} + \frac{[\mathrm{PFHxS}]}{0.047} + \frac{[\mathrm{PFOA}]}{0.035} + \frac{[\mathrm{PFOS}]}{0.015}$$

The United States EPA has only established criteria for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), set at 70 ng/L total for both compounds, that is less stringent than MDH’s guidance.

Historical PFAS and HI data for Well #3 in Cottage Grove are shown in Table 1-2 and a snapshot comparison of East Metro PFAS impacted public water supply wells is shown in Table 1-3.

Table 1-2: Historical PFAS and HI Calculation for Well #3

Date	PFBA (µg/L)	PFBS (µg/L)	PFPeA (µg/L)	PFHxA (µg/L)	PFHxS (µg/L)	PFOA (µg/L)	PFOS (µg/L)	HI
2/26/2020	0.98	0.13	0.064	0.051	0.081	0.023	0	2.84
11/6/2019	0.98	0.12	0.062	0.047	0.073	0.022	0	2.62
8/14/2019	0.98	0.12	0.064	0.047	0.077	0.023	0	2.73
5/28/19	1	0.15	0.067	0.051	0.086	0.02	0	2.87
2/14/19	0.98	0.12	0.064	0.04	0.072	0.026	0	2.67
12/5/18	0.97	0.13	0.063	0.026	0.067	0.027	0	2.53
8/23/18	0.98	0.13	0.06	0.046	0.06	0	0	1.71
5/22/18	1	0.12	0.068	0.047	0.066	0.02	0	2.41
3/14/18	1	0.14	0.066	0.044	0.07	0.019	0	2.47
10/18/17	0.95	0.14	0.06	0.044	0.082	0.027	0	2.94
6/21/17	0.97	0.16	0.061	0.048	0.1	0.017	0	3.07
4/20/17	0.86	0.13	0.045	0.038	0.077	0.022	0	2.64
10/10/16	0.91	0.14	0.069	0.03	0.089	0.027	0	3.02
5/11/16	0.85	0.11	0.055	0.042	0.071	0.025	0	2.61
11/4/15	0.9	0.13	0.055	0.039	0.07	0.015	0	2.31
9/9/15	0.9	0.13	0.052	0.053	0.07	0.017	0	2.43
6/3/15	0.91	0.14	0.056	0.043	0.067	0.015	0	2.27
1/28/15	0.93	0.12	0.055	0.037	0.074	0	0	1.95

While this study was carried out in Cottage Grove, PFAS contamination is a widespread problem across the Twin Cities south-east metropolitan region. A 2019 snapshot of the PFAS contamination in other east-metro communities’ public water supply wells is presented in Table 1-3.

Table 1-3: Snapshot of East-Metro PFAS Impacted Public Water Supply Wells

Supply Well	PFBA (µg/L)	PFBS (µg/L)	PFPeA (µg/L)	PFHxA (µg/L)	PFHxS (µg/L)	PFOA (µg/L)	PFOS (µg/L)	HI
Cimarron Park #1	**0.110**	0.000	**0.011**	0.000	0.000	0.000	0.000	0.02
Cimarron Park #2	**0.140**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.02
Cottage Grove #1	**0.780**	**0.020**	**0.026**	**0.009**	0.000	0.000	0.000	0.17
Cottage Grove #2	**0.630**	**0.110**	**0.048**	**0.031**	**0.060**	**0.019**	0.000	2.12
Cottage Grove #3	**0.980**	**0.120**	**0.064**	**0.040**	**0.072**	**0.026**	0.000	2.67
Cottage Grove #4	**1.100**	**0.120**	**0.066**	**0.056**	**0.090**	**0.031**	0.000	3.30
Cottage Grove #5	**1.000**	**0.022**	**0.063**	**0.026**	0.000	**0.026**	0.000	1.03
Cottage Grove #6	**0.110**	0.000	0.000	0.000	0.000	0.000	0.000	0.02
Cottage Grove #7	**0.870**	**0.018**	**0.067**	**0.020**	0.000	**0.040**	0.000	1.38
Cottage Grove #8	**0.860**	**0.050**	**0.053**	**0.021**	**0.035**	**0.020**	0.000	1.57
Cottage Grove #9	**0.660**	**0.026**	**0.032**	**0.012**	**0.015**	**0.016**	0.000	0.94
Cottage Grove #10	**0.910**	**0.021**	**0.059**	**0.030**	**0.027**	**0.061**	0.000	2.61
Cottage Grove #11	**0.530**	0.000	**0.020**	0.000	0.000	0.000	0.000	0.08
Cottage Grove #12	**0.063**	0.000	0.000	0.000	0.000	0.000	0.000	0.01
Hastings #3	**0.320**	0.000	0.000	0.000	0.000	0.000	0.000	0.05
Hastings #4	**0.250**	0.000	0.000	0.000	0.000	0.000	0.000	0.04
Hastings #5	**0.640**	0.000	**0.040**	**0.014**	0.000	**0.010**	0.000	0.45
Hastings #6	**0.190**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.03
Hastings #7	**0.180**	0.000	**0.009**	0.000	0.000	0.000	0.000	0.03
Hastings #8	**0.220**	0.000	**0.010**	0.000	0.000	**0.020**	0.000	0.60
Lake Elmo #1	**1.000**	0.000	**0.015**	**0.020**	0.000	**0.046**	0.000	1.56
Lake Elmo #2	**0.085**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.01
Lake Elmo #4	**0.077**	0.000	**0.013**	0.000	0.000	0.000	0.000	0.01
Newport #1	**0.230**	0.000	**0.017**	0.000	0.000	0.000	0.000	0.03
Newport #2	**0.390**	0.000	**0.019**	0.000	0.000	0.000	0.000	0.06
Oakdale #1	**0.320**	0.000	**0.015**	**0.029**	0.000	**0.088**	**0.066**	7.11
Oakdale #2	**0.260**	0.000	**0.013**	**0.021**	**0.009**	**0.059**	**0.055**	5.69
Oakdale #3	**0.120**	0.000	0.000	0.000	0.000	0.000	0.000	0.02
Oakdale #5	**1.200**	**0.024**	**0.037**	**0.090**	**0.043**	**0.390**	**0.630**	54.69
Oakdale #7	**1.200**	**0.028**	**0.045**	**0.091**	**0.039**	**0.310**	**0.330**	32.33
Oakdale #8	**0.760**	**0.013**	**0.023**	**0.030**	0.000	**0.140**	**0.180**	16.27
Oakdale #9	**1.300**	**0.034**	**0.059**	**0.120**	**0.059**	**0.410**	**0.490**	46.44
Oakdale #10	**0.049**	0.000	0.000	0.000	0.000	0.000	0.000	0.01
St. Paul Park #2	**1.100**	0.000	**0.056**	**0.012**	0.000	**0.020**	0.000	0.79
St. Paul Park #3	**0.920**	**0.009**	**0.045**	**0.013**	0.000	**0.040**	0.000	1.34
St. Paul Park #4	**1.100**	0.000	**0.045**	**0.013**	0.000	**0.029**	0.000	1.05
Woodbury #1	**0.180**	0.000	0.000	**0.016**	0.000	**0.030**	0.000	0.96
Woodbury #2	**0.270**	0.000	**0.013**	0.000	0.000	0.000	0.000	0.04
Woodbury #3	**0.200**	0.000	0.000	0.000	0.000	**0.014**	0.000	0.43
Woodbury #4	**0.320**	0.000	**0.012**	**0.015**	0.000	**0.014**	0.000	0.52
Woodbury #5	**0.230**	0.000	**0.011**	0.000	0.000	0.000	0.000	0.03
Woodbury #6	**0.430**	0.000	0.000	**0.019**	0.000	**0.045**	0.000	1.44
Woodbury #7	**0.410**	0.000	**0.015**	**0.015**	0.000	**0.040**	0.000	1.28
Woodbury #8	**0.280**	0.000	0.000	0.000	0.000	0.000	0.000	0.04
Woodbury #9	**0.340**	0.000	0.000	**0.014**	0.000	**0.030**	0.000	0.98
Woodbury #10	**0.300**	0.000	0.000	0.000	0.000	0.000	0.000	0.04
Woodbury #11	**0.170**	0.000	0.000	0.000	0.000	0.000	0.000	0.02
Woodbury #12	**0.250**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.04
Woodbury #13	**0.340**	**0.017**	**0.015**	**0.011**	**0.055**	**0.012**	**0.021**	3.03
Woodbury #14	**0.270**	0.000	0.000	0.000	0.000	0.000	0.000	0.04
Woodbury #15	**0.210**	0.000	0.000	0.000	0.000	0.000	0.000	0.03
Woodbury #16	**0.350**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.05
Woodbury #17	**0.200**	0.000	0.000	0.000	0.000	**0.023**	0.000	0.69
Woodbury #18	**0.150**	0.000	0.000	0.000	0.000	0.000	0.000	0.02
Woodbury #19	**0.240**	0.000	**0.010**	0.000	0.000	0.000	0.000	0.03

Currently, granular activated carbon (GAC) is the only technology approved by MDH for treating PFAS in public drinking water applications. To allow other effective treatments to be available during the evaluation of permanent facility design, the Minnesota Pollution Control Agency (MPCA), MDH, and impacted communities were interested in demonstrating ion exchange (IX) resin as a viable treatment alternative for removal of PFAS. IX treatment for PFAS has the potential to significantly reduce footprint size when compared to GAC treatment and may provide longer media life than GAC media. To demonstrate the effectiveness of IX treatment, a pilot skid was installed at one of Cottage Grove's contaminated wells to evaluate the performance and costs of two NSF drinking water approved IX resin media in direct comparison to a GAC media. The following report is a summary of the results of this pilot study. The full Pilot Test Plan can be found in Appendix A.

1.2 GOALS AND OBJECTIVES

The primary goal of this study was to evaluate IX as a potential treatment process for PFAS removal from groundwater both as a stand-alone process and in conjunction with GAC. Three objectives were developed to support this goal:

1. Demonstrate IX operability and PFAS removal performance.
2. Assess comparative cost estimates for IX, GAC, and mixed GAC-IX treatment.
3. Provide information to develop a policy for alternative treatment for PFAS removal.

1.3 PILOT DESIGN

The pilot was located at the City of Cottage Grove's Well #3 Interim Treatment Facility. The pilot received raw water directly from the City's system upstream of GAC treatment at the Interim Facility, allowing the pilot to directly evaluate the raw drinking water source rather than relying on an inactive well or other proxy source. The pilot evaluated three different media types for PFAS removal performance, a GAC media from Norit® (1240 Plus), an IX media from Purolite (Purofine® PFA 694E), and an IX media from Evoqua Water Technologies (DOWEX™ PSR-2 Plus). The medias were evaluated in five different treatment columns:

1. GAC: Norit® GAC only
2. IX1: GAC followed by Purolite Purofine® 694E
3. IX2: GAC followed by Evoqua DOWEX™ PSR2 Plus
4. IX3: Purolite Purofine® 694E
5. IX4: Evoqua DOWEX™ PSR2 Plus only

Due to City water demand, Well #3 provides an intermittent water supply. To maximize the number of bed volumes treated over the course of the pilot study, water storage tanks were included upstream of the pilot to allow the pilot to run continuously. Fundamental details of the pilot design are shown in Table 1-4, and a general pilot schematic is shown below in Figure 1-1. A full detailed description of the pilot facility, sampling procedures, and analytical methods is provided in Appendix B. Although PFAS is the primary contaminant of concern in Cottage Grove Well #3, background water chemistry can significantly impact the effectiveness of GAC and IX treatment.

Significant pretreatment was not anticipated to be necessary at the outset of the pilot study due to the relatively low levels of iron and manganese in the source water, with concentrations of 0.14 mg/L and 0.06 mg/L, respectively. Evoqua indicated that they observed fouling with the DOWEX™ PSR2 Plus media in a previous study, but the iron concentrations at that pilot were at times over 1 mg/L, significantly higher than the concentration in the Well #3 raw water. On this basis, it was anticipated that a 5-µm bag filter to remove particulates would provide sufficient pretreatment.

Full background water quality parameters can be found in the Pilot Test Plan in Appendix A.

Table 1-4: Fundamental Pilot Design Information

Parameter	GAC	IX1	IX2	IX3	IX4
Media	Norit® GAC	Purofine® IX	DOWEX™ IX	Purofine® IX	DOWEX™ IX
Influent Water Source	Raw Water	GAC Effluent	GAC Effluent	Raw Water	Raw Water
Column Diameter	8”	3”	3”	3”	3”
Goal Media Bed Depth	90”	36”	36”	36”	36”
Goal Empty Bed Contact Time	10 min	2.5 min	2.5 min	2.5 min	2.5 min
Goal Flowrate	1.94 gpm	0.45 gpm	0.45 gpm	0.45 gpm	0.45 gpm

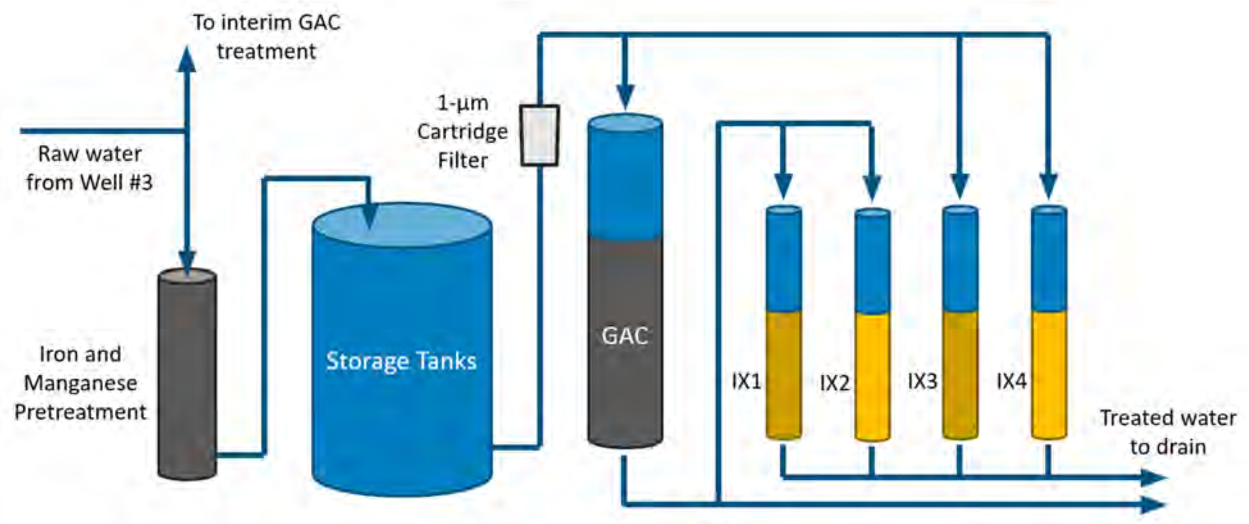

Figure 1-1: Pilot facility schematic after addition of pretreatment

2.0 TREATMENT RESULTS

2.1 PRETREATMENT NEEDS, EFFORTS AND RESULTS

Initial efforts to operate the pilot without pretreatment exhibited immediate physical fouling of the IX media by particulate, along with slow fouling of the GAC media, despite the 5-µm bag filter included between the storage tanks and media columns. It is hypothesized that the IX columns experienced worse fouling than the GAC columns due to the smaller media size and higher surface loading rate. Laboratory analysis of the fouled media indicated that the fouling particles contained significant oxidized iron, suggesting that iron precipitated after the bag filter or that the bag filter was unable to remove the particulates. Iron fouling was also observed in the full-scale interim GAC treatment facility located at the same site, but at a diminished rate. It is hypothesized that the storage tanks prior to the pilot allowed iron in the raw water to oxidize and precipitate prior to the IX and GAC media treatment, which accelerated the fouling process. Fouling was observed through an increase in differential pressure (DP) across the columns. Figure 2-1 depicts the DP values across the five pilot columns during the first 16 days of pilot operation, after which the pilot was shut down. It is preferential to keep the differential pressure below 25 psi in adsorption media columns to avoid operational disturbances, such as strain on upstream pumps or lower flow rates. This level would have been exceeded had the pilot continued to operate without pretreatment.

In order to remove iron prior to the media columns, BIRM media filters were added upstream of the storage tanks, as shown in Figure 1-1. BIRM media utilizes manganese dioxide in conjunction with a pressurized air pocket for iron oxidation, precipitation and removal. BIRM media was selected because this was the pretreatment technology used by Evoqua at a previous pilot which had experienced iron fouling. Later in the pilot study the BIRM media was replaced by Filox media, a more potent manganese dioxide media which removes both iron and manganese. The effectiveness of the implemented pretreatment at removing iron and manganese is illustrated in Figure 2-2 and Figure 2-3.

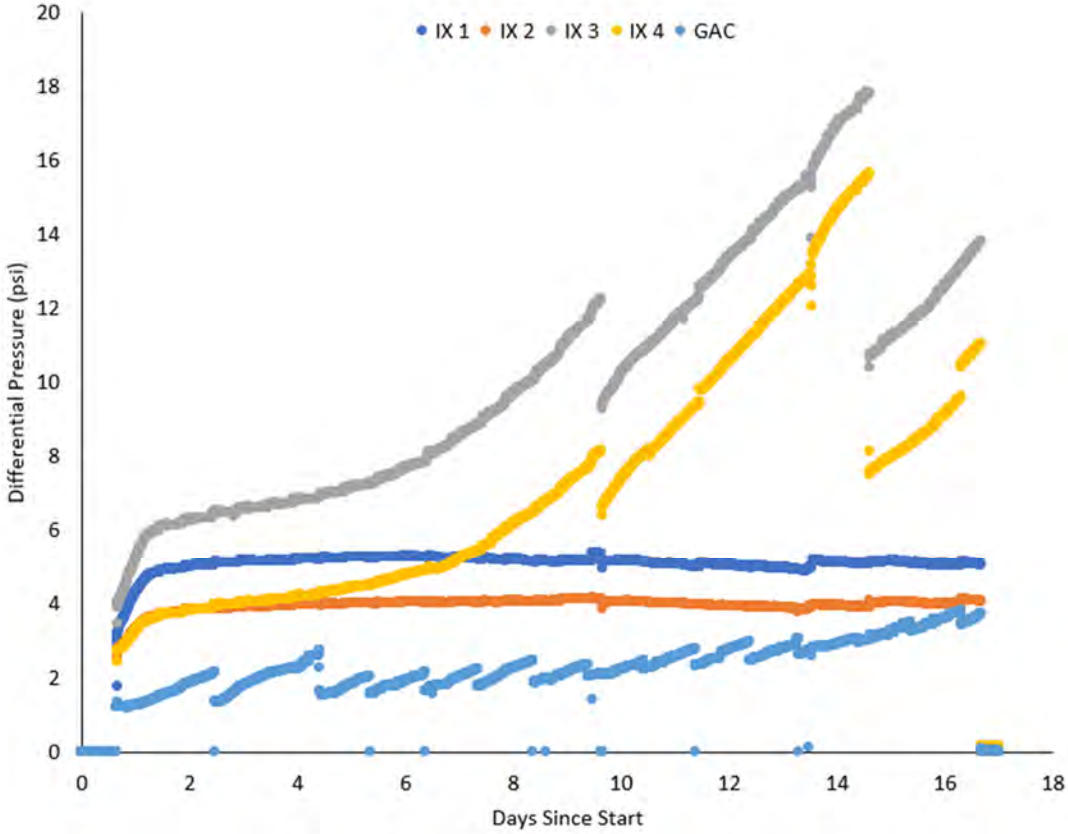

Figure 2-1: Differential Pressure from Iron Fouling Event

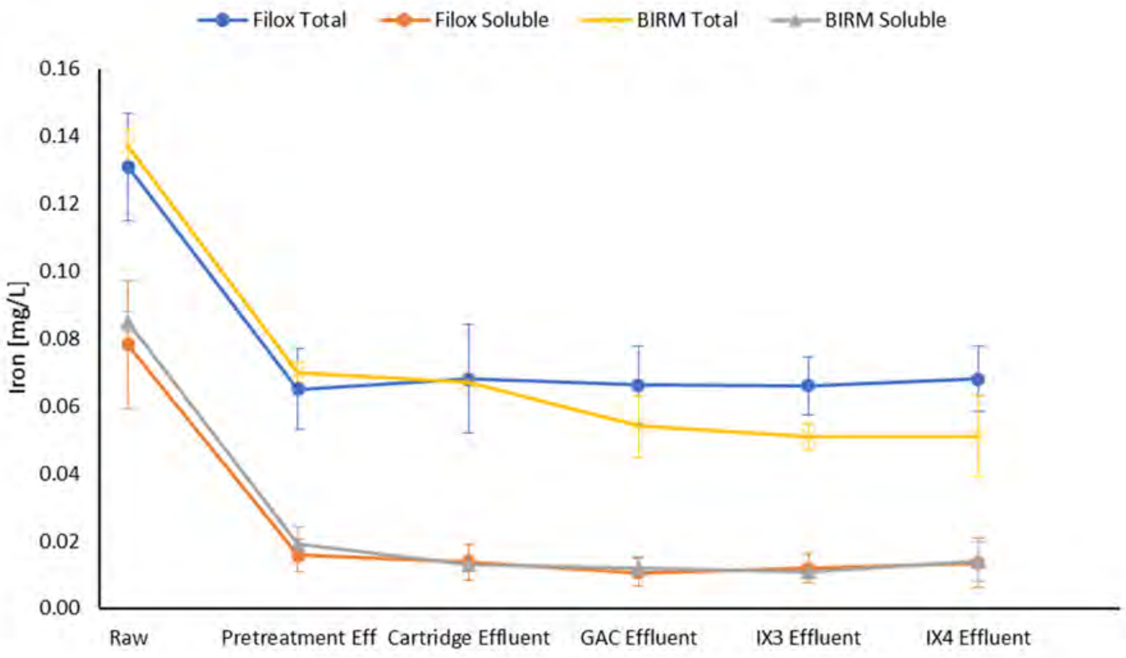

Figure 2-2: Iron Profile with Filox and BIRM Pretreatment

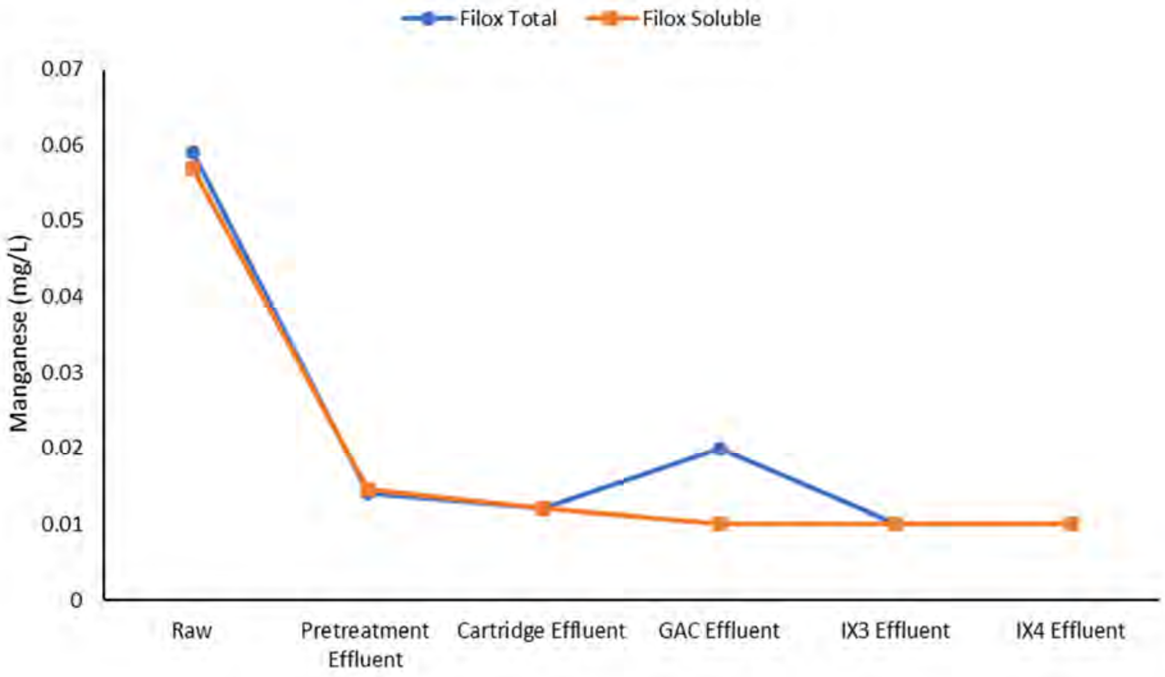

Figure 2-3: Manganese Profile for Filox

BIRM and Filox successfully reduced total iron by approximately 50% compared to raw water levels and reduced soluble iron by approximately 80% compared to raw water levels. Filox successfully reduced total and soluble manganese levels by approximately 75% compared to raw levels. BIRM and Filox required backwashing 3 times a week at minimum to maintain proper pretreatment function. Along with the addition of pretreatment, the 5-µm bag filter was replaced by a 1-µm cartridge filter. The cartridge filter was replaced as needed, typically once every two weeks.

Following these changes, the GAC and IX medias were replaced, and the pilot was restarted. The GAC and IX medias were not replaced again for the remainder of the study.

2.2 PILOT OPERATIONS

Several operational characteristics were tracked during the pilot run, including differential pressure (DP), flow rate, and empty bed contact time (EBCT). The results of DP monitoring are discussed below, while results of flow rate and empty bed contact time can be found in Appendix C.

2.2.1 Operational Challenges

Several mechanisms were in place to facilitate smooth pilot operation. Operators were onsite a minimum 3 days a week for pretreatment backwashing, during which time they also conducted inspection of the pilot facility. The pilot skid was equipped with remote monitoring capability, as well as the ability to remotely adjust flow rates to each column. Text message-based alarms were established to alert team members to pump failures and low water levels in the storage tanks. Unfortunately, these precautionary measures were unable to eliminate pilot complications. Flooding events, electrical outages, and low water levels in the storage tanks all caused shutdowns during the pilot study, but care was taken to minimize the effect of these shutdowns on the study results.

2.2.2 Differential Pressure

One of the key operational parameters of interest during the pilot study was the DP across each of the columns, because changes to DP can serve as an indicator for a number of process changes that might occur during the pilot. Rising DP can indicate flow hinderance in the form of column compaction or fouling, while falling DP can indicate a reduction in flow or column expansion.

Pressure transmitters on each column monitored and continuously logged the DP across the media bed in each of the pilot columns. As shown in Figure 2-4, DP increased significantly in three of the five treatment columns throughout the study. The two columns that did not experience appreciable DP increase were IX1 and IX2, which treated GAC effluent and as a result were shielded from fouling particles in the raw water. Figure 2-4 illustrates the DP progression during pilot operation from the restart on June 6, 2020 to October 12, 2021, after the last PFAS sample was collected. Abrupt inconsistencies in DP can be seen at varying time intervals during the pilot study, which were caused by pilot shutdowns. During shutdowns the pilot media relaxed, or in some instances was disrupted by water backflow, and although the media was reconsolidated prior to restarting the pilot changes to the DP across each column during these events were inevitable.

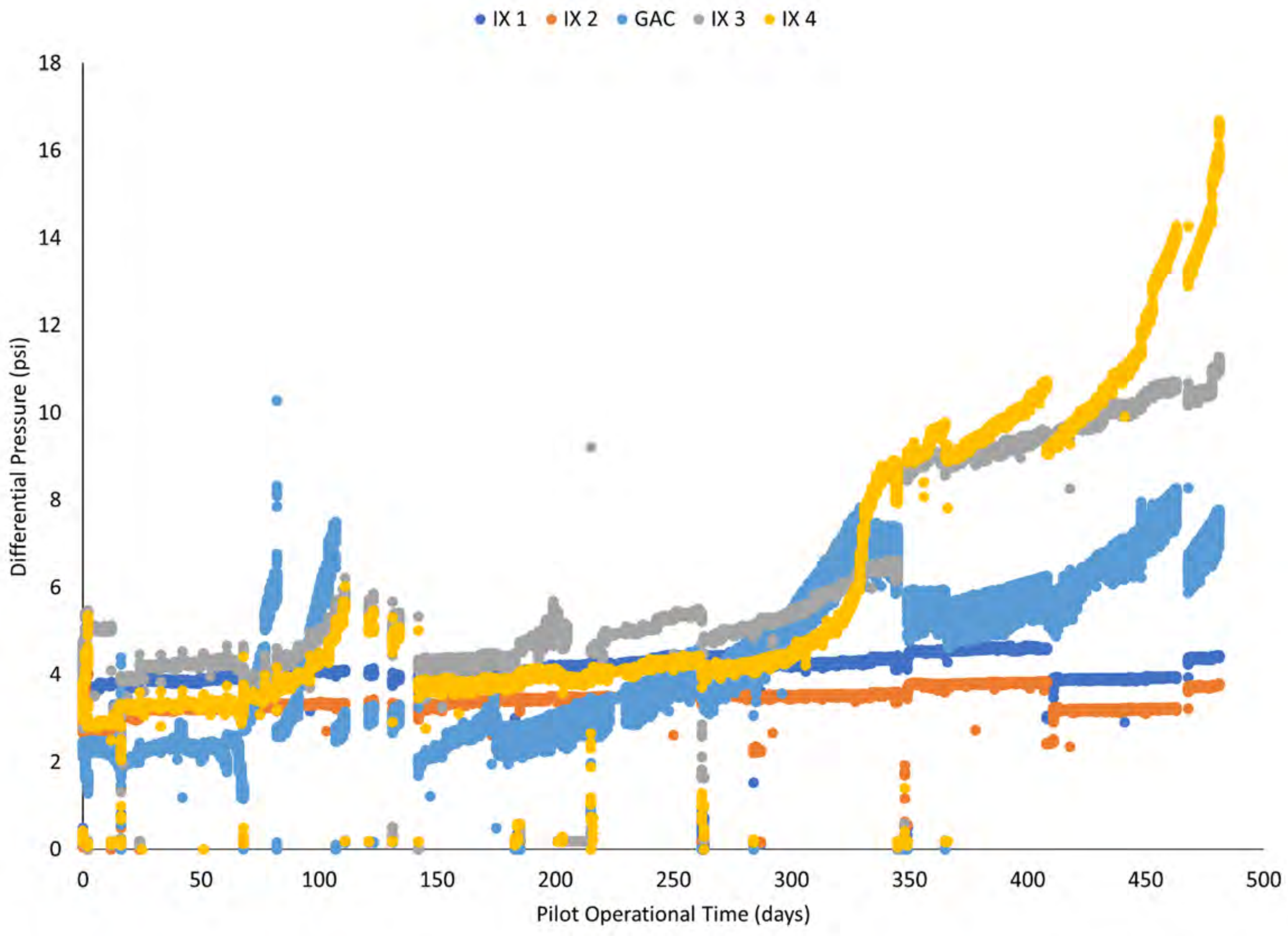

Figure 2-4: Column Differential Pressure from Pilot Start-up to End

Several potential influences could have contributed to media fouling, as outlined in Table 2-1. The columns remained at a steady state for approximately 60 days following the installation of BIRM pretreatment, then the DP across the GAC media began increasing rapidly. The GAC was backwashed twice to combat this fouling, corresponding to the large decreases in DP around days 80 and 100. The BIRM media was removed and replaced with Filox, a more durable form of manganese dioxide designed for iron and manganese treatment with a longer anticipated service life than BIRM, around day 120. At this time the media columns were gently backwashed to remove fouling particles. Laboratory analysis of particulate removed from backwashing indicated that the fouling particles contained significant oxidized manganese. In retrospect, this fouling may have been caused by the breakdown of BIRM media, which has a manganese dioxide coating.

The Filox media also began to degrade or lose potency over time, as another increase in differential pressure began around day 300, leading to Filox replacement around day 330. Although the new Filox was rinsed several times, it is believed that fine dust particles from the new Filox were inadvertently passed into the pilot system, causing further increase in DP, particularly in IX4. It is unknown how these particles bypassed the 1-μm cartridge filter or why IX3 was not similarly affected. Further increase of DP through IX3, IX4 and GAC was observed over the final 150 days of the study, potentially due to degradation of the second round of Filox, though the media was not replaced as the study was approaching close-out.

Another potential reason for increased DP over the final 150 days of the study was biological growth within the columns. Filamentous green algae-like growth was observed on column walls and on the top of the GAC media bed and a pale tan biofilm was observed on column walls, though it is unknown if growth of either penetrated the bed itself. While the growth was likely exacerbated by sunlight penetrating the clear pilot columns, biological fouling has been reported by full-scale treatment systems as well. To prevent the growth of biofilm, the entire GAC column and the head space of the IX3 and IX4 columns were wrapped with aluminum foil after 400 days of operation, which appeared to reduce algae growth but did not appreciably reduce DP. Visible space was left at the top and bottom of the columns to allow for column operation inspections.

Table 2-1: Summary of potential causes of media fouling

Fouling Mechanism	Associated Observations
Metal precipitation	Oxidizing conditions of water storage tanks; initial fouling had distinct rust color; lab testing confirmed significant presence of iron and manganese in particulate fouling
Pretreatment media physical breakdown	Media was intended for “home style” system rather than industrial drinking water treatment process; repeatedly backwashed under significant pressure; black dust observed on cartridge filter
Pretreatment media chemical breakdown by chlorine	Unlikely; media was backwashed with unchlorinated water
Biological growth	Green filamentous and biofilm growth observed in columns; clear columns let in sunlight
Dust introduced by new pretreatment media	Jump in DP of IX4 after Filox media change-out

2.3 WATER QUALITY

Water quality samples were tested on a regular basis to monitor the water chemistry throughout the system. For brevity, all water quality results are shown in Appendix D.

2.4 PFAS TREATMENT RESULTS

As raw water flows through media columns PFAS adsorb or otherwise stick to the treatment media. Initially, this results in no or low PFAS in the column effluent. However, treatment media have finite capacity to take up PFAS, and over time PFAS begin to break through the media columns, forming what is known as a breakthrough curve. If the system is allowed to run for a long enough time, the effluent PFAS concentration will be the same as the influent PFAS concentration. One of the primary purposes of this study was to evaluate how long the system can run before the media needs to be changed out, known as the media life.

2.4.1 Using Ports for PFAS Treatment Results

Breakthrough curves were generated for each pilot column for each of the different PFAS analyzed. Breakthrough curves are dependent upon the number of bed volumes treated by the system, and as such it was beneficial to experimentally test as high a number of bed volumes as possible. Given the time constraints placed on the pilot study, sample ports were installed at discrete intervals along the columns. Three intermediate ports were installed in each IX column, spaced every 9 inches, while two intermediate ports were installed in the GAC column, spaced every 30 inches. These ports provided insight into treatment at various points throughout the media column. Samples collected at the sample ports had only been treated by a fraction of the full media column, and because the volume of media was lower the equivalent bed volumes for samples taken from the ports was much higher, as described in the equation below. For example, at the end of the pilot the full GAC column had treated just under 57,000 bed volumes of water, but at the first GAC port this equated to treatment of over 163,000 bed volumes of water.

$$\text{Bed Volumes} = \frac{\text{Volume of Water Treated}}{\text{Volume of Media Bed}}$$

In order to verify that the ports provided an accurate representation of the full-column treatment process, HI breakthrough data from column ports was overlayed with data from column effluent for GAC, IX3 and IX4 columns, as shown in Figure 2-5 through Figure 2-7. As can be seen from these figures, the port data and effluent data track quite closely for all the columns, although the agreement was not quite as close for the GAC column as the two IX columns. This finding is significant because it shows that PFAS breakthrough is consistent across treated bed volumes for the tested EBCTs, allowing the results from the ports to be later scaled using the full-column EBCT when predicting full-scale run time.

Additionally, in all three cases full column treatment outperformed treatment at the ports. As such, any design information obtained using port data would appear to be conservative when compared to full column effluent data. This information gave the team confidence to use port data to determine full-scale run time design parameters for each of the columns.

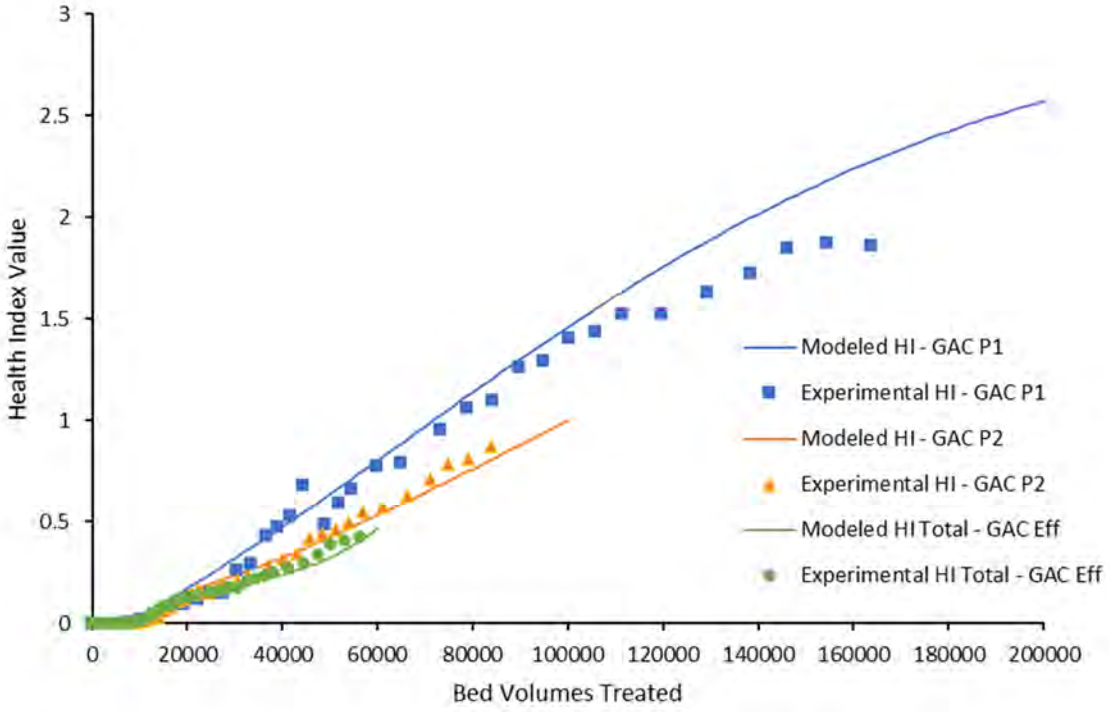

Figure 2-5: Overlap of GAC Port HI Breakthrough

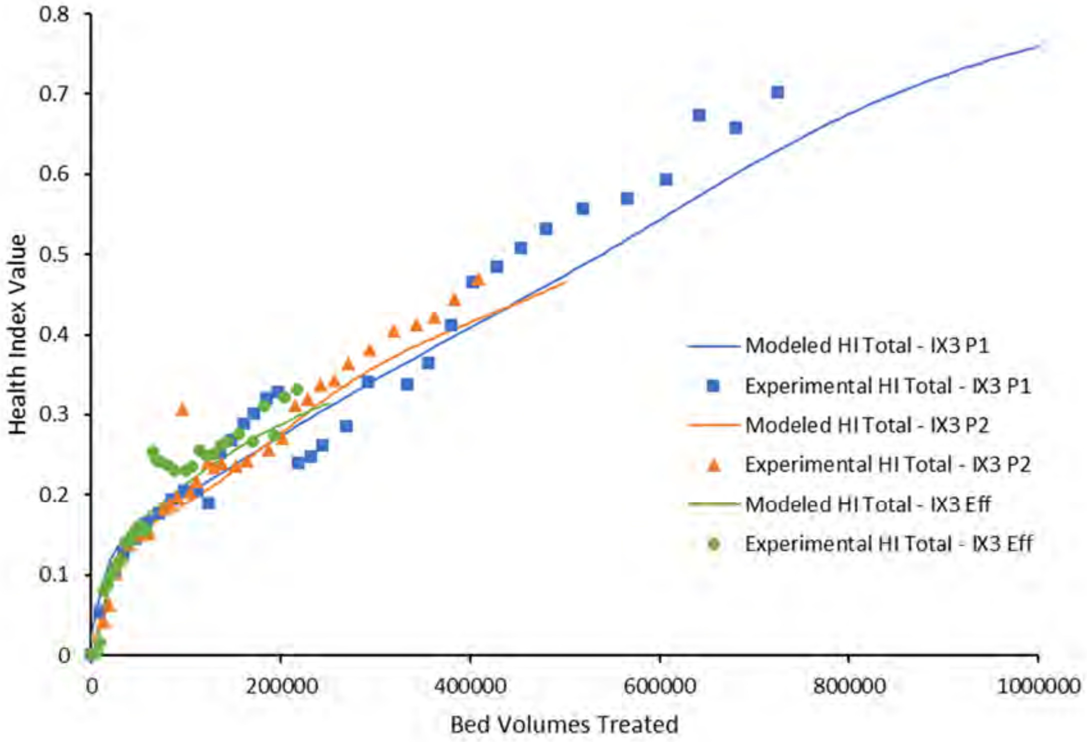

Figure 2-6: Overlap of IX3 Port HI Breakthrough

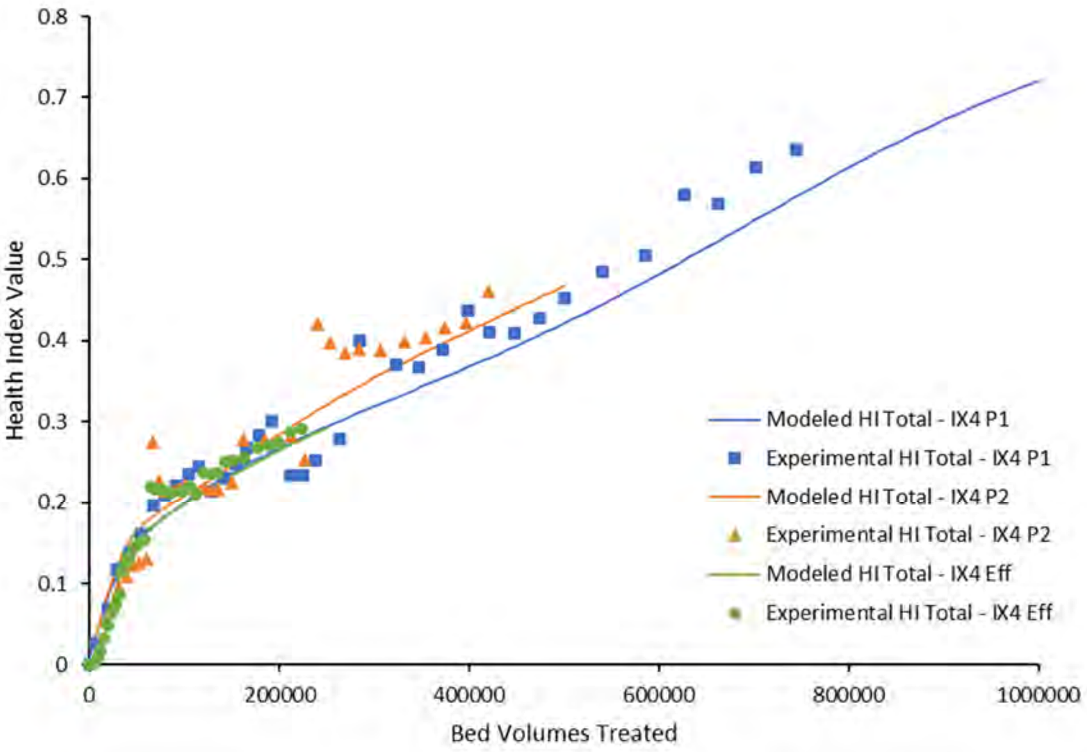

Figure 2-7: Overlap of IX4 Port HI Breakthrough

2.4.2 PFAS Breakthrough Results

Breakthrough of individual PFAS compounds through the second port of GAC and the first port of IX3 and IX4 columns is shown below in Figure 2-8 through Figure 2-10. Data from the first IX sample port was used for this analysis because this was the only port with sufficient data generation, with an HI value near 0.5 by the end of the study. The second port was chosen for the GAC column because samples collected from this port reached an HI value >0.5 by the end of the study and HI breakthrough from this port more closely aligned with the effluent HI breakthrough than the HI breakthrough from the first port.

Breakthrough curves shown in Figure 2-8 through Figure 2-10 also include best-fit models to describe the breakthrough curves. Six potential models were evaluated for each compound breakthrough curve. Three of these were common empirical models: the Dose-Response model, the Yoon-Nelson model, and the Clark model. However, these models were not able to take into account cases of PFAS desorption, which occurs due to differences in adsorption affinity between compounds and leads to the effluent concentration of a compound exceeding the influent concentration. This phenomenon is well-documented for PFAS systems with multiple compounds and was observed in several compounds during this study. In cases such as this, a modified version of these three models was used to fit the breakthrough curve. In each case the best-fit model was determined using the Adjusted R^2 metric. These breakthrough curves are equivalent to PFAS breakthrough out of the lead vessel in a lead-lag configuration. To determine the equivalent continuous full-scale run time, the number of bed volumes was multiplied by the full-scale EBCT and converted to days. This can be done because, as shown in Figure 2-5 through Figure 2-7, breakthrough was dependent on bed volumes treated independent upon EBCT for the EBCTs tested in this study.

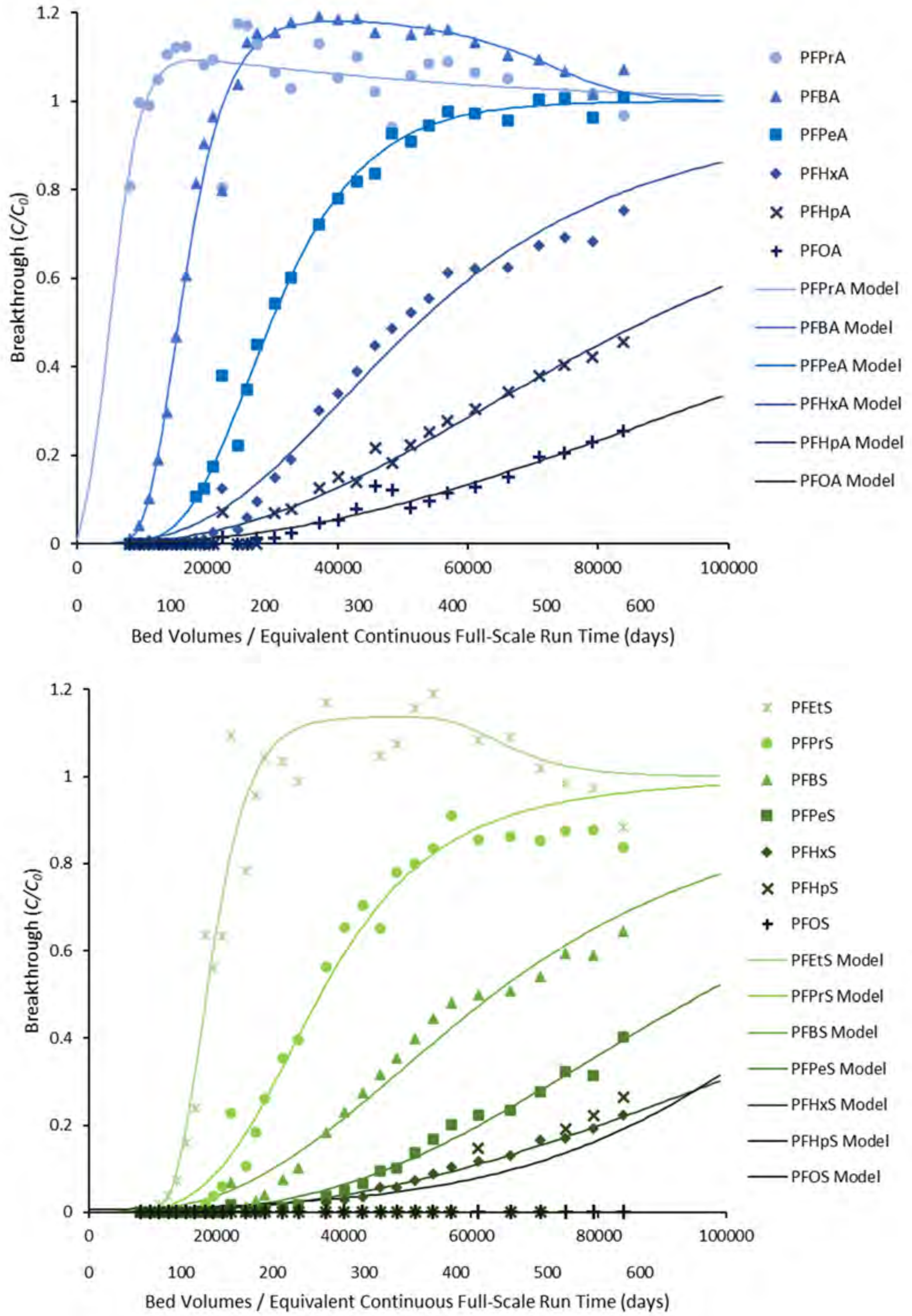

Figure 2-8: PFAS Breakthrough at GAC Port 2

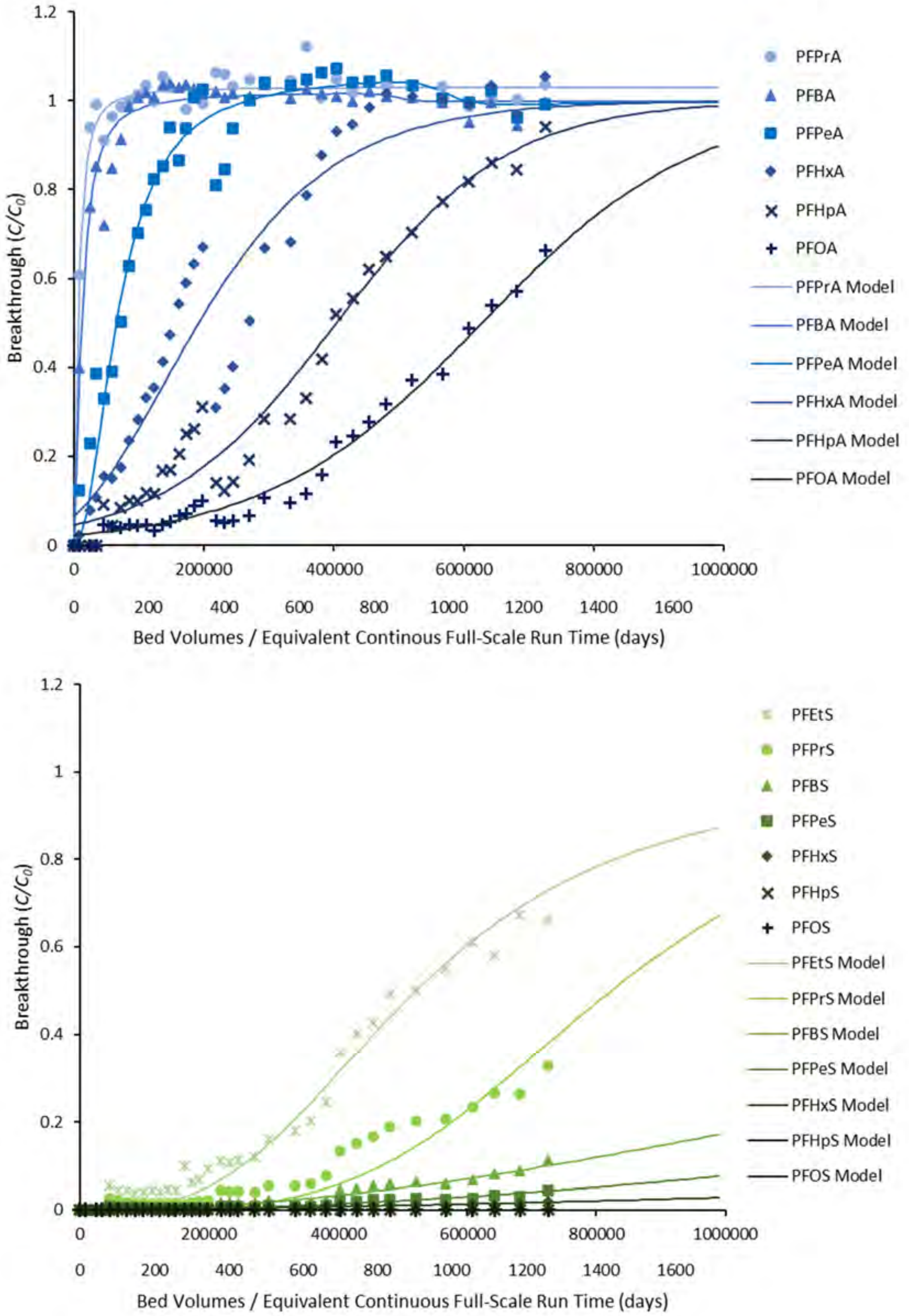

Figure 2-9: PFAS Breakthrough at IX3 Port 1

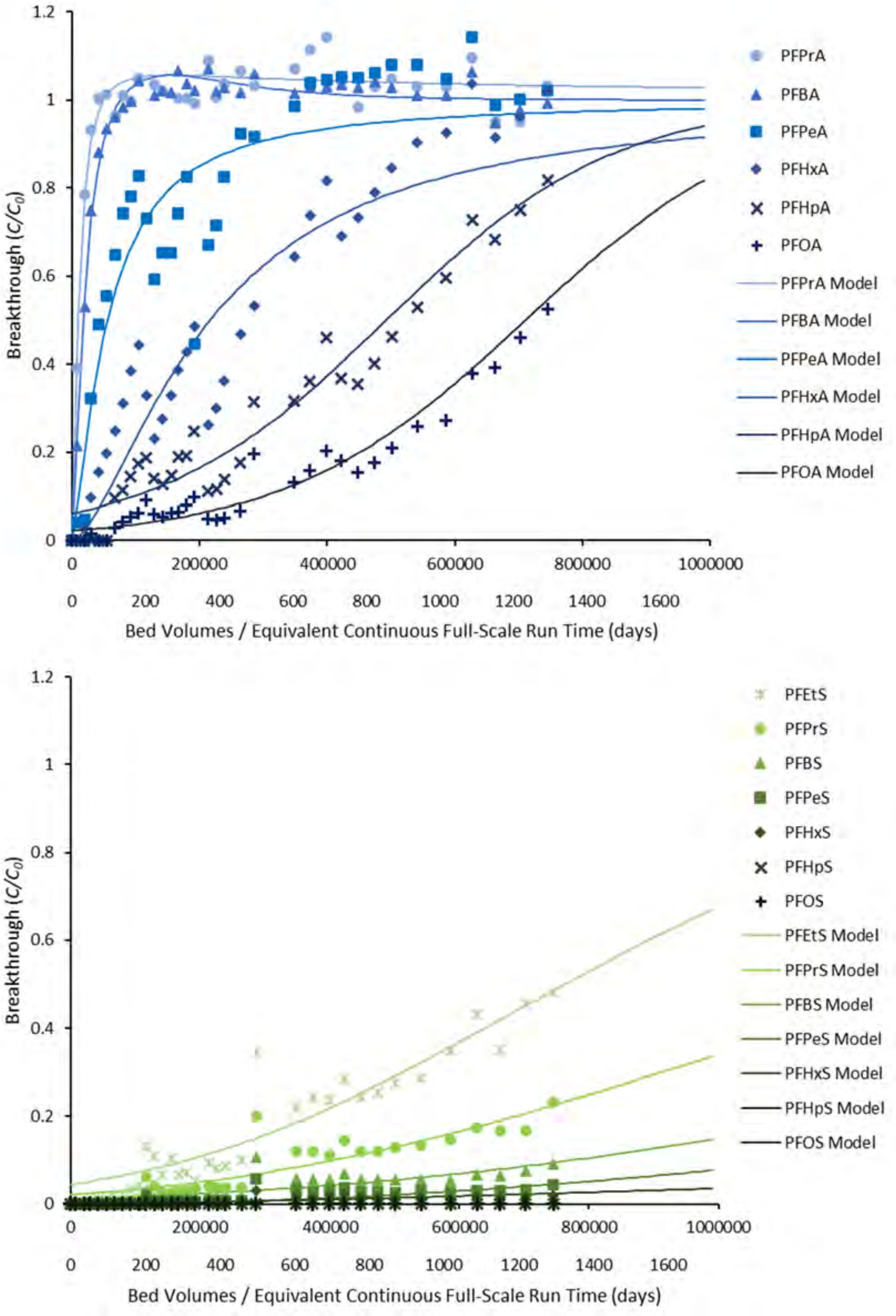

Figure 2-10: PFAS Breakthrough at IX4 Port 1

The largest take-away from these breakthrough curves is that the Purolite (used in IX3) and Evoqua (used in IX4) IX medias appears to delay breakthrough of PFSAs longer than GAC media. Breakthrough of long-chain PFCAs, such as PFOA, was also delayed longer by IX than GAC. In contrast, breakthrough of short-chain PFCAs, such as PFBA, was better delayed by GAC. The equivalent continuous full-scale run times until 10% compound breakthrough are shown in Table 2-2, along with which media type better delayed 10% breakthrough. Looking specifically at those compounds which contribute to the HI, it was found that compounds which contribute 14% of HI in the raw water were better removed by GAC, while compounds which contribute 84% of HI in the raw water were better removed by IX. Further investigation of these trends is provided in Appendix E.

Table 2-2: Approximate continuous full-scale run times until 10% breakthrough

Compound	**GAC Run Time**	**Purolite IX Run Time**	**Evoqua IX Run Time**	**Better Media Type**	**% HI in Raw Water**
	days	days	days		
			PFCAs		
PFPrA	21[1]	<9[1]	9[1]	GAC	-
PFBA	58[1]	13[1]	22[1]	GAC	5%
PFPeA	125	39[1]	52[1]	GAC	-
PFHxA	167	78[1]	87	GAC	9%
PFHpA	250	191	174	GAC	-
PFOA	361	451	521	IX	16%
			PFSAs		
PFEtS	97	434	313	IX	-
PFPrS	146	816	712	IX	-
PFBS	201	1,267	>1,300	IX	3%
PFPeS	326	>1,300	>1,300	IX	-
PFHxS	410	>1,300	>1,300	IX	64%
PFHpS	465	>1,300	>1,300	IX	-
PFOS	>600	>1,300	>1,300	Likely IX	3%

[1] Data taken from effluent port rather than intermediate port due to speed of breakthrough

2.4.3 Health Index Breakthrough

The HI value for each experimental sample was calculated using the formula provided in Section 1.1. Additionally, HI breakthrough over time was modeled by combining the best-fit models for individual PFAS. The modeled and experimental HI values at IX3 port 1, IX4 port 1, and GAC port 2 are shown below in Figure 2-11 through Figure 2-13. As can be seen from these figures, the modeled HI values trend well with the experimental HI values. The modeled HI plots are also broken down by individual PFAS compound. As can be seen in the figures, the majority of initial HI contribution is due to rapid PFBA breakthrough, while later HI breakthrough is dominated by PFHxA and PFHxS for the GAC column and PFHxA and PFOA for the IX columns.

An HI value of greater than 1.0 indicates that the water supply does not pass the requirement for safe drinking water as determined by MDH, but the conceptual drinking water supply plan has identified that a health index goal of 0.5 may be appropriate as a basis of design. For this reason, it has been assumed that lead value change-outs will be completed once a HI value of 0.5 is reached.

The final sample point corresponded to roughly 600 continuous days treated by the GAC vessel, compared to roughly 1,300 continuous days for IX However, the GAC column's HI reached 0.8, while the IX columns' HI only just reached 0.5. Clearly the run time prior to a 0.5 HI breakthrough of the IX resins were significantly greater compared to the runtime of the GAC media. These pilot results indicate that the GAC lead vessel effluent would reach a health index value of 0.5 and need to be replaced every 58,000 bed volumes, or approximately every 1.1 years of continuous run time. The results indicate that the Purolite IX resin (used in column IX3) effluent would reach a health index value of 0.5 and would need to be replaced every 540,000 bed volumes, equivalent to 2.6 years of continuous run time, while the Evoqua IX resin (used in column IX4) effluent would reach a health index value of 0.5 after 630,000 bed volumes, equivalent to 3.0 years of continuous run time.

It should again be noted that the yearly run times assume continuous operation of the treatment system. The actual media life would be extended if the system was only operated for a fraction of each day, though this will be specific to each facility.

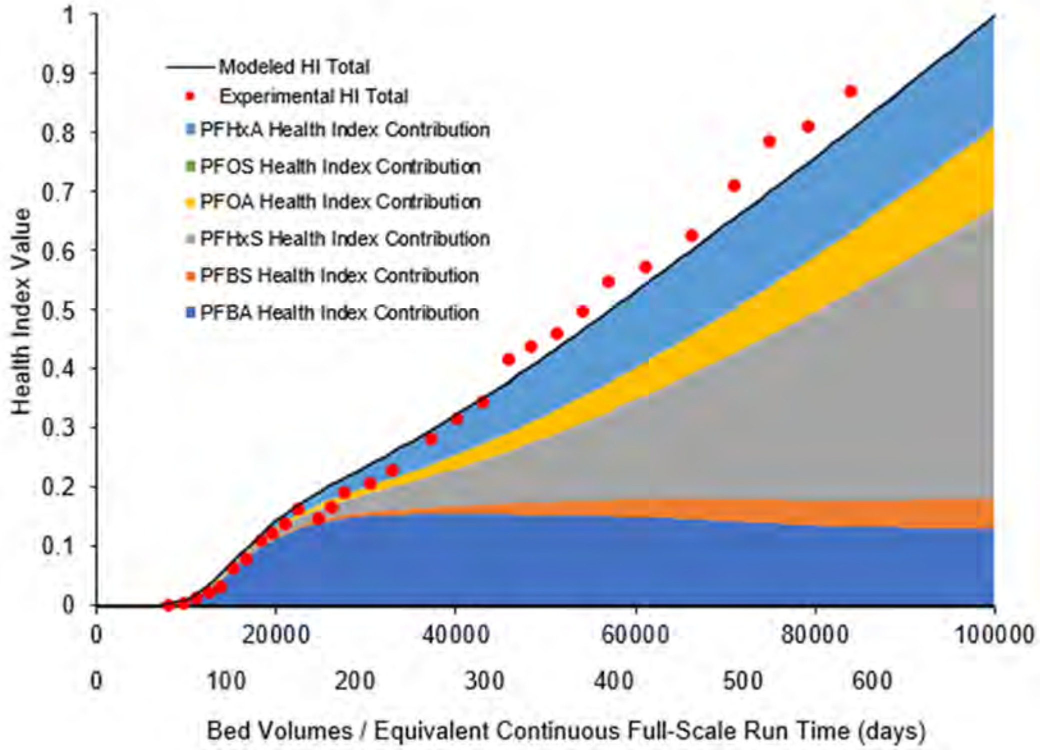

Figure 2-11: Health Index Breakthrough at GAC Port 2

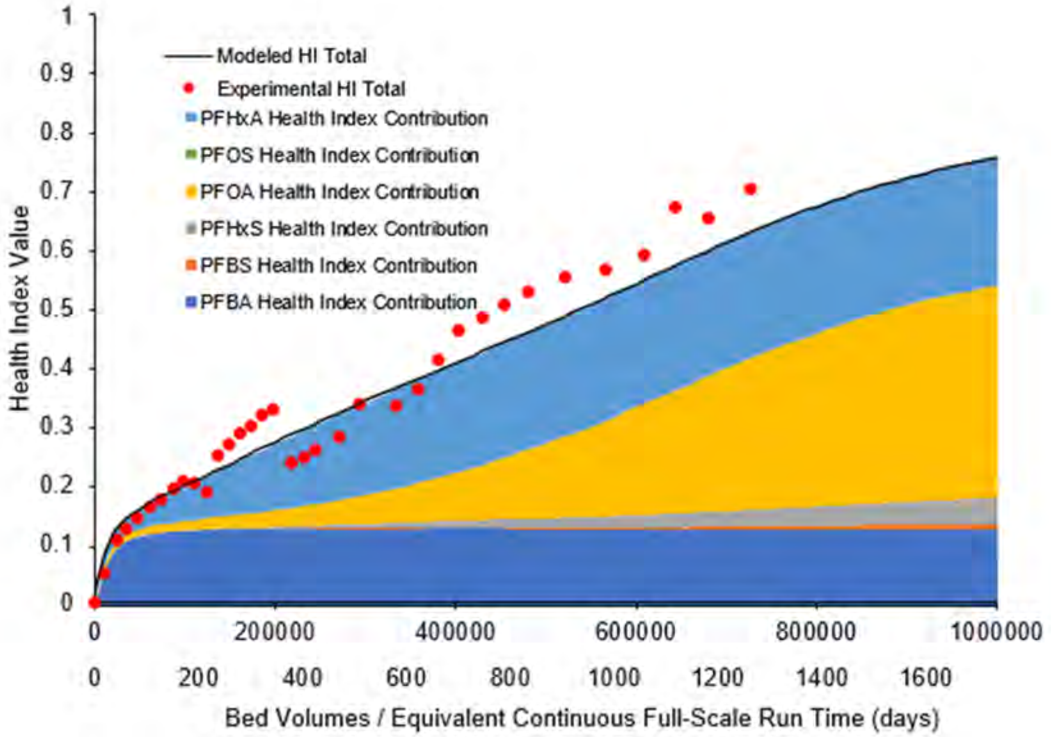

Figure 2-12: Health Index Breakthrough at IX3 Port 1

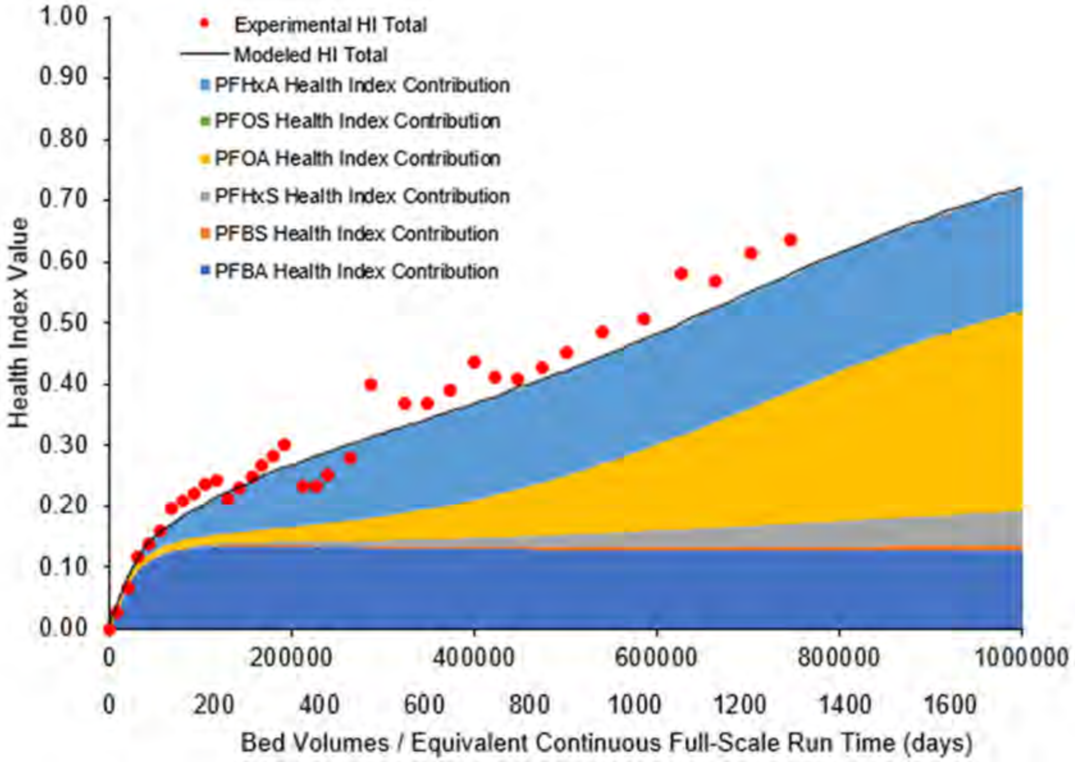

Figure 2-13: Health Index Breakthrough at IX4 Port 1

2.4.4 GAC-IX Treatment Results

Breakthrough of individual PFAS compounds was observed through the first port of IX1 and IX2 columns. However, limited breakthrough was seen from these columns because the influent water had already been treated by the GAC column.

Breakthrough of individual PFAS compounds through the second port of GAC and the first port of IX1 and IX2 columns is shown below in Figure 2-14 and Figure 2-15. As with the previous treatment result analysis, breakthrough curves shown in Figure 2-14 and Figure 2-15 also include best-fit models to describe the breakthrough curves. However, the bed volumes treated by IX1 and IX2 cannot be scaled to equivalent days run time in the same way in which the bed volumes treated by IX3 and IX4 were scaled, because doing so would effectively scale the treatment of the lead GAC column in addition to the lag IX column. Because of this, the results from the GAC-IX dual treatment portion of the pilot can be used to qualitatively show that this option has thus far performed well as a treatment option for PFAS, but based on the current duration of pilot run-time no quantitative result has been generated as to specific media life for the lag IX media.

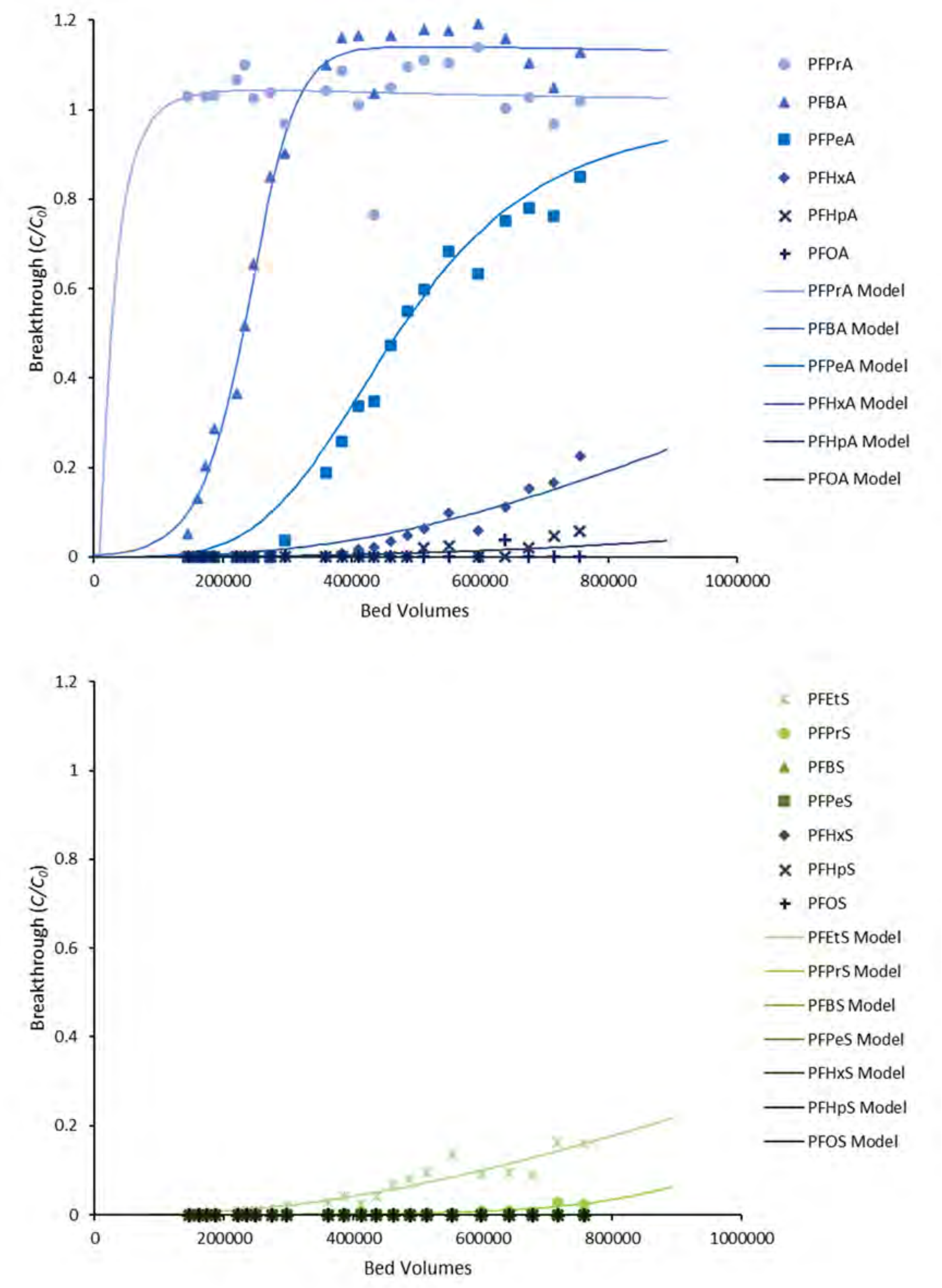

Figure 2-14: PFAS Breakthrough at IX1 Port 1

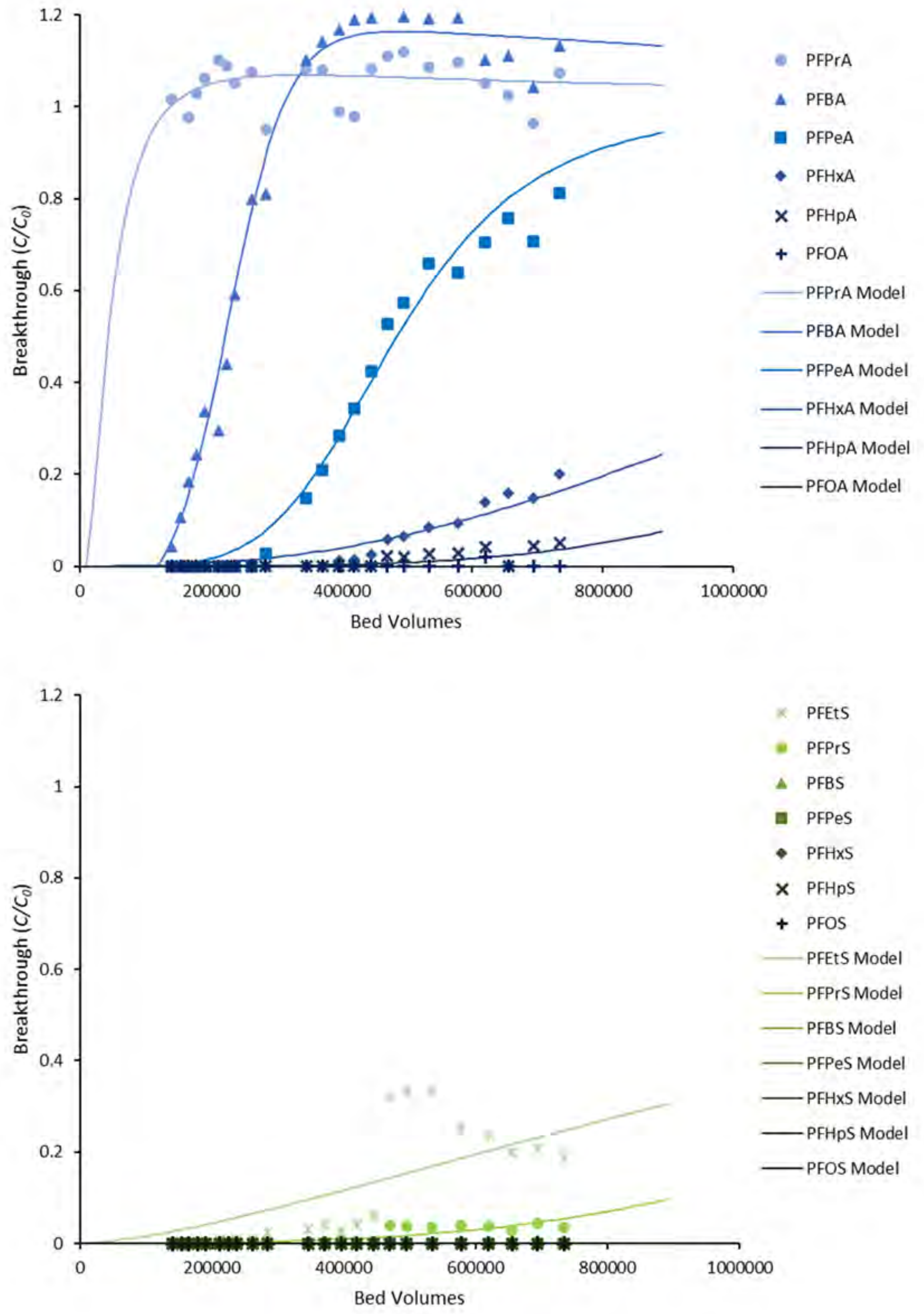

Figure 2-15: PFAS Breakthrough at IX2 Port 1

2.4.5 Final HI Breakthrough

While the above discussion focused on effluent from the ports of each treatment column, it is important to recognize that the HI breakthrough in the effluent of all columns remained below 0.5 through the end of the study, in keeping with the extended run-times predicted by the port data. Table 2-3 shows the bed volumes treated by each full column over the course of the study as well as the resulting concentrations of the HI constituents, compared to the concentrations in the raw influent.

Table 2-3: Table of HI breakthrough in column effluent by end of study

Column	**Effluent Bed Volumes**	**PFAS Monitored in Minnesota**						
		PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS	**HI**
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	**-**
Well #3 Raw Water	-	0.896	0.127	0.047	0.074	0.014	0.001	**2.78**
GAC	56,429	1.012	0.052	0.023	0.005	0.001	0.000	**0.42**
IX3: Purolite IX	217,958	0.922	0.002	0.035	0.000	0.001	0.000	**0.33**
IX4: Evoqua IX	224,970	0.913	0.001	0.029	0.000	0.001	0.000	**0.29**
IX1: GAC - Purolite	227,714	1.035	0.000	0.005	0.000	0.000	0.000	**0.17**
IX2: GAC - Evoqua	225,629	1.038	0.000	0.003	0.000	0.000	0.000	**0.16**

3.0 COST COMPARISON

A cost comparison was completed for GAC, IX, and GAC-IX treatment facilities of various flow rates to determine a cost to flow rate curve for each type of facility. Cost estimates were developed using a work-breakdown structure approach to develop cost estimates for GAC and IX facilities of 1.0 MGD, 4.5 MGD, and 10 MGD flow rates. Cost estimates included both capital and operational costs to determine the net present value of each treatment. All costs were determined assuming construction of a greenfield facility in 2021 dollars.

3.1 CAPITAL COST

Capital costs were developed for GAC and IX facilities of 1.0 MGD, 4.5 MGD, and 10 MGD flow rates. A variety of assumptions were made during the cost estimating process, which generally were directed toward the construction of a permanent facility with provisions for pretreatment, intermediate and final clear wells, and backwash reclaim. In order to better understand capital cost breakdown for GAC and IX facilities the capital costs were broken down into three categories: building capital costs, total process capital costs, and PFAS treatment only process costs. Building capital costs and total process capital costs sum to the full capital costs for each option, while the PFAS treatment only process costs are a subset of total process costs that only cover the bare minimum of a simple PFAS treatment facility. Table 3-1 identifies the capital cost components that were included in each cost category, while Table 3-2 summarizes the capital cost estimating results. The capital cost to flow rate curve for each type of facility is shown in Figure 3-1. Capital costs were not given a contingency as part of this evaluation, and due to the significant differences in site layout, water sources, and building material preferences between facilities these cost estimates should broadly be viewed as Class 4 of the AACE International Cost Classifications, with an expected range of accuracy of -30% to +50%.

Table 3-1: Capital costs items included in each treatment category

	Building Capital Costs	Total Process Capital Costs	PFAS Only Process Capital Costs
General (insurance, bond, mobilization, etc)	X		
Building excavation	X		
Drive, parking, erosion control, site preparation	X		
Connections to existing water main		X	
Building sanitary plumbing	X		
Concrete for building foundation, base slab	X		
Concrete for clearwells and gravity filters		X	
Tip-up panels for building walls	X		
Precast ceiling	X		
Concrete masonry for office, bathroom, electrical	X		
Concrete masonry for chemical rooms		X	
Building roof system, insulation, weather proofing	X		
Doors and windows	X		
Paint	X		
Pretreatment filter mechanical components		X	
Pressure filters for GAC/IX		X	X
Pumps		X	
Pump hoist	X		
Chemical feed systems – chlorine and fluoride		X	X
Chemical feed systems – pretreatment filtration		X	
Process pipe necessary for PFAS treatment system		X	X
Process pipe necessary for pretreatment and clearwells		X	
HVAC	X		
Electrical	X		

Table 3-2: Estimated capital costs for each treatment category

		Building Capital Cost	Total Process Capital Cost	PFAS Only Process Capital Cost	Total Facility Capital Cost with Pretreatment	Total Facility Capital Cost without Pretreatment	Percent of Total Cost for Pre-treatment
1.0 MGD	GAC	$2.54M	$2.83M	$1.51M	$5.37M	$4.04M	25%
	IX	$2.48M	$2.53M	$1.17M	$5.01M	$3.65M	27%
	GAC-IX	$2.54M	$2.90M	$1.57M	$5.43M	$4.11M	24%
4.5 MGD	GAC	$5.5M	$9.2M	$5.0M	$14.7M	$10.5M	28%
	IX	$5.4M	$8.7M	$4.6M	$14.1M	$10.0M	29%
	GAC-IX	$5.5M	$9.5M	$5.4M	$15.0M	$10.8M	28%
10 MGD	GAC	$8.9M	$17.0M	$9.6M	$25.9M	$18.5M	28%
	IX	$8.4M	$16.2M	$9.0M	$24.6M	$17.3M	30%
	GAC-IX	$8.9M	$17.6M	$10.3M	$26.5M	$19.2M	28%

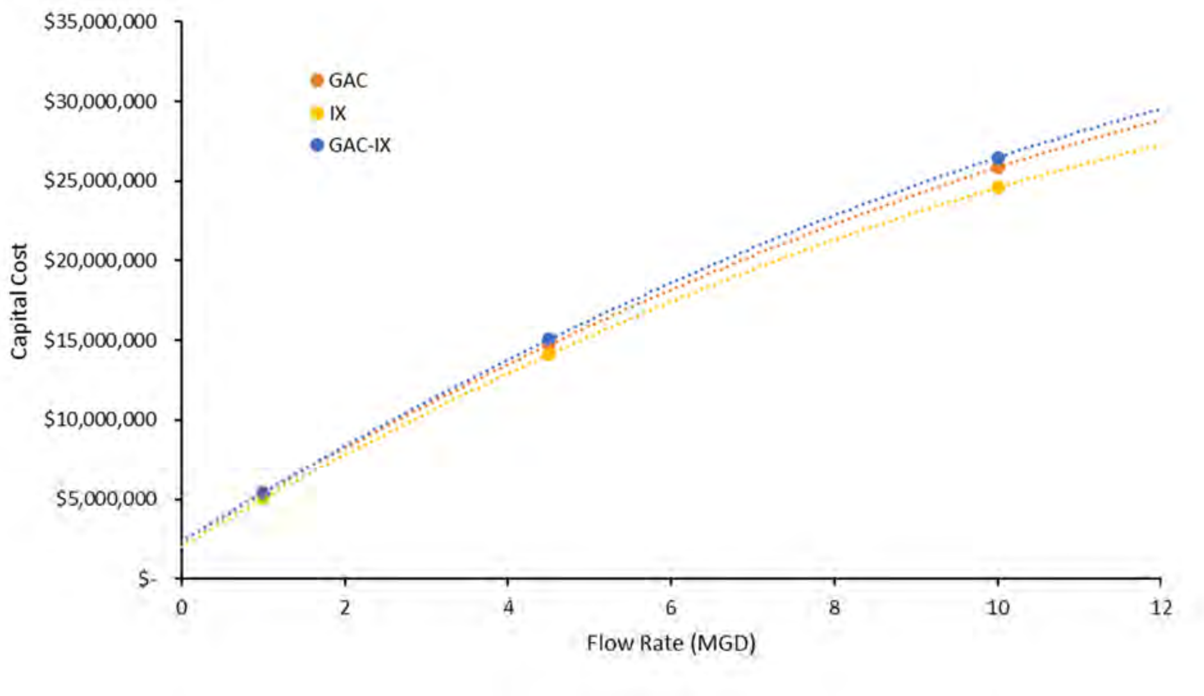

Figure 3-1: Capital cost verse flow rate curve

3.2 OPERATIONAL COST

Annual operational costs were determined for each treatment option by evaluating media, chemical, and electrical costs on per year basis. The full table of operational costs is shown in Table 3-3 and illustrated as cost to flow rate in Figure 3-2.

Media costs were determined based on media unit prices for new media and disposal of old media as provided by the manufacturers. Media life calculations for GAC-GAC and IX-IX lead-lag systems assumed that the lead vessel would be changed out once the lead vessel effluent health index value reached 0.5, at which point the lag vessel would become the new lead vessel.

Since most drinking water facilities do not operate continuously, the expected media life must be adjusted to account for daily rune time. For this analysis, a daily run time of 15 hours per day was used based on the average run time of Well #3. Based on a daily run time of 15 hours per day, the pilot results indicated that the media life for the lead GAC vessel would be approximately 1.8 years, while the media life for the lead Purolite and Evoqua IX vessels would be approximately every 4.1 years and every 4.8 years, respectively.

Operation of the GAC-IX system assumed that the GAC vessel would be allowed until the effluent reached a health index value of 1.0, or approximately every 3.0 years based on a daily run time of 15 hours per day, at which point it would be replaced. It was assumed that the IX vessel, which would remain the lag vessel throughout GAC change-outs, would be changed out every 4.1 years and every 4.8 years for Purolite and Evoqua IX vessels, respectively.

Chemical costs for chlorine, fluoride, and pretreatment were determined based on a typical dose at each flow rate and unit costs provided by vendors. Pumping electrical costs were calculated based on anticipated pumping time, pump energy use, and a cost of 0.09$/kWh. Electrical costs included pumping along intermediate stages of the water treatment facility as well as high serves pumps serving the distribution system, but do not include the submersible pumps drawing the well water, due to significant variation between individual installations. Submersible well pump capital and operational costs will nevertheless be an important aspect of overall treatment for utilities to consider.

Cost estimations and media life provided in this study assume that the system is running 15 hrs/day.

Table 3-3: Estimated annual operational costs

	O&M Breakdown	**GAC**	**Purolite Resin**	**Dow/Evoqua Resin**	**GAC and Putolite Resin**	**GAC and Evoqua/Dow Resin**
1.0 MGD	Pumping	$22,000	$22,000	$22,000	$22,000	$22,000
	Chemical	$10,000	$10,000	$10,000	$10,000	$10,000
	Media	$98,000	$19,000	$25,000	$78,000	$84,000
	Total	**$131,000**	**$51,000**	**$57,000**	**$110,000**	**$117,000**
4.5 MGD	Pumping	$92,000	$92,000	$92,000	$92,000	$92,000
	Chemical	$45,000	$45,000	$45,000	$45,000	$45,000
	Media	$425,000	$108,000	$142,000	$344,000	$374,000
	Total	**$562,000**	**$245,000**	**$278,000**	**$480,000**	**$511,000**
10 MGD	Pumping	$193,000	$193,000	$193,000	$193,000	$193,000
	Chemical	$100,000	$100,000	$100,000	$100,000	$100,000
	Media	$850,000	$217,000	$283,000	$688,000	$748,000
	Total	**$1,143,000**	**$509,000**	**$576,000**	**$981,000**	**$1,041,000**

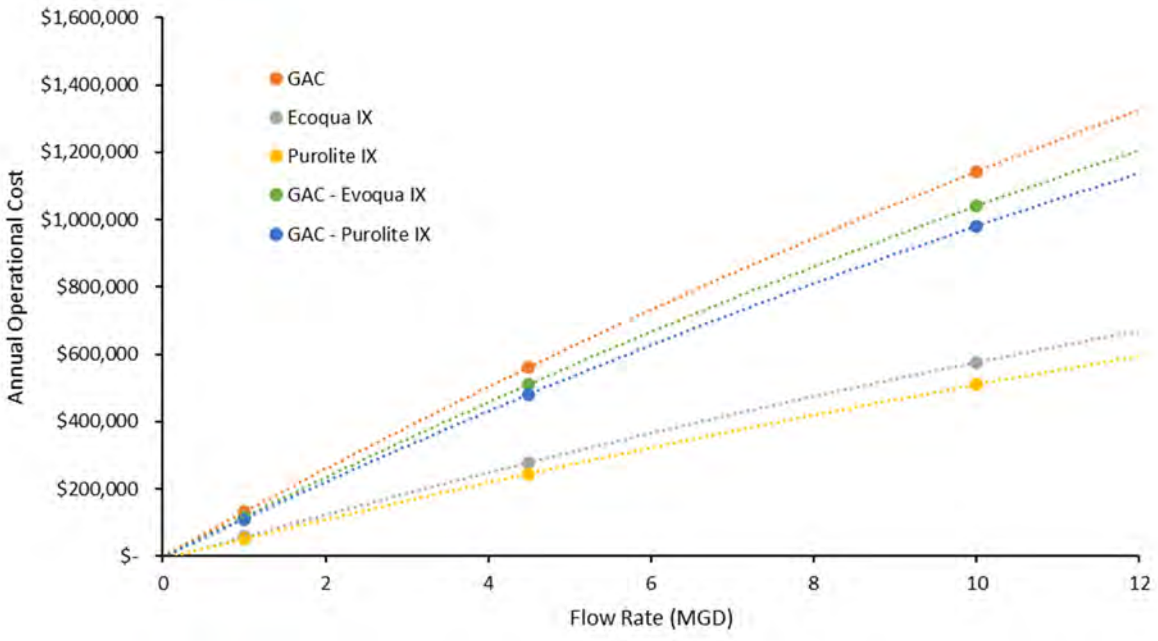

Figure 3-2: Annual operational cost verse flow rate curve

3.3 NET PRESENT VALUE

The net present value (NPV) for each option was calculated over a 20-year life cycle, which allowed for a more rigorous assessment of the costs associated with each option. The NPV analysis assumed a 3% discount rate. The results of the NPV analysis are shown in Table 3-4 and Figure 3-3 through Figure 3-5.

Table 3-4: Estimated 20-year net present values

	GAC	Purolite Resin	Dow/Evoqua Resin	GAC and Purolite Resin	GAC and Evoqua/Dow Resin
1.0 MGD	$7.3M	$5.8M	$5.9M	$7.1M	$7.2M
4.5 MGD	$23.1M	$17.8M	$18.3M	$22.2M	$22.7M
10 MGD	$42.9M	$32.2M	$33.2M	$41.1M	$42.0M

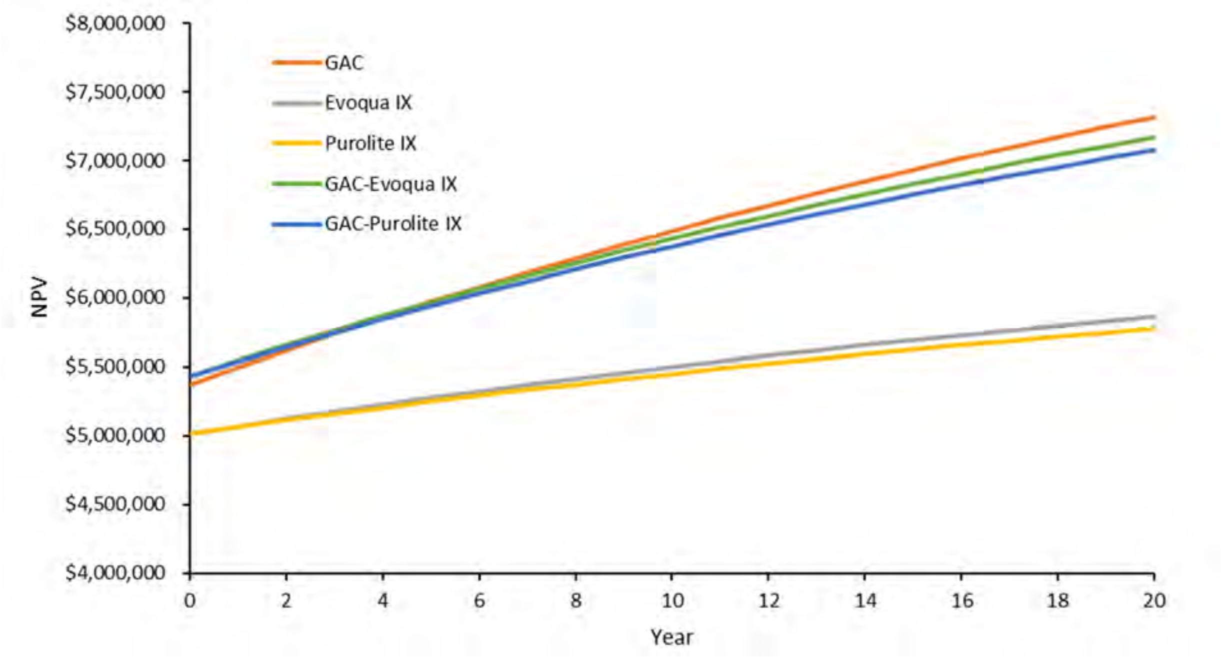

Figure 3-3: Net Present Value for a 1 MGD facility over 20 years

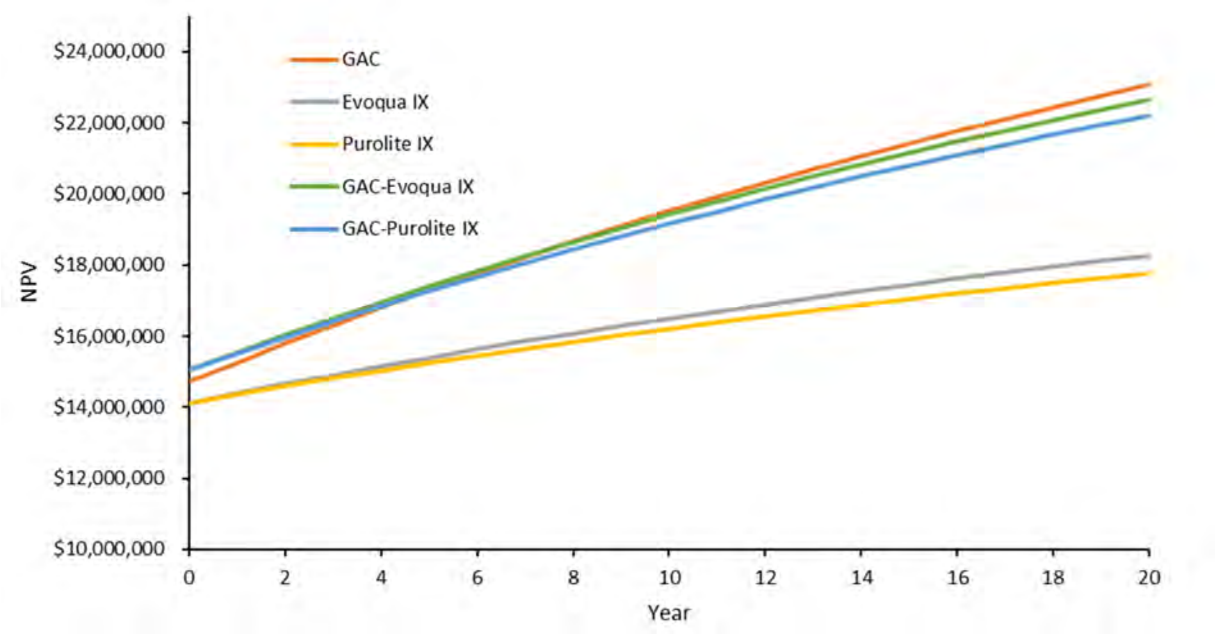

Figure 3-4: Net Present Value for a 4.5 MGD facility over 20 years

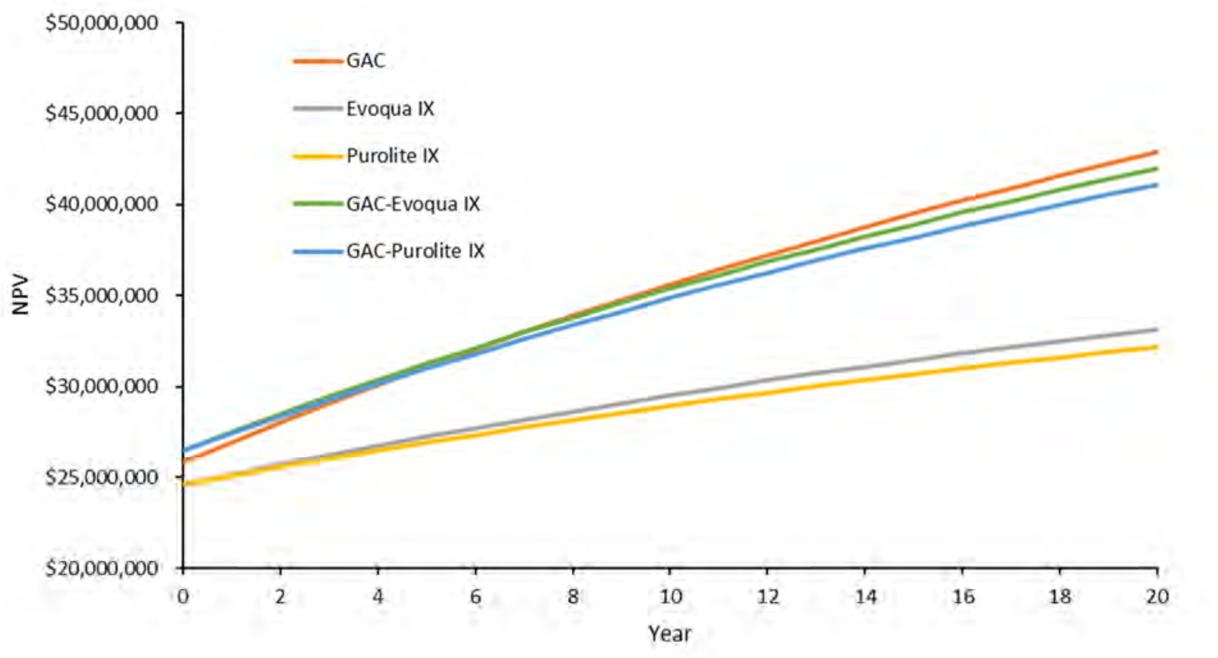

Figure 3-5: Net Present Value for a 10 MGD facility over 20 years

4.0 SUMMARY AND CONCLUSIONS

4.1 PFAS TREATMENT CAPABILITIES AND COST

This pilot study found that both GAC and IX media were able to remove PFAS from the source water, although it appeared that IX media provides a longer run time prior to Health Index breakthrough to a level of 0.5.

This study found that different groups of PFAS broke through the different media at different rates. Short-chain perfluorocarboxylic acid compounds, such as PFBA, quickly achieved breakthrough of both media, though the study found that they broke through IX resin faster than they broke through GAC media. Long-chain perfluorocarboxylic acids, on the other hand, such as PFOA, broke through GAC and IX media at a similar rate. All PFSA compounds, in contrast, were removed by IX media significantly better than by GAC media. Many of the compounds that drive the Health Index value for East Metro communities are PFSA compounds, and it is for this reason treatments incorporating IX medias are likely to provide better long-term treatment than GAC media.

In addition to the longer life of IX media, this study found that the net present value of an IX facility with pretreatment would be lower than that of a similarly sized GAC facility with pretreatment, primarily due to reduced operating costs. While GAC-IX dual media treatment shows promise from a treatment perspective, the duration of the pilot only allowed for limited data on media bed life, necessitating conservative assumptions in the cost estimate, making the net present value similar to that of GAC only treatment. However, it is important to reiterate that these are high level cost estimates, and costs for specific projects might vary considerably.

Pilot study learnings that may inform the development of PFAS Pilot Study Guidelines are provided in Appendix F.

4.2 PRETREATMENT MAY BE REQUIRED

Based on the results of this pilot study, PFAS treatment media are best implemented in conjunction with pretreatment for source waters similar to that of Well #3. The study found that the GAC media tested was more resilient to fouling than the IX media. Several communities in the East Metro have installed and are operating GAC interim PFAS treatment facilities without pretreatment, including a facility at the site of the pilot. These facilities have been operating successfully without pretreatment, likely due to the fact that the completely sealed treatment systems minimize dissolved oxygen levels in the water and thereby mitigate metal precipitation. Nevertheless, fouling has been observed at least one of these installations, and it is possible that PFAS treatment could be improved for GAC with the inclusion of pretreatment.

The results of the study also indicate that the media life of IX resins implemented on raw water sources similar to Well #3 might be significantly reduced by fouling unless pretreatment is included.

4.3 CONTINUED INVESTIGATION

One of the key learnings from this pilot study was that PFAS treatment technologies are changing rapidly, and continued investigation of these technologies will be imperative to understand how to most efficiently treat PFAS contamination long-term. Even in the two years since the pilot was proposed, promising new IX resins have been developed that warrant testing. To this end, we recommend allocating funds for a permanent research facility within a new full-scale PFAS treatment facility for continued investigation of treatment technology. Such a facility, with space to pilot up to three new technologies at a time, would have regional level impacts and position Minnesota as a leader in advanced water treatment technologies for years to come.

APPENDICES

Appendix A PILOT TEST PLAN

Attach is the final version of the pilot test plan.

EVALUATION OF ION EXCHANGE FOR REMOVAL OF PERFLUOROALKYL SUBSTANCES (PFAS) FROM A MINNESOTA EASTERN METROPOLITAN REGION GROUNDWATER

Pilot Test Plan (Revised 12/9/19)

Prepared by

Stantec
Johns Hopkins University

Submitted to

The Minnesota Pollution Control Agency

December 2019

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1. BACKGROUND

The communities within Minnesota’s Twin Cities east metropolitan region are served by groundwater that contains perfluoroalkyl substances (PFAS) resulting from prior industrial manufacturing activities at a 3M Company facility. Health-based standards issued by the Minnesota Department of Health (MDH) for perfluorooctanoic acid (PFOA) of 35 ng/L and perfluorooctane sulfonic acid (PFOS) of 15 ng/L are lower than the U.S. EPA values of 70 ng/L. These values, together with the MDH cumulative noncancer Health Risk Index (HRI) requirement of <1 for five (5) PFAS (PFOS, PFOA, PFHxS, PFBS, PFBA) prompted several east metropolitan communities to implement interim wellhead treatment in order to meet peak water demands. The City of Cottage Grove installed interim granular activated carbon treatment facilities at their Well #10 and Well #3 in order to lift a watering ban that resulted when eight (8) of their 11 wells exceeded the newly established HRI value. The City of Oakdale installed a long-term carbon treatment system in 2006 and St. Paul Park recently bid on an interim carbon treatment system.

The Minnesota Pollution Control Authority (MPCA) and impacted east metropolitan communities are interested in demonstrating ion exchange (IX) as a viable treatment alternative for mitigation of HRI exceedances through removal of PFAS. This demonstration will provide a side-by-side evaluation of IX performance capabilities and costs relative to granular activated carbon (GAC). In fulfillment of this demonstration, a pilot facility will be operated at the City of Cottage Grove to directly compare these two treatment technologies and demonstrate the key operational parameters needed to achieve effective ion-exchange performance.

IX is a promising treatment technology for removal of PFAS, particularly for the smaller chain compounds not as well removed by adsorption. The IX process should provide greater operational bed volumes than GAC. However, the higher unit cost of IX media makes the demonstration of cost-effectiveness an important objective. As with GAC, IX media is NSF/ANSI/CAN 61 certified for single-pass operation and spent IX media requires appropriate disposal.

The primary goal of this research is to compare the pilot-scale performance of two NSF/ANSI/CAN 61 certified ion exchange resins with the performance of an NSF/ANSI/CAN 61 approved activated carbon for the removal of PFAS compounds present in an east metropolitan groundwater well. The objectives supporting this goal include: (1) demonstration of IX operability with adequate detail to allow the MDH to draft a policy for piloting of ion exchange as an alternative treatment process for PFAS removal for the State of Minnesota; (2) performance of reconnaissance level cost estimates for full-scale implementation of IX resins for comparison with existing full-scale interim carbon treatment performance costs; and (3) performance of reconnaissance level cost estimates for full-scale implementation of GAC/IX in-series for comparison with existing full-scale interim carbon treatment performance costs.

These objectives will be accomplished through performance of the following two major tasks: (1) pilot installation and start-up and (2) pilot assessment of routine performance of the different media operated in parallel and in-series. A specially designed and fabricated pilot system will be provided by Stantec. Testing of the pilot process will be conducted using Well #3 groundwater, the location of one of the interim carbon treatment facilities in operation at the City of Cottage Grove. Routine pilot monitoring will be performed by Stantec staff and analytical support will be provided by the Johns Hopkins University Bloomberg School of Public Health.

If the IX performance proves to be a promising cost-effective alternative to GAC, several pertinent additional objectives could be addressed as part of a future study. These additional objectives include: investigation of the performance and cost enhancements achievable with a lead-lag configuration design of IX followed by GAC; evaluation of an RO process for performance comparison to the IX/GAC lead-lag configuration; and utilization of the RO concentrate for testing elevated loading of PFAS, assuming issues of handling high concentrations of PFAS can be adequately addressed.

2. DESCRIPTION OF PILOT-PROCESS

The pilot will consist of five test columns operated in parallel, with two columns containing NSF/ANSI/CAN 61 approved Purolite PFA694E anion exchange resin, two columns containing NSF/ANSI/CAN 61 approved DOW PSR2 anion exchange resin, and the fifth column containing the NSF/ANSI/CAN 61 approved Norit® GAC 1240 PLUS in use at Cottage Grove's Well #3 interim treatment facility. The columns will be operated in down-flow mode with up-flow capabilities for initial media washing and as-required backwashing. The duplicate IX columns will receive influent feed from the GAC effluent instead of the holding tank containing Well #3 water. The schematic of the pilot process is included in Figure 2-1. The IX and carbon treatment systems will be located within the building housing the interim carbon treatment system for Well #3. Break tanks for rinse water and influent well water and storage tanks for treated effluent will be housed at this location. The following section provides a description of the different components of the pilot treatment train.

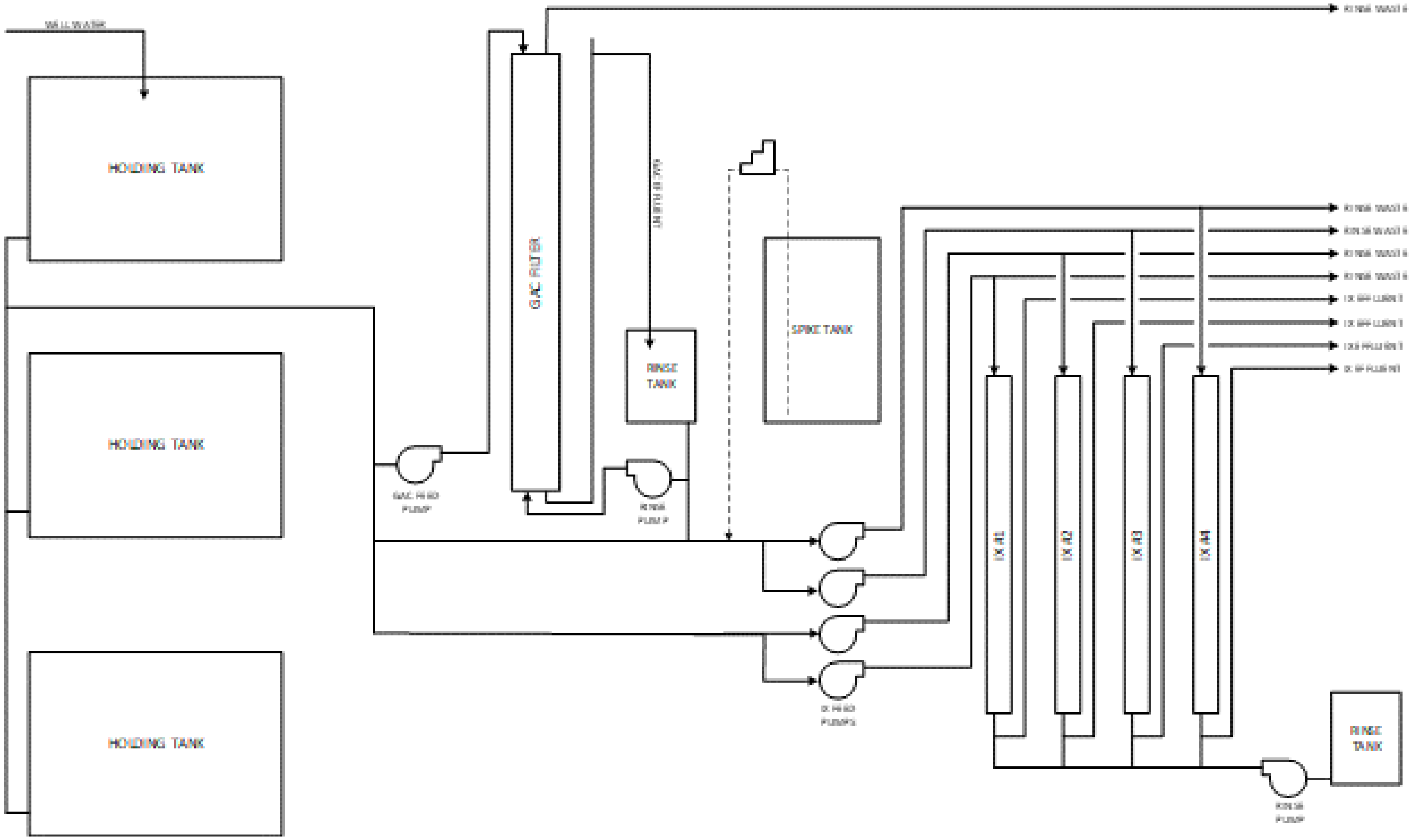

Figure 2-1
Schematic of the Pilot Plant

2.1 Influent Test Water

The Cottage Grove Well #3 test water will be plumbed to three 2,000-gallon break tanks at the pilot location for testing purposes. If needed, a feed pump will be supplied to fill the tanks. The influent line will have an electric ball valve to control the level of the break tanks via a level sensor and the PLC. The effluent from the break tanks will flow through a 5-micron bag filter and in-line dissolved oxygen sensor before splitting to the GAC and IX columns.

2.2 Ion Exchange Test Columns

The IX pilot will include four (4) parallel test columns. Each IX column will be operated independently, with loading in down-flow operation and initial backwashing in up-flow operation. The columns will be constructed of 3” clear sch. 40 PVC pipe. The lower ends of each column will be fitted with a media retaining nozzle to prevent media loss and provide even flow distribution. Each column will have three (3) ¼” SS sample ports evenly distributed along the bed depth. One sample port will be located 9 inches up from the lower media support, two (2) more will be located at 9-inch intervals above the first location. Sample port stems will extend into the center of the column and will be fitted with a stainless-steel screen to prevent media loss during sampling. Each column will be fitted with an air release valve (ARV) at the top of the IX column. Each IX column will also be fitted with a pressure differential transmitter for monitoring and data logging the pressure difference through the test resins.

Each of the four (4) IX columns will be fitted with a progressive cavity style feed pump capable of variable speed and controlled via PID loop to maintain a selected flow rate. Influent flow to each column will be monitored via a magnetic style flow meter or equivalent for data logging and flow rate control. A 0.5-micron cartridge filter will be installed on the inlet to each IX column. The effluent of the cartridge filter will be plumbed to the top of the IX column to allow for the down flow process configuration.

2.3 Ion Exchange Rinse System

A tank for IX rinse water will be plumbed to a common pumping system. The draw line from the rinse tank will be fitted with a ball valve so the operator may select the draw source water for the rinse pump. The pump effluent will be fitted with a rotameter and diaphragm valve for manual flow control. A common pipe header will be plumbed to the bottom of each of the four (4) IX columns and be fitted with valves so the operator can select the flow path of regen/rinse water. The waste from the media rinsing will exit the top of the columns and be sent to waste.

2.4 Ion Exchange Media

Two (2) of the columns will be loaded with Purolite polystyrenic gel resin (Purofine® PFA694E, USA) and the other two (2) columns will be loaded with Dow polystyrenic gel resin (Dowex™ PSR-2 Plus, USA). The first column of each resin type will be operated to simulate design loading and ambient water quality conditions. The second column of each resin type will be configured to receive GAC effluent water and simulate the performance of GAC/IX. The type of resin to be utilized, dimensions of the IX pilot system, and operational parameters are summarized in Table 2-1.

Table 2-1
Media Type, Column Dimensions, Operational Parameters, Regeneration and Rinse Information

Parameter	Units	Values
Resin or Carbon Type		
Resin Name	**Purofine® PFA 694E**	**Strong base anion polystyrenic gel**
Exchange Capacity	meq/mL	1.30
Mean Diameter	µm	675 ± 75
Uniformity Coefficient (Max)	-	1.3
Specific Gravity	g/mL	1.05
Resin Name	**DOWEX™ PSR-2 Plus**	**Strong base anion polystyrenic gel**
Exchange Capacity	meq/mL	0.65 to ≥0.7
Mean Diameter	µm	700±50
Uniformity Coefficient	-	≤1.1
Specific Gravity	g/mL	1.07
Carbon Name	**Norit® GAC 1240 Plus**	**Acid-washed bituminous coal**
Iodine Number Molasses Number	mg/g	950 210
Particle Size Range (95%)	mm	0.425 – 2.00
Apparent Density	kg/m^3	500
Column Specifications		
Column Material	Clear rigid PVC	Schedule 40
Column Diameter	inch	3 (IX) 8 (GAC)
Resin Bed Depth	inch	36 (IX) 90.36 (GAC)
Bed Volume (BV)	ft^3	0.15 (IX) 2.59 (GAC)
Operational Parameters		
Flow-mode	Type	Down-flow
EBCT	min	2.5 (IX) 10 (GAC)
Flowrate	gpm	0.45 (IX) 1.94 (GAC)
Surface Loading Rate	gpm/ft^2	8.98 (IX) 5.63 (GAC)
Rinse Information		
Flow-mode	-	Down-flow
Rinse Volume	bed volumes	3-4

2.5 GAC Test Column

The GAC column will be constructed of 8” clear sch. 40 PVC pipe. The column diameter was sized to provide enough effluent flow to accommodate the simultaneous lead-lag GAC/IX studies. The bottom of the column will be fitted with a media retaining nozzle to prevent media loss and provide even flow distribution. The GAC column will have three (3) ¼” stainless sample ports evenly distributed along the bed depth. One sample port will be located 22.5 inches up from the lower media support, two (2) more will be located at 22.5-inch intervals above the first location. Sample port stems will extend into the center of the column and will be fitted with a SS screen to prevent media loss during sampling. The column will be fitted with an air release valve (ARV) at the top of the GAC column. The GAC column will also be fitted with a pressure differential transmitter for monitoring and data logging the pressure difference through the test GAC.

The GAC column will be fitted with a progressive cavity style feed pump capable of variable speed and controlled via a PID loop to maintain a selected flow rate. Influent flow will be monitored via a magnetic style flow meter or equivalent for data logging and flow rate control. The effluent of the flow meter will be plumbed to the top of the GAC column to allow for down flow process.

The process effluent of the GAC column will be plumbed to a stand-pipe type constant head device to prevent the column from syphoning and be routed to a clear well tank for the purpose of supplying the IX columns operated in parallel and for backwashing the GAC. The clear well tank will have an overflow configured to draw excess overflow water from the lower portion of the break tank and be plumbed to an appropriate waste location.

2.6 GAC Backwash System

The GAC clear well will be plumbed to a backwash pump system. The backwash pump effluent will be fitted with a rotameter and diaphragm valve for manual flow control. A pipe header will be plumbed to the bottom of the GAC column to allow for upflow backwash of the GAC.

The waste from the GAC backwash will exit the top of the columns and be plumbed to waste. The GAC backwash effluent connection will be fitted with a Y-strainer, mounted vertically to the top of the GAC column. The screen mesh of this Y-strainer will be of a size to prevent GAC from exiting the column during a backwash and allow fines and other buildup to exit through it.

2.7 GAC Media

The fifth column will be loaded with Norit® GAC 1240 Plus, an acid washed bituminous GAC produced by steam activation of select grades of coal. The column will be operated under design flow and ambient water quality conditions that mimic the Cottage Grove interim treatment facility conditions.

2.8 Data Logging

Data logging will be provided for influent flow rates and pressure differential readings for the four (4) ion exchange columns and the GAC column. The system is designed to accommodate 10 points to be logged with a few extra points available for future add-ons if needed.

3. PILOT SITE DESCRIPTION

Pilot testing will be conducted at the Cottage Grove, Minnesota Well #3 interim GAC treatment facility. The pilot columns will be placed in the northeast corner of the well 3 interim facility. Raw water holding tanks will be placed adjacent to the pilot columns to provide water to the system when the well is not running. Previously measured PFAS concentrations at this location are included in Table 3-1 and background water quality is provided in Table 3-2. This water is representative of other east metro groundwaters and the low levels of competing anions such as nitrate and sulfate make this water a good candidate for PFAS removal by IX. The groundwater at this site is contaminated with approximately 1 µg/L of PFBA and lower levels of the four other PFAS compounds (PFBS, PFHxS, PFOS, PFOA) that comprise Minnesota's HRI for PFAS. The running average for the HRI at Well #3 prior to treatment (calculated by summing the ratio of each compound's measured groundwater concentration to its health-based guidance value) has fluctuated between three (3) and four (4) since 2008. Although PFBA occurs at the highest concentration, it is the presence of PFHxS, and PFOA with their considerably lower health-based values that result in most of the HI violations without carbon treatment.

Table 3-1
Historical PFAS and HI Data for Well #3 (Cottage Grove, MN)

Date	PFBS (µg/L)	PFBA (µg/L)	PFHxS (µg/L)	PFHxA (µg/L)	PFOS (µg/L)	PFOA (µg/L)	PFPeA (µg/L)	HI	HI(RA)
5/28/19	0.15	1	0.086	0.051	0	0.02	0.067	2.62	2.24
2/14/19	0.12	0.98	0.072	0.04	0	0.026	0.064	2.47	2.13
12/5/18	0.13	0.97	0.067	0.026	0	0.027	0.063	2.40	2.08
8/23/18	0.13	0.98	0.06	0.046	0	0	0.06	1.48	2.16
5/22/18	0.12	1	0.066	0.047	0	0.02	0.068	2.18	2.49
3/14/18	0.14	1	0.07	0.044	0	0.019	0.066	2.25	2.56
10/18/17	0.14	0.95	0.082	0.044	0	0.027	0.06	2.72	2.72
6/21/17	0.16	0.97	0.1	0.048	0	0.017	0.061	2.83	2.64
4/20/17	0.13	0.86	0.077	0.038	0	0.022	0.045	2.45	2.46
10/10/16	0.14	0.91	0.089	0.03	0	0.027	0.069	2.87	2.39
5/11/16	0.11	0.85	0.071	0.042	0	0.025	0.055	2.40	2.18
11/4/15	0.13	0.9	0.07	0.039	0	0.015	0.055	2.11	2.03
9/9/15	0.13	0.9	0.07	0.053	0	0.017	0.052	2.17	2.07
6/3/15	0.14	0.91	0.067	0.043	0	0.015	0.056	2.05	2.11
1/28/15	0.12	0.93	0.074	0.037	0	0	0.055	1.77	2.18

A snapshot comparison of the PFAS composition of Cottage Grove Well #3 with the other East Metro PFAS impacted public water supply wells is presented in Table 3-3. In order to capture IX performance for contaminants either absent in Cottage Grove Well #3 (e.g., PFOS) or observed at higher concentrations in other community wells (e.g., PFOA, PFBA, PFHxA), the potential for PFAS challenge testing of IX columns has been built into the pilot equipment for optional future studies designed to encompass other regional scenarios.

Table 3-2
Background Water Quality at Well #3 (Cottage Grove, MN)

Parameter (Unit)	Typical Value
Alkalinity, Bicarbonate (mg/L)	240
Alkalinity, Carbonate (mg/L)	1.6
Alkalinity, Total (mg/L)	240
Ammonia Nitrogen, Total (mg/L)	<0.05
Arsenic (µg/L)	1.47
Barium (µg/L)	<20
Bromide (mg/L)	0.0314
Ca as CaCO3 (mg/L)	190
Chloride (mg/L)	22.3
Dissolved Oxygen (mg/L)	0.1
Hetero. Plate Count (MPN/mL)	<2
Iron (µg/L)	<140
Manganese (µg/L)	54.5
Mg as CaCO3 (mg/L)	130
Nitrate + Nitrite Nitrogen, Total (mg/L)	<0.05
Nitrite Nitrogen, Total (mg/L)	<0.01
Oxidation Reduction Potential (mV)	70.3
pH (units)	7.9
Phosphate, Total (mg/L)	<0.03
Potassium (mg/L)	<5
Sodium (mg/L)	6.43
Specific Conductance (µS/cm)	544
Strontium (mg/L)	90
Sulfate (mg/L)	52.7
Temperature (deg C)	8.97
Total Organic Carbon (mg/L)	<1

Table 3-3
Snapshot Comparison of East Metro PFAS Impacted Public Water Supply Wells
(units in µg/L for samples collected early 2019)

Supply Well	PFOS	PFOA	PFBA	PFPeA	PFHxA	PFBS	PFHxS
Hastings #3	0.000	0.000	**0.320**	0.000	0.000	0.000	0.000
Hastings #4	0.000	0.000	**0.250**	0.000	0.000	0.000	0.000
Hastings #5	0.000	**0.010**	**0.640**	**0.040**	**0.014**	0.000	0.000
Hastings #6	0.000	0.000	**0.190**	**0.010**	0.000	0.000	0.000
Hastings #7	0.000	0.000	**0.180**	**0.009**	0.000	0.000	0.000
Hastings #8	0.000	**0.020**	**0.220**	**0.010**	0.000	0.000	0.000
Lake Elmo #1	0.000	**0.046**	**1.000**	**0.015**	**0.020**	0.000	0.000
Lake Elmo #2	0.000	0.000	**0.085**	**0.010**	0.000	0.000	0.000
Lake Elmo #4	0.000	0.000	**0.077**	**0.013**	0.000	0.000	0.000
Cimarron Park #1	0.000	0.000	**0.110**	**0.011**	0.000	0.000	0.000
Cimarron Park #2	0.000	0.000	**0.140**	**0.010**	0.000	0.000	0.000
Newport #1	0.000	0.000	**0.230**	**0.017**	0.000	0.000	0.000
Newport #2	0.000	0.000	**0.390**	**0.019**	0.000	0.000	0.000
Oakdale #1	**0.066**	**0.088**	**0.320**	**0.015**	**0.029**	0.000	0.000
Oakdale #2	**0.055**	**0.059**	**0.260**	**0.013**	**0.021**	0.000	**0.009**
Oakdale #3	0.000	0.000	**0.120**	0.000	0.000	0.000	0.000
Oakdale #5	**0.630**	**0.390**	**1.200**	**0.037**	**0.090**	**0.024**	**0.043**
Oakdale #7	**0.330**	**0.310**	**1.200**	**0.045**	**0.091**	**0.028**	**0.039**
Oakdale #8	**0.180**	**0.140**	**0.760**	**0.023**	**0.030**	**0.013**	0.000
Oakdale #9	**0.490**	**0.410**	**1.300**	**0.059**	**0.120**	**0.034**	**0.059**
Oakdale #10	0.000	0.000	**0.049**	0.000	0.000	0.000	0.000
St. Paul Park #2	0.000	**0.020**	**1.100**	**0.056**	**0.012**	0.000	0.000
St. Paul Park #3	0.000	**0.040**	**0.920**	**0.045**	**0.013**	**0.009**	0.000
St. Paul Park #4	0.000	**0.029**	**1.100**	**0.045**	**0.013**	0.000	0.000
Woodbury #1	0.000	**0.030**	**0.180**	0.000	**0.016**	0.000	0.000
Woodbury #2	0.000	0.000	**0.270**	**0.013**	0.000	0.000	0.000
Woodbury #3	0.000	**0.014**	**0.200**	0.000	0.000	0.000	0.000
Woodbury #4	0.000	**0.014**	**0.320**	**0.012**	**0.015**	0.000	0.000
Woodbury #5	0.000	0.000	**0.230**	**0.011**	0.000	0.000	0.000
Woodbury #6	0.000	**0.045**	**0.430**	0.000	**0.019**	0.000	0.000
Woodbury #7	0.000	**0.040**	**0.410**	**0.015**	**0.015**	0.000	0.000
Woodbury #8	0.000	0.000	**0.280**	0.000	0.000	0.000	0.000
Woodbury #9	0.000	**0.030**	**0.340**	0.000	**0.014**	0.000	0.000
Woodbury #10	0.000	0.000	**0.300**	0.000	0.000	0.000	0.000
Woodbury #11	0.000	0.000	**0.170**	0.000	0.000	0.000	0.000
Woodbury #12	0.000	0.000	**0.250**	**0.010**	0.000	0.000	0.000
Woodbury #13	**0.021**	**0.012**	**0.340**	**0.015**	**0.011**	**0.017**	**0.055**
Woodbury #14	0.000	0.000	**0.270**	0.000	0.000	0.000	0.000
Woodbury #15	0.000	0.000	**0.210**	0.000	0.000	0.000	0.000
Woodbury #16	0.000	0.000	**0.350**	**0.010**	0.000	0.000	0.000
Woodbury #17	0.000	**0.023**	**0.200**	0.000	0.000	0.000	0.000
Woodbury #18	0.000	0.000	**0.150**	0.000	0.000	0.000	0.000
Woodbury #19	0.000	0.000	**0.240**	**0.010**	0.000	0.000	0.000

4. PILOT TEST PLAN

The overall pilot testing will be conducted in two sequential phases:

- **Mobilization and Start-up**: Mobilization and start-up will include loading and conditioning the test media, verifying hydraulic performance of the pilot systems, establishing/documenting routine operations and challenge test conditions, establishing/documenting any required minor modifications to the testing protocol and verifying proper adherence to the quality assurance program.

- **Steady-state operation for IX, GAC and GAC/IX**: During this phase, two IX columns, one GAC column and two additional IX columns receiving feedwater from the GAC column will be operated to breakthrough under ambient loading rates. Breakthrough will be determined as both the point when PFBA is present in the effluent and when HI violations occur in the effluent. Early evidence of initial breakthrough will be evaluated through sample collection from intermediate sampling ports located down the length of the columns. It is anticipated that the columns may take 12-18 months to reach breakthrough.

The following subsections describe the test plan for these phases in further detail.

4.1 Phase I: Mobilization and Start-up

The activities of the mobilization and start-up phase are presented below:

4.1.1 Mobilization

Objective: To verify proper design and operation of the pilot facility and the absence of PFAS study site contamination issues.

Work Plan: The fabricated pilot facility will be verified against design specifications, installed at the prepared pilot site pad, hydraulically tested for leaks and verified for automated processes. An initial quality control check will verify the absence of PFAS contamination within the fabricated pilot by analyzing PFAS-free water cycled through the pilot header, each empty column and associated piping. Due to the volumes required, this water will be supplied from the carbon interim-treated effluent at Cottage Grove Well #3. Diagnostics and correct action will be taken if contamination is found, prior to loading the columns with media ahead of the startup phase.

As noted above, two of the columns will be loaded with potable water grade microporous polystyrenic gel anion exchange resin containing a complex amino functional group (Purolite PFA694E, USA). This resin is principally applied for the removal of perfluoroalkyl and polyfluoroalkyl substances and has a mean diameter of 675 ± 75µm, a maximum uniformity coefficient of 1.3 and a specific gravity of 1.05. The service flow rate is anticipated to fall between 10-40 BV/h, dependent upon the seasonality of the testing (temperature of the test water) and the effectiveness of the cartridge filters in alleviating column pressure drop. The two other IX columns will be loaded with a different manufacturer's potable water grade microporous polystyrenic gel strong base anion exchange resin containing a quaternary amine functional group (Dow DOWEX™ PSR-2, USA). This resin selectively removes trace contaminants from potable water and has a particle diameter of 700±50μm, a uniformity coefficient of ≤1.1 and a particle density of 1.07 g/mL. The fifth column will be loaded with the same Norit® GAC 1240 PLUS in use at the full-scale interim treatment facility and will serve as a control column by which to assess the accuracy of the pilot test results in predicting full-scale performance. The specifications for this carbon include a minimum iodine number of 950, a minimum molasses number (USA) of 210, a minimum abrasion number (AWWA) of 70, a maximum particle size >2.00 mm of 5%, a maximum particle size <0.425 mm of 0.5%, and an apparent density of 500 kg/m^3. The service flow rate is anticipated to fall between 2-8 BV/h and will match the loading rate of the interim facility.

Schedule: This task will be conducted over a 3-week period.

4.1.2 Startup

Objective: To finalize routine operational and challenge test conditions and familiarize the pilot operator with the detailed operational and data collection protocols to be followed during the subsequent Phase II baseline testing.

Work Plan:
Initial up-flow backwashing of the IX columns with PFAS-free water will be performed to expand the bed volumes to at least 1.5 times their initial volume for a minimum period of 30 minutes in order to remove voids, particulate matter, and trapped air bubbles that will minimize pressure-drop during routine loading operations. The GAC column will be expanded 30% during initial backwashing for a minimum period of 30 minutes. The columns will then be operated in down-flow mode at the service loading rates and other operational parameters specified in Table 2-1.

Once initial backwashing has been completed, down-flow loading of the pilot columns with the PFAS-free water will occur for at least 2 hours in order to verify proper media settling, hydraulic performance of each loaded column and to provide operator acclimation with daily operation and data acquisition protocols.

Schedule: This test phase will be conducted over a 1-week period

4.2 Phase II: Baseline Testing of Pilot Process

The activities of the baseline testing are presented below:

4.2.1 Evaluation of the IX Process under Ambient Loading Conditions

Objective: To obtain comparative performance and reconnaissance level cost data for the two (2) ion exchange columns, one (1) activated carbon, and (2) GAC/IX in series columns operated under identical ambient loading conditions.

Work Plan: Baseline testing will provide comparative performance data for the different selected media under identical ambient pilot loading conditions. The parameters to be evaluated during baseline testing under ambient conditions include: (1) breakthrough timeframe (and resulting bed volumes) for PFAS (most likely to be manifested as PFBA detection), HI >1 and change in concentration of competing matrix ions as determined from laboratory analysis of temporally collected samples; (2) pressure drop dependence on temperature and flow rate variations; (3) visual changes to media as a result of iron or manganese adsorption with measured concentration changes in these parameters before and after passage through each resin column; and (4) breakthrough profile plots of PFAS, HI>1 and competing water matrix anions as a function of bed volumes and loading rates. The detailed sampling plan for the baseline testing is shown in Table 5-1.

The IX and IX/GAC in-series processes will be operated until end-of-column breakthrough of PFBA occurs, even if HI violations are observed earlier. During this operation, routine anions (chloride, bicarbonate, nitrite/nitrate, phosphate and sulfate concentrations), iron and manganese, other routine water quality parameters such as pH, temperature, turbidity and a target list of 24 PFAS compounds will routinely be measured in both influent and effluent samples and selected port samples. Comparative breakthrough profiles of the anions, individual PFAS compounds and the calculated hazard index will be plotted. The ambient feedwater run length of each IX process will be derived from the time to PFBA breakthrough (or whichever PFAS compound is observed to breakthrough first) and the running average PFAS hazard index will be assessed for compliance to values <1 during this period.

Schedule: This task will be conducted over a period of 18 months or end when breakthrough is observed. It is anticipated that the columns may begin to show signs of breakthrough from samples collected at various column port locations, but full breakthrough will take considerably longer. Quarterly data presentation reports will be provided and ongoing interaction with Cottage Grove will underlie any decisions concerning the ultimate duration for the unchallenged column trials.

5. SAMPLING AND ANALYTICAL PLAN

The routine water quality parameters to be analyzed during pilot testing analysis is summarized in Table 5-1.

Once weekly influent and effluent water samples will be collected and analyzed for PFAS compounds, while critical anions, iron, manganese, alkalinity, total dissolved solids (TDS), total organic carbon (TOC), will be analyzed every other week. Onsite parameters will be analyzed every week. Timed weekly effluent samples will be collected to develop breakthrough curves for the PFAS compounds and evaluate the behavior of major anions and other relevant water quality parameters. Timed port samples will be collected at a lower frequency interval.

Table 5-1
Sampling and Analytical Plan

PARAMETER	METHOD	ANALYSIS LOCATION	PILOT GAC, IX, & GAC/IX SAMPLING FREQUENCY				
			Influent	Per Effluent†	Per Port #1	Per Port #2*	Per Port #3*
Flowrate	Rotameter	onsite	online	NA	NA	NA	NA
Temperature	SM2550B	onsite	1/day	1/day	NA	NA	NA
Pressure	Pressure gauge	onsite	1/day	1/day	NA	NA	NA
24 PFAS	Modified EPA 537	JHU	1/week	1/week	1/month	1/quarter	1/quarter
Alkalinity, Total	SM2320B	JHU	1/every other week	1/every other week	NA	NA	NA
Bicarbonate	SM 4500 CO$_2$D	JHU	1/every other week	1/every other week	NA	NA	NA
Chloride	EPA 300.1	JHU	1/every other week	1/every other week	NA	NA	NA
Iron	Hach	JHU	1/every other week	1/every other week	NA	NA	NA
Manganese	Hach	JHU	1/every other week	1/every other week	NA	NA	NA
Nitrite	EPA 300.1	JHU	1/every other week	1/every other week	NA	NA	NA
Nitrate	EPA 300.1	JHU	1/every other week	1/every other week	NA	NA	NA
Sulfate	EPA 300.1	JHU	1/every other week	1/every other week	NA	NA	NA
pH	SM 4500H+	onsite	1/week	1/week	NA	NA	NA
EC	SM2510B	onsite	1/week	1/week	NA	NA	NA
Turbidity	SM2130B	onsite	1/week	1/week	NA	NA	NA
TDS	SM2510B Calc	onsite	1/week	1/week	NA	NA	NA
TOC	SM5310C	JHU	1/every other week	1/every other week	NA	NA	NA
DO	SM4500-O G	onsite	1/week	1/week	NA	NA	NA

†Pilot consists of 5 effluents (i.e, GAC, IX#1, IX#2, GAC/IX#1, and GAC/IX#2).

*Sampling frequencies will be increased once breakthrough is observed for Port #1.

6. QUALITY ASSURANCE AND QUALITY CONTROL

This section describes quality assurance/quality control (QA/QC) checks that will be used throughout the project.

6.1.1 Ion-Exchange and GAC Pilot Process

- **Pilot Column Units**: All columns will be checked for PFAS contamination prior to loading of media by running 3 bed volumes of PFAS-free water through each column and then collecting the first 250-mL of sample from each column into PFAS sampling containers to verify lack of PFAS contamination from the column walls. This same test will then be performed after the columns are loaded with media and backwashed in accordance with manufacturer directions in order to verify lack of PFAS contamination from the media.

- **Pilot Auxiliary Units**: All equipment related to the pilot equipment such as pressure gauges, flow meters, and safety switches will be calibrated on-site during the pilot start up period and verified at a minimum on a bi-weekly basis.

- **On-line Monitoring Devices**: Any on-line monitoring devices will be calibrated bi-weekly on-site.

6.1.2 Laboratory Analyses

All samples will be carefully collected according to the sampling procedure described in the *Standard Methods for Water and Wastewater* or the cited EPA method. Proper QA/QC will also be implemented by JHU on all instruments used for analysis. All samples will be collected in proper sample bottles, refrigerated and analyzed within the holding time period of the parameter.

Analysis of PFAS will be performed by liquid chromatography tandem mass spectrometry (LC-MS/MS) with initial solid-phase extraction (SPE) instead of direct injection for achieving lower reporting limits. At the present time, there is no approved methodology for PFAS analysis in matrices other than finished drinking water (EPA Method 537 Rev. 1.1 or EPA Method 537.1). The pilot samples will be analyzed for PFAS by SPE-LC-MS/MS using isotope dilution, a quantitation technique considered the most accurate for PFAS in all matrices. The isotope dilution method is commonly referred to as “EPA 537 modified” within the analytical community. This method utilizes known amounts of stable isotope labelled PFAS (either carbon-13 (^{13}C) or deuterium (D)) as internal standards. The internal standards are spiked into all samples prior to sample extraction. Quantification is performed using external standards that contain different concentrations of target PFAS but the same amount of labelled PFAS as added to the field samples. The use of isotopically labeled internal standards allows to account for both losses during the sample extraction as well as matrix effects observed during LC-MS/MS analysis and thus assures that both the compound identification and compound quantification is of the highest degree of precision and accuracy possible. All detected PFAS compounds will be correctly reported as their acid form with their corresponding Chemical Abstracts Service (CAS) number. Reporting limits of 2-4 ng/L are targeted using isotope and external standards obtained from Wellington Laboratories, Guelph, Canada. A summary of the 24 target compounds that will be reported for all analyzed samples is provided in Table 6-1 and a summary of the 19 stable isotope labelled internal standards used for quantification of PFAS is provided in Table 6-2.

Table 6-1
Summary of PFAS Analytes to be Reported

	Analyte Name	**Acronym**	**CAS Number**
N-1	Perfluorotetradecanoic acid	PFTreA	376-06-7
N-2	Perfluorotridecanoic acid	PFTriA	72629-94-8
N-3	Perfluorododecanoic acid	PFDoA	307-55-1
N-4	Perfluoroundecanoic acid	PFUnA	2058-94-8
N-5	Perfluorodecanoic acid	PFDA	335-76-2
N-6	Perfluorononanoic acid	PFNA	375-95-1
N-7	Perfluorooctanoic acid	PFOA	335-67-1
N-8	Perfluoroheptanoic acid	PFHpA	375-85-9
N-9	Perfluorohexanoic acid	PFHxA	307-24-4
N-10	Perfluoropentanoic acid	PFPeA	2706-90-3
N-11	Perfluorobutanoic acid	PFBA	375-22-4
N-12	Perfluorodecanesulfonic acid	PFDS	335-77-3
N-13	Perfluorononanesulfonic acid	PFNS	68259-12-1
N-14	Perfluorooctanesulfonic acid	PFOS	1763-23-1
N-15	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
N-16	Perfluorohexanesulfonic acid	PFHxS	355-46-4
N-17	Perfluoropentanesulfonic acid	PFPeS	2706-91-4
N-18	Perfluorobutanesulfonic acid	PFBS	375-73-5
N-19	Perfluorooctanesulfonamide	PFOSA	754-91-6
N-20	Fluorotelomer sulfonic acid 8:2	FtS 8:2	39108-34-4
N-21	Fluorotelomer sulfonic acid 6:2	FtS 6:2	27619-97-2
N-22	Fluorotelomer sulfonic acid 4:2	FtS 4:2	757124-72-4
N-23	2-(N-Ethylperfluorooctanesulfonamido)acetic acid	NEtFOSAA	2991-50-6
N-24	2-(N-Methylperfluorooctanesulfonamido)acetic acid	NMeFOSAA	2355-31-9

Table 6-2
Summary of Stable Isotopes used for PFAS Quantitation

	Analyte Name	Acronym
IS-1	Perfluoro-n-[$^{13}C_4$]butanoic acid	PFBA-IS
IS-2	Perfluoro-n-[$^{13}C_5$]pentanoic acid	PFPeA-IS
IS-3	Perfluoro-n-[1,2,3,4,6-$^{13}C_5$]hexanoic acid	PFHxA-IS
IS-4	Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	PFHpA-IS
IS-5	Perfluoro-n-[$^{13}C_8$]octanoic acid	PFOA-IS
IS-6	Perfluoro-n-[$^{13}C_9$]nonanoic acid	PFNA-IS
IS-7	Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid	PFDA-IS
IS-8	Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid	PFUnA-IS
IS-9	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid	PFDoA-IS
IS-10	Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid	PFTreA-IS
IS-11	Perfluoro-1-[$^{13}C_8$]octanesulfonamide	PFOSA-IS
IS-12	2-(N-Methyl-D_3-perfluorooctanesulfonamido)acetic acid	NMeFOSAA-IS
IS-13	2-(N-Ethyl-D_5-perfluorooctanesulfonamido)acetic acid	NEtFOSAA-IS
IS-14	Perfluoro-n-[2,3,4-$^{13}C_3$]butanesulfonic acid	PFBS-IS
IS-15	Perfluoro-n-[2,3,4-$^{13}C_3$]hexanesulfonic acid	PFHxS-IS
IS-16	Perfluoro-[$^{13}C_8$]octanesulfonic acid	PFOS-IS
IS-17	[1,2-$^{13}C_2$]fluorotelomer sulfonic acid 4:2	FTS 4:2-IS
IS-18	[1,2-$^{13}C_2$]fluorotelomer sulfonic acid 6:2	FTS 6:2-IS
IS-19	[1,2-$^{13}C_2$]fluorotelomer sulfonic acid 8:2	FTS 8:2-IS

Solid phase extraction (SPE) Procedure

Polystyrenedivinylbenzene (SDVB) SPE cartridges (Agilent Technologies) are rinsed with methanol (5x 2-mL) followed by reagent water (5x 2-mL) without allowing the water to drop below the top edge of the packing. Afterwards, 4-5 mL of reagent water are added to each cartridge before samples are placed on a vacuum extraction manifold and sample transfer tubes are connected. Prior to extraction, stable isotope labelled internal standards are added to all water samples. After extraction, SPE cartridges are dried for 30 min under vacuum prior to elution of PFCs using 5x 2-mL methanol. The extract is concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1-mL volume with 96:4% (vol/vol) methanol:water.

LC-MS/MS analysis

LC-MS/MS analysis will be conducted using a TSQ quantiva triple quadrupole mass spectrometer coupled to a Vanquish Flex UHPLC (both Thermo Scientific). The mass spectrometer is equipped with a heated electrospray ionization (H-ESI) probe. The H-ESI source is used in the negative ionization mode and analytes are detected using Selected Reaction Monitoring (SRM) mode with specified retention time segments to achieve highest sensitivity. Chromatographic separation of all analytes and corresponding internal standards is accomplished using a Hypersil GOLD C18 reversed phase column (100mm x 1mm; 1.9 µm particle size) at a flow rate of 0.1 mL min^{-1} and ammonium acetate (20 mM) and methanol used as eluents. Quantification is performed using a calibration spanning a concentration range of at least 2-3 orders of magnitude and a minimum of 5 calibration points. Limits of detection (LODs) and limit of quantification (LOQs) are determined by spiking reagent water with different concentrations of the analytes prior to extraction and analysis as described for field samples.

Laboratory Quality control

All reagents, labware and consumables have been carefully selected to minimize PFAS contamination. The tubing used in the SPE extraction and in the UHPLC system has been replaced by PEEK and polypropylene tubing, respectively. In addition, an isolator column (Hypersil GOLD C18, 50mm x 2.1mm; 3 µm; Thermo Fisher) is installed after the LC pump and prior to the injection valve to eliminate potential contamination from solvents.

Laboratory blanks, spikes, duplicates and instrument calibration are performed at the frequency, evaluated with the acceptance criterion and addressed with the corrective action outlined in Table 6-3.

Table 6-3
Frequencies, Acceptance Criteria, and Corrective Actions for Laboratory QC

QC Sample Type	Frequency	Acceptance Criterion	Corrective Action
Laboratory blank	Per set of 20	Below method reporting limit (MRL)	Identify source of contamination and reanalyze associated samples
Laboratory duplicate(a)	Per set of 20	RPD ± 25%	Reanalyze.
Laboratory spike(a)	Per set of 20	75-125% recovery	Respike and reanalyze.
Calibration(b)	Per sample run	5-point calibration curve ($r^2 > 0.997$). The concentration of the lowest standard equal to the reporting limit.	Investigate the problem, resolve the problem, and recalibrate.
Calibration check	Per set of 20	Mid-range calibration solution (RPD± 15%)	Investigate the problem, resolve the problem, and recalibrate if necessary.

(a) Analytical duplicate and spike are conducted on representative samples.
(b) If the sample concentration exceeds the highest calibration standard, the sample will be diluted and reanalyzed; if the sample concentration is lower than the lowest calibration standard, it will be reported as <MDL.

If the QA requirements for a critical parameter are not met, the parameter will be considered suspect and flagged. Under this circumstance, both the analyst and principle investigator will investigate the cause of the discrepancy. If the discrepancy is due to an analytical problem, the sample will be reanalyzed or another sample will be collected and analyzed. In any event, the data will be flagged with a data qualifier and the qualifier will be included and explained in the subsequent literature.

6.1.3 Field Quality control

Field QC checks will consist of field blanks and field duplicates. Three field blanks, three influent duplicates, three IX duplicates and three GAC effluent duplicates will be collected at the start of the pilot to verify initial performance and then occur at a frequency of one field blank and one duplicate sample per 20 routine field samples or weekly (whichever is more frequent). The location of the continuing field duplicates will be the influent or one of the column or port effluents and these locations will rotate on a continual basis.

The field blank will check for pilot site contamination by transferring aliquots of PFAS-free reagent water or Cottage Grove Well #3 interim GAC treated effluent into sample bottles at the pilot facility during collection of field samples. The field blanks will undergo identical handling and laboratory analytical processing as all other collected field samples. Contaminant levels must remain at or below the method reporting limit for the analyzed compounds. If levels begin to exceed these limits, they will be compared against the laboratory blanks to verify whether contamination is occurring at the pilot site during sample collection and/or transport. If the contamination source is coming from the field, trip blanks will be instituted to determine if contamination is arising from transportation. Once the contamination source is identified, the necessary corrective action to eliminate the contamination will be verified before analytical work is resumed.

The field duplicate will verify the precision of the field collection protocols and the laboratory spiking of the field duplicate will verify lack of bias in the analytical protocols. Collectively, these will demonstrate the accuracy of the generated results.

In addition to the collection of these field QC samples, the following procedures will be followed during pilot operation to ensure the integrity of PFAS measurements through minimization of background contamination:

- The pilot facility will be inspected for elimination of common PFAS sources of contamination prior to initiation of pilot activities. These include aluminum foil, PTFE products, and inappropriate tubing (i.e.,Teflon™, silicone, etc.) or tape for equipment pumps and plumbing.
- Onsite glassware and other collection equipment will be cleaned and stored in accordance with EPA Method 537.1 protocols. Alconox® or Liquinox® cleaning reagents will be used, followed by potable water and deionized PFAS-free water rinses. Verification of cleanliness will be verified by including their use (as appropriate) in preparation of the site blanks accompanying sample batches shipped to JHU for analysis. A site blank will be collected with every batch of shipped samples.
- Sample collection containers will be HDPE or polypropylene containers with HDPE or polypropylene caps. Only regular ice will be used to cool samples for shipment, as Blue ice® is a contamination source.
- The pilot operator will not wear clothing that may be contaminated with PFAS to the pilot site. These include garments that have been treated with Gore-Tex® or other synthetics for water or stain repellency. Clothing worn to the pilot site should be cotton and will not have been washed with fabric softeners or dried with dryer sheets.

- The pilot operator will carefully wash hands with a plain unperfumed soap (i.e., lye and solid fat only) before coming to the pilot site and restrict use of grooming products to those that do not contain fragrances, perfumes, sunscreen, insect repellent or volatile ingredients.
- The pilot operator will not bring any packaged or wrapped food to the pilot site and will leave the premises for all meals and snacks.
- During field documentation, no waterproof/treated paper or field books, Post-its or other adhesive paper products, plastic clipboards or water-proof markers will be allowed on the premises. Only plain untreated sheets of paper held together on a metal clipboard and ballpoint pens will be allowed.
- The pilot operator will use new nitrile gloves during sample collection and collect PFAS samples ahead of other sample analytes. The PFAS sample bottle cap cannot be placed on any surface and the operator will avoid contact with the inside of the sample bottle or cap. Once the PFAS samples are collected, they must be placed into individual sealed plastic bags (e.g. Ziploc®) separate from all other sample parameter bottles.
- There will be no preservative in the PFAS sample collection bottles, as the preservative Trizma is not recommended for unchlorinated water samples. Two (2) - 125 mL HDPE bottles will be collected per sample.

6.1.4 Data Analyses

Data collected on-site will be regularly merged with data obtained from off-site laboratory samples. This will result in a comprehensive database, which can be used for data analysis, retrieval, reporting and graphics. All data will be checked and verified by the project engineer before and after entry into the database.

7. HEALTH AND SAFTEY AND SCHEDULE

A separate health and safety plan will provide operational guidelines and emergency procedures that must be followed during the mobilization, operation and tear-down of the pilot facility. The plan will cover all aspects of operation, maintenance and associated sampling activities of the pilot facility in order to ensures the health and safety of onsite personnel.

The tentative schedule of the proposed pilot testing is presented in Table7-1. One month will be needed for pilot mobilization and start-up verification of performance. Baseline testing is anticipated to occur for 18-24 months (until break-through is observed).

If effective IX or GAC/IX performance is successfully demonstrated, a future study could improve clarity on design and operational optimization issues and the adaptability of this process to additional water supplies. Effective performance will be demonstrated in terms of: (1) continuous production of effluent quality in conformance with HRI requirements prior to breakthrough; (2) cost-effective operation relative to the GAC pilot and interim full-scale data; and (3) lack of any serious operational deficiencies during pilot operation. The future study would focus on evaluation of RO performance, estimation of tolerable well supply interruption rates and exploration of performance with additional water supplies or utilization of RO concentrate to performance challenge water testing.

Table 7-1
Tentative Schedule of the Pilot Testing

Activity	Duration
Phase 1: Pilot Mobilization	3 Weeks
Phase 1: Pilot Startup	1 Week
Phase 2: GAC, IX, and GAC/IX Testing	Anticipated to be 18-24 months
Future Phase: IX/GAC, RO, Challenge Testing	Optional

Appendix B MATERIALS AND METHODS

B.1 DESCRIPTION OF PILOT PROCESS TRAINS

The pilot test was conducted at the Interim GAC Treatment Facility located at Well #3 in Cottage Grove, MN. The pilot consists of five test columns operated in parallel, with two columns (IX1 & IX3) containing NSF/ANSI/CAN 61 approved Purolite PFA694E anion exchange resin, two columns (IX2 & IX4) containing NSF/ANSI/CAN 61 approved DOW PSR2 anion exchange resin, and the fifth column containing the NSF/ANSI/CAN 61 approved Norit® GAC 1240 PLUS. The columns were operated in down-flow mode with up-flow capabilities for initial media washing and as-required backwashing. All pilot systems were located within the building housing the interim carbon treatment system for Well #3.

Raw water from Well #3 entered the interim facility, passed through pretreatment for iron and manganese, then routed to three holding tanks, adjacent to the pilot columns, to provide continuous water to the system when the well was inactive. Water from the holding tanks was passed through a 1-micron cartridge filter to achieve particulate removal. After the filter, three streams were diverted to IX3, IX4, and GAC. The IX1 and IX2 columns received influent feed from the GAC effluent instead of the holding tank. Figure B-1 shows a picture of the pilot columns. The following sections provide detailed descriptions of the different components of the pilot treatment train.

B.1.1 Raw Water Supply

The raw water supply for the pilot was taken from Cottage Grove Well #3. The influent supply was controlled by a solenoid valve that automatically opened when the well pump was running, and shut when the well pump turned off.

B.1.2 Pretreatment

Following the initial pilot run which was cut short due to iron fouling, the influent water was routed to iron removal filters as pretreatment prior passing through the pilot.

Initially, a series of three filter tanks containing BIRM media were installed on the raw water line prior to the holding tanks, as shown in Figure B-2. Raw water flowed downward through the media and the effluent was routed to the storage tanks. BIRM media has a manganese oxide coating that oxidizes iron to form particulates, which are removed through filtration by the BIRM media. Backwashing was carried out 3 times a week.

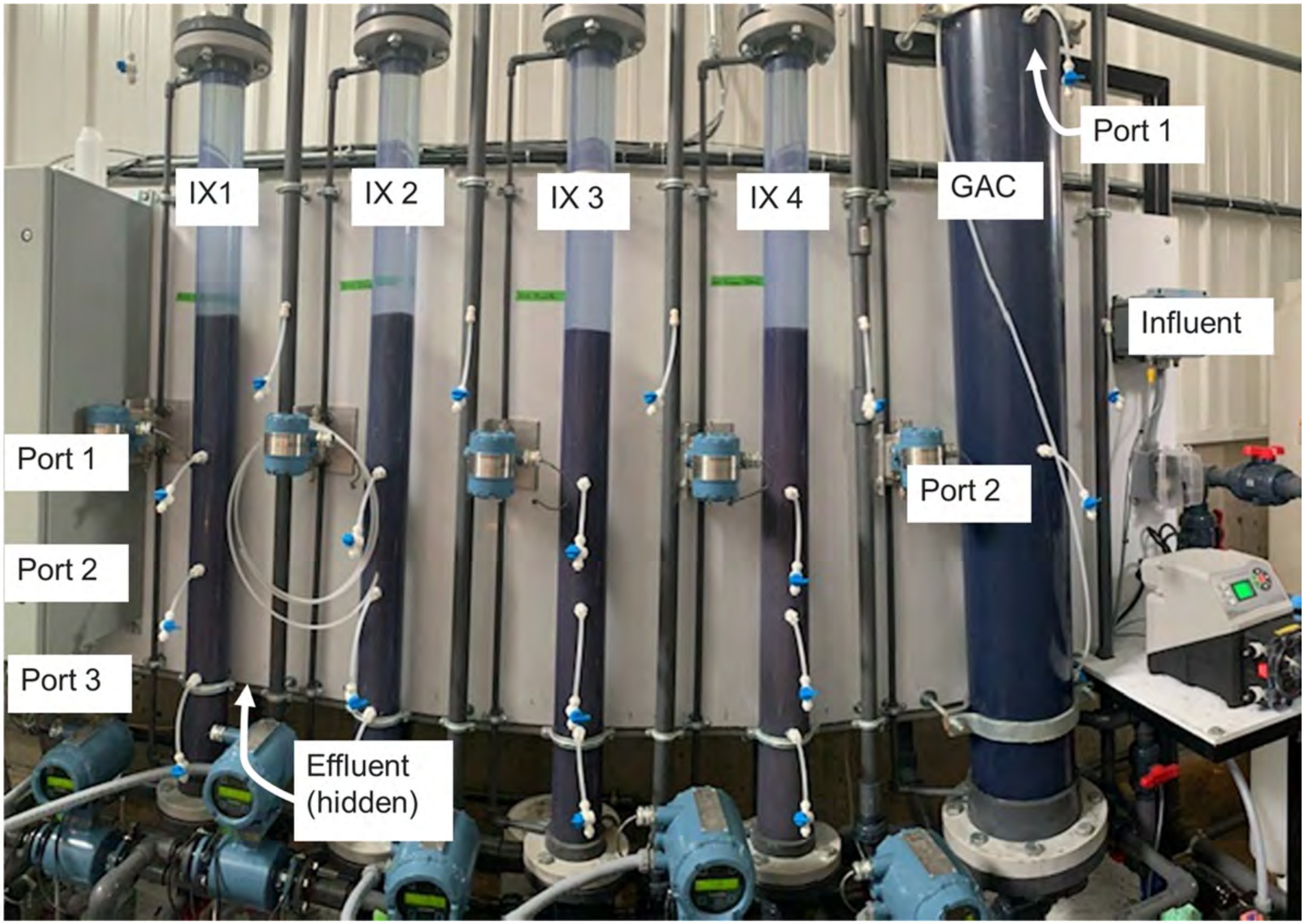

Figure B-1: Pilot skid layout

Figure B-2: Pretreatment system

After approximately four months the BIRM media was replaced with Filox media, which was selected for its ability to remove manganese as well as iron. Filox media also had a higher flow rate, allowing all pilot flow to pass through one pretreatment vessel, at which point the others were decommissioned. The Filox media was replaced again after another six months.

See Appendix C for the differential pressure increase in GAC that caused concern for manganese fouling and resulted in the media change.

B.1.3 Storage Tanks

Three 2,000 gallon tanks provided water storage for the pilot so that the columns could continue to run even when the Well #3 pump was off. A level sensor in one of the tanks provided level control that would shut the solenoid when water level hit an operator set high-level. The level sensor also provided a low-level alarm that was sent directly to the operators’ phones when the water level in the tanks began to get too low.

B.1.4 Cartridge Filter

Following the storage tanks water passed through a 1 µm cartridge filter to remove particulate upstream of the PFAS treatment columns. The cartridge filter was replaced by as necessary, typically between twice a week and once every two weeks.

B.1.5 Ion Exchange Test Columns

The pilot included four parallel IX test columns, constructed of 3” clear schedule 40 PVC pipe. The columns were operated in a downward flow configuration, with media retaining nozzles to prevent media loss and provide even flow distribution.

Each column had three ¼” sample ports arranged at 9” intervals along the bed depth. Each sample port stem was extended into the center of the column and fitted with stainless-steel screen to prevent media loss during sampling. Each column was fitted with an air release valve at the top of the IX column and fitted with a pressure differential transmitter for monitoring and logging the pressure difference across the media bed.

The four IX columns were fitted with a progressive cavity style feed pump capable of variable speed and controlled via PID loop to maintain a flow rate of 0.45 gpm, corresponding to an empty bed contact time of approximately 2.5 minutes. Influent flow to each column was monitored via a magnetic flow meter for data logging and flow rate control.

Two of the IX columns (IX1 & IX3) were loaded with Purolite polystyrenic gel resin (Purofine® PFA694E, USA) and the other two columns (IX2 & IX4) were loaded with Dow polystyrenic gel resin (Dowex™ PSR-2 Plus, USA). One column of each resin type (IX3 & IX4) was operated to simulate design loading and ambient water quality conditions. The second column of each resin type (IX1 & IX2) was configured to receive GAC effluent water and simulate the performance of GAC-IX dual media treatment. Further details regarding the IX resins and column design are shown in Table B-1.

B.1.6 Ion Exchange Effluent Tank

IX column effluent was collected in a ~100-gallon tank, with piped overflow to a floor drain. This tank was used to provide backwash rinse water to the IX columns.

The IX backwash rinse system was used at start-up to remove fines from the IX resins and occasionally to help reconsolidate the media bed after a disruption to the pilot operation. A common backwash pump drew water from the IX effluent tank, and backwash flow could be controlled by the operator using a globe valve and rotameter. A common pipe header was plumbed to the bottom of each of the four IX columns and fitted with valves to direct the flow path of to any of the IX columns. After exiting out the top of the column the backwash water was wasted to a floor drain. The IX backwash effluent connections were fitted with a Y-strainer, mounted vertically to the top of the columns. The screen mesh of this Y-strainer was small enough to prevent IX resin beads from exiting the column during a backwash but allow fines and other small particles to exit through it.

B.1.7 GAC Test Column

The GAC column was constructed of 8” clear schedule 40 PVC pipe. The column diameter was sized to prevent side-wall effect and to provide enough effluent flow to accommodate the simultaneous lead-lag GAC/IX studies. The bottom of the column was fitted with a media retaining nozzle to prevent media loss and provide even flow distribution. The GAC column had two ¼” stainless sample ports evenly distributed at 30-inch intervals along the bed depth. Each sample port stem was extended into the center of the column and fitted with stainless-steel screen to prevent media loss during sampling. The column was fitted with an air release valve (ARV) at the top of the GAC column. The GAC column will also be fitted with a pressure differential transmitter for monitoring and data logging the pressure difference through the test GAC.

The GAC column was fitted with a progressive cavity style feed pump capable of variable speed and controlled via a PID loop to maintain a selected flow rate. Influent flow to the column was monitored via a magnetic flow meter for data logging and flow rate control.

The GAC column was loaded with Norit® GAC 1240 Plus, an acid washed bituminous GAC produced by steam activation of select grades of coal. The column was operated under design flow and ambient water quality conditions that mimic the Cottage Grove interim treatment facility conditions (i.e. approximately 10 min EBCT). Further details regarding the GAC media resins and column design are shown in Table B-1

B.1.8 GAC Effluent Tank

GAC column effluent was collected in a ~100-gallon tank, with piped overflow to a floor drain. This tank was used to provide backwash rinse water to the GAC column.

The GAC backwash rinse system was used at start-up to remove fines from the GAC media and occasionally to help reconsolidate the media bed after a disruption to the pilot operation or remove fouling material.

Backwash flow could be controlled by the operator using a globe valve and rotameter. The waste from the GAC backwash exited the top of the column and discharged to a floor drain. The GAC backwash effluent connection was fitted with a Y-strainer, mounted vertically to the top of the GAC column. The screen mesh of this Y-strainer was small enough to prevent GAC from exiting the column during a backwash but allow fines and other small particles to exit through it.

B.2 DESCRIPTION OF SAMPLING PROCEDURES

A variety of samples were collected for PFAS analysis or water quality analysis over the course of the pilot study. Sampling locations and frequency are covered in Table B-2. Detailed sampling procedures are provided in the following sections.

Table B-1: Media Type, Column Dimensions, Operational Parameters, Regeneration and Rinse Information

Parameter	Units	Values
Resin Name	**Purofine® PFA 694E**	**Strong base anion polystyrenic gel**
Exchange Capacity	meq/mL	1.30
Mean Diameter	µm	675 ± 75
Uniformity Coefficient (Max)	-	1.3
Specific Gravity	g/mL	1.05
Resin Name	**DOWEX™ PSR-2 Plus**	**Strong base anion polystyrenic gel**
Exchange Capacity	meq/mL	0.65 to ≥0.7
Mean Diameter	µm	700±50
Uniformity Coefficient	-	≤1.1
Specific Gravity	g/mL	1.07
Carbon Name	**Norit® GAC 1240 Plus**	**Acid-washed bituminous coal**
Iodine Number	mg/g	950
Molasses Number	mg/g	210
Particle Size Range (95%)	mm	0.425 – 2.00
Apparent Density	kg/m^3	500
Column Specifications		
Column Material	Clear rigid PVC	Schedule 40
Column Diameter	inch	3 (IX) 8 (GAC)
Resin Bed Depth	inch	36 (IX) 90.36 (GAC)
Bed Volume (BV)	ft^3	0.15 (IX) 2.59 (GAC)
Operational Parameters		
Flow-mode	Type	Down-flow
EBCT	min	2.5 (IX) 10 (GAC)
Flowrate	gpm	0.45 (IX) 1.94 (GAC)
Surface Loading Rate	gpm/ft^2	8.98 (IX) 5.63 (GAC)
Rinse Information		
Flow-mode	-	Up-flow
Rinse Volume	bed volumes	3-4

Table B-2: Sampling and Analytical Plan

PARAMETER	METHOD	ANALYSIS LOCATION	PILOT GAC, IX, & GAC/IX SAMPLING FREQUENCY				
			Raw Influent	Per Effluent†	Per Port #1	Per Port #2*	Per Port #3*
Flowrate	Rotameter	onsite	online	NA	NA	NA	NA
Temperature	SM2550B	onsite	1/week	1/week	NA	NA	NA
Pressure	Pressure gauge	onsite	online	online	NA	NA	NA
PFAS	Modified EPA 537	JHU	1/week	1/ week	1/ week	1/ week	1/ week
Iron	Hach	onsite	1/every other week	1/every other week	NA	NA	NA
Manganese	EPA 200.7	RMB Labs	1/month	1/month	NA	NA	NA
pH	SM 4500H+	onsite	1/week	1/week	NA	NA	NA
EC	SM2510B	onsite	1/week	1/week	NA	NA	NA
Turbidity	SM2130B	onsite	1/week	1/week	NA	NA	NA
TDS	SM2510B Calc	onsite	1/week	1/week	NA	NA	NA
TOC	SM5310C	JHU	1/every other week	1/every other week	NA	NA	NA
Alkalinity, total	SM2320B	JHU	1/every other week	1/every other week	1/every other week	1/every other week	1/every other week
Nitrite	EPA 300.1	JHU	1/every other week	1/every other week	1/every other week	1/every other week	1/every other week
Nitrate	EPA 300.1	JHU	1/every other week	1/every other week	1/every other week	1/every other week	1/every other week
Chloride	EPA 300.1	JHU	1/every other week	1/every other week	1/every other week	1/every other week	1/every other week
Sulfate	EPA 300.1	JHU	1/every other week	1/every other week	1/every other week	1/every other week	1/every other week
DO	SM4500-O G	onsite	online	NA	NA	NA	NA

†Pilot consists of 5 effluents (i.e, GAC, IX#1, IX#2, GAC/IX#1, and GAC/IX#2).

*Sampling frequencies were decreased once breakthrough was observed at Port #1.

* Pretreatment, tank and cartridge effluent sampling occurred at the same frequency as column effluent sampling

B.2.1 PFAS Sampling

PFAS samples were collected in new 250 mL polypropylene sample bottles. Prior to sample collection, the sample line was flushed to remove any stagnant water. Each collection bottle was then rinsed with sample water, which was wasted, and then filled and capped. Sample bottles were labeled with column_location_YYYYMMDD / time and operator (i.e. IX3_EFF_20200210 / 3 PM HCC).

Samples were generally collected from most treated to least treated, starting with column effluent and progressing to GAC influent and raw water. For quality control measures, a duplicate sample and a control sample of distilled water were collected after a full set of port samples had been collected.

Sample ports include:

1. Raw
2. GAC Inf
3. GAC P1
4. GAC P2
5. GAC Eff
6. IX1 Eff
7. IX1 P1
8. IX2 Eff
9. IX2 P1
10. IX3 P1
11. IX3 P2
12. IX3 P3
13. IX3 Eff
14. IX4 P1
15. IX4 P2
16. IX4 P3
17. IX4 Eff
18. Field Blank
19. IX3 P2_b (duplicate)

Packaged samples were sent in a cooler with ~2L of ice in designated polypropylene bottles and a temperature sensor that started logging when the first sample was added to cooler to ensure the temperature limit was not exceeded. The cooler was priority shipped to the John Hopkins University lab and received the next day for analysis.

B.2.2 Field Quality Control - PFAS

Field QC consisted of field blanks and field duplicates. Three field blanks, influent duplicates, IX duplicates and GAC effluent duplicates were collected at the start of the pilot to verify initial performance and then occurred at a frequency of one field blank and one duplicate sample per routine field sampling.

Field blanks used a store-bought distilled water. The field blanks underwent identical handling and analytical processing as all other collected field samples. If field plank PFAS levels began to exceed the method reporting limits, they were compared against the laboratory blanks to verify whether contamination was occurring at the pilot site during sample collection and/or transport.

The purpose of the field duplicate was to verify the precision of the field collection protocols and sample preparation methods in order to demonstrate the repeatability of results.

In addition to the collection of these field QC samples, the following procedures were followed during pilot operation to ensure the integrity of PFAS measurements through minimization of background contamination:

- The pilot facility was inspected for elimination of common PFAS sources of contamination prior to initiation of pilot activities. These include aluminum foil, PTFE products, and inappropriate tubing (i.e.,Teflon™, silicone, etc.) or tape for equipment pumps and plumbing.
- Sample collection containers were HDPE or polypropylene containers with HDPE or polypropylene caps. Only regular ice was used to cool samples for shipment, as Blue ice® is a contamination source.
- The pilot operator did not wear clothing that may have been contaminated with PFAS to the pilot site. These include garments that have been treated with Gore-Tex® or other synthetics for water or stain repellency.
- The pilot operator used new nitrile gloves during sample collection and collected PFAS samples ahead of other sample analytes. The PFAS sample bottle caps were not placed on any surface and the operator avoided contact with the inside of the sample bottle or cap.
- There was no preservative in the PFAS sample collection bottles, as the preservative Trizma is not recommended for unchlorinated water samples.

B.2.3 TOC Sampling

John Hopkins supplied 20 mL amber vials with acid preservative for collection. Sample ports matched PFAS sample ports except no field blank or duplicate was necessary. As with PFAS sample collection, the sample line was flushed prior to sample collection. The vials contained preservative; therefore, no rinse occurred. The vials were slowly filled the neck, to ensure no reagent overflowed from the sample, until water reached the neck of the bottle. The fragile glass vials required robust packaging in bubble wrap and placed in the cooler with the PFAS samples to send to JHU.

B.2.4 Water Quality Sampling

Water quality parameters turbidity, pH, temperature, and conductivity were tested at the Pilot site on a weekly basis. Samples were collected at each of the following locations:

- Raw water
- Filox Effluent
- Tank Effluent
- Cartridge Filter Effluent
- GAC Effluent
- IX1 Effluent

- IX2 Effluent
- IX3 Effluent
- IX4 Effluent

Temperature, pH and Conductivity Analysis

Samples for temperature, pH, and conductivity analysis were collected in 250 mL polypropylene bottles. The polypropylene sample was filled up to an inch below the shoulder of the 250 mL bottle to leave space in the bottle for probes.

A Hach HQ 40d Multi Meter equipped with pH and conductivity probes was used to measure pH, conductivity, and temperature. Both probes were rinsed and calibrated prior to analysis. Probes were placed within the sample bottle so that their ends were fully submerged. Results were recorded for each sample.

Turbidity Analysis

Turbidity analysis was carried out with a Cole-Parmer Turbidimeter Kit. The Turbidimeter was calibrated using 800, 100, 20, and 0.2 NTU standards prior to analysis. Samples were collected in the kit vials, and care was taken to remove all air bubbles to achieve accurate results. The sample was placed in the turbidimeter, cover closed and proceeded to read turbidity. Three replicates were taken for each sample, and the average was recorded.

B.2.5 Iron Sampling

To ensure pretreatment was functioning as intended, iron samples were collected and processed on a bi-weekly basis from:

- Raw water
- Filox Effluent
- Cartridge Filter Effluent
- GAC Effluent
- IX3 Effluent
- IX4 Effluent

Duplicate samples were collected for each sample location, and each sample analyzed for soluble and total iron concentrations.

Soluble Iron Analysis

Materials needed:

1. Hach HPT 251 Ultra Low Range Iron Test
2. Hach TNT 890 Metals Digestion kit
3. 15 mL centrifuge tube
4. 10 mL syringe
5. 0.45 um filter syringe attachment
6. 5 mL disposable pipette and pipette bulb
7. Kim wipes

8. DR 3900
9. 250 mL polypropylene sample bottle

Iron samples were initially collected in 250 mL polypropylene sample bottles, which were rinsed with DI water and then rinsed with sample water prior to actual sample collection. Using a syringe, slightly more than 10 mL of water, was pushed through a 0.45 um filter into a 15 mL centrifuge tube. This filtered out particulate iron in order to obtain a soluble iron measurement.

The filtered water was processed with the Hach HPT 251 Ultra Low Range Iron Test by following the instructions on the box. The cuvette was then placed in the Hach DR3900 spectrophotometer for soluble iron measurement. Used cuvettes and any contaminated waste were discarded in a hazardous waste container.

Total Iron Analysis

Materials needed:

1. Hach TNT 890 Metals Digestion kit
2. Hach HPT 251 Ultra Low Range Iron Test
3. 1, 5, 10 mL disposable pipettes and pipette bulb
4. 15 mL digestion vials
5. Kim wipes
6. DR 3900
7. Digestion block
8. 250 mL polypropylene sample bottle

Processing total iron requires an intermediate step of digestion. Unfiltered sample water was processed with the Hach TNT 890 Metals Digestion kit following instructions on the box.

After digestion, the samples were treated with the Hach HPT 251 Ultra Low Range Iron Test and measured using a Hach DR3900 spectrophotometer with HPT 251 Ultra Low Iron software. Used cuvettes and any contaminated waste were discarded in a hazardous waste container.

B.2.6 Manganese Sampling

The following sampling procedure is meant to provide insight on manganese sample collection at the pilot facility and analyzation at a local facility: RMB labs. Samples were collected and processed monthly from:

- Raw water
- Filox Effluent
- Cartridge Filter Effluent
- GAC Effluent
- IX3 Effluent
- IX4 Effluent

Duplicate samples were collected for each port, one of which was analyzed for soluble manganese and the other sample for total manganese.

Manganese samples were collected in new 250 mL polypropylene sample bottles, which were rinsed with sample water prior to actual sample collection. The bottles were labeled with the sample location he samples location and “Soluble” or “Total” for RMB labs reporting. The samples were dropped off in a cooler at the lab.

B.3 PFAS SAMPLES LABORATORY ANALYSIS

All samples were collected and analyzed in accordance with guidelines and best practices established in the Standard Methods for Water and Wastewater or the cited EPA method. Proper QA/QC was implemented by JHU on all instruments used for analysis.

A targeted analysis of 32 unique PFAS was performed by solid phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) following a modified protocol based on EPA Method 537.1 Rev 1 for the analysis of finished drinking water.[1] Details of this methodology were published recently by JHU in peer-reviewed scientific literature for the analysis of various groundwater- and municipal-sourced bottled waters (Chow et al. 2021).[2] Samples collected in 250 mL volumes were extracted and concentrated using mixed-mode weak anion exchange solid-phase extraction (WAX-SPE), which facilitated high recovery and sensitive part-per-trillion level detection of both short and long-chain PFAS for analysis. Prior to extraction, samples were fortified with equal amounts of 20 different stable isotopes of PFAS analytes as internal standards. This internal standardization process allows reproducible and accurate quantification of target analytes, accounting for sample loss during extraction and matrix effects during analysis. Sample concentrations were quantitated based on the relative response of analyte to its isotopically labelled internal standard calibrated to standards of known concentration fortified with an equal amount of internal standard. All detected PFAS concentrations were correctly reported in their acid form.

Reference standards and isotopically labelled internal standards were obtained from Wellington Laboratories as methanolic solutions (Guelph, Canada) except for PFPrA, which was prepared as a standard from neat chemical (Sigma Aldrich). A summary of the 32 target compounds analyzed is provided in Table B-3 including their associated isotopically-labelled internal standards used for quantitation.

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[1] Shoemaker, J.; Tettenhorst, D. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS); Analytical Method EPA/600/R-18/352; U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment: Washington, DC, 2018.

[2] Chow, S. J.; Ojeda, N.; Jacangelo, J. G.; Schwab, K. J. Detection of Ultrashort-Chain and Other per- and Polyfluoroalkyl Substances (PFAS) in U.S. Bottled Water. Water Research 2021, 201, 117292. https://doi.org/10.1016/j.watres.2021.117292.

Table B-3: Summary of PFAS Analytes to be Reported

Acronym	Analyte Name	CAS Number	Internal Standard
Perfluorocarboxylic Acids			
PFPrA	Perfluoropropanoic acid	422-64-0	$[^{13}C_4]$ PFBA
PFBA	Perfluorobutanoic acid	375-22-4	$[^{13}C_4]$ PFBA
PFPeA	Perfluoropentanoic acid	2706-90-3	$[^{13}C_5]$ PFPeA
PFHxA	Perfluorohexanoic acid	307-24-4	$[^{13}C_5]$ PFHxA
PFHpA	Perfluoroheptanoic acid	375-85-9	$[^{13}C_4]$ PFHpA
PFOA	Perfluorooctanoic acid	335-67-1	$[^{13}C_8]$ PFOA
PFNA	Perfluorononanoic acid	375-95-1	$[^{13}C_9]$ PFNA
PFDA	Perfluorodecanoic acid	335-76-2	$[^{13}C_6]$ PFDA
PFUdA	Perfluoroundecanoic acid	2058-94-8	$[^{13}C_7]$ PFUdA
PFDoA	Perfluorododecanoic acid	307-55-1	$[^{13}C_2]$ PFDoA
PFTriA	Perfluorortridecanoic acid	72629-94-8	$[^{13}C_2]$ PFTreA
PFTreA	Perfluorotetradecanoic acid	376-06-7	$[^{13}C_2]$ PFTreA
Perfluorosulfonic Acids			
PFPrS	Perfluoropropane sulfonic acid	423-41-6	$[^{13}C_3]$ PFBS
PFBS	Perfluorobutane sulfonic acid	375-73-5	$[^{13}C_3]$ PFBS
PFPeS	Perfluoropentane sulfonic acid	2706-91-4	$[^{13}C_5]$ PFHxA
PFHxS	Perfluorohexane sulfonic acid	355-46-4	$[^{13}C_3]$ PFHxS
PFHpS	Perfluorheptane sulfonic acid	375-92-8	$[^{13}C_8]$ PFOS
PFOS	Perfluorooctane sulfonic acid	1763-23-1	$[^{13}C_8]$ PFOS
PFNS	Perfluorononane sulfonic acid	68259-12-1	$[^{13}C_6]$ PFDA
PFDS	Perfluorodecane sulfonic acid	335-77-3	$[^{13}C_7]$ PFUdA
Fluorotelomer Sulfonates			
4:2 FTS	4:2 fluorotelomer sulfonate	757124-72-4	$[^{13}C_2]$ 4:2 FTS
6:2 FTS	6:2 fluorotelomer sulfonate	27619-97-2	$[^{13}C_2]$ 6:2 FTS
8:2 FTS	8:2 fluorotelomer sulfonate	39108-34-4	$[^{13}C_2]$ 8:2 FTS
Perfluorosulfonamides			
FBSA	Perfluorobutane sulfonamide	30334-69-1	$[^{13}C_3]$ PFHxS
FHxSA	Perfluorohexane sulfonamide	41997-13-1	$[^{13}C_8]$ PFOS
PFOSA	Perfluorooctane sulfonamide	754-91-6	$[^{13}C_8]$ PFOSA
Sulfonamidoacetic acids			
N-MeFOSAA	N-Methyl-perfluoro-1-octanesulfonamidoacetic acid	2355-31-9	$[^{2}D_3]$ N-MeFOSAA
N-EtFOSAA	N-Ethyl-perfluoro-1-octanesulfonamidoacetic acid	2991-50-6	$[^{2}D_5]$ N-EtFOSAA
Fluoroethers			
HFPO-DA	Hexafluoropropylene oxide-dimer acid	13252-13-6	$[^{13}C_3]$ HFPO-DA
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	$[^{13}C_3]$ PFHpA
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1	$[^{13}C_8]$ PFOS
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	$[^{13}C_7]$ PFUdA

B.3.1 Solid phase extraction (SPE) Procedure

Weak anion exchange cartridges (Water Oasis WAX, 150 mg, 6 cc) were conditioned with sequential rinses of solvent (2×3 mL methanol, 2×3 mL methanol + 0.5% NH_4OH, 2×3 mL reagent water) immediately before use. Prior to extraction, 250 ml of each collected sample were acidified below pH 3.5 with H_2SO_4 and fortified with 2.5 ng of each internal standard. Samples were drawn through PP transfer tubing into a vacuum extraction manifold and extracted dropwise. After extraction, cartridges were rinsed with reagent wanted water and sodium acetate buffer and dried under vacuum for 30 minutes. Analytes were then eluted from the cartridge with 4×2 mL methanol + 0.5% NH_4OH and concentrated to 0.5 mL by air sparging. Samples were effectively concentrated by a factor of 500× in comparison to the original 250 mL sample volume. Sample extracts were centrifuged and aliquoted for LC-MS/MS immediately. The remaining extract volume was stored sealed at 4°C to minimize storage losses in the event of re-analysis.

B.3.2 LC-MS/MS Analysis

LC-MS/MS analysis was conducted using a TSQ Quantiva triple quadrupole mass spectrometer coupled to a Vanquish Flex UHPLC (both Thermo Scientific). Samples were introduced to the instrument for analysis in fluoropolymer-free PP autosample vials as 50/50 mixtures of sample extract and aqueous acetate buffer. Analytes were separated by reverse-phase chromatography based on hydrophobic interactions using a solid-core C18 column (Thermo Fisher Accucore) using a linear water-methanol eluent gradient amended with ammonium acetate buffer. Samples were introduced to the MS using heated electrospray ionization, and the MS was operated in negative ionization mode. Individual analytes were specifically targeted for detection by selected reaction monitoring (SRM), which selects and quantifies PFAS by a unique combination of parent molecular ion and characteristic fragmentation products within a defined retention time window (Table B-4). Analytes were quantified using 8-point internal-standardized calibration curves using standards in methanol ranging from 0.125-250 µg/L, except for PFBA, which also included an additional 500 µg/L calibration standard. Calibration curves were fitted linearly using a *1/concentration* weighing factor.

Table B-4: Summary of Analyte LC Parameters and Calculated Method Detection Limits (MDLs)

Analyte	Retention Time (min)	Precursor Ion (m/z)	Quantifier Product Ion (m/z)	Method Detection Limit (ng/L)
Perfluorocarboxylic Acids (PFCA)				
PFPrA	1.6	163	119	0.45
PFBA	3.5	213	169	0.49
PFPeA	6	263	219	0.36
PFHxA	8.5	313	269	0.3
PFHpA	10	363	319	0.13
PFOA	11.3	413	369	0.17
PFNA	12.4	463	419	0.21
PFDA	13.29	513	469	0.24
PFUdA	14.04	563	519	0.29
PFDoA	14.67	613	569	0.43
PFTriA	15.14	663	619	2.82
PFTreA	15.41	713	669	0.44
Perfluorosulfonic Acids (PFSA)				
PFPrS	4.45	249	80	0.11
PFBS	6.6	299	80	0.18
PFPeS	8.6	349	80	0.16
PFHxS	10.45	399	80	0.26
PFHpS	11.4	449	80	0.24
PFOS	12.3	499	80	0.41
PFNS	13.27	549	80	0.47
PFDS	14	599	80	0.68
Fluorotelomer Sulfonates				
4:2 FTS	8	327	307	0.2
6:2 FTS	11.25	427	407	10.31
8:2 FTS	13.25	527	507	0.27
Perfluorosulfonamides				
FBSA	9.6	298	78	0.54
FHxSA	12.47	398	78	0.45
PFOSA	14.31	498	78	0.29
Sulfonamidoacetic acids				
N-MeFOSAA	13.93	570	419	0.54
N-EtFOSAA	14.35	584	419	0.89
Fluoroethers				
HFPO-DA	8.8	285	169	0.11
ADONA	10.2	377	251	0.14
9Cl-PF3ONS	12.88	531	351	0.41
11Cl-PF3OUdS	14.34	631	451	1.04

B.3.3 Laboratory Quality Control

All reagents, labware and consumables were carefully selected to minimize PFAS contamination. Samples and working chemical stocks were all stored in new, clean, PP containers. The tubing used in the SPE extraction and in the UHPLC system was replaced by PP and PEEK tubing, respectively. In addition, an isolator column (Hypersil GOLD C18, 50mm x 2.1mm; 3 µm; Thermo Fisher) was installed after the LC pump and prior to the injection valve to eliminate potential contamination from solvents.

Method detection limits (MDLs), calculated according to EPA standard methods, were utilized as the minimum reportable concentration used to determine breakthrough of pilot filter beds (Table B-5). These MDL values were determined as either the greater of the calculated concentration value yielding >99% statistical confidence of being significantly greater than zero or the maximum concentration detected within a blank sample during initial performance evaluation. Using this determination, MDLs considered both analytical variability and background contamination in stated method sensitivity. MDL values for analytes detected and tracked in this study were all below the part-per-trillion level (0.11-0.54 ng/L).

Within each sample batch, laboratory blanks, spikes, duplicates, and instrument calibration were performed at the frequency, evaluated with the acceptance criterion, and addressed with the corrective action outlined in Table B-5. Laboratory blanks accounted for potential contamination during sample handling in the JHU analytical lab. Field blanks accounted for potential contamination during sample collection at the field site and during shipment. Sample duplicates ensured reproducible quantitation and collection of samples. Calibration standards ensured reproducible instrument quantitation with each sample batch. Laboratory-spiked blanks assessed the reproducibility and recovery of the extraction and analytical method for each target analyte.

Table B-5: Frequencies, Acceptance Criteria, and Corrective Actions for Laboratory QC

QC Sample Type	Frequency	Acceptance Criterion	Corrective Action
Laboratory blank	Per set of 20	Below method detection limit (MDL)	Identified source of contamination and reanalyzed associated samples
Field blank	Per set of 20	Below method detection limit (MDL)	Identified source of contamination, determined whether systemic contamination occurred, and rejected samples from batch.
Sample duplicate(a)	Per set of 20	RPD ± 25%	Identified source of variation. Reanalyzed.
Laboratory spiked blank	Per set of 20	75-125% recovery	Identified source of analytical inaccuracy and reanalyzed.
Calibration(b)	Per sample run	8-point calibration curve ($r^2 > 0.99$). Analyte RPD ± 25%. ISTD RPD ± 30%	Investigated the source of analytical variability, resolved the problem, and recalibrated.

(a) Sample was randomly selected from one of the active pilot sample ports during each week of pilot sample collection.

Appendix C PILOT OPERATIONAL RESULTS

C.1 FLOW RATES

Each column's influent flow was monitored via a magnetic flow meter for data logging and flow rate control. IX columns had a target flow rate of 0.45 gpm to achieve an EBCT of 2.5 minutes. The GAC column had a target flow rate of 1.94 gpm to achieve an EBCT of 10 minutes. Over the course of the pilot flow rates tended to oscillate around the design points and pump frequencies were manually adjusted to fix variations in flow caused by differential pressure, storage tank head, and pump hardware. The column pumps contained stators, and flow rates would severely oscillate when the stator was degraded or damaged and required replacement.

Figure C-1 and Figure C-2 provide flow rate data over the course of the study. Despite the variability in flow rate, all columns averaged the desired flow rate over the course of the pilot, as shown in Table C-1.

C.2 EMPTY BED CONTACT TIME

Although the goal flow rates were all achieved over the course of the pilot, the resulting empty bed contact times (EBCTs) were marginally longer than desired EBCTs due to slight expansions of the media beds. The desired and actual media bed depths and EBCTs are shown along with flow rates in Table C-1.

Table C-1: Pilot design basics

Parameter		GAC	IX1	IX2	IX3	IX4
Flowrate	Goal	1.94 gpm	0.45 gpm	0.45 gpm	0.45 gpm	0.45 gpm
	Actual	1.93 gpm	0.45 gpm	0.45 gpm	0.45 gpm	0.45 gpm
Media Bed Depth	Goal	90.4”	36.0”	36.0”	36.0”	36.0”
	Actual	92.0”	38.7”	39.0”	38.6”	38.7”
EBCT	Goal	10.0 min	2.5 min	2.5 min	2.5 min	2.5 min
	Actual	10.5 min	2.6 min	2.6 min	2.6 min	2.6 min

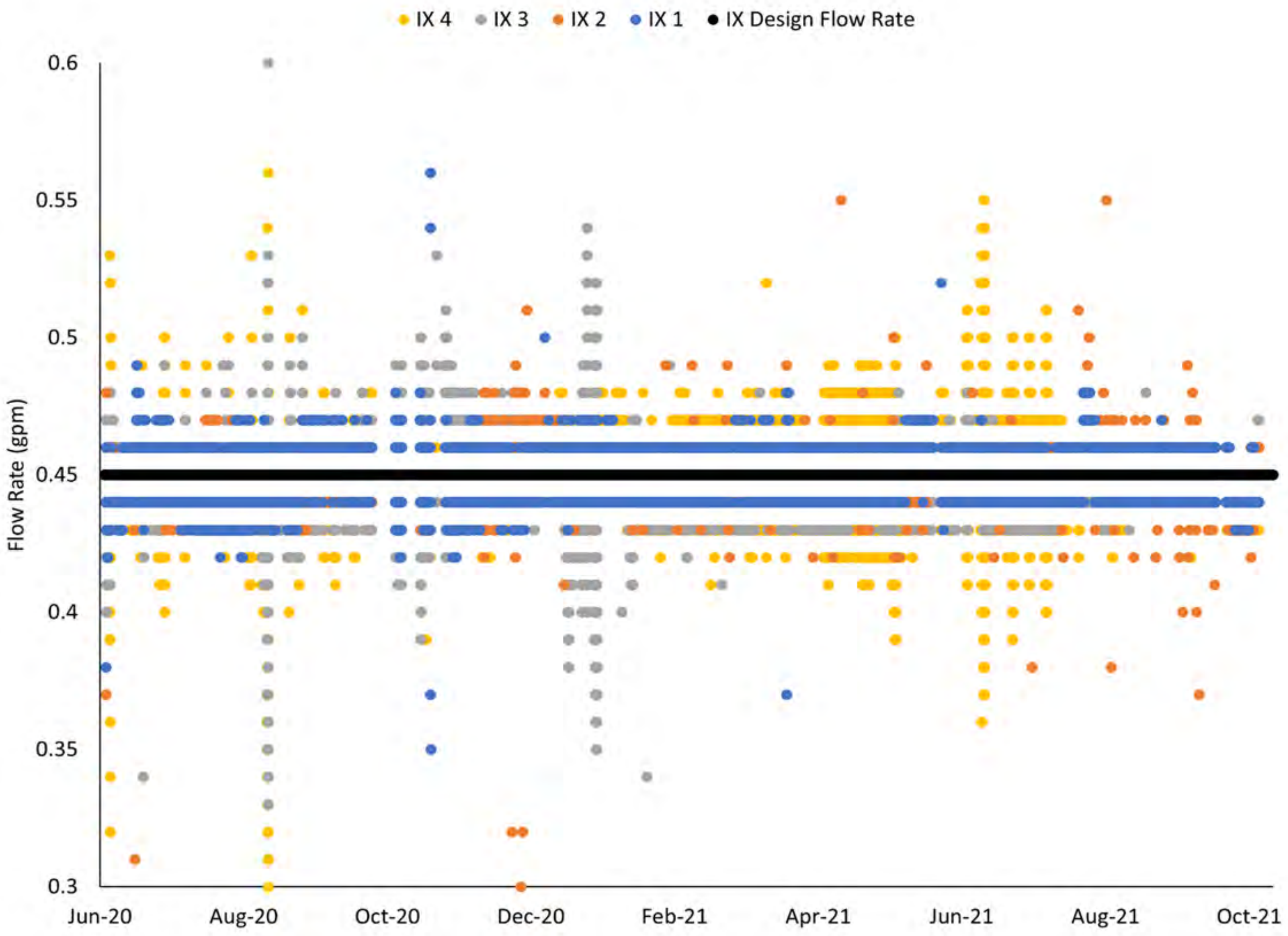

Figure C-1: Ion Exchange Columns Flow Rate

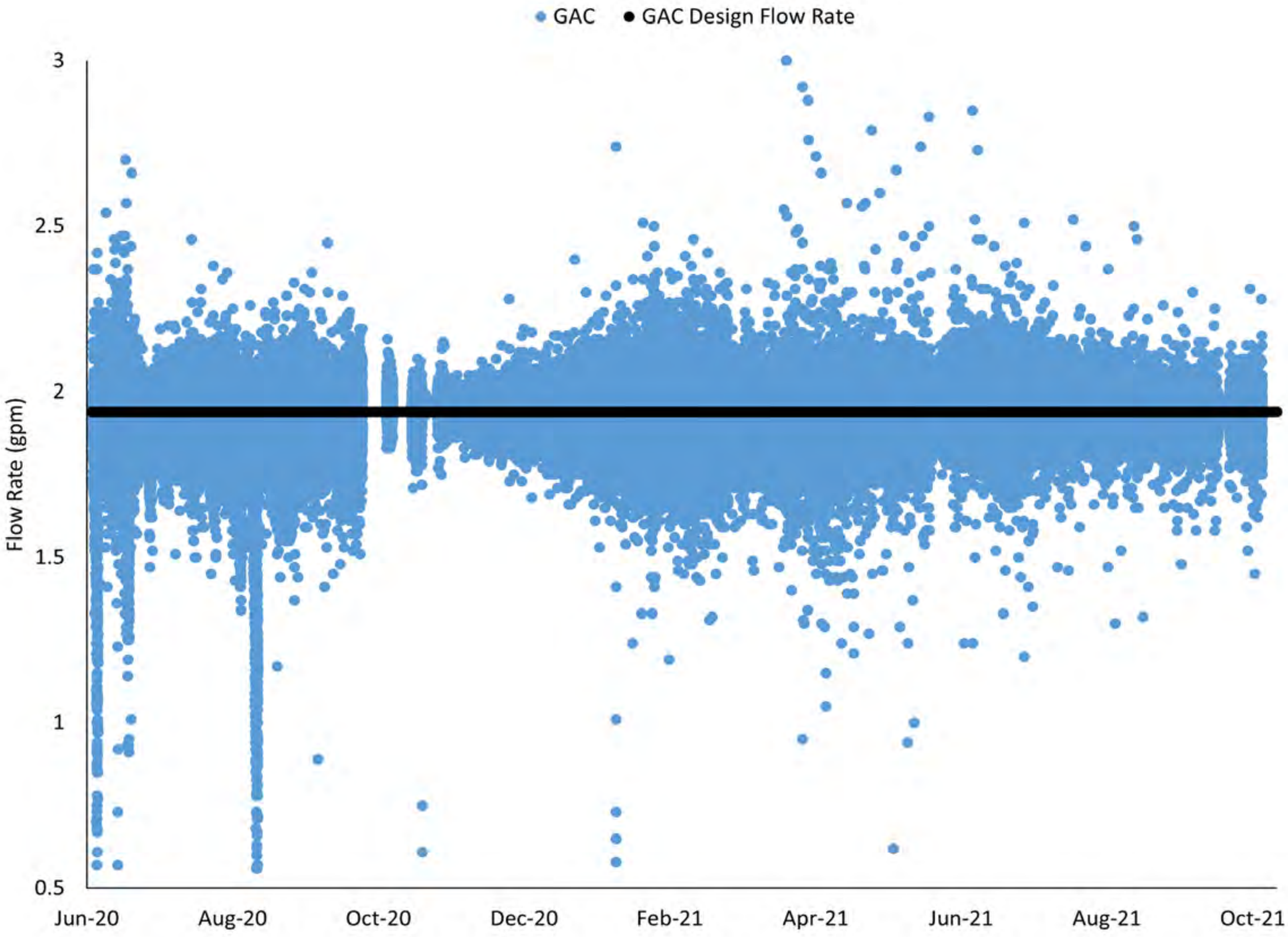

Figure C-2: GAC Column Flow Rate

Appendix D WATER QUALITY

Properly characterizing the background water quality during the pilot study was important because the GAC and IX treatment processes utilized in the pilot can be significantly impacted by background parameters such as total organic carbon, turbidity, and iron. These parameters, along with several others, were tested on a regular basis to ensure good water quality throughout the pilot system over time. The full results of this water quality sampling are shown in Table D-1 and Table D-2.

Table D-1: JHU Analyzed Water Quality Parameters Mean and Standard Deviation with Filox Pretreatment

	TOC (mg/L)	Alkalinity (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
Raw	0.90 ± 0.90	217 ± 15	37.2 ± 2	0.76 ± 0.13	57.8 ± 2.4
GAC Influent	0.85 ± 0.79	227 ± 28	35.3 ± 8	0.75 ± 0.16	57.7 ± 2.2
GAC Port 1	0.98 ± 1.26		36.3 ± 3	0.79 ± 0.12	57.6 ± 2.4
GAC Port 2	1.35 ± 2.50		37.0 ± 2	0.82 ± 0.12	57.3 ± 2.2
GAC Effluent	1.65 ± 3.65	227 ± 21	36.4 ± 3	0.77 ± 0.12	56.9 ± 4.3
IX 1 Port 1	0.83 ± 0.77		37.3 ± 2	0.81 ± 0.10	57.1 ± 1.9
IX 2 Port 1	0.65 ± 0.51		37.7 ± 2	0.81 ± 0.09	58.2 ± 1.6
IX3 Port 1	1.86 ± 4.93		37.1 ± 2	0.76 ± 0.13	58.3 ± 1.6
IX4 Port 1	1.07 ± 0.92		37.4 ± 2	0.77 ± 0.14	58.4 ± 1.4
IX3 Port 2	0.76 ± 0.68		37.1 ± 2	0.76 ± 0.12	58.1 ± 1.6
IX4 Port 2	0.87 ± 0.74		37.1 ± 2	0.75 ± 0.13	58.0 ± 1.9
IX3 Port 3	1.00 ± 1.6		37.0 ± 2	0.76 ± 0.13	58.1 ± 1.6
IX4 Port 3	1.72 ± 4.3		37.4 ± 2	0.78 ± 0.14	58.5 ± 1.3
IX1 Effluent	2.15 ± 4.43	227 ± 22	37.0 ± 2	0.79 ± 0.17	57.8 ± 2.1
IX2 Effluent	0.69 ± 0.73	217 ± 17	36.9 ± 2	0.77 ± 0.13	57.5 ± 2.3
IX3 Effluent	1.18 ± 1.54	229 ± 34	36.9 ± 2	0.78 ± 0.17	57.8 ± 2.5
IX4 Effluent	1.19 ± 2.19	228 ± 31	37.2 ± 2	0.77 ± 0.13	58.2 ± 2.2

*Nitrite levels were non-detectable

Table D-2: Basic and Metal Water Quality Parameters Mean and Standard Deviation with Filox Pretreatment

	pH N=29	**Turbidity (NTU) N=29**	**Conductivity (µs/cm) N=29**	**Temperature (ºC) N=29**	**Total Mn (ug/L) N=5**	**Soluble Mn (ug/L) N=5**	**Total Fe (g/L) N=9**	**Soluble Fe (mg/L) N=9**
Raw	7.51 ± .12	0.14 ± 0.08	634 ± 11	10.9 ± 0.6	60 ± 10	60 ± 10	0.131 ± 0.016	0.078 ± 0.019
Pretreatment Effluent	7.53 ± .13	0.35 ± 0.51	635 ± 10	11.0 ± 0.8	20 ± 10	20 ± 10	0.065 ± 0.012	0.016 ± 0.005
Tank Effluent	7.50 ± .12	0.16 ± 0.08	639 ± 7	11.0 ± 0.5				
Cartridge Effluent	7.50 ± .14	0.12 ± 0.05	642 ± 11	11.1 ± 0.4	10 ± 10	10 ± 10	0.068 ± 0.016	0.014 ± 0.005
GAC Effluent	7.49 ± .13	0.10 ± 0.05	641 ± 7	11.2 ± 0.4	20 ± 10	<10	0.066 ± 0.011	0.011 ± 0.004
IX1 Effluent	7.58 ± .09	0.10 ± 0.04	641 ± 8	11.9 ± 0.6				
IX2 Effluent	7.55 ± .10	0.11 ± 0.07	642 ± 7	11.8 ± 0.5				
IX3 Effluent	7.50 ± .11	0.11 ± 0.06	642 ± 7	11.6 ± 0.6	<10	<10	0.066 ± 0.009	0.012 ± 0.004
IX4 Effluent	7.48 ± .14	0.10 ± 0.05	642 ± 7	11.4 ± 0.5	<10	<10	0.068 ± 0.010	0.013 ± 0.007

*Reporting Limit for Manganese was 10 ug/L at RMB Labs. In average value calculations, measurements reported as less than 10 ug/L were assumed to be 10 ug/L.

Temperature and conductivity marginally increased throughout the treatment train. Figure D-1 is the turbidity profile. Precipitated metals and Filox grains escaped pretreatment vessels increasing effluent turbidity. Particulates then settled out in the break tanks and particles larger than 1 micron were captured in the cartridge filter. Turbidity decreased as the water traveled through the rest of the treatment train.

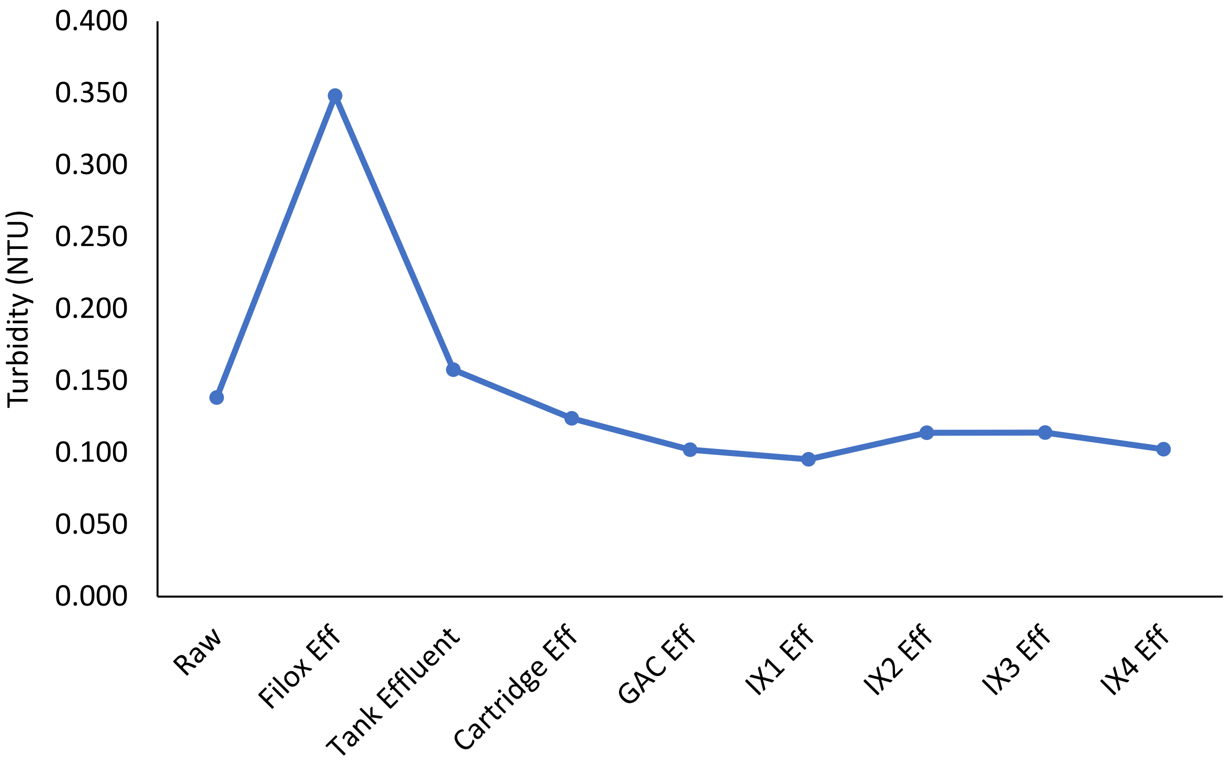

Figure D-1: Treatment Train Effluent Turbidity

The dissolved oxygen (DO) sensor, located on the pilot influent line, measured the DO concentration following the break tanks. The DO sensor accumulated sludge buildup and required cleaning every 6 months.

Pretreatment backwash includes an aeration step to provide an oxidizer for iron causing increased DO during backwash, three times a week. After the pretreatment, DO is undesirable within the columns because of its potential to precipitate metals and react with the media. Figure D-2 is a snapshot of one month's dissolved oxygen pattern.

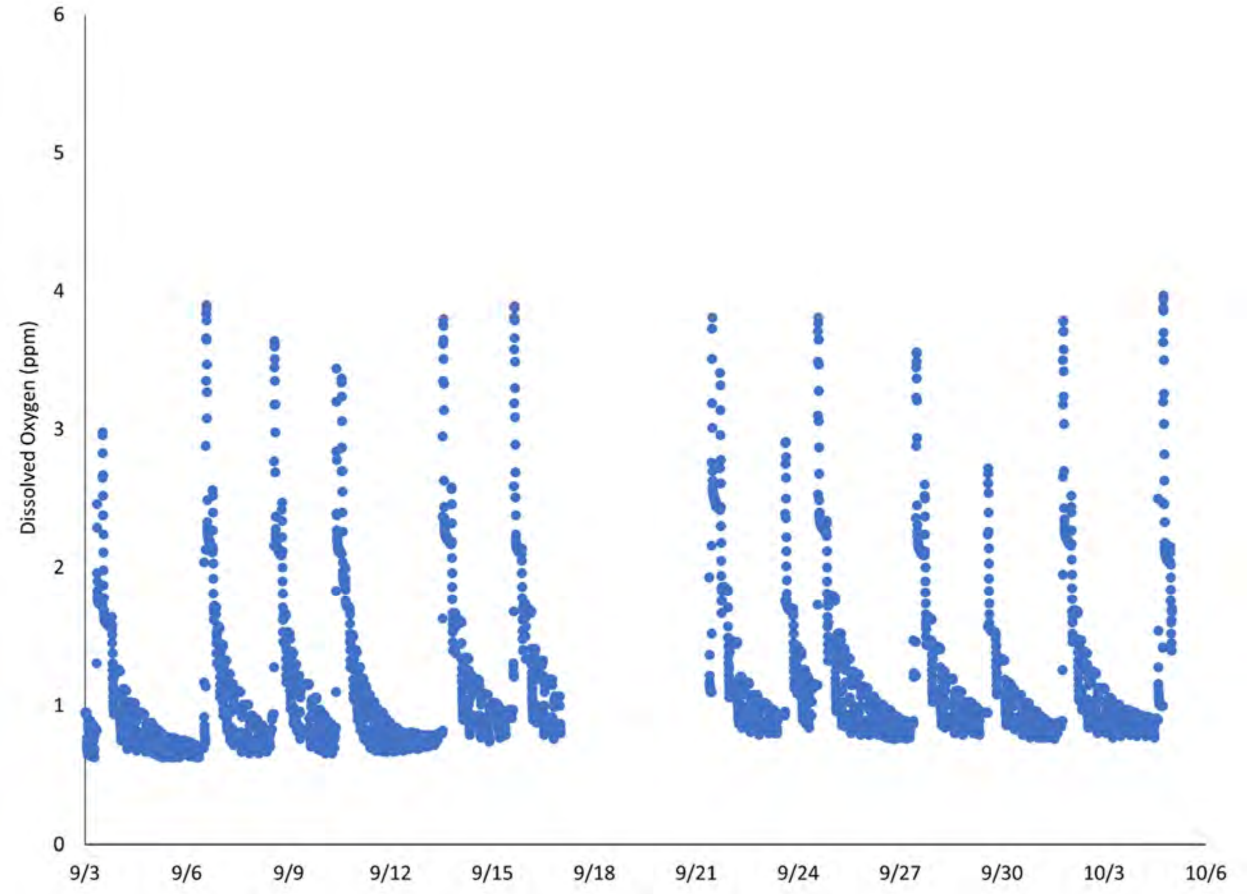

Figure D-2: Influent GAC Column Dissolved Oxygen Concentration

Appendix E ADDITIONAL PFAS TREATMENT RESULTS

The PFAS treatment results were further analyzed by cumulative loading capacity in terms of millimole of PFAS per liter of media (mmol PFAS/L of media) and by the relationship between time to 10% breakthrough and chain length.

E.1 CUMULATIVE LOADING CAPACITY

The cumulative loading capacity of the medias at Port 1 were calculated over the course of the pilot by using the difference between the influent and effluent concentrations and integrating over the flow to each column between discrete sample intervals as shown in Figure E-1. As PFAS sorbed to the media, the sorbed concentrations increase, but then as some PFAS begin to desorb the concentrations of those compounds decrease. In the case of PFPrA, the Reimann sum indicated that more of the compound desorbed than initially adsorbed, leading to a negative cumulative sorbed concentration. However, this is almost certainly due to fluctuations in influent concentrations between sample times for these compounds that resulted in a negative mass balance.

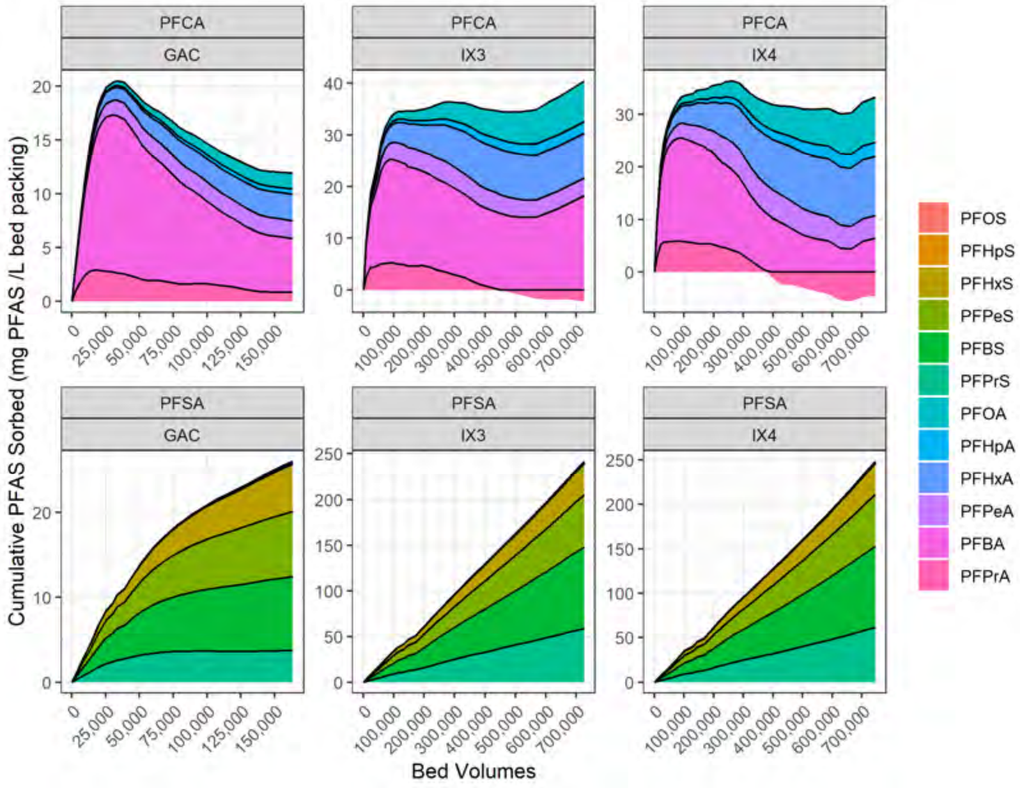

Figure E-1: Cumulative mass density of PFAS sorbed to each column over the course of pilot operation at Port 1. Mass density represented as cumulative stacked plots, normalized to the total bed volume within the analyzed column segments.

As can be seen from Figure E-1, both GAC and the IX resins evaluated had a similar maximum capacity for PFCAs over the course of the pilot, on the order of 20-40 mg PFAS/L of media. However, the retention of these maximum PFCA molar capacities was significantly different between the GAC and IX medias. In the case of the GAC media, the cumulative sorbed concentration of PFCAs decreased in relation to the increase of cumulative sorbed concentration of PFSAs. This seems to indicate that there was a finite sorption capacity available in the GAC media, which for the case of this pilot appeared to be approximately 36 mg PFAS/L of media. In contrast, the cumulative sorbed concentration of PFCAs on the IX media was maintained at approximately 35 mg PFAS/L of media even as PFSAs were adsorbed at significantly higher cumulative concentrations. This appeared to indicate that, like GAC, the IX medias had a finite number capacity for the sorption of PFCAs. However, the significant increase in cumulative concentration of PFSAs over the course of the pilot, which showed no signs of plateauing, suggest that there was significantly more sorption capacity in IX media (>270 mg/L) available for PFSAs, perhaps because they are stronger acids than PFCAs.

It is important to note that the cumulative sorption capacities shown above are specific to the source water, due to sorption competition between individual PFAS, background anions, and other foulants, and cannot be used as generally as isotherm information.

E.2 BREAKTHROUGH AND CHAIN LENGTH

While the relationship between compound chain length and time to breakthrough was discussed in the body of the report, a more formal examination is provided here. Specifically, the number of bed volumes to 10% breakthrough of each compound was plotted against compounds for each class ordered by chain-length, as shown in Figure E-2. This study found that the relationship between time to 10% breakthrough and the fluorinated carbon chain length was approximately linear for the GAC media but followed an exponential relationship for the IX medias. These differing relationships demonstrate the increased efficacy of IX versus GAC media for longer-chain compounds, a difference that is particularly strong for PFSA compounds.

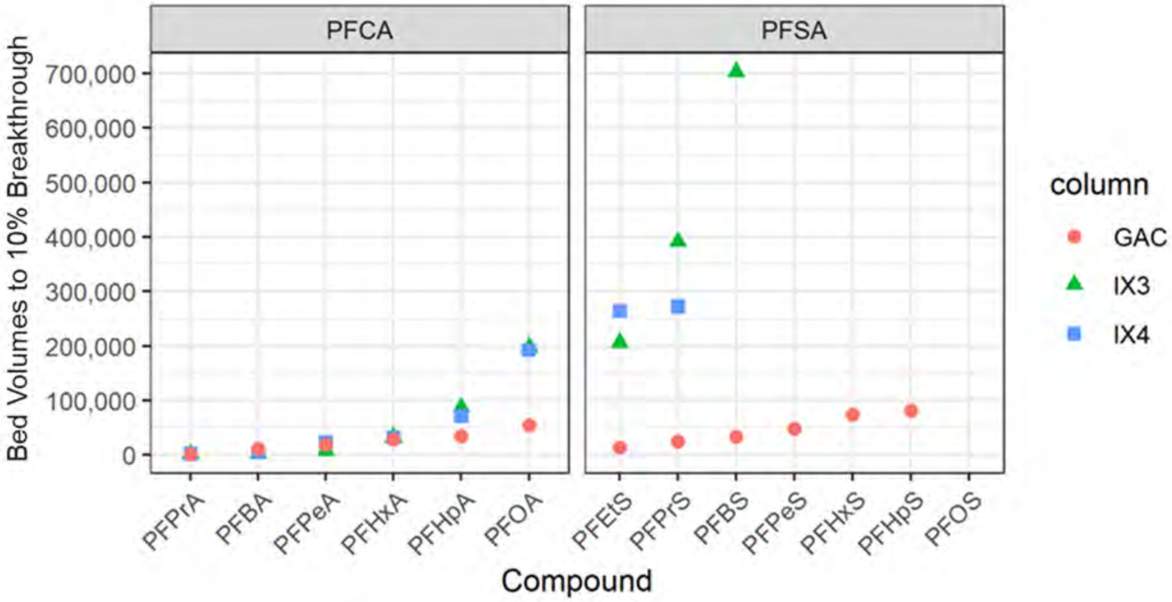

Figure E-2: Initial breakthrough bed volumes for PFCA and PFSA compounds in each column, ordered by increasing chain-length

Appendix F PILOT STUDY POLICY GUIDANCE

Several of the elements of this pilot study inform key aspects to be considered in the development of an ion exchange pilot study policy. These elements are summarized in brief in the following points.

- Pilot column diameters should be large enough to prevent side-wall effects.
- Effort should be made to limit raw water exposure to the atmosphere, provided this is the anticipated full-scale treatment configuration. Should full-scale treatment be anticipated to expose raw water to the atmosphere this should be replicated within the pilot.
- Pilots should be designed with pretreatment or with a contingency to add pretreatment in a timely manner.
- The use of intermediate ports was helpful to allow detection of early breakthrough within the media bed.
- Online monitoring of differential pressure across media beds was a helpful tool to track fouling.
- PFAS samples should be collected and analyzed no less frequently than once a month to reliably establish breakthrough curves for the different PFAS present in source water. Weekly sampling should be considered for the first month.
- The pilot run time should be sufficient to allow for reasonable evaluation of media bed life as needed for full-scale facility design. Depending on the media being evaluated and the PFAS concentrations within the raw water this could require a long study (>1 year).
- Pilot column construction using clear columns was helpful for media observation, however clear columns should be covered when not under visual observation.