



May 29, 2019

Environmental Review Commission
Jeffrey Hudson, Commission Counsel
300 North Salisbury Street, Suite 545
Raleigh, NC 27603

NCLG Fiscal Research Division
Mark Trogon, Director
300 North Salisbury Street, Suite 619
Raleigh, NC 27603

Re: Session Law 2018-5, Section 13.1.(e) Final Report on activities related to grant-in-aid to Cape Fear Public Utilities Authority (CFPUA) in the amount of \$450,000 to perform large scale pilot testing on Granular Activated Carbon (GAC) and Ion Exchange (IX) media for per- and poly-fluoroalkyl substances (PFAS)

Dear Sir or Madam,

Cape Fear Public Utility Authority has completed activities compliant with Session Law 2018-5 Section 13.1.(e) and is pleased to submit this Final Report of technical findings in the form of the attached Pilot Report prepared by HDR. The Pilot Report presents the activities and findings of the pilot test and includes Appendix F prepared by the UNCW Marine and Atmospheric Chemistry Research Laboratory which provides Analysis of non-Targeted Perfluoroalkyl Substances in Water Treated for Aquifer Storage and Recovery.

Thank you for the opportunity to conduct this research. Please contact me for any additional information related to this pilot project.

Sincerely,

A handwritten signature in black ink, appearing to read 'J. R. Flechtner', is written over a light blue horizontal line.

James R. Flechtner, P.E.
Executive Director

Attachment



Pilot Report

Granular Activated Carbon and Ion Exchange
Groundwater Treatment Pilot Test Report

Cape Fear Public Utility Authority

Wilmington, NC
May 24, 2019



5/24/19

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Glossary of Terms

Term	Definition
Aquifer Storage and Recovery (ASR)	The direct injection of water into an aquifer for later use.
Bed volume	The volume occupied by the GAC bed.
Breakthrough	The time when the concentration exceeds the treatment objective in the effluent.
Compound of Emerging Concern (CEC)	A group of compounds with no regulatory standard that has recently been detected in water and may pose negative effects to public health or the environment. This includes pharmaceuticals, personal care products, industrial chemicals and endocrine disruptors.
Empty bed contact time (EBCT)	A measure of the time when water is in contact with the media bed in a filter. Calculated by dividing the total volume of the media bed (including pore space) by the flow rate across the bed.
Granular activated carbon (GAC)	A form of particulate carbon manufactured with increased surface area per unit mass to enhance the adsorption of soluble contaminants.
Heating, Ventilating, and Air Conditioning (HVAC)	A system that provides heating, ventilation, and air conditioning.
Health Advisory Level (HAL)	The concentration in drinking water at which there are no adverse health effects.
Ion exchange (IX)	A water treatment process by which one or more contaminants is removed from water by exchanging with another substance imbedded in a manufactured resin.
Lead/Lag (LL)	A configuration where two processes are operated in series.
Maximum Contaminant Level (MCL)	The maximum level allowed of a contaminant in water which is delivered to a user of a public water system.
Method detection limit (MDL)	The minimum concentration of a substances that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.
No observed adverse effect level (NOAEL)	The highest dosage level at which chronic exposure to the substance shows no adverse health effects.
Poly- and Perfluoroalkyl Substances (PFAS)	A group of man-made chemicals containing primarily carbon-fluorine bonds and carbon-carbon bonds that are used in industrial processes, are found in aqueous film forming foam, and found in a variety of consumer products.
Secondary Maximum Contaminant Level (SMCL)	A non-enforceable guideline established by the EPA for constituents that are not considered to present a risk to human health.
Supervisory Control and Data Acquisition (SCADA)	A control system that uses computers, networked data communications, and graphical user interfaces to control, monitor and gather information, and process real-time data.
Total organic carbon (TOC)	A measure of the amount of organic carbon found in a water sample, often used as a non-specific indicator of water quality.
UV Absorbance at 254 nm (UV254)	Provides an indication of the concentration of organic matter, specifically those that contain aromatic rings or unsaturated bonds in their molecular structures. Often a surrogate for TOC.

Executive Summary

In the past several years, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), two long-chain poly and perfluoroalkyl substances (PFAS), have been detected in drinking water sources throughout the U.S. and worldwide. PFOS and PFOA have Environmental Protection Agency (EPA) lifetime drinking water health advisory levels (HALs) set for 70 ng/L, individually or combined. Long-chain PFAS (those with ≥ 8 carbons in their chemical formula) are generally considered to be more bioaccumulative, although easier to remove through certain treatment processes compared to short-chain PFAS (those with < 8 carbons in their chemical formula).

The Cape Fear Public Utility Authority (Authority) operates an Aquifer Storage and Recovery (ASR) system to supplement their potable water supply through the storage of treated water from the Sweeney Water Treatment Plant (WTP) in the Peedee Aquifer. Industrial discharge into the Cape Fear River has led to both long- and short-chain PFAS detections, including GenX, in the Sweeney WTP intake and finished drinking water. Consequently, PFAS contamination has been detected in ASR water. As a result of PFAS contamination, the ASR system is currently out of service and 50 million gallons of ASR water have been withdrawn from the Peedee aquifer and discharged to the James A. Loughlin (Northside) Wastewater Treatment Plant (WWTP).

As a result of PFAS contamination at the ASR site, the Division of Water Infrastructure (DWI) of the Department of Environmental Quality (DEQ) has granted the Authority funds, per North Carolina Session Law 2018-5, to perform non-targeted sampling of finished water in its ASR system. Additionally, funds have been provided to perform pilot-testing to determine the relative effectiveness of granular activated carbon (GAC) and ion exchange (IX) to treat contaminated water. GAC and IX are two well-established technologies in drinking water treatment. GAC uses carbon media while IX uses a synthetic resin to achieve constituent removal from water. These treatment technologies remove constituents such as organic carbon, color, taste and odor compounds, compounds of emerging concern (CEC), and PFAS through adsorption and ion exchange mechanisms.

GAC and IX main pilots and GAC, IX, and GAC/IX lead/lag mini columns operated continuously for 13 weeks, from January through April 2019, to evaluate the efficacy of these technologies for PFAS removal at the ASR site. GAC and IX main pilot flow rates ranged from 130 to 250 gallons per minute (gpm) and GAC, IX, and GAC/IX mini columns operated at 0.2, 1.0, and 0.2/0.2 gpm, respectively. 42 PFAS were monitored weekly to evaluate the extent of contamination and evaluate treatment efficacy of GAC and IX treatment on both long-chain and short-chain PFAS. Additionally, traditional water quality parameters (e.g. organics, color, etc.) were routinely measured, and CECs and a select group of non-routine water quality parameters were periodically monitored in influent and effluent of the main pilot units.

Results from the pilot study show that GAC provided superior total PFAS, TOC, and UV254 removal compared to the IX pilot, and total PFAS removal did not plateau as quickly in the GAC pilot compared to the IX pilot. Additionally, the GAC main pilot provided superior removal of long-chain PFAS compounds, GenX, and many CECs compared to the IX pilot. For these reasons, GAC treatment is the recommended PFAS removal technology for the Peedee Aquifer.

Introduction

The Cape Fear Public Utility Authority (Authority) operates an Aquifer Storage and Recovery (ASR) system to supplement their potable water supply through the storage of treated water from the Sweeney Water Treatment Plant (WTP) in the Peedee Aquifer. The purpose of the Westbrook ASR system is to provide potable water that can later be withdrawn during peak demand times. The ASR system has a capacity of 1 million gallons per day (mgd).

In 2016, the Environmental Protection Agency (EPA) established a lifetime drinking water health advisory level (HAL) for two poly- and perfluoroalkyl substances (PFAS): perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), individually or combined, of 70 ng/L. Short-chain PFAS, including GenX, have been developed as an alternative PFAS to PFOS and PFOA. Industrial discharges have increased the concern regarding GenX release in source water that impacts the Sweeney WTP. The North Carolina Department of Health and Human Services (NC DHHS) has established a health goal for GenX of 140 ng/L in drinking water. In July of 2017, NC DHHS determined that adverse health effects to the most vulnerable population (bottle-fed infants) could be realized over a lifetime of consuming water with levels greater than 140 ng/L. The GenX health goal is based on intermediate (sub-chronic) health effects from animal studies using an uncertainty factor of 1,000 and a no-observed-adverse-effect-level (NOAEL) of 0.1 mg/kg/day.

Due to PFAS contamination largely comprised of GenX in the Cape Fear River and technology limitations at the Sweeney WTP, the Sweeney WTP finished water injected into the ASR system was contaminated with PFAS. Consequently, the ASR system is currently out of service and 50 million gallons of water have been withdrawn from the aquifer and disposed by the Authority at the James A. Loughlin (Northside) Wastewater Treatment Plant (WWTP).

As a result of PFAS contamination in the ASR site, the Division of Water Infrastructure (DWI) of the Department of Environmental Quality (DEQ) granted the Authority funds, per NC Session Law 2018-5, to perform non-targeted sampling of finished water in its ASR system. Additionally, funds have been provided to perform pilot-testing to determine the relative effectiveness of granular activated carbon (GAC) and ion exchange (IX) to treat this contaminated water.

The primary goal of this study was to evaluate GAC and IX treatment efficacy of PFAS, specifically GenX, from the ASR site. Secondary goals of this project included evaluating flexibility for additional constituent removal, such as contaminants of emerging concern (CECs), anions, and metals. The last objective was to determine design and operational parameters for a full scale treatment system, including media/resin regeneration/replacement frequency and flow rates.

The purpose of this memorandum is to present an overview of the CFPUA pilot-testing and determinations made for PFAS treatment. Included are the materials and methods employed during pilot operation, including pilot procurement and operating parameters. Additionally, this memorandum presents main pilot (up to 250 gpm) and mini pilot results (0.2 gpm and 1.0 gpm) for PFAS, CECs, and other relevant water quality and operational parameters. Lastly, recommendations for full-scale treatment implementation and estimated capital costs are provided.

Materials and Methods

Both pilot trains were installed by the same contractor, Water and Waste Systems Construction, Inc., who was selected through a public bidding process as the lowest responsive, responsible bidder. The contractor's equipment vendor, Calgon, Inc., provided pilot equipment as well as on-site service during start-up and operation of the main pilot trains and mini pilot columns. Figure 1 presents a timeline of events leading up to continuous pilot operation in January of 2019.

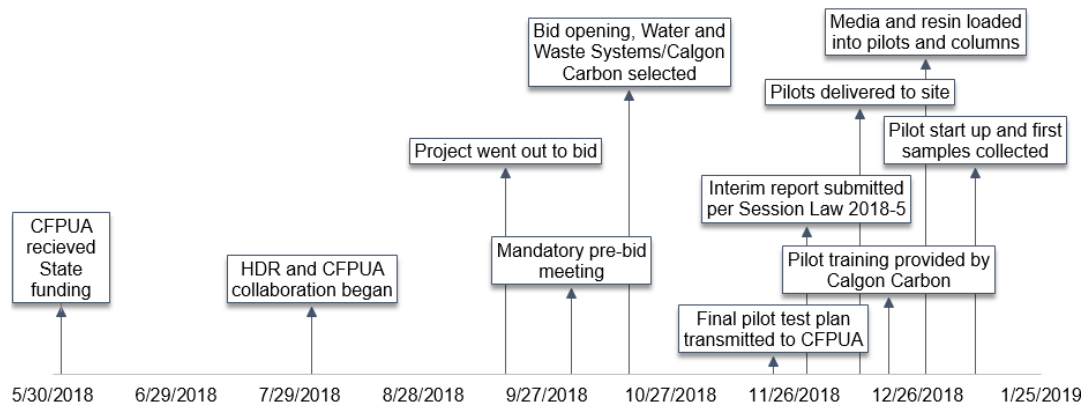


Figure 1. Pilot Procurement Timeline

Pilot System Overview

The Senate bill established the following test conditions: i) install temporary IX and GAC systems suitable to treat a minimum 500 gpm flow; ii) after installation of the temporary treatment systems, test the water weekly, before and after treatment, over a six week period at increasing flow rates to determine the relative effectiveness of IX and GAC at reducing PFAS, including GenX; iii) after determination of the most successful treatment technology at a high flow of 500 gpm, continue sampling at two week intervals thereafter.

The existing ASR pump has a maximum capacity of 700 gpm; therefore it was not possible to operate both pilots at 500 gpm. Additionally, it was desired to evaluate both GAC and IX at multiple empty bed contact times (EBCTs), since EBCT is a key design parameter related to PFAS removal capabilities. Furthermore, operating the IX and GAC one at a time was not feasible due to the short time constraints. Feasible treatment options were reviewed with the NC DEQ and approval was obtained to operate pilots in parallel under equal conditions at all times, with flow rates up to 250 gpm per train. Three scenarios were operated in parallel according to Table 1, and a simplified schematic of main pilot trains and mini pilot columns is shown in Figure 2.

Table 1. Testing Scenarios

Test Scenarios	Purpose
GAC and IX Main Pilot Trains in Parallel	To evaluate GAC and IX simulating large-scale ASR potable water treatment.
GAC and IX Mini Pilot Columns in Parallel	To evaluate PFAS breakthrough in GAC and IX processes. Mini pilot columns will be scaled-down versions of the pilot trains.
GAC-IX Mini Pilot Columns in Series	To determine the PFAS breakthrough in a GAC/IX lead/lag configuration.

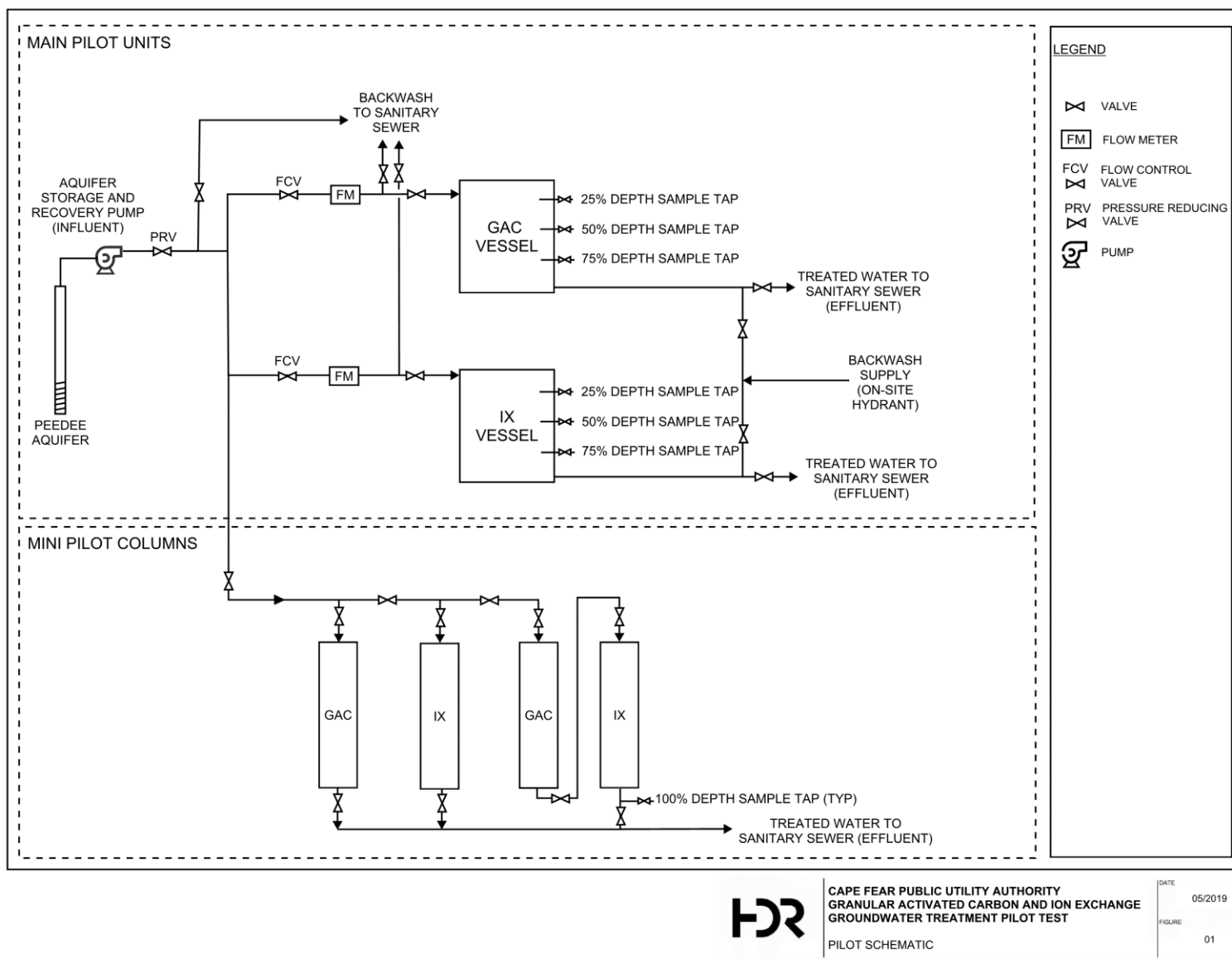


Figure 2. Main Pilot and Mini Pilot Column Schematic

GAC and IX main pilot vessels and mini pilot columns are shown in Figure 3. Detailed main pilot train drawings provided by Calgon are presented in Appendix A. The 4-inch diameter mini pilot columns used for this project were previously used at the Sweeney WTP.



Figure 3. Main Pilot Trains (left) and Mini Pilot Columns (right)

It was expected that breakthrough may not be reached in the main pilots due to the short timeframe of this project; therefore, intermediate sample ports at 25%, 50%, and 75% bed depths in addition to the 100% bed depth sampling port were provided for depth-wise sampling. Figure 4 shows sampling port taps located at the three partial bed depths. Drawings provided by Calgon show a profile of intermediate sampling port locations in Appendix A.



Figure 4. 25%, 50% and 75% Bed Depth Sampling Ports

Pilot Operation

Main pilot train flow rates were periodically increased throughout this study to evaluate the removal of PFAS at multiple flow rates and maximum treatment conditions. Additionally, evaluating GAC and IX at various EBCTs was desired since research has shown that increased EBCTs often result in increased constituent removal. Table 2 presents flow rates and EBCTs evaluated, along with the duration of each operating scenario. Flow rates remained equal between the two main pilot trains during the entire period of operation. A period of at least six weeks was required for evaluations using the high flow rate per Session Law 2018-5. IX media generally requires less contact time compared to GAC media for comparable PFAS removal; therefore, values presented in Table 2 show lower EBCTs for IX compared to GAC. The lower EBCT requirement for IX resin is due to the differences between IX resin and GAC media. For example, IX resins generally have larger surface areas compared to GAC media and thus require much lower EBCTs to effectively treat the same volume as GAC. Calgon Filtrasorb 400 GAC media (main pilot bed depth = 50") and Calgon CalRes 2301 IX resin (main pilot bed depth = 28") was evaluated in this pilot study. The GAC main pilot train was able to be operated at a higher EBCT compared to the IX main pilot train by containing additional media. An example EBCT calculation is provided below using the GAC mini pilot column, which had a diameter of 4 inches and a media depth of 26 inches.

$$Area = \frac{\pi}{4} \left[(4 \text{ in}) \left(\frac{1 \text{ ft}}{12 \text{ in}} \right) \right]^2 = 0.0872 \text{ ft}^2$$

$$Column \text{ Volume} = (0.0872 \text{ ft}^2)(36 \text{ in}) \left(\frac{1 \text{ ft}}{12 \text{ in}} \right) = 0.26 \text{ ft}^3$$

$$EBCT = \frac{Volume}{Flow \text{ Rate}} = \frac{0.26 \text{ ft}^3 * 7.48}{0.2 \text{ gpm}} = 10 \text{ minutes}$$

Table 2. Main Pilot Train Flow Rates and EBCTs Evaluated

Flow Rate (gpm)	GAC EBCT (min)	IX EBCT (min)	Start Date	End Date	No. Weeks
130	20	4	1/9/2019	1/25/2019	2.5
175	15	3	1/25/2019	2/12/2019	2.5
250	10	2	2/12/2019	4/8/2019	8

Alternatively, mini pilot columns operated at consistent flow rates and EBCTs throughout this study, as shown in Table 3. Keeping mini pilot column flow rates consistent allowed media and resin performance and PFAS breakthrough to be characterized under steady state conditions.

Table 3. Mini Pilot Column Flow Rates and EBCTs Evaluated

Column	Flow Rate (gpm)	EBCT (minutes)	No. Weeks
GAC Mini	0.2	10	13
IX Mini	1.0	2	13
GAC / IX (Lead / Lag)	0.2 / 0.2	10 / 7.6	13

Data Collection

Routine water quality monitoring was performed on samples collected from a common influent sample port in addition to GAC and IX main pilot train effluent sample ports and mini pilot columns. Main pilot train operational and water quality parameters were collected according to Table 4. Flow rate measurements and PFAS samples were the only parameters collected from the mini pilot columns. Data were entered into a spreadsheet by Authority staff and transmitted weekly to HDR for analysis. In some cases, analytical measurement of PFAS samples by the certified lab required two to four weeks before transmittal to Authority.

Daily samples were collected as close to the same time each day as possible, and parameters collected three times per week and weekly were collected on the same days of the week every week, when possible. A complete list of the 42 PFAS and 29 CECs/non-routine compounds evaluated is presented in Appendix B. A wide range of PFAS was selected for analysis to evaluate the efficacy of GAC and IX at removing both long- and short-chain compounds. Sampling for PFAS and CECs/non-routine water quality compounds was conducted by Catlin Engineers and Scientists (Catlin) and analyzed by GEL Laboratories, LLC (GEL) or Eurofins Eaton Analytical (Eurofins). Eurofins also provided analytical services for some of the more traditional water quality parameters, including total organic carbon (TOC). The University of North Carolina at Wilmington (UNCW) conducted an analysis of non-targeted PFAS at the ASR site. UNCW results are presented in Appendix F.

Table 4. Main Pilot Parameters, Frequency, and Entity Responsible for Sampling and Analysis

Parameter	Frequency	Entity/Lab
Flow Rate	Daily	Authority
Water Pressure	Daily	Authority
Cumulative Volume	Daily	Authority
pH	Daily	Authority
Temperature	Daily	Authority
Dissolved Oxygen	Daily	Authority
Conductivity	Daily	Authority
Total Organic Carbon	3 times per week	Authority/Eurofins
UV254	3 times per week	Authority/Eurofins
Redox Potential	1 time per week	Authority
Turbidity	1 time per week	Authority
Alkalinity	1 time per week	Authority/Eurofins
Hardness	1 time per week	Authority/Eurofins
Total Dissolved Solids	1 time per week	Authority/Eurofins
Iron	1 time per week	Authority/Eurofins
Manganese	1 time per week	Authority/Eurofins
PFAS	1 time per week	Catlin/GEL
CECs and non-routine compounds	Weeks 1, 6 and 13	Catlin/Eurofins

IX Main Pilot Backwashing Event

During pilot operation, PFAS sample collection was strategically completed to align with expected PFAS breakthrough depths. For example, early in the study, it was not expected for PFAS to breakthrough the media/resin beds past the 50% depth sample port. As a result, collecting PFAS samples from the 75% bed depth port was delayed for the first four weeks since 75% breakthrough was not expected. Once 75% bed depth sampling was initiated in the IX vessel due to partial 50% bed depth breakthrough (2/13/19), the project team continued to monitor sample depth breakthrough at all bed depths. PFAS results over the next several weeks were non-detect in the 75% sampling port, and significant PFAS concentration variability was observed between other sampling ports (25% and 50% bed depths) from week to week. For these reasons, it was suspected that an issue known as “short-circuiting” was occurring. Short-circuiting in a vessel arises when preferential flow pathways form tunnels within the filter bed and cause a portion of the media to be bypassed.

To address potential short-circuiting, the main IX pilot was backwashed on 3/18/19, in attempt to re-establish the IX resin bed and homogenize resin distribution. Backwashing was conducted by introducing potable water from a nearby hydrant with backflow prevention into the pilot through the effluent pipe and directing flow up through the underdrain. The backwash event took approximately 33 minutes. The first 10 minutes was spent ramping up flow to 45 gpm, which was maintained for 18 minutes prior to ramping flow back down for the remaining 5 minutes.

Following the backwash event, PFAS were detected in samples collected from the 75% and 50% sampling ports at reasonable concentrations. Sampling at the 25% bed depth was halted at this time due to suspected complete breakthrough. It is assumed that since samples collected from the IX 100% sampling port revealed expected trends in TOC and UV254 levels, the PFAS results collected from this location were valid.

Results

The primary purpose of this project was to evaluate GAC and IX technologies for PFAS removal. In addition to PFAS results, TOC and UV absorbance at 254 nm (UV254) results are also presented. TOC and UV254 are common water quality monitoring parameters for GAC and IX performance and were monitored more frequently than PFAS. Additionally, CEC and non-routine compound results, including anions and metals, are also discussed. It is important to note the following during a review of TOC, UV254, PFAS, and CEC and non-routine compound results:

- Figures show constituent concentrations and/or removal as a function of date and/or bed volumes. IX main pilot trains treated more bed volumes than GAC main pilot trains since IX operated at a lower EBCT compared to GAC.
- Vertical lines are shown to represent when flow rate (EBCT) changes were made and when the IX main pilot was backwashed, as noted in the figures.
- “Total PFAS” refers to the sum of the 42 individual PFAS evaluated.
- 75% sampling ports were not sampled for PFAS until 2/13/19, since breakthrough at this port prior to this time was not anticipated.

- 25% sampling ports were not sampled for PFAS after 2/27/19, since complete breakthrough was reached.
- CECs and non-routine compound results from sampling events that took place on 1/9/19, 2/20/19, and 4/3/19 are discussed.

Total Organic Carbon

TOC is a measure of the amount of organic carbon in a water sample, and is often found in raw water ranging from < 1 to 20 mg/L. Finished water TOC is often < 2 mg/L, although this is site-specific, and depends on water source and treatment methods. GAC and IX are two technologies that can be used for TOC removal from drinking water. GAC removes TOC through adsorption, and it is important to note that other organic compounds comprising TOC will compete with PFAS for GAC adsorption sites. IX works by exchanging contaminants for the mobile counterion on the resin, which is based on the regeneration salt used to condition the resin. Similarly to GAC, PFAS and TOC will compete for resin sites, although the resin used in this project was PFAS-selective.

TOC samples were collected three times per week throughout pilot operation from the 100% effluent sampling ports. Figure 5 presents TOC concentrations from main pilot influent and effluent samples as a function of date. Influent TOC remained relatively consistent, ranging from 1.3 mg/L to 1.6 mg/L throughout pilot operation, with an average TOC concentration of 1.5 mg/L.

TOC was slightly higher in IX pilot effluent compared to GAC pilot effluent throughout the course of this project. TOC removal is somewhat dependent on influent TOC concentration, where a higher influent TOC often resulted in a higher effluent TOC in both GAC and IX main pilots, as observed on 1/25/19 and 2/8/19. For GAC and IX, TOC removal decreased as operation continued, indicating GAC media and IX resin was becoming exhausted. Despite this, average GAC effluent TOC during the 250 gpm testing period was 0.71 ± 0.15 mg/L, and average IX effluent TOC during the 250 gpm testing period was 1.0 ± 0.09 mg/L.

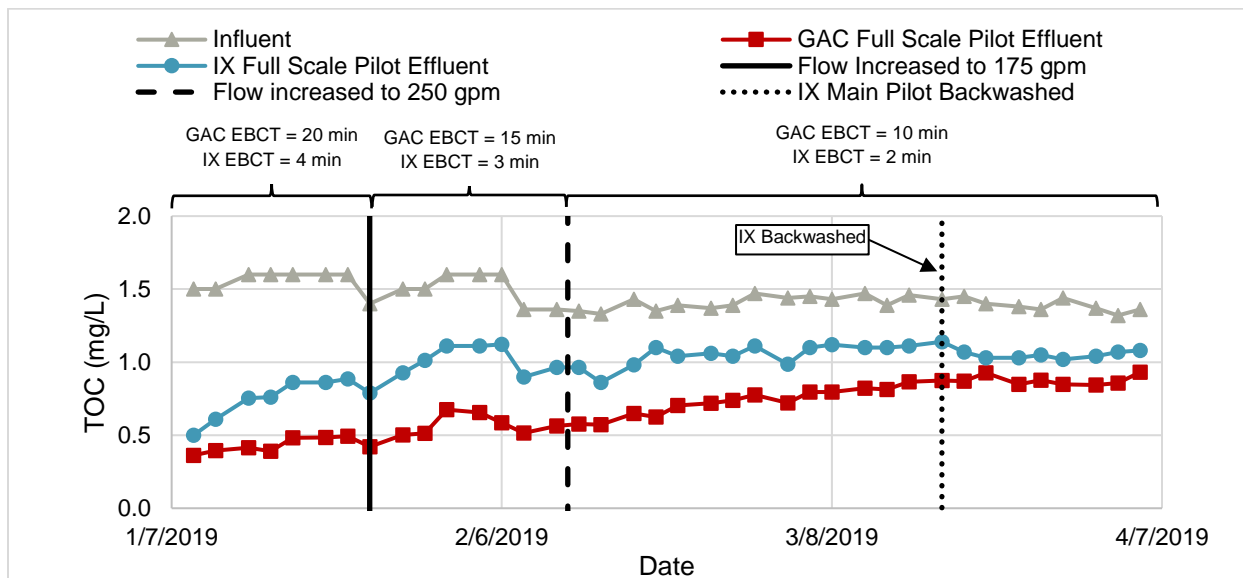


Figure 5. GAC and IX Main Pilot TOC Results

UV254

UV254 is a surrogate parameter for the measurement of organic compound concentrations in water, and can often be correlated to TOC or dissolved organic carbon (DOC). UV254 is a measure of the light that passes through a water sample at a wavelength of 254 nm. UV254 can often be measured as an alternative to TOC due its relatively quick and simple analysis, and is expressed in terms of cm^{-1} .

Figure 6 presents UV254 results from GAC and IX main pilot trains. UV254 results were collected at the same time as TOC results, three times per week, from the GAC and IX main pilot train 100% effluent sampling ports. The first four UV254 results were omitted due to unexpectedly high influent concentrations ($> 2.5 \text{ cm}^{-1}$) observed during start-up, which was attributed to the initiation of pumping from the ASR well to the pilots. With the exception of start-up, UV254 is relatively consistent in influent samples, ranging from 0.020 to 0.034 cm^{-1} with an average value of 0.030 cm^{-1} .

The GAC pilot consistently removed UV254 with slightly more success relative to the IX pilot. Both pilots showed a gradual decrease in UV254 removal as operation progressed. Average UV254 in GAC effluent during the 250 gpm testing period was $0.010 \pm 0.005 \text{ cm}^{-1}$. Average UV254 in IX effluent during the 250 gpm testing period was $0.017 \pm 0.004 \text{ cm}^{-1}$. Similar to TOC results, UV254 removal is somewhat dependent on influent concentration, where higher influent UV254 corresponds to a higher effluent UV254 in the GAC and IX pilots, as observed on 1/28/19, and lower influent UV254 corresponds to lower effluent UV254, as observed on 3/27/19.

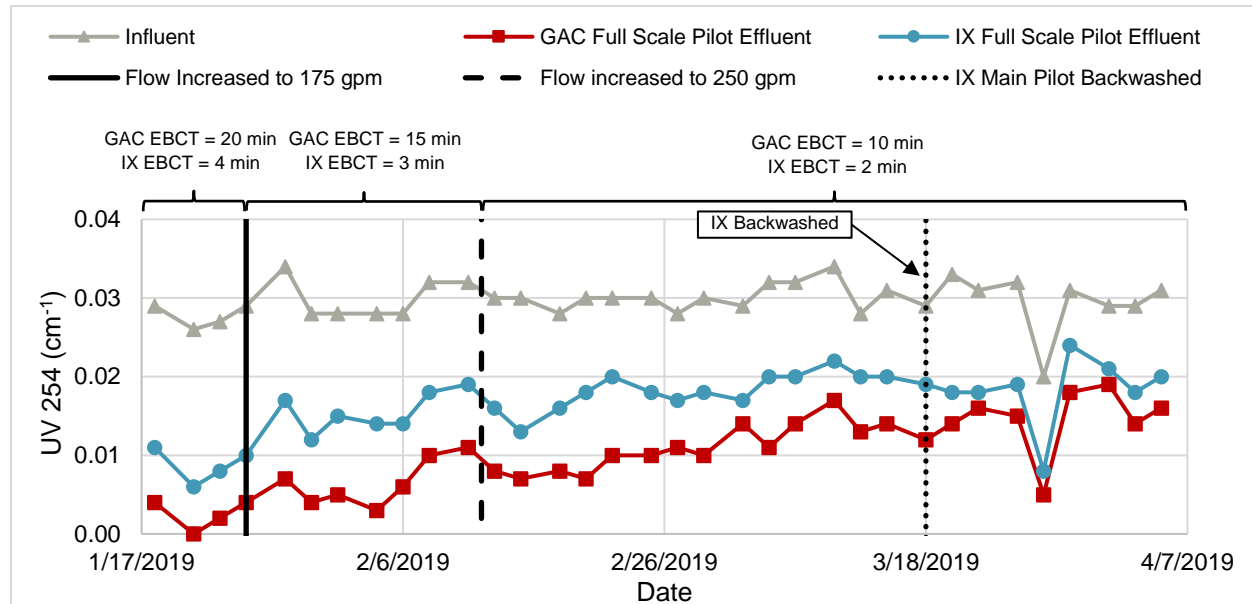


Figure 6. GAC and IX Main Pilot UV254 Results

PFAS

Main Pilot Trains

Figure 7 presents total PFAS results from samples collected from the 100% effluent sampling ports of the GAC and IX main pilots. Influent total PFAS concentrations ranged from 828 to 2,691 ng/L, with an average concentration of 2,036 ng/L. Total PFAS concentrations in effluent samples increase first in the IX pilot, followed by the GAC main pilot.

Total PFAS IX effluent concentrations remained relatively consistent from 2/20/19, after 17,700 bed volumes, until the end of the pilot study. Total PFAS concentrations in the GAC main pilot did not begin to increase until 2/13/19, after 3,600 bed volumes, and GAC and IX main pilot effluent concentrations are similar by the end of the study. Data in Figure 7 suggest that the influent total PFAS concentration influences total PFAS removal from the IX main pilot, which was observed for TOC and UV254 data as well. Generally, a higher influent concentration often resulted in higher effluent concentrations, as observed on 2/20/19 and 3/13/19. This trend was not observed in the GAC main pilot. It is important to note that both GAC and IX approach breakthrough around the same time (late March/early April), although GAC released a lower mass of PFAS throughout the run, which could be attributed to operating at a greater EBCT.

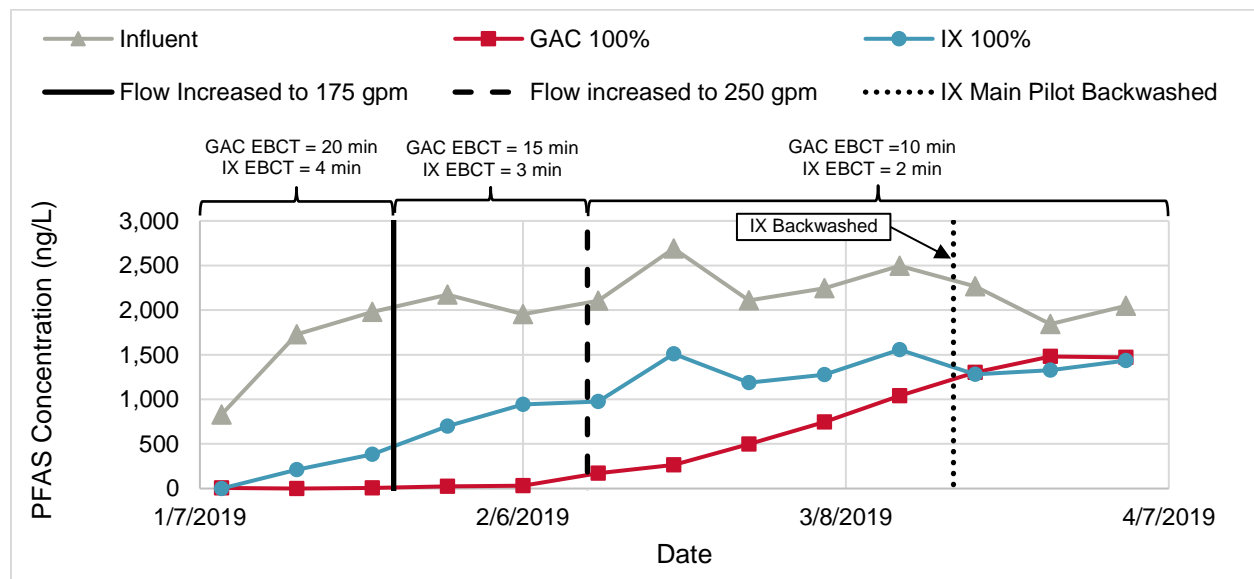


Figure 7. GAC and IX Main Pilot Total PFAS Results

Figure 8 presents total PFAS results from samples collected at each GAC sampling port throughout this project as a function of bed volume. As expected, total PFAS removal was initially relatively high at the start of the pilot ($\geq 80\%$) due to the abundance of available adsorption sites that had not yet been exhausted. Total PFAS removal decreases as adsorption sites become exhausted through the bed. GAC adsorption sites from the top of the media bed to the 25% sampling port were exhausted after approximately 5,700-6,000 bed volumes. Adsorption sites from the 25% sampling port to the 50% sampling port were exhausted after approximately 10,000 bed volumes. At the 75% and 100% sampling port locations, media had reached 90% and 80% breakthrough, respectively, by the end of the pilot study (~10,000 to 11,000 bed volumes).

Breakthrough could be delayed in the GAC pilot if routine backwashing was performed, although the pilot study duration was not long enough to evaluate a backwash event.

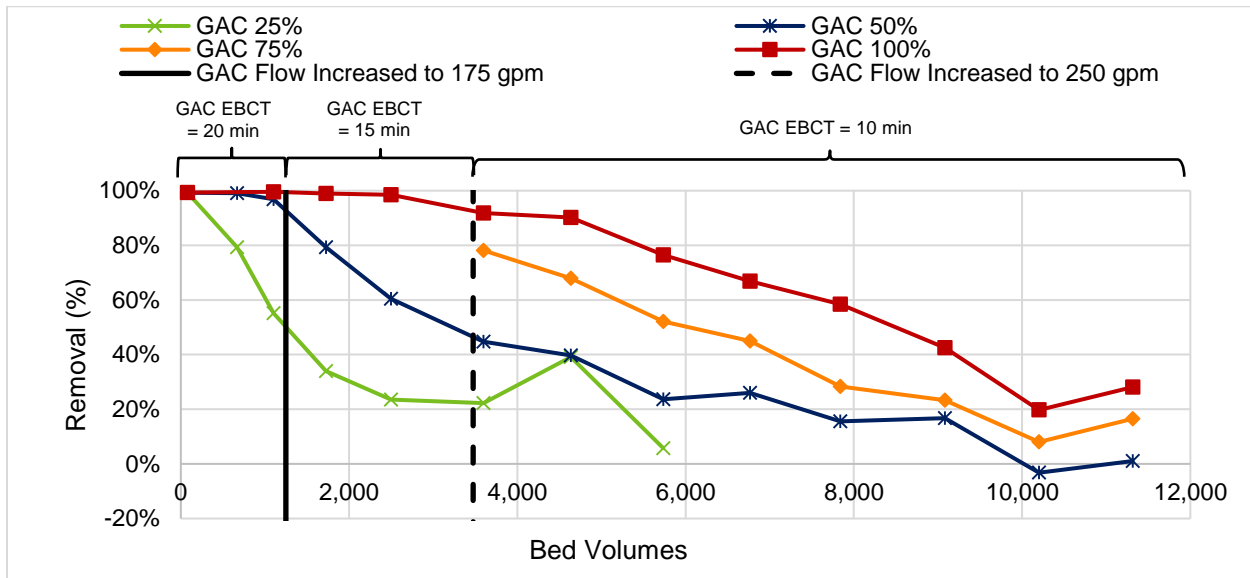


Figure 8. GAC Total PFAS Removal vs. Bed Volume

Figure 9 presents total PFAS removal for each of the main IX pilot sampling ports as a function of bed volumes. As mentioned previously, it was suspected that short-circuiting was occurring since 75% effluent sampling ports initially revealed PFAS samples as non-detect (from samples collected between ~15,000 to ~28,000 bed volumes). Additionally, PFAS results at 25% and 50% sampling ports were variable, and did not follow the anticipated removal trend that was observed in the GAC main pilot. Backwashing was conducted to alleviate bed distribution short-circuiting by slowly ramping up flow for 10 minutes to a steady flow rate of 45 gpm, which remained constant for 18 minutes prior to ramping flow rate back down for 5 minutes. PFAS were detected in the 75% sampling port after backwashing. However, breakthrough cannot be determined from the 25%, 50%, or 75% sampling ports since the number of bed volumes that actually passed through these sections of the IX vessel is unknown due to short-circuiting.

PFAS results from the 100% effluent sampling port followed an expected removal trend, and TOC and UV254 results from this sampling location were as anticipated; therefore, it is assumed that PFAS results from this sampling location are accurate. The 100% sampling port location IX media had reached 70% total PFAS breakthrough.

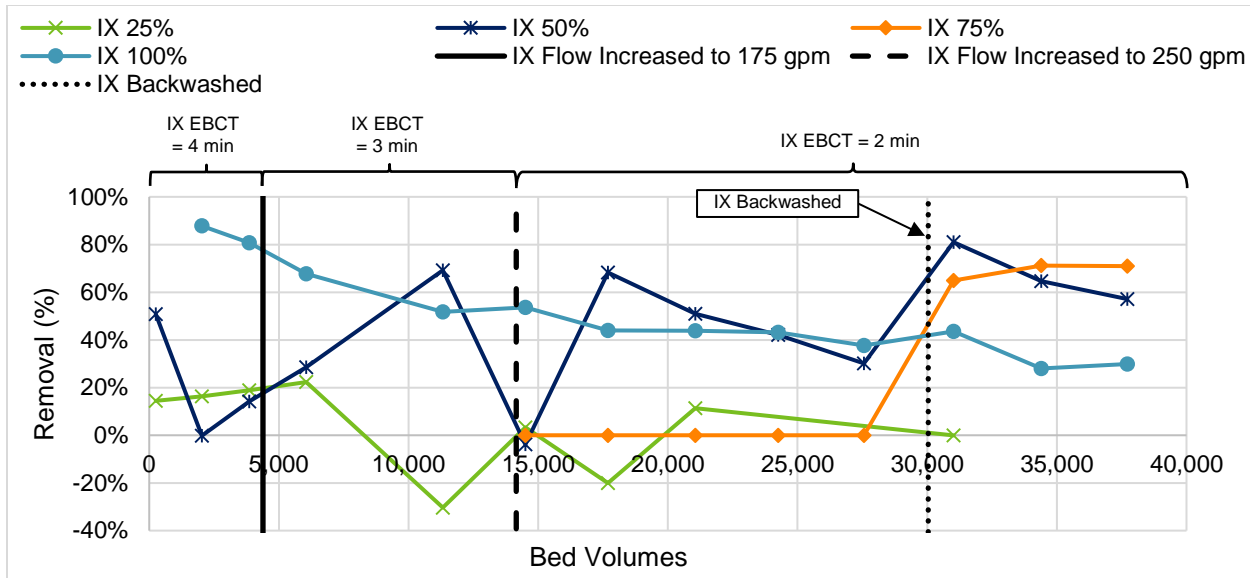


Figure 9. IX Total PFAS Removal vs. Bed Volume

Figures 10 and 11 present GAC and IX main pilot results, respectively, as the effluent total PFAS concentration (C_e) divided by the influent total PFAS concentration (C_i) as a function of bed volume. Showing the results in this format provides a quick determination of constituent breakthrough and shows a clear trend in breakthrough patterns. Complete breakthrough is reached when C_e is equal to C_i . Approximately 80% breakthrough of total PFAS was reached in the GAC pilot by the conclusion of the pilot study, indicating complete breakthrough would likely have been reached in the near future if pilot operation continued. The IX main pilot reached approximately 70% breakthrough of total PFAS by the end of pilot operation. The IX pilot was backwashed after approximately 30,000 bed volumes.

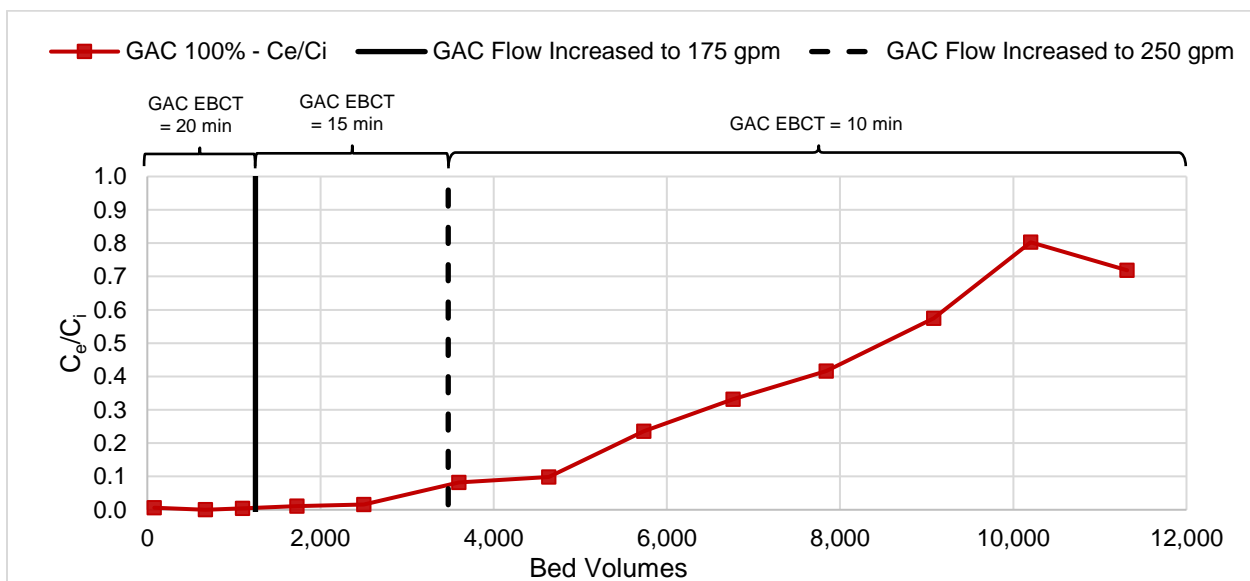


Figure 10. GAC Total PFAS C_e/C_i vs. Bed Volumes

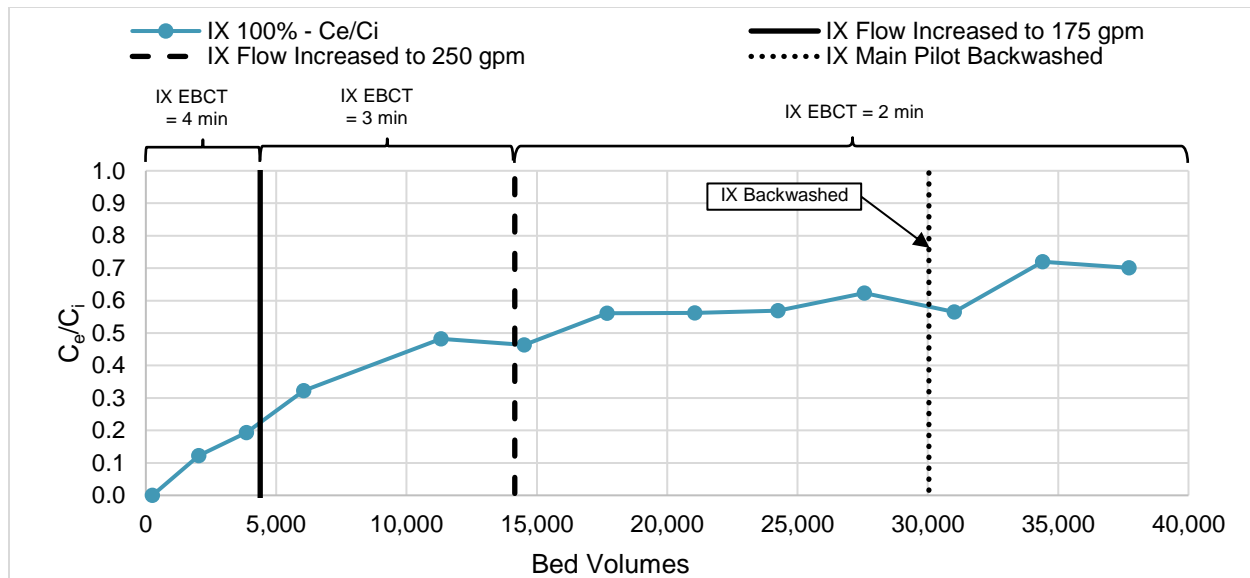


Figure 11. IX Total PFAS C_e/C_i vs. Bed Volumes

Figures 12 and 13 present individual PFAS removal as a function of bed volume for samples collected from GAC and IX main pilot train 100% sample ports, respectively. Individual PFAS data points shown on Figures 12 and 13 represent PFAS that were detected in a majority of samples; therefore PFAS below detection are not shown. Numbers in figure legends shown in parenthesis represent the number of carbons that the individual PFAS contains. Appendix D provides a summary table showing percent removal of individual PFAS and number of carbons contained in each compound.

Figure 12 demonstrates that long-chain PFAS such as PFOS and PFOA, were successfully removed from the GAC pilot compared to short-chain PFAS (e.g. PFMOAA and PFO₂HxA), as expected. It is important to note that PFOS and PFOA influent concentrations were relatively low, with average values of 2.8 and 2.5 ng/L, respectively. Generally, PFAS adsorbability decreases with decreasing carbon chain length. It is important to note that PFO₄DA, a 6-carbon PFAS, and PFOA were below detection in each of the 100% GAC effluent samples. PFOS was below detection in a majority of 100% GAC main pilot effluent sampling ports. Alternatively, shorter chain compounds removal began to decrease after approximately 3,600 bed volumes.

It is interesting to note that GenX, a 6-carbon PFAS with a fluoropolymer structure, did not follow the same pattern as compounds with similar carbon lengths (e.g. PFO₄DA and PFO₃OA) in the GAC main pilot. It would be expected that GenX removal would be similar or better than PFO₃OA, a 5-carbon PFAS, based on its chain length. Alternatively, GAC removal of GenX was reduced to 40% by the end of the pilot study, where PFO₃OA removal remained near 80% by the end of the project.

Figure 13 shows that individual PFAS removal from the IX main pilot was also dependent on carbon chain length, where long-chain PFAS generally had better removal compared to short-chain PFAS. GenX removal is similar for both main pilots, reaching approximately 40% breakthrough by the end of the project for both pilots.

However, there are several differences to note between individual PFAS removal from GAC and IX main pilot trains. First, long-chain PFAS removal was not as successful in the IX main pilot compared to the GAC main pilot. PFOS, PFOA, and PFO4DA had reached approximately 50% breakthrough in the IX main pilot whereas these compounds were still removed to below detection in the GAC main pilot by the end of the pilot study.

Second, PFAS removal decreases sooner in the IX main pilot compared to the GAC main pilot. For example, PFAS removal in the IX pilot decreases during the second sampling event after approximately 2,000 bed volumes, while a majority of PFAS removal does not decrease until approximately 3,600 bed volumes in the GAC pilot. This could be due to short-circuiting that was likely occurring in the IX pilot that the team attempted to remediate with backwashing.

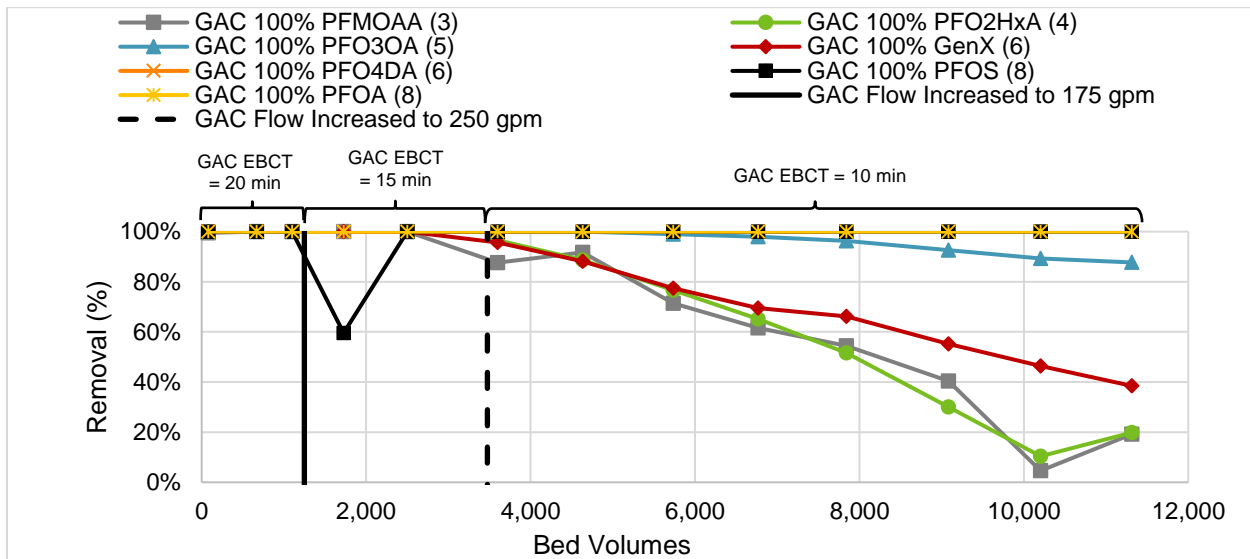


Figure 12. GAC Main Pilot Individual PFAS Removal

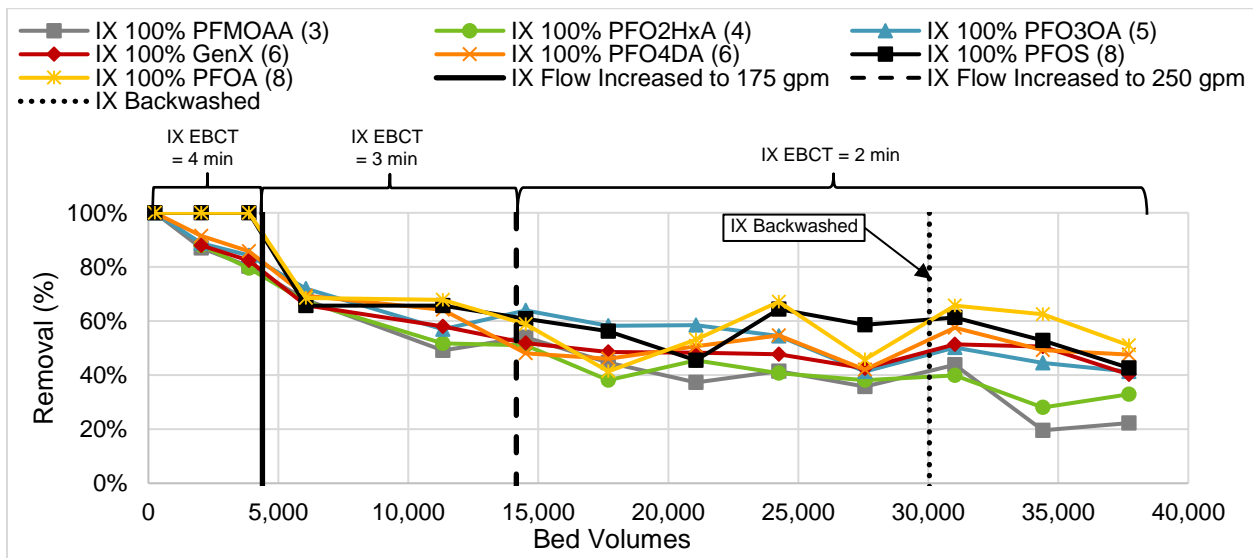


Figure 13. IX Main Pilot Individual PFAS Removal

Mini Columns

Figure 14 shows total PFAS results for GAC, IX, and GAC/IX lead/lag mini columns. Mini column effluent PFAS concentrations were relatively low in each of the columns during the first 1.5 months of operation, indicating adsorption sites had not been exhausted yet. Effluent concentrations collected from each of the mini columns slowly start to increase in mid- to late-February. IX mini column effluent concentrations increase more rapidly, whereas PFAS concentrations collected from GAC and GAC/IX mini column effluent increase gradually.

The IX mini column reached complete breakthrough of total PFAS prior to the end of the study, around 3/20/19, since the effluent total PFAS concentration exceeded the influent concentration. GAC and GAC/IX mini columns had not reached complete breakthrough by the end of the pilot study.

Throughout operation, mini column data was variable, but the data was overall consistent with main pilot operation and did not yield significantly different findings. One set of mini pilot column results was removed (3/27/19) since results were possible outliers.

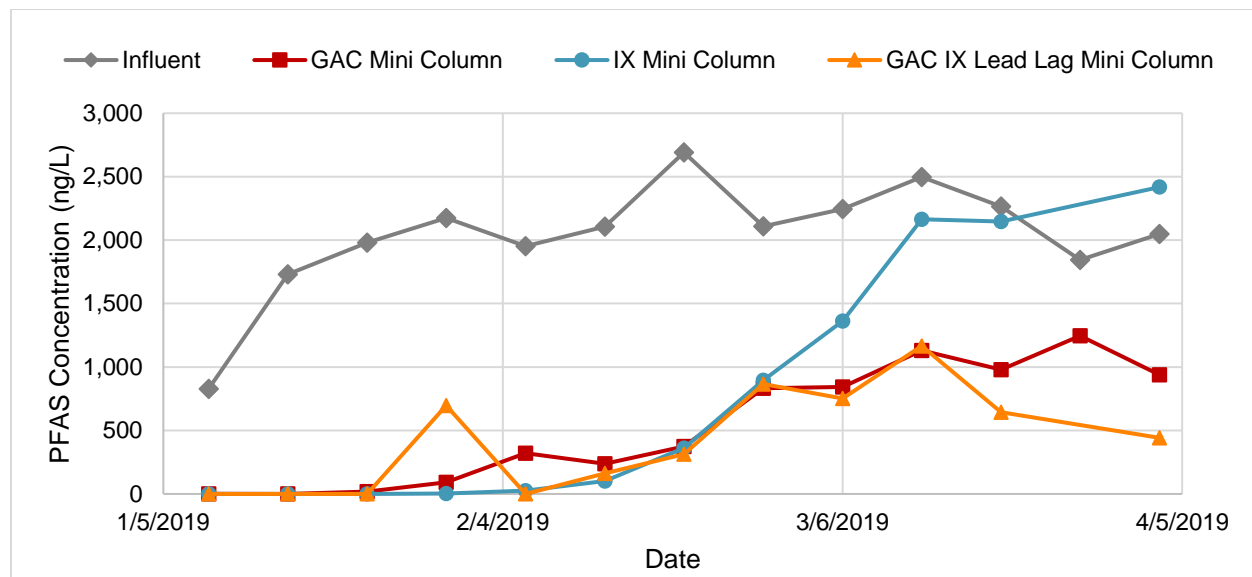


Figure 14. GAC, IX, and GAC/IX Mini Column Total PFAS Results

CECs and Non-Routine Compounds

A complete list of CECs and non-routine compounds is presented in Appendix B, and compounds below detection limits are presented in Appendix C. Table 5 presents CECs and non-routine compounds that were detected in at least one of the two influent samples collected during the course of this project, but were not removed or had negligible (< 5%) removal using both GAC and IX main pilots. Maximum contaminant levels (MCLs) and secondary MCLs are also shown in Table 5. Each of the constituents listed in Table 5 that had MCLs or SMCLs were below their respective MCLs or SMCLs throughout testing.

Table 5. CECs and Non-Routine Compounds Detected but Not Removed

Compound	Average Influent Concentration	MCLs	SMCLs	GAC Impact on Removal	IX Impact on Removal
Bromide	0.22 mg/L	None	None	Negligible	None
Chloride	56 mg/L	None	250 mg/L	None	None
Fluoride*	0.39 mg/L	4 mg/L	2 mg/L	None	None
Calcium	51 mg/L	None	None	None	None
Magnesium	10 mg/L	None	None	None	None
Potassium	6.6 mg/L	None	None	None	Negligible
Total Silica	16 mg/L	None	None	None	None
Sodium	42 mg/L	None	None	None	None
Barium	4.7 µg/L	2 mg/L	2 mg/L	None	Negligible
Boron	97 µg/L	None	None	None	Negligible
Manganese	5.0 µg/L	None	0.05 mg/L	None	None
Strontium	253 µg/L	None	None	None	None
Zinc*	5.3 µg/L	None	5.0 mg/L	None	Negligible
Tris (chloropropyl) phosphate	0.01 µg/L	None	None	None	None

*Only detected in one influent sample.

Constituents that were detected and at least partially removed from the GAC main pilot, IX main pilot, or both, included color, sulfate, DOC, TOC, arsenic, nickel, 1,4-dioxane, and sucralose. These constituents will be discussed in the following paragraphs.

Color removal was 50% for both pilots during the first two sampling events, and 33% for the third sampling event. Sulfate was removed by 6% and 70% in the GAC and IX pilots, respectively, during the first round of sampling, but was negligibly removed by both pilots during the second and third sampling events. IX is generally considered a successful technology for the removal of anions, such as bromide, chloride, fluoride, and sulfate. The resin tested in this project was developed to be preferential to PFAS, which would explain why the IX pilot did not provide substantial removal of monovalent ions, but did provide removal of PFAS and a divalent ion (sulfate) during the first sampling event. As expected, DOC and TOC were removed by both the GAC and IX main pilots, with decreasing removal as operation continued due to the exhaustion of adsorption sites.

Arsenic was partially removed from the GAC and IX pilots, although not substantially. Arsenic removal during the first sampling event was 6% and 10% for GAC and IX pilots, respectively.

During the second sampling event, arsenic removal was zero and 6% for GAC and IX pilots, respectively. During the third sampling event, arsenic removal using both pilots was negligible. Nickel was only detected during the first sampling event and was only removed from the IX main pilot at 9%. No nickel removal was observed from the GAC main pilot.

1,4-dioxane was detected during the three sampling events with influent concentrations of 0.14, 0.35, and 0.27 µg/L, respectively. 1,4-dioxane was removed by 50%, 39%, and 0% by the GAC main pilot during the three sampling events, respectively, but was not removed using the IX main pilot during any of the three sampling events.

Sucralose was detected in pilot influent at levels of 0.063, 0.089, and 0.086 µg/L during the three sampling events, respectively. Sucralose was removed to below detection limits (< 0.025 µg/L) in the GAC pilot effluent during the first two events, and was at the detection limit during the third sampling event. Sucralose had removals of 38% and 15% using the IX main pilot during the first two events, although the sucralose concentration in the IX pilot effluent was higher compared to the influent, suggesting desorption from the resin.

Conclusions and Recommendations

It is recommended that GAC be utilized if full-scale treatment of the ASR site is desired based on total PFAS and GenX removal results. GAC provided superior total PFAS, TOC, and UV254 removal compared to the IX pilot, and total PFAS removal did not plateau as quickly in the GAC pilot when compared to the IX pilot. Additionally, the GAC main pilot provided superior removal of long-chain PFAS and many CECs compared to the IX pilot. It is anticipated that increasing the EBCT in either the GAC or IX pilot would result in improved constituent removal and greater number of bed volumes treated. However, it is important to note there is potential for greater biological growth at longer EBCTs. Increasing EBCT can be accomplished by using a larger media volume or by decreasing the flow rate. Furthermore, periodic backwashing of GAC could delay the time of breakthrough; however this impact could not be evaluated due to the short duration of this project.

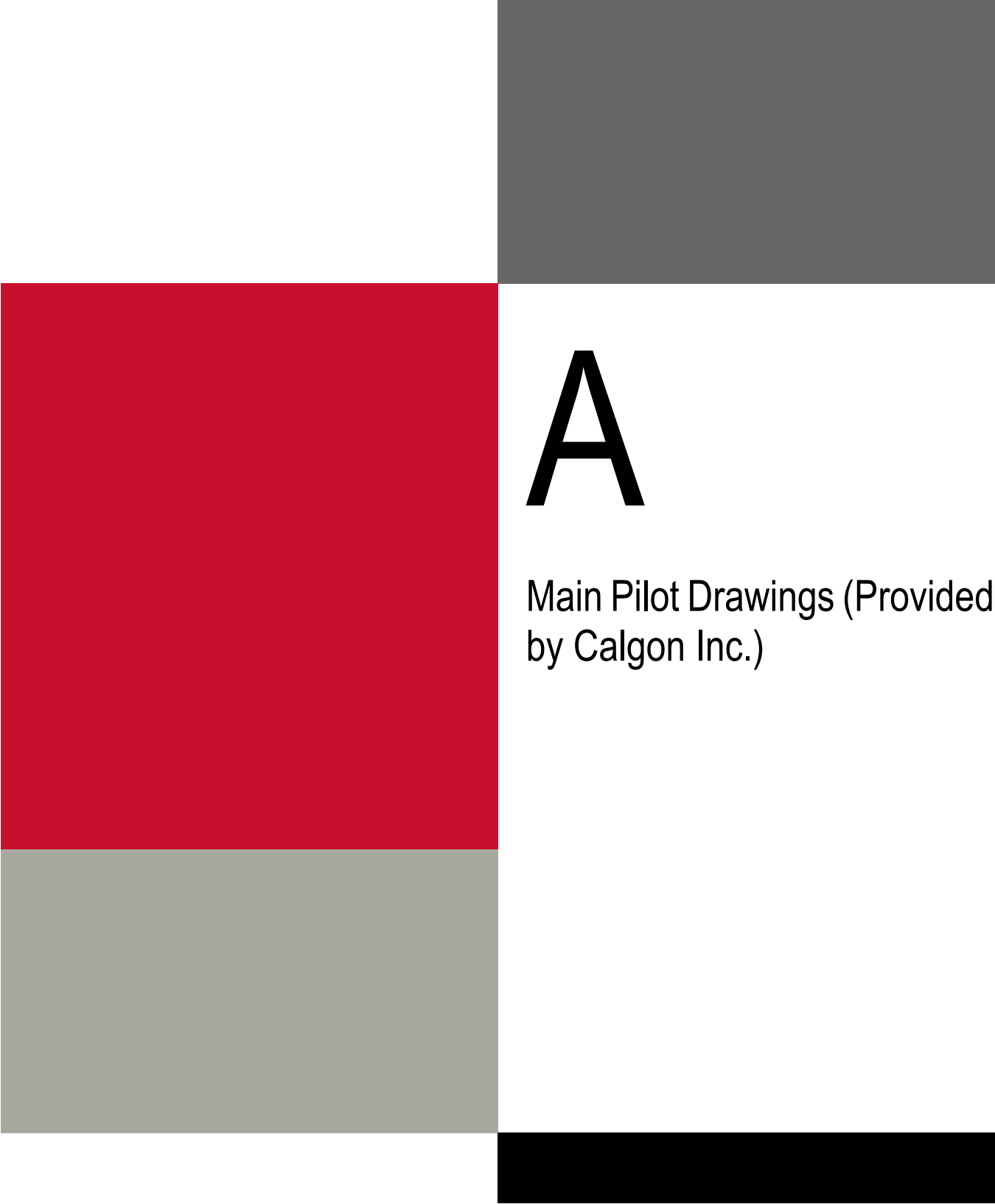
An engineer's opinion of the probable construction cost was generated for a full-scale GAC treatment system using the following assumptions, and a detailed cost estimate is provided in Appendix E.

- 25% contingency
- 7.0% sales tax
- 10% general conditions
- 5% contractors fee
- 15% for engineering design, permitting, and construction support

It is expected that the total project cost for full-scale GAC implementation at the Westbrook ASR site would be \$3,500,000. This includes the following major equipment and activities that would be required for successful installation:

- Two lead/lag GAC skids (10" diameter vessels containing 20,000 lbs. GAC media each) including media, delivery, and start up
- One pre-fabricated building (1,600 sf)
- Wastewater pump station for spent backwash
- Site restoration and improvements
- Electrical and controls
- SCADA instrumentation
- HVAC installation

The estimated exhaustion rate for the carbon evaluated in this project (Filtrisorb-400) is approximately 83 days, requiring an estimated change-out frequency of 4.4 times per year. This exhaustion rate is based on treatment until complete total PFAS breakthrough, which is estimated at 12,000 bed volumes. Bed life could be extended if backwashing measures are taken. It is estimated that the cost per GAC replacement would be approximately \$64,000, or \$280,000 per year, using an exhaustion rate of 83 days.



A

Main Pilot Drawings (Provided
by Calgon Inc.)



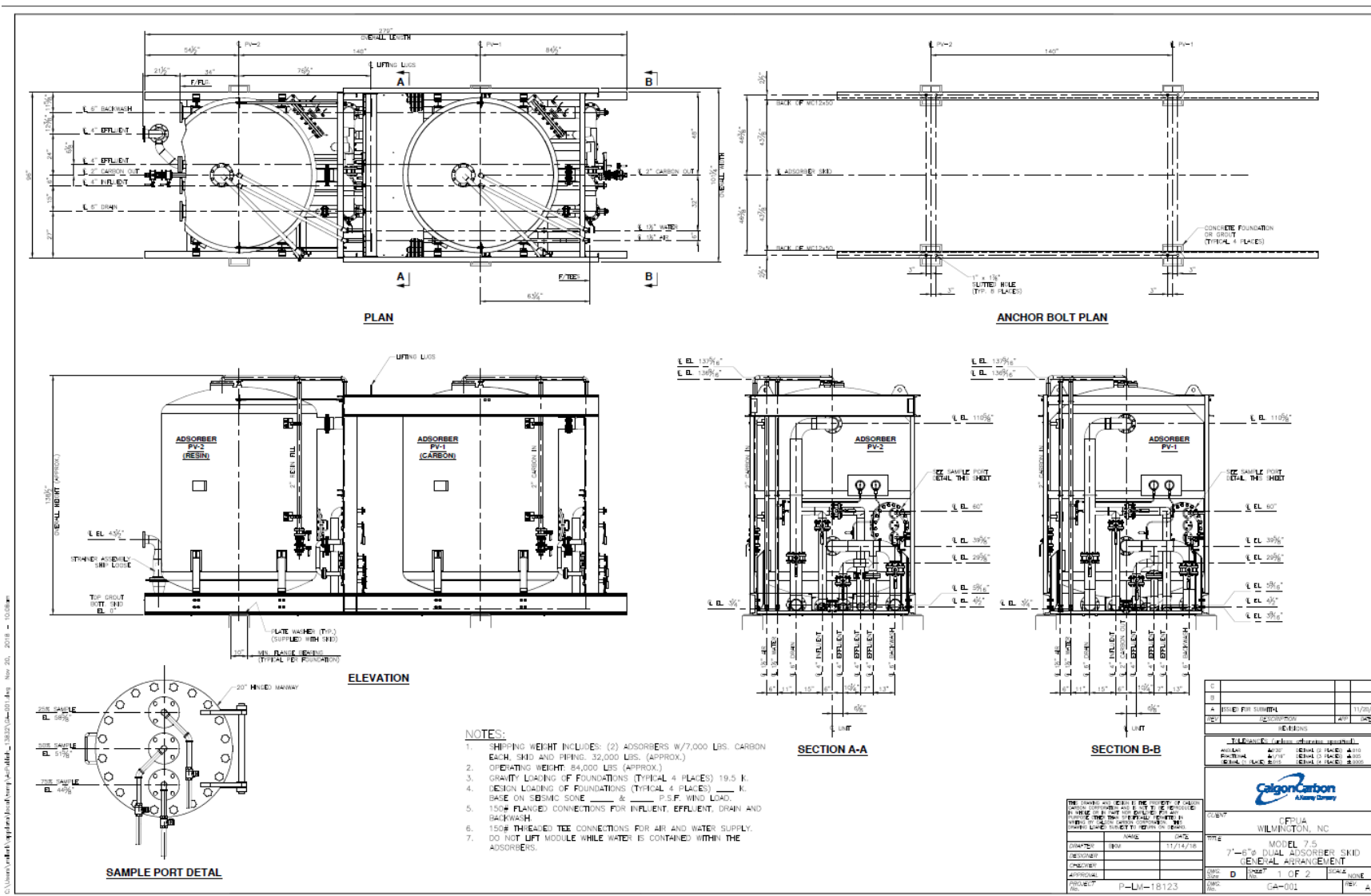


Figure A-2. Pilot Details (Provided by Calgon Inc.)



B

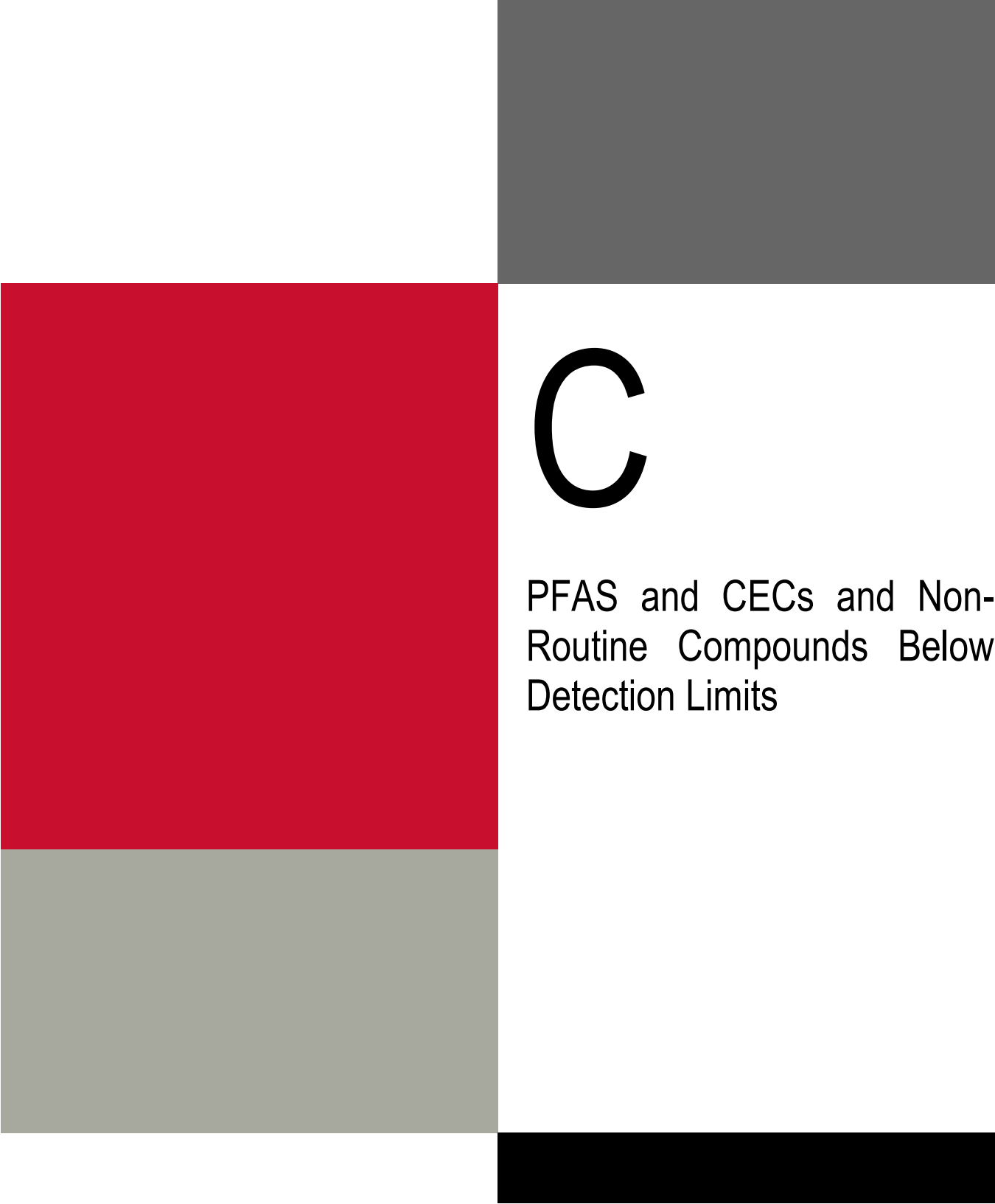
Complete List of PFAS and
CECs Evaluated

Table B-1. PFAS Analyzed

PFAS	Abbreviation
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	PF3OUdS
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	PFPrOPrA, GenX
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-EtFOSE
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-MeFOSE
4-(Heptafluoroisopropoxy) hexafluorobutanoic acid	PFECA-G
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	No abbreviation
Fluorotelomer sulfonate 10:2	10:2 FTS
Fluorotelomer sulfonate 4:2	4:2 FTS
Fluorotelomer sulfonate 6:2	6:2 FTS
Fluorotelomer sulfonate 8:2	8:2 FTS
N-ethylperfluoro-1-octanesulfonamide	N-EtFOSA
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA
N-methylperfluoro-1-octanesulfonamide	N-MeFOSA
N-methylperfluoro-1-octanesulfonamidoacetic acid	N-MeFOSAA
Nafion Byproduct 1 ^a	NBP1
Nafion Byproduct 2 ^a	NBP2
Perfluoro(3,5,7,9-tetraoxadecanoic) acid ^a	PFO4DA
Perfluoro(3,5,7-trioxaoctanoic) acid ^a	PFO3OA
Perfluoro(3,5-dioxahexanoic) acid ^a	PFO2HxA
Perfluoro-2-methoxyacetic acid ^a	PFMOAA
Perfluoro-3-methoxypropanoic acid ^a	PFMOPrA
Perfluoro-4-methoxybutanoic acid ^a	PFMOBA
Perfluorobutanesulfonate	PFBS
Perfluorobutyric acid	PFBA
Perfluorodecanesulfonate	PFDS
Perfluorodecanoic acid	PFDA
Perfluorododecanoic acid	PFDoA
Perfluoroheptanesulfonate	PFHpS
Perfluoroheptanoic acid	PFHpA
Perfluorohexanesulfonate	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluorononanesulfonate	PFNS
Perfluorononanoic acid	PFNA
Perfluorooctanesulfonamide	PFOSA
Perfluorooctanesulfonate	PFOS
Perfluorooctanoic acid	PFOA
Perfluoropentanesulfonate	PFPeS
Perfluoropentanoic acid	PFPeA
Perfluorotetradecanoic acid	PFTeDA
Perfluorotridecanoic acid	PFTTrDA
Perfluoroundecanoic acid	PFUdA
Sodium dodecafluoro-3H-4,8-dioxanonanoate	ADONA

Table B-2. CECs and Non-Routine Compounds Analyzed

Group Name	Compound
General Chemistry	Color (Apparent)
	Bromide
	Chloride
	Fluoride
	Sulfate
	Dissolved Organic Carbon
	Total Organic Carbon
Metals	Calcium
	Magnesium
	Potassium
	Total Silica
	Sodium
	Antimony
	Arsenic
	Barium
	Beryllium
	Boron
	Cadmium
	Chromium
	Manganese
	Molybdenum
	Nickel
	Strontium
	Thallium
	Zinc
Volatile Organic Compounds	1,4-Dioxane
EEA Methods	Tris(2-chloroethyl) phosphate
	Tris(chloropropyl) phosphate
	Sucralose



C

PFAS and CECs and Non-
Routine Compounds Below
Detection Limits

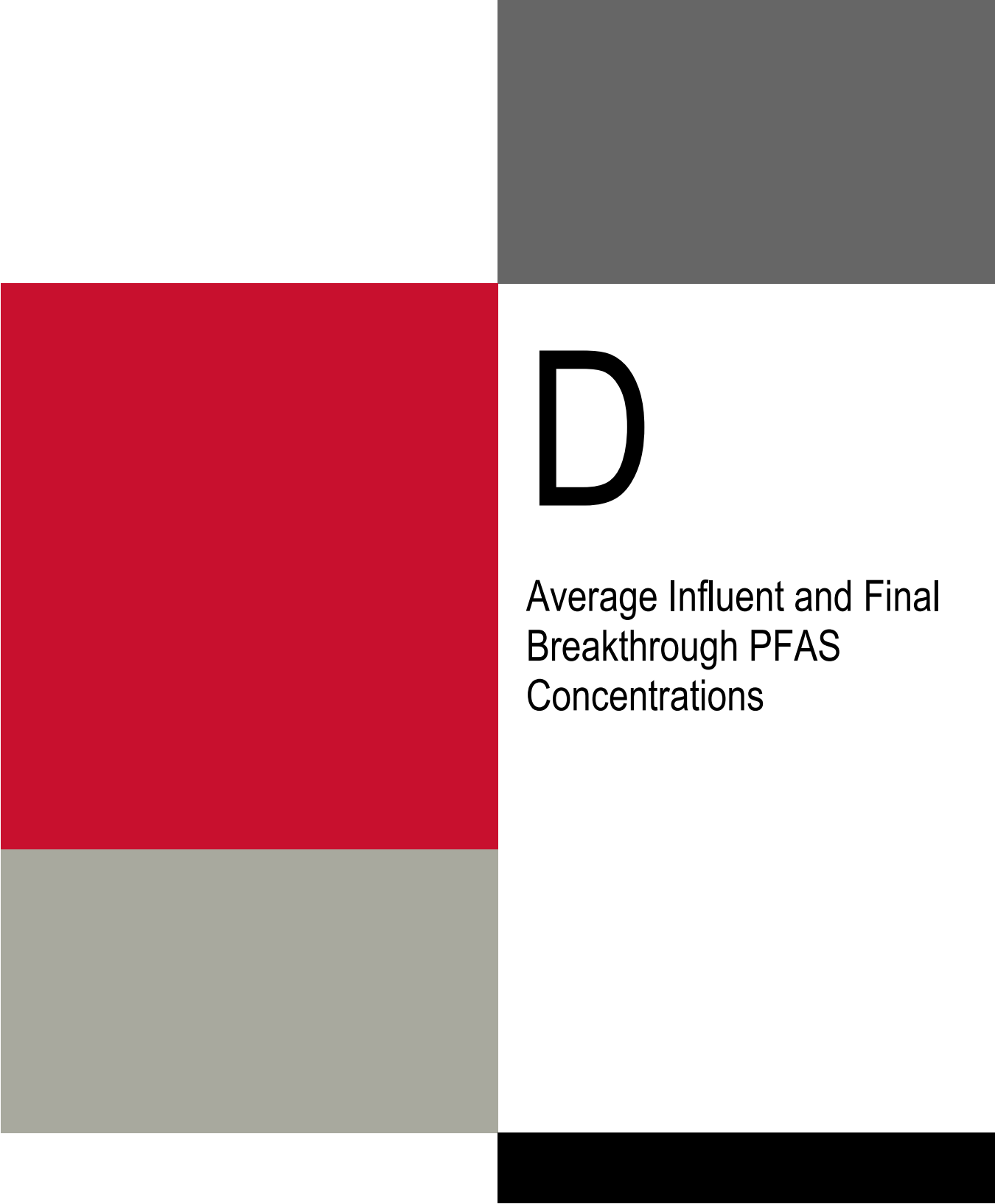
Table C-1 presents a list of PFAS that were not detected in any sample during this project, and Table C-2 presents a list of CECs and non-routine compounds that were not detected in this project. Method detection limits (MDLs) for PFAS generally ranged from 0.6 to 1.3 ng/L.

Table C-1. PFAS below Detection Limits

PFAS	Abbreviation
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	PF3OUdS
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-EtFOSE
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-MeFOSE
4-(Heptafluoroisopropoxy) hexafluorobutanoic acid	PFECA-G
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	No abbreviation
Fluorotelomer sulfonate 10:2	10:2 FTS
Fluorotelomer sulfonate 4:2	4:2 FTS
Fluorotelomer sulfonate 6:2	6:2 FTS
Fluorotelomer sulfonate 8:2	8:2 FTS
N-ethylperfluoro-1-octanesulfonamide	N-EtFOSA
N-ethylperfluoro-1-octanesulfonamidoacetic acid	N-EtFOSAA
N-methylperfluoro-1-octanesulfonamide	N-MeFOSA
Nafion Byproduct 1 ^a	No abbreviation
Perfluorodecanesulfonate	PFDS
Perfluorododecanoic acid	PFDoA
Perfluoroheptanesulfonate	PFHpS
Perfluorononanesulfonate	PFNS
Perfluorooctanesulfonamide	PFOSA
Perfluoropentanesulfonate	PFPeS
Perfluorotridecanoic acid	PFTrDA
Sodium dodecafluoro-3H-4,8-dioxanonoate	ADONA

Table C-2. CEC and Non-Routine Compounds Below Detection Limits

Compound	Method Detection Limit (µg/L)
Antimony	< 1
Beryllium	< 0.3
Cadmium	< 1
Chromium	< 0.9
Molybdenum	< 2
Selenium	< 2
Thallium	< 0.3
Tris(2-chloroethyl) phosphate	< 0.01



D

Average Influent and Final
Breakthrough PFAS
Concentrations

Table D-1. Average Influent PFAS and Final Breakthrough PFAS, and Final Bed Volumes Treated

PFAS	Number of Carbons	Bed Volumes	12,777	42,039	10,947	69,165	5,355
		Average Influent (ng/L)	GAC Main Pilot (ng/L)	IX Main Pilot (ng/L)	GAC Mini Column (ng/L)	IX Mini Column (ng/L)	GAC/IX Lead/Lag Mini Column (ng/L)
GenX	6	69	49	47	53	45	19
NBP2	7	6.7	ND	2.5	2.5	ND	1.2
PFO4DA	6	37	ND	20	8.2	8.9	8.2
PFO3OA	5	209	25	118	67	124	44
PFO2HxA	4	830	696	582	397	1,140	185
PFMOAA	3	843	660	635	375	1,060	174
PFMOPrA	4	11	19	12	17	14	4.3
PFMOBA	5	6.6	8.6	3.3	4.6	7.5	1.7
PFBS	4	0.62	ND	ND	ND	ND	ND
PFBA	4	1.9	2.3	1.9	2.0	2.4	ND
PFDA	10	0.2	ND	ND	ND	ND	ND
PFHpA	7	2.7	ND	1.6	1.4	0.95	0.61
PFHxS	6	1.1	ND	ND	ND	ND	ND
PFHxA	6	3.0	1.1	1.9	1.7	2.3	0.72
PFNA	9	0.69	ND	ND	ND	ND	ND
PFOS	8	2.8	ND	1.2	0.90	ND	0.67
PFOA	8	2.5	ND	1.2	0.98	0.60	0.70
PFPeA	5	8.8	11	8.3	7.7	13	2.8
Total PFAS	Not Applicable	2,048	1,472	1,435	938	2,418	442

*ND = not detected



E

Detailed Cost Estimate





**Cape Fear Public Utility Authority
Westbrook ASR GAC Contactor Addition**


HDR Project No. 10130082

Level 5

Opinion of Probable Construction Cost

May 1, 2019

Item No.	Area of Work	Subtotals
1	Mobilization	\$21,000
2	Building Floor Foundation	\$30,000
3	Excavation	\$9,000
4	Spoils Disposal	\$600
5	4" Ductile (above grade)	\$15,300
6	4" Ductile 90 fitting	\$13,000
7	4" Ductile Tee Fitting	\$4,800
8	6" Ductile Backwash Feed and Discharge to Sewer	\$300,000
9	6" Gate Valve	\$5,000
10	6" Flow Meter	\$10,000
11	6" Backflow Preventer	\$10,000
12	Crane Rental	\$1,600
13	Site Restoration and Improvements	\$100,000
14	GAC Vessel Purchase, Lead/Lag	\$600,000
15	Installation	\$30,000
16	Butler Building	\$72,000
17	Electrical and Controls	\$85,000
18	Wastewater Pump Station (for backwash and filter-to-waste)	\$600,000
19	SCADA Instrumentation and TRU	\$50,000
20	HVAC	\$50,000
Subtotal base Costs Before Mark-Ups		\$2,007,300
Contingency (25%)		\$501,825
Subtotal		\$2,509,125
Sales Tax (7%)		\$175,639
General Conditions (10%)		\$250,913
Contractor Fee (5%)		\$125,456
Subtotal		\$3,061,133
Engineering Design, Permitting, Construction Administration (15%)		\$459,170
Opinion of Probable Construction Cost		\$3,520,302

An abstract graphic design featuring a large, bold, black letter 'F' positioned to the right of a large red rectangle. The red rectangle is situated in the middle-left portion of the image. To the right of the red rectangle, there is a dark gray rectangle at the top and a black rectangle at the bottom. Below the red rectangle is a light gray rectangle. The overall composition is minimalist and geometric.

F

Analysis of Non-Targeted
PFAS in Water Treated for
Aquifer Storage and
Recovery (UNC Wilmington)

Final Report

Analysis of non-Targeted Perfluoroalkyl Substances in Water Treated for Aquifer Storage and Recovery

Marine and Atmospheric Chemistry Research Laboratory

1.0 Introduction

Water in the aquifer storage facility of the Cape Fear Public Utility Authority (CFPUA) has not been examined for non-targeted PFAS compounds. This facility has historically been injecting treated Sweeney Water into it and therefore may contain compounds in addition to those identified in finished water from the Sweeney plant after reports of GenX contamination. The Marine and Atmospheric Chemistry Research Laboratory (MACRL) at UNCW performed a study to determine previously unidentified PFAS in aquifer storage recovery (ASR) water. In addition to identification, the efficiency of removal of these non-targeted PFAS compounds by both granulated activated charcoal (GAC) and ion exchange (IX) was determined. CFPUA set up a system at the ASR site in Wilmington where ASR feed-water (FW) was split and sent through a GAC and IX simultaneously. This report describes findings to date as described in the initial scope of work.

2.0 Materials and Methods:

2.1 Sample collection

Previously published sample processing and QA/QC procedures were followed throughout the study¹⁻². Briefly, water samples were collected at three different time points over the course of the study. The first sampling event was at week 1 (January 9, 2019), week 7 (February 20, 2019) and Week 13 (March 27, 2019). Samples were collected at three specific

locations during each sampling event. The first location was the aquifer influent (ASR influent), the second was the granulated activated carbon effluent (GAC effluent), and the third was the ion exchange resin effluent (IX effluent). Samples were collected in methanol-rinsed 500 mL high density polyethylene (HDPE) bottles which have been shown in previous studies to minimize PFAS loss by adsorption. A travel blank was included for each sampling event that consisted of PFAS-free high purity water from a Millipore Milli-Q Reference system. The MQ water was poured into a separate cleaned 500 mL bottle when the last sample was collected and processed as described below.

Sample analysis began with brief sonication of the 500 mL container before measuring into a graduated cylinder. After transferring to the graduated cylinder, the sample collection bottle was rinsed with 5 mL of methanol which was combined with the measured aliquot and the sample volume was recorded.

Isolation and preconcentration of PFAS from raw and finished waters were performed using Oasis WAX Plus cartridges (500 mg; Waters Corp., Milford, MA). Cartridges were conditioned with 20 mL of methanol followed by 20 mL deionized water, each at a flow rate of 10 mL/min. A 500-mL aliquot of each water sample was loaded onto the preconditioned cartridges at a flow rate of 10 mL/min with HDPE large volume sampler transfer lines. The cartridges were washed with 10 mL of 25 mM sodium acetate buffer followed by 10 mL of methanol. Cartridges were dried completely by purging with high-purity nitrogen gas for 10 min after which analytes were eluted from the SPE into polypropylene centrifuge tubes with 4 mL of methanol with 0.28% ammonium hydroxide at a flow rate of 1 mL/min. The centrifuge tube was placed under a gentle stream of UHP grade nitrogen (1 mL/minute) to approximately 1000 μ L using a TurboVap system.

2.2 Liquid chromatography-high resolution mass spectrometric analysis

Non-targeted analysis of each sample was carried out using an Agilent 1290 LC coupled to a Bruker microQTOF II high resolution mass spectrometer. An electrospray ionization source operated in the negative mode was used for all analyses. The UPLC column was a Phenomenex Luna 50 mm x 2.1 mm with 1.6 μ m C18 phase. The solvents used were water (A) and methanol (B) both with 2mM NH_4OAc . The injection volume was 10 μ L for all samples. The gradient used for all analyses is described in Table 1.

During each analysis the mass axis was calibrated using the Agilent low tune mix. Each LC-QTOF analysis was screened against a suspect PFAS list to remove previously identified and reported compounds. Remaining suspect peaks observed in the LC were further explored if a negative mass defect resulting from several F and O atoms was observed and there was a signal to noise ratio >3 . The high resolution and subsequent mass accuracy of the QTOF was used to generate molecular formulas after calibration using Bruker Data Analysis Package 4.2 with general elemental composition limits of: carbon 1-60, hydrogen 0-60, fluorine 0-100, oxygen 0-15, nitrogen 0-1, sulfur 0-1, chlorine 0-1 and Na 0-1. These were refined depending on several observations such as isotope patterns.

Proposed molecular formulas generated were further checked against several metrics. The first was agreement of the isotopic pattern between experimental and matched formulas within ten percent. If the isotopic pattern between experimental and matched formulas was within 10 percent then a combination of dimer and adducts was used to confirm the molecular formula. Once a molecular formula was identified, the Chemical Abstract Services database was searched for possible CAS numbers. CAS numbers should not be used as a definitive measure to identify the compound, rather they should be viewed as an additional tool for structure

elucidation. Lastly, MS/MS was performed to aid in the characterization of the proposed structures. A variety of blanks was analyzed which included travel, method and instrumental with no PFAS compounds detected. The deprotonated molecular ion was used to integrate each of the compounds described in this study.

3. Results/Discussion

Samples analyzed by LC-QTOF high resolution mass spectrometry had several chromatographically resolved peaks that were tentatively identified based upon their molecular formulas (Figure 2). No commercially available standards were available at the time of this study to confirm these structures and provide concentration data. Until standards become available structures must be considered tentative and area counts under the chromatographically resolved peak reported in lieu of concentration data. Total areas of all compounds detected during the course of the study are presented in Figure 3. Even though we could not quantify the areas give a relative idea of total concentrations for the sum of these compounds. The first two sample points, ASR 1 and ASR 10, were collected September 22, 2017 and November 22, 2017 respectively prior to the current study. These samples represent water pumped out of the aquifer and are included in this report as a reference point for comparison. Samples collected from the aquifer are reported as ASR. The total area of ASR 1 is the highest representing maximum PFAS impacted waters present in the aquifer as a result of exposure to water that originated from the Cape Fear River water. As the pumping continued there was a decrease in total area of PFAS compounds in ASR 10. These two sampling events are important because they put the historical PFAS distribution in the aquifer in perspective compared to the present study. ASR influent samples during weeks 1, 7 and 13 were variable in total area counts suggesting that there is not a consistent PFAS background in these samples. PFAS total area counts in weeks 1, 7 and 13

decreased significantly relative to ASR 1 and 10. Total area counts of PFAS in the effluent of each treatment are always less relative to the area counts of the influent suggesting that both media were effective at removing some fraction of the PFAS initially present in the influent. GAC was always more effective at removing PFAS relative to ion exchange, however as sampling progressed from week 1 to week 13 the efficacy of removal decreased in both media indicating that their effectiveness declined with use. Presenting the same data as a fraction remainder (Figure 4), GAC was more efficient at removing PFAS compared to ion exchange over the course of study where ion exchange removed approximately 10% of the PFAS total area counts whereas GAC removed 40% at week 13.

Distributions of detected PFAS in ASR 1 and ASR 10 are very similar to the distribution of PFAS dominated by NVHOS at > 93% (Figure 5). The distribution was not the same when comparing the ASR influent to each filtering treatment over the course of this study. Pie charts in Figure 6 are the percentage of each compound relative to the total area for that sample. ASR influent during the first sampling event (week 1) was predominantly contained NVHOS. This compound was primarily found in the ASR 1 and ASR 10 samples. Comparing the GAC and IX effluents in Figure 6 to the ASR influent gives an idea of how the distribution of compounds changed after passing through the media. Data in Figure 6 suggest that GAC was more effective at removing PFAS compounds with more carbon atoms (e.g. PFO5DOA) and NVHOS. When compared to IX, NF BP 4 increased in relative percentage in the effluent. Week 7 ASR influent PFAS distribution (Figure 7) was very similar to week 1 and ASR 1 and ASR 10 since the dominant PFAS present was NVHOS. However, the GAC and IX effluents were very different compared to Week 1 in that NVHOS was the major PFAS present. By week 13 the GAC and IX

effluents were similar in distribution as the ASR influent (Figure 8?) with NVHOS dominating the PFAS distribution.

The change in PFAS distribution on the GAC and IX effluents between each of the weeks is striking. During initial sampling the linear sulfonate NVHOS is completely removed while the branched compounds such as PEPA and PMPA were not completely eliminated. This distribution changed during week 7 and 13 where NVHOS was not removed and dominated the PFAS make up in the effluent. There is little in the peer reviewed literature to explain the behavior of these replacement PFAS compounds during GAC and IX filtration and what data exist suggests incomplete removal of replacement PFAS compounds during drinking water treatment ³⁻⁵.

More research is available on the legacy compound removal by GAC and IX. For example, legacy PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTeDA; FOSA; PFBS, PFHxS, PFOS) were monitored for >200 days in simulated drinking water as it passed through GAC and IX columns ⁶. Overall, there appeared to be selective removal of PFAS based upon dissolved organic matter (DOM) and PFAS loading. The authors found PFAS with a carboxylate functional group had a clear trend in removal efficiency and chain length whereas PFAS with a sulfonate functional group showed greater removal efficiency. Breakthrough volume, when the response of analyte in effluent is equal to influent, was greatest for longer chain sulfonate relative to carboxylate PFAS for both GAC and IX.

The role dissolved organic carbon (DOC) concentration plays in the removal of emerging PFAS by GAC and IX is another important variable to consider ⁷. Kothawala et al. (2017) suggested that ion exchange was effective at removing PFAS from drinking water even at DOC concentration of 8 mg/L. In the same study, PFAS removal with GAC was dependent on

chain length and differed at various DOC concentrations. The chemical parameters over the course of this study are presented in Table 1 and include total organic carbon (TOC), dissolved organic carbon (DOC), and UV_{254} . TOC measurements represent the combined dissolved and particulate organic carbon present whereas DOC measurements represent the dissolved organic carbon pool. Both TOC and DOC samples were acidified prior to analysis thus removing inorganic carbon. Note that these measurements were collected as ancillary data during the course of the study and were not analyzed by UNCW. ASR influent TOC concentrations for all three sample events were fairly constant, ranging between 1.4 and 1.5 mg/L. TOC concentrations in GAC and IX effluents were always less than the ASR influent, however as the study progressed values increased. Comparing dissolved organic carbon (DOC) concentrations during sampling events indicates the effectiveness of filter media at removing DOC from the influent (Table 1). ASR influent samples had very similar DOC values whereas effluents for both GAC and IX were less than the influent, suggesting removal of DOC by both media. Temporal analysis of week 1 to week 7 shows that there was a slight increase in DOC concentration in both effluents suggesting the media effectiveness at removing DOC changed with use.

Composition of chromophoric DOM can be assessed with UV_{254} measurement since aromatic moieties and conjugated systems absorb in this region of the electromagnetic spectrum. ASR influent UV_{254} was similar for each sampling event and ranged from 0.02 to 0.03 cm^{-1} (Table 1). GAC and IX effluents were always lower in UV_{254} compared to influent samples with GAC consistently lower than IX. A recent peer reviewed publication suggests that UV_{254} does not accurately predict legacy PFAS retention behavior on GAC⁸. More research is needed to fully understand the behavior of PFAS on GAC in the presence of DOM.

The breakthrough bed volumes of PFAS determined in this study provide a final metric regarding performance of the filter media. The ratio of PFAS areas in effluent /influent to bed volume points to a clear trend in filter performance with time (Figure 9). The second sampling point (7 weeks of filter usage) suggests the efficacy of GAC (90% removal) is different relative to IX media (60 % removal. The 13 week data further illustrate this trend where GAC removed 40% of PFAS while IX removed only 10%. From these data it is clear GAC is more efficient at removing PFAS relative to IX but the efficiency of both media significantly decreases with extended usage.

4.0 Summary

High resolution mass spectrometry with liquid chromatographic separation allowed the detection of several tentatively identified PFAS compounds. There are currently no commercially available standards to confirm and quantify these compounds. Filter media had different affinities and removal efficiencies for the PFAS compounds detected over the course of the study. The change of PFAS removal performance may be attributed to several possibilities including molecular attributes (linear vs. branched; carboxylate vs. sulfonate) as well as dissolved organic matter composition and concentration. Lastly, GAC was more efficient at removing the suite of PFAS compounds but over reduced bed volume compared to IX.

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Table 1: Water parameters collected as a part of the study. Note, UNCW did not perform these measurements.

Sampling Week	Date of Collection	TOC mg/L			DOC (mg/L)			UV ₂₅₄ (cm ⁻¹)			Bed Volume		
		ASR Influent	GAC Full Scale Pilot Effluent	IX Full Scale Pilot Effluent	ASR Influent	GAC Full Scale Pilot Effluent	IX Full Scale Pilot Effluent	ASR Influent	GAC Full Scale Pilot Effluent	IX Full Scale Pilot Effluent	ASR Influent	GAC Full Scale Pilot Effluent	IX Full Scale Pilot Effluent
1	Jan. 9, 2019	1.5	0.4	0.5	1.3	<0.5	<0.5	0.026	-0.001	0.005	na	81	252
7	Feb. 20, 2019	1.4	0.6	1.1	1.4	0.7	1.0	0.030	0.007	0.018	na	4634	17693
13	March 27, 2019	1.4	0.9	1.1	nd	nd	nd	0.020	0.005	0.008	na	10203	34403

Figure Captions

Figure 1: Schematic illustrating sampling locations at ASR influent, GAC effluent and IX effluent.

Figure 2: Structures of per- and polyfluoroalkyl substances detected by LC- high resolution QTOF mass spectrometer. The numbers underneath each compound are the corresponding CAS identifier.

Figure 3: The total area of compounds described in this study to sample event. Notice the break in y-axis.

Figure 4: Removal efficiency of compounds detected in this study to treatment type and sample event.

Figure 5: Distribution as a percentage of compounds detected in this study for ASR 1(a) and ASR 10 (b).

Figure 6: Week 1 distribution as a percentage of compounds detected in this study for ASR influent (a), GAC effluent (b) and IX effluent (c).

Figure 7: Week 7 distribution as a percentage of compounds detected in this study for ASR influent (a), GAC effluent (b) and IX effluent (c). The two pie charts under each letter indicated by a Roman numeral is duplicate analyses.

Figure 8: Week 13 distribution as a percentage of compounds detected in this study for ASR influent (a), GAC effluent (b) and IX effluent (c).

Figure 9: The ratio of detected compounds in this study plotted against bed volumes for both GAC and IX filter media. The two symbols at the second time point are duplicate analysis.

Pilot Schematic

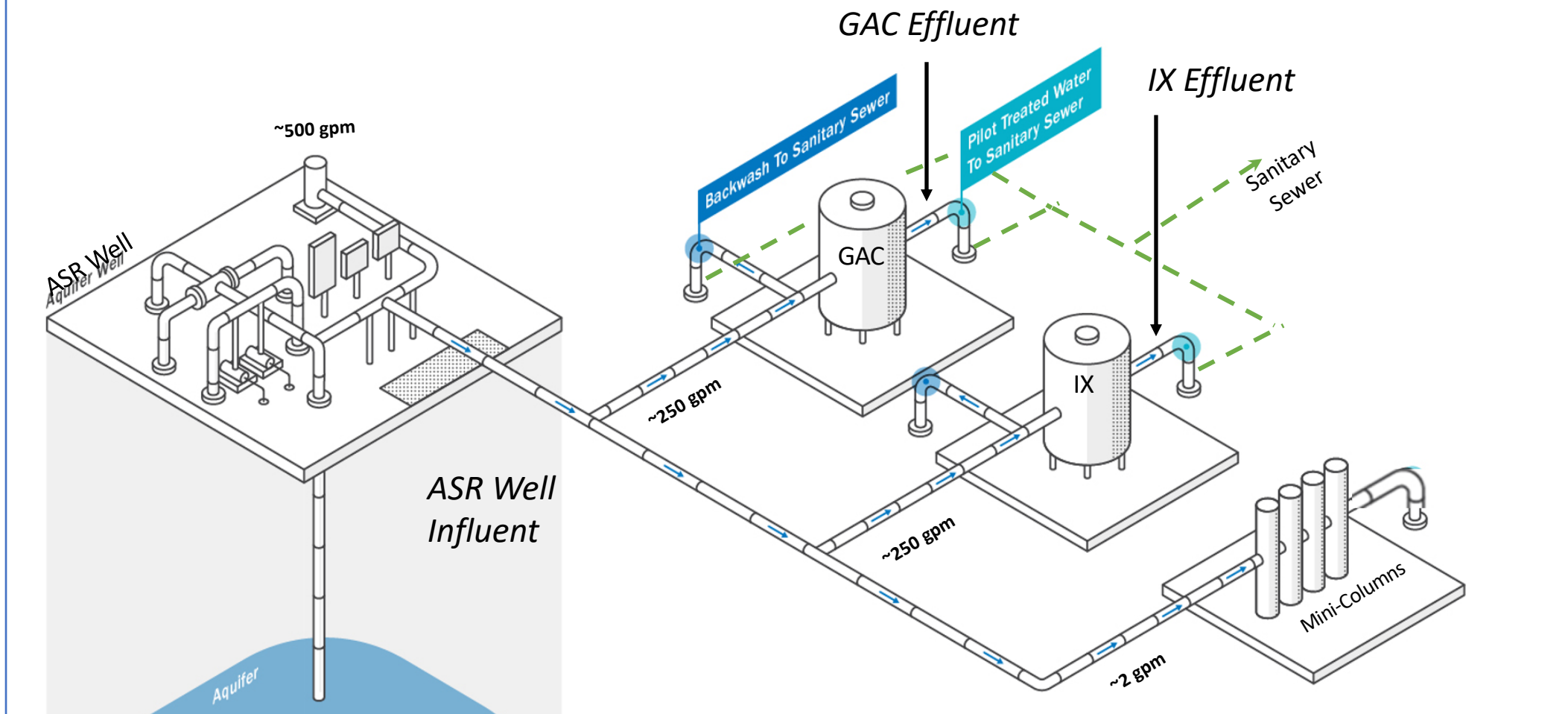


Figure 2

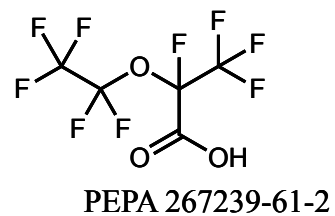
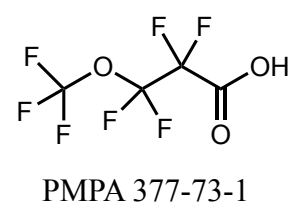
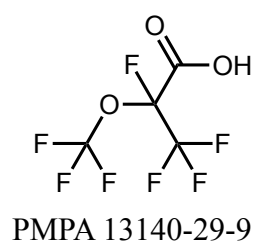
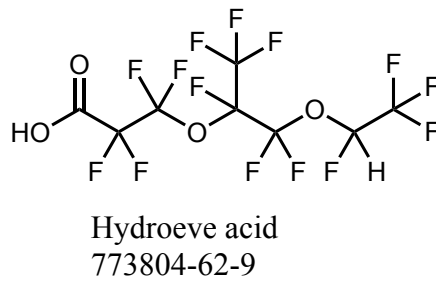
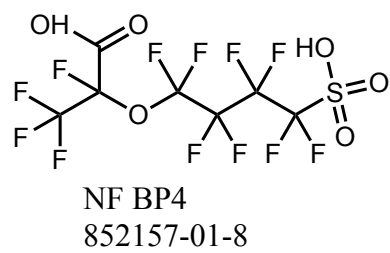
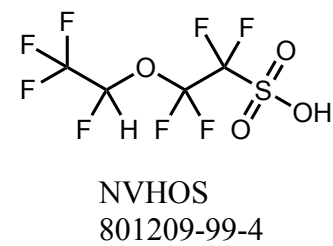
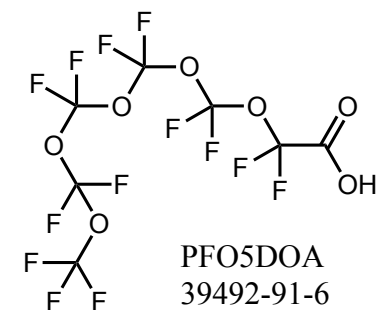


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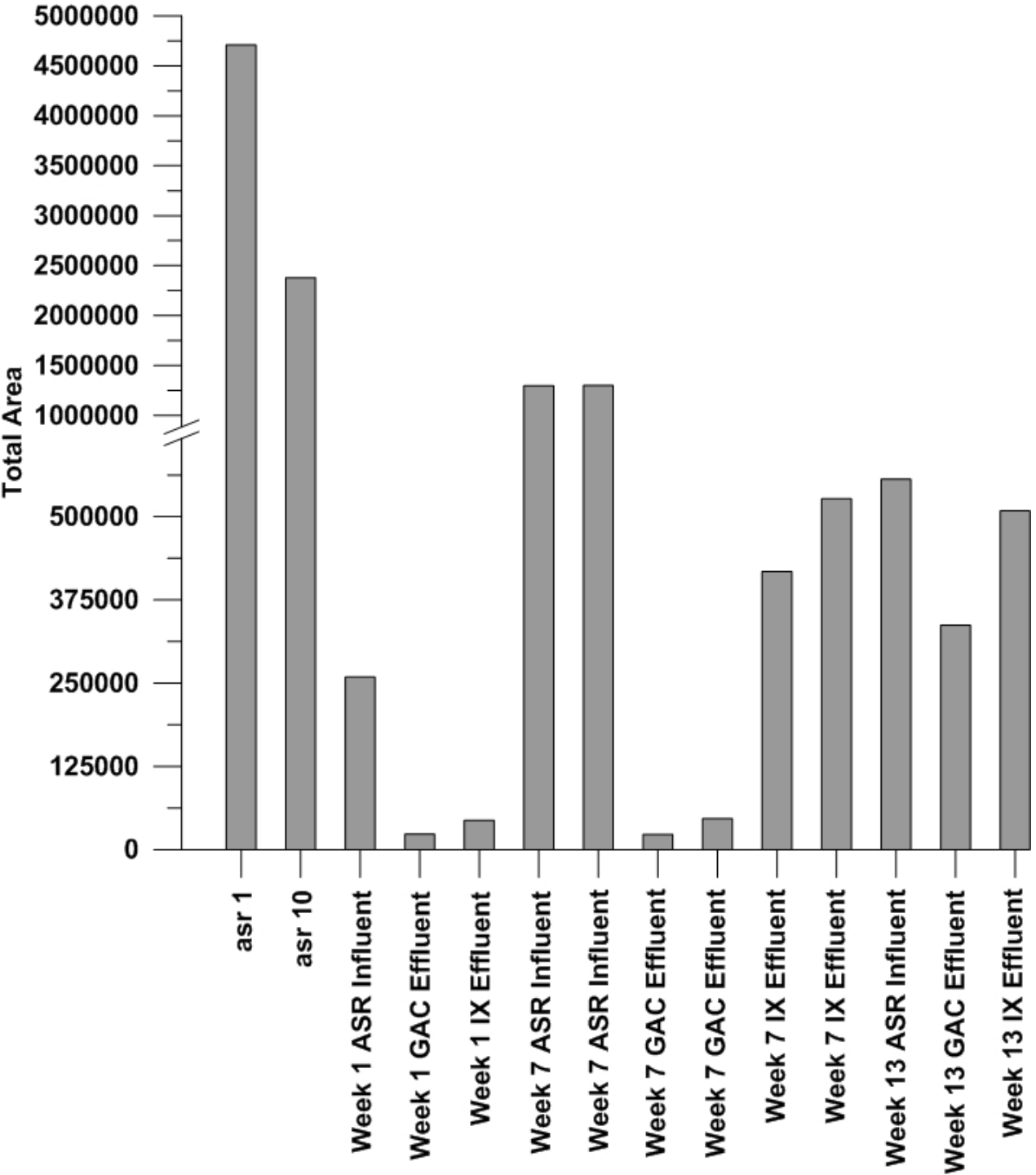


Figure 4

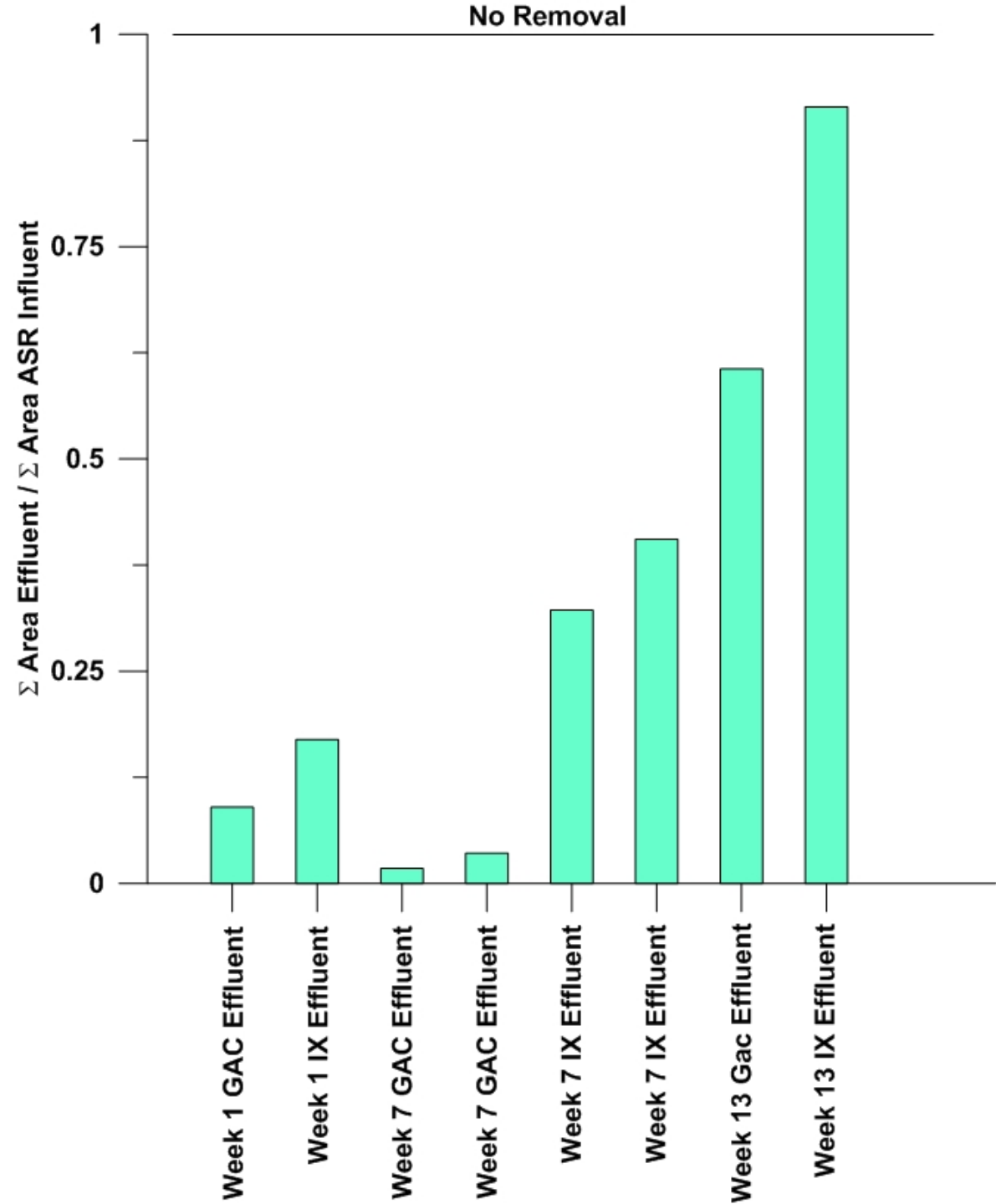
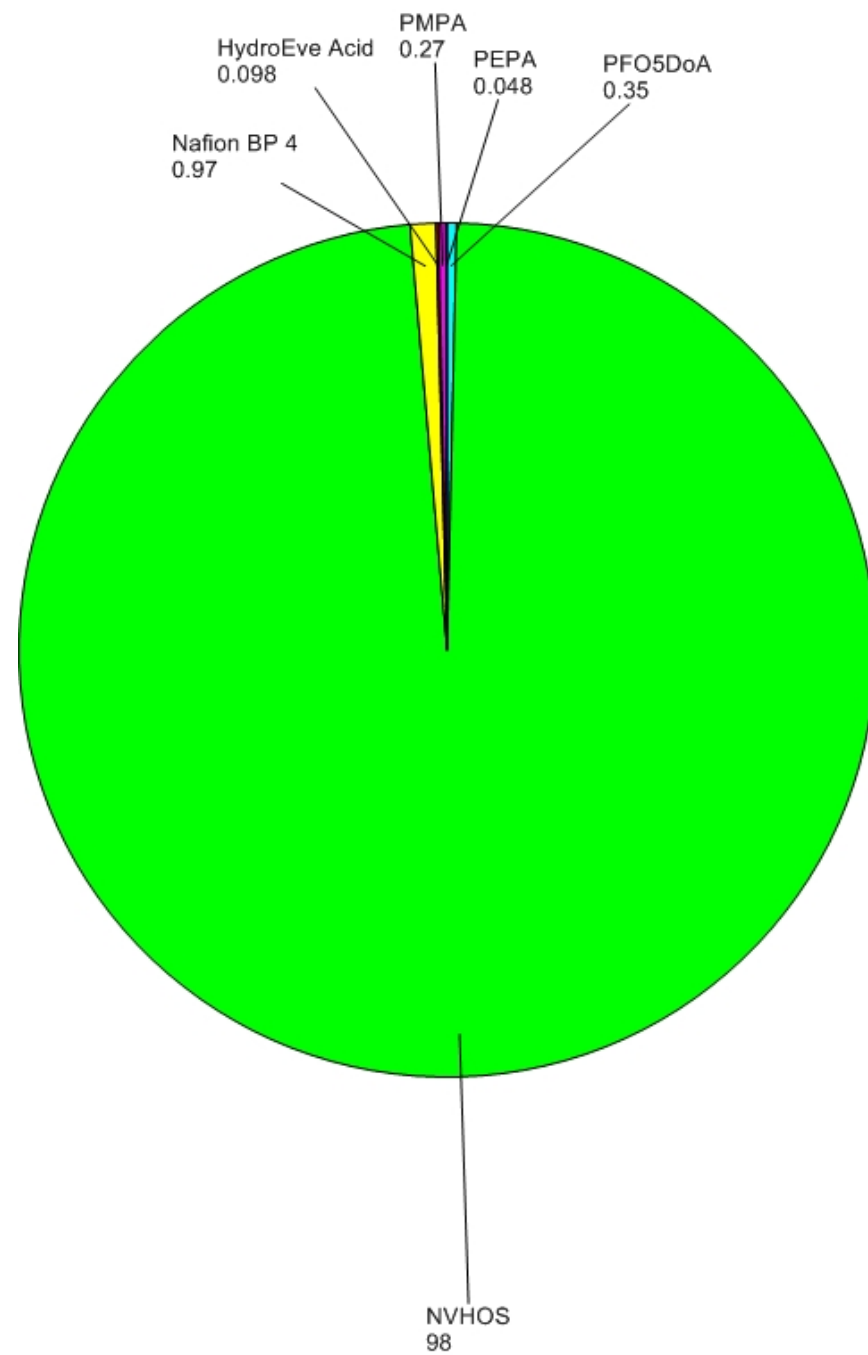


Figure 5

a.



b.

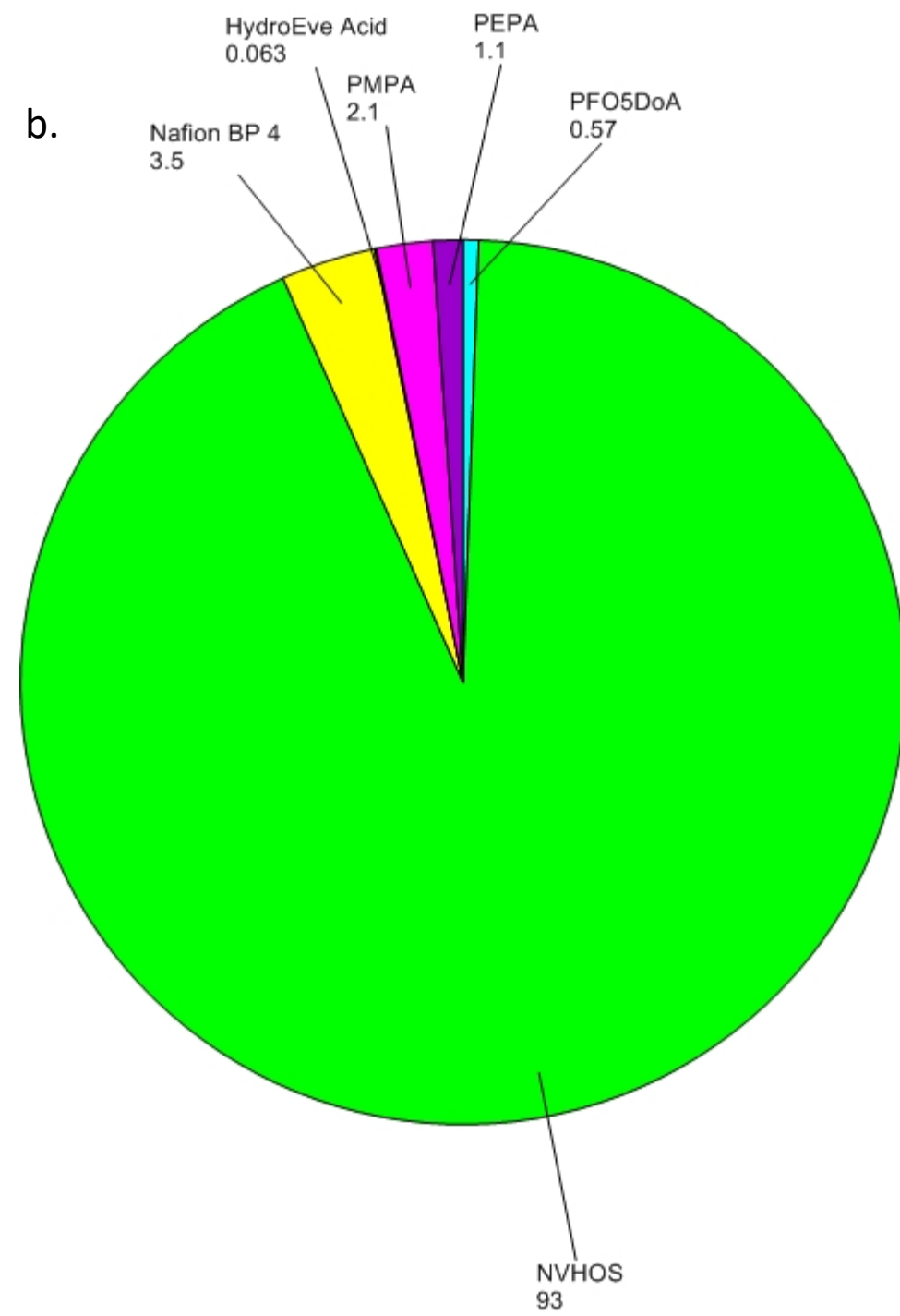
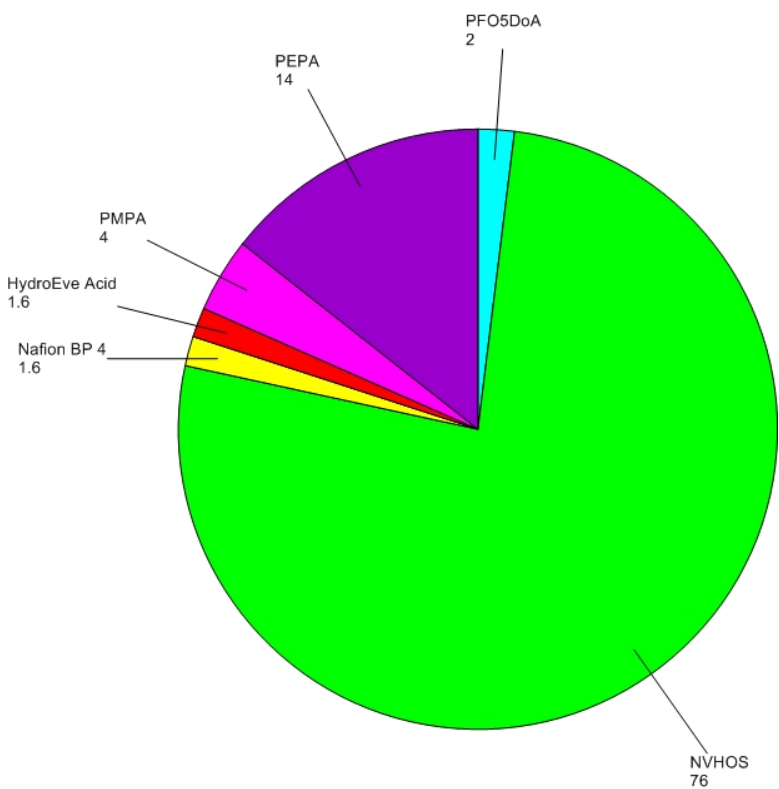
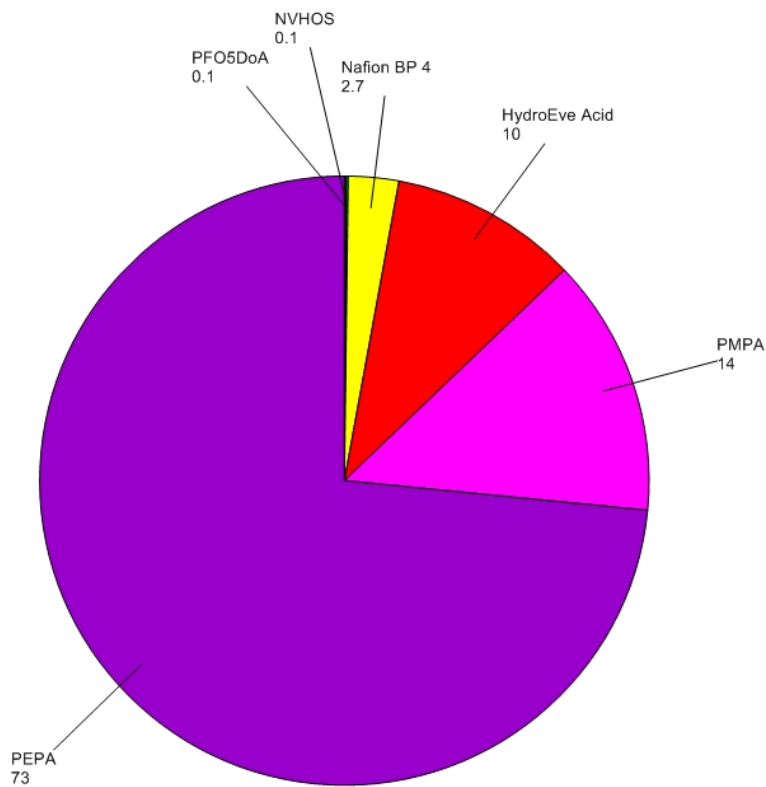


Figure 6

a.



b.



c.

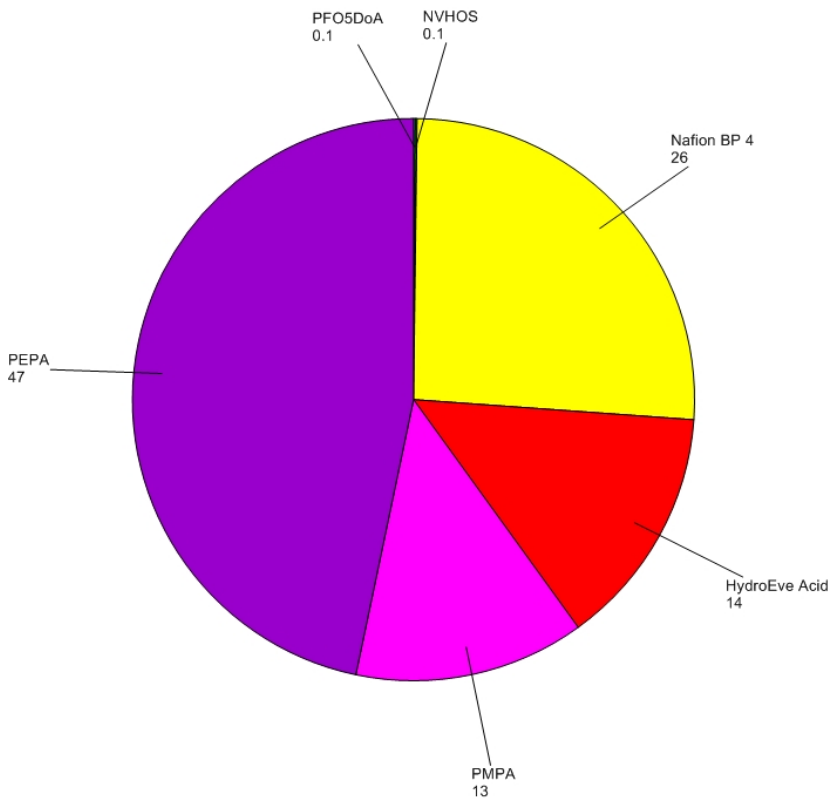


Figure 7

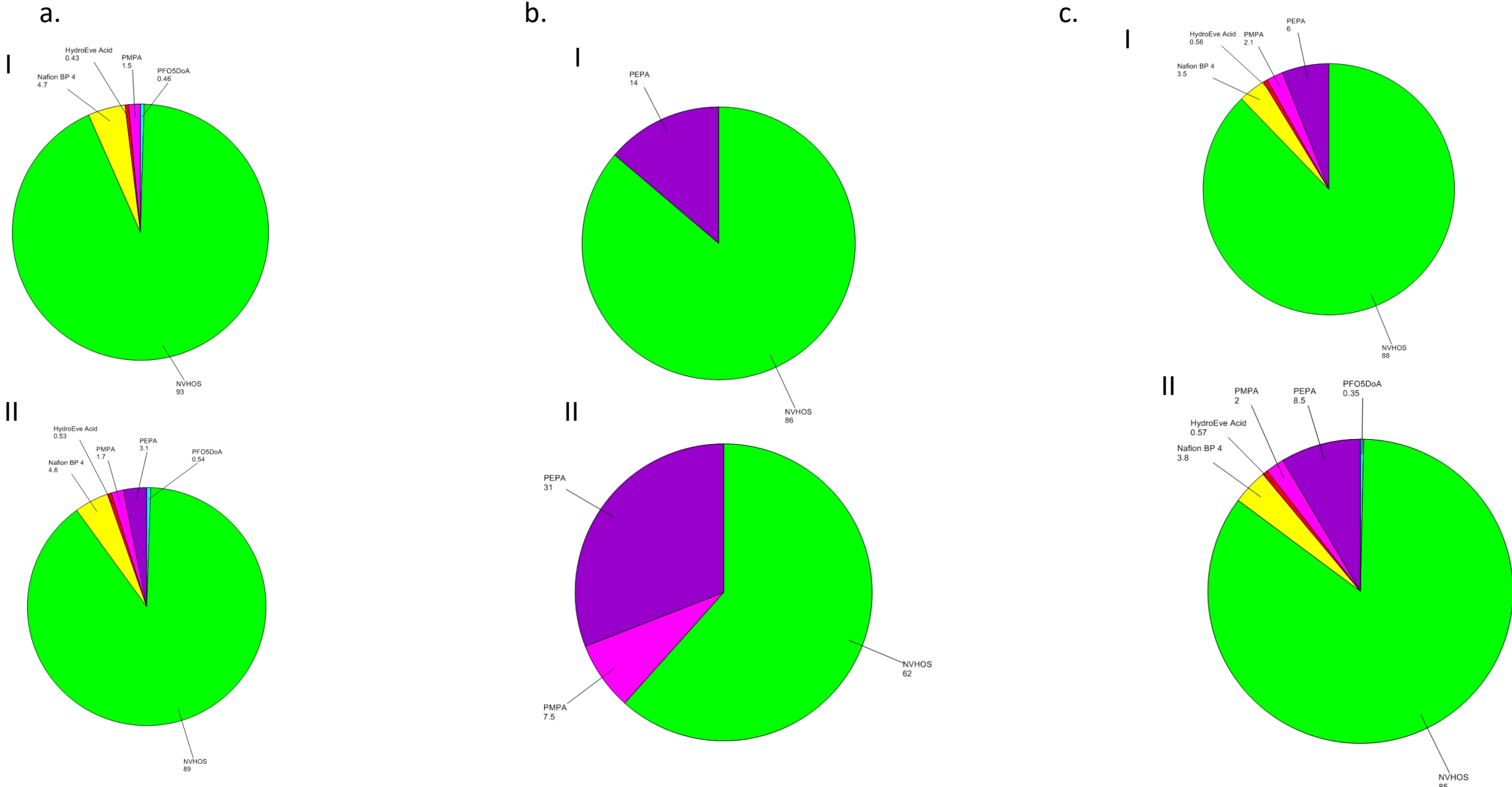
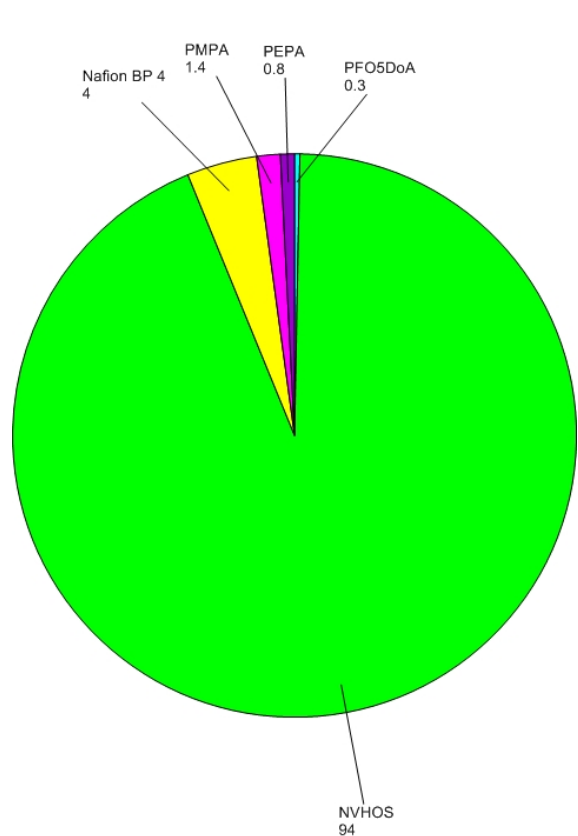
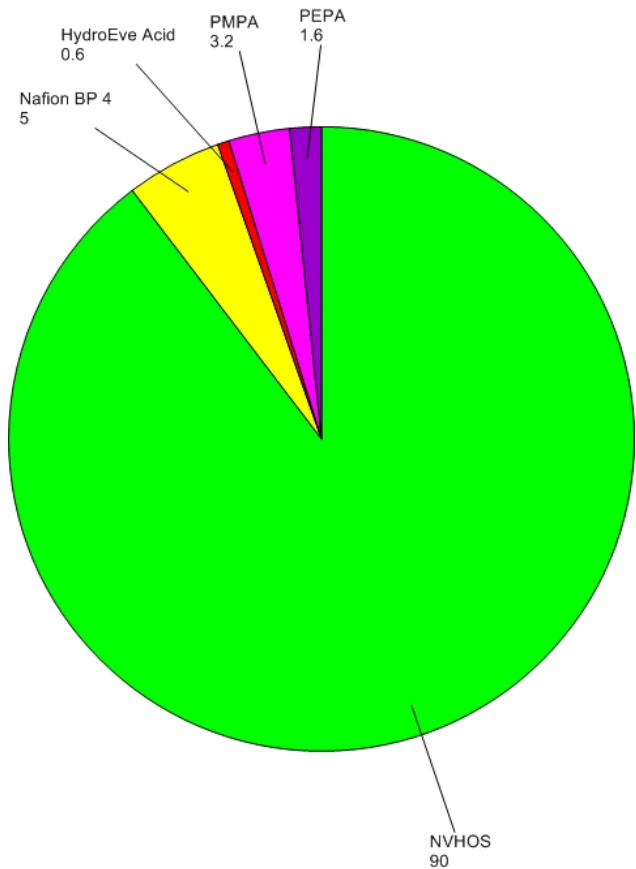


Figure 8

a.



b.



c.

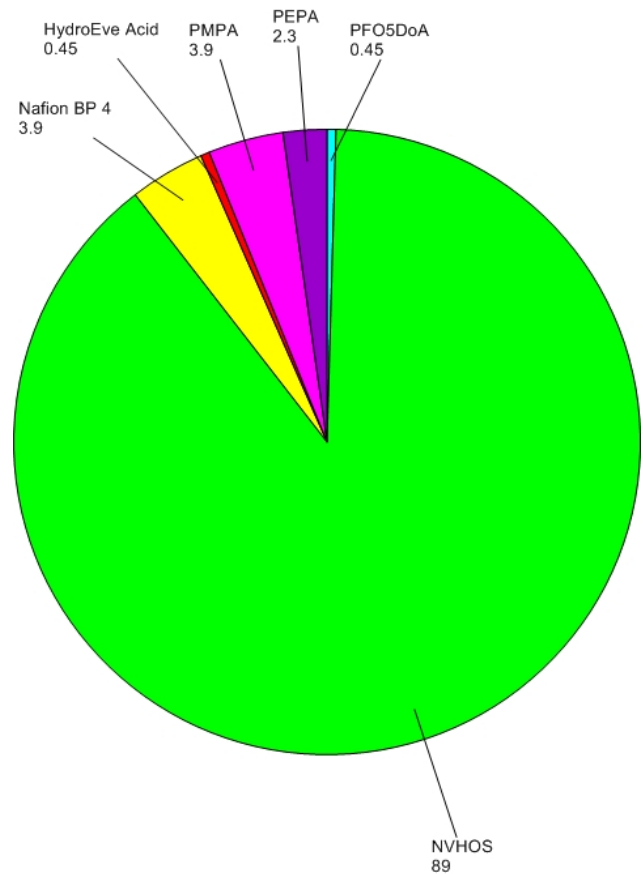
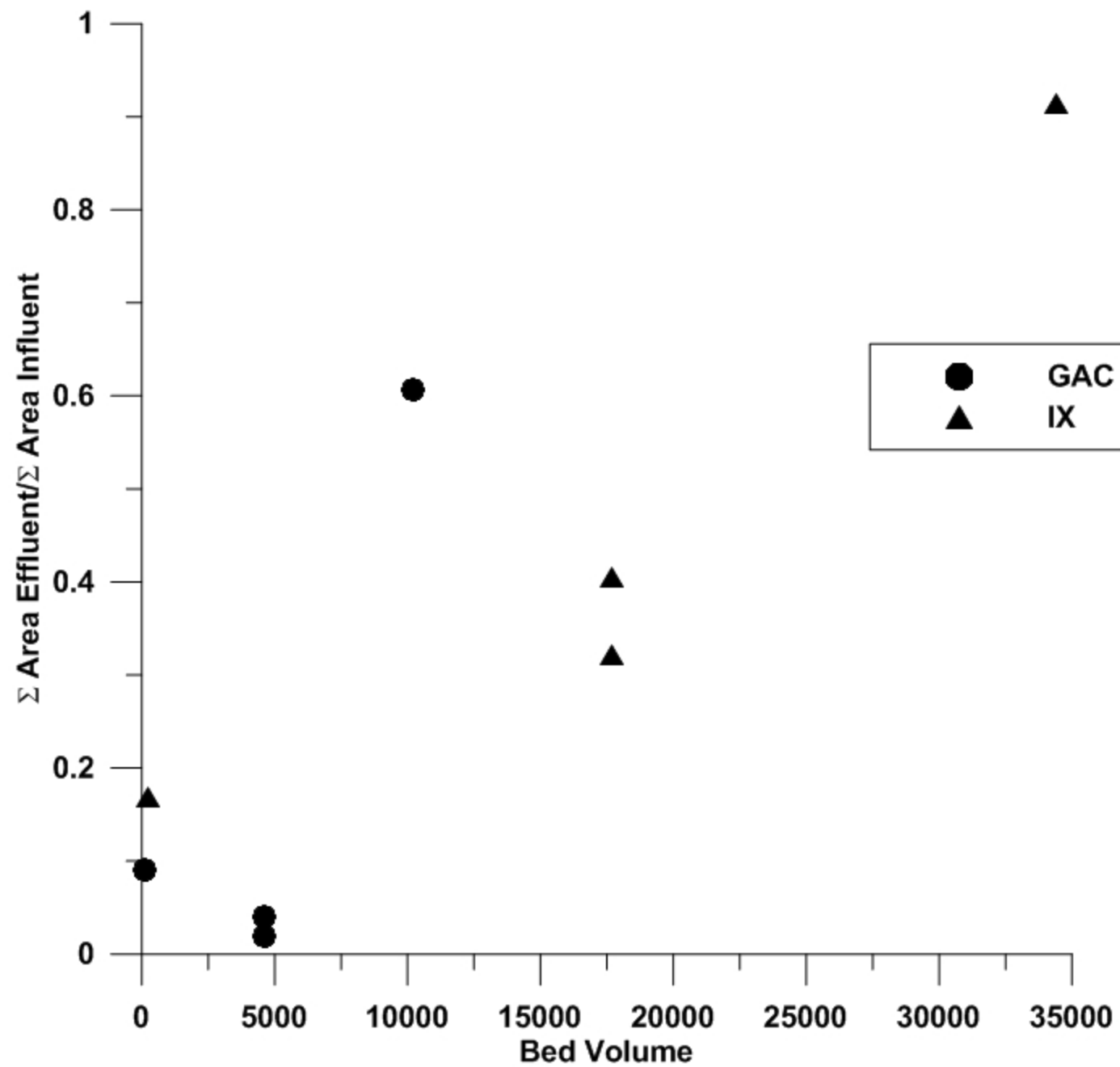


Figure 9





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