The Pennsylvania State University

The Graduate School

ANALYSIS OF GRANULAR ACTIVATED CARBON REMOVAL EFFICIENCY OF PER-
AND POLYFLUOROALKYL SUBSTANCES IN GROUNDWATER

A Paper in

Environmental Engineering

by

Andrew D. Crew

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Master of Environmental Engineering

December 2021

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made contaminants that are highly persistent in the environment and bioaccumulate within humans. PFAS contaminants the environment through industries such as aviation, chemical manufacturers, and processing facilities. The increasing discovery of PFAS in groundwater sources for drinking water has raised concerns since studies have shown PFAS to be potentially carcinogenic. Routine exposure through drinking water could lead to long-term health effects depending on the concentration and duration of exposure. Due to this health concern, the Environmental Protection Agency (EPA) set an health advisory limit (HAL) of 70 parts per trillion (ng/L), thus requiring numerous contaminated water systems to begin treating for PFAS.

The objective of this study is to review the granular activated carbon (GAC) removal efficiency for per- and polyfluoroalkyl substances (PFASs) at contaminated groundwater sites. PFAS treatment data were collected from three full scale granular activated carbon (GAC) systems that are currently treating PFAS. The data were graphed to analyze the behavior of PFAS with GAC treatment. The study looked at raw water and treatment characteristics that could be contributing to GAC's effectiveness at removing PFAS from drinking water. Factors that contribute to the removal efficiency include water quality, design characteristics, adsorbent characteristics, and contaminate properties.

Many pilot studies have shown GAC to be an effective form of treatment, but there are limited studies that show this on a full-scale over a long duration of time. This study showed that the GAC system was effective at reducing concentrations of PFOS and PFOA greater than 95% dependent on the quantity of water treated expressed as media bed volumes. The study also confirmed that GAC treatment is not as effective for short-chained PFAS such as PFBS and

PFHxA. At one treatment site, PFHxA demonstrated an increase concentration leaving the lag vessel indicating that desorption was occurring. A comparison between the three different treatment sites media replacement cost showed that switching the lead and lag vessel prior to the replacement of media in the original lag vessel reduced the media replacement cost by nearly half.

A theoretical PFAS breakthrough bed volume calculation was performed using Freundich's equation to compare to the actual breakthrough observed at each treatment site. The theoretical calculation typically uses conservative values and applies a safety factor since there are several unaccounted factors that affect adsorption. These factors include water quality, competition for adsorption, total PFAS concentrations and more. Due to the number of variables that affect the adsorption behavior of GAC, a pilot study to develop specific treatment data is normally encouraged since the theoretical calculation cannot be solely relied on.

Several factors that affect the adsorption of GAC were not examined in detail within this study. Other articles have shown that the type of TOC present in water affects the GAC adsorption efficiency more or less than other types. Other contaminants, such as VOC's have different properties that could compete with PFAS for adsorption sites. The competition for adsorption sites has mainly been commented on among the different forms of PFAS, but not among other contaminants. The data presented provides an overall trend of PFAS treatment, but due to the numerous factors that affect adsorption it cannot always be directly correlated to other treatment sites believed to have similar water quality.

Contents

Tables

Figures

Acronyms and Abbreviations

AFFF	Aqueous film-forming foam
AIX	Anion exchanged
AOP	Advanced oxidation process
ATSDR	Agency for Toxic Substances and Disease Registry
AWWA	American Water Works Association
BOD	Biological oxygen demand
CCL	Contaminant canditate list
CF	Cubic Feet
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
EPA	U.S. Environmental Protection Agency
EU	European Union
GAC	Granular activated carbon
GPM	Gallons per minute
KOW	Log of the octanol-water partition coefficient
LOAEL	Lowest-observed-adverse effect-level
MCL	Maximum contaminant level
NEtFOSAAN	Ethylperfluorooctanesulfonamido acetic acid
NMeFOSAA	N-Methylperfluorooctane sulfonamidoacetic acid
NO	Nanofiltration
NOM	Natural organic matter
PCFAs	Perfluorinated carboxylic acids
PFBS	Perfluorobutanesulfonic acid
PFC	Perfluorinated compounds
PFDA	Perfluorodecanoic acid

PFDOA	Perfluorododecanoic acid
PFHXA	Perfluorohexanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFSA	Perfluoroalkane sulfonic acids
PFTA	Perfluorotetradecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFUnA	Perfluorouoecanoic acid
PHFpA	Perfluoroheptanoic acid
POP	Persistent organic pollutant
PPARS	Peroxisome proliferator-activated receptor
NG/L	Parts per trillion
RO	Reverse osmosis
RSSCT	Rapid small-scale column tests
SDWA	Safe drinking water act
TCE	Trichloroethylene
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
VOC	Volatile organic compound

ACKNOWLEDGEMENTS

1.0   INTRODUCTION

Over the last two decades, a group of emerging contaminants known as poly-perfluoroalkyl substances (PFASs) have raised concern in drinking water systems due to significant detection levels in groundwater sources. PFAS are a human made substance used for extensive surface coating purposes that are extremely persistent. Surface and groundwater sources are exposed to PFAS through industry practice. Examples of industries that use these chemicals include paper products, cookware, aviation, pesticides, firefighting, military uses and more (ATSDR et al., 2021). Research articles have shown PFAS to contain carcinogenic properties and thus raising concern.

The objective of this article is to review the granular activated carbon (GAC) removal efficiency of per- and polyfluoroalkyl substances (PFASs) at contaminated groundwater sites. This paper focused on gathering in-situ PFAS data from contaminated groundwater sites that utilize granular activated carbon (GAC) technology for treatment. The data was collected at the groundwater site treatment by the water system operators using standard PFAS sampling techniques. Samples were collected before and after the GAC system approximately every month and shipped to a third-party laboratory for analysis. Raw water quality data such as total suspended solids (TSS), total phosphorus (TP), total organic carbon (TOC), pH, temperature and more were collected from previous water testing. The data was used to correlate and calculate the removal of PFAS compounds. Concurrently, various parameters that affect the efficiency of GAC for removing PFAS will be discussed.

Research to support the conclusion drawn from the provided data was gathered by accessing papers related to the topic via Penn State resources. These papers were taken from ScienceDirect, Wiley, ATSDR, Environmental Science and various articles. Source types

included AWWA papers, presentations, discussion with engineers, conferences, GAC manufactures, and resources from an engineering firm. Research was also conducted to provide a recommendation to improve the GAC removal efficiency.

A better understanding on PFAS removal with GAC treatment will result in improved treatment practices thus ultimately providing safer drinking water to the public. Improved practices will also help reduce the cost of treatment. Raising awareness will also encourage technological advances to occur that will improve PFAS removal.

2.0   LITERATURE REVIEW

2.1   Physical Properties

The chemical structures of PFAS are extremely stable and persistent in the environment. PFAS are categorized into two functional groups; one consists of hydrophobic nonionic strong carbon-fluorine chain. The second anionic group has a negative charge consisting of a carboxylates, sulfonate or sulfonamide head (Kothawala et al., 2017). The strong bond makes PFAS an effective surfactant repelling substances such as oils, fats and water (ASTDR et al., 2021). There are two different types of PFAS considered based on the number of atoms. If the PFAS molecule contains more than seven (7) carbon atoms, it is considered a long-chain. If less than seven (7) atoms, than it is considered a short-chain compound. Due to regulation, long-chained PFAS has been phased of production. As a result, short chained PFAS production has seen an increase over the past couple of decades. Though slightly easier to degrade, larger amounts of short-chained PFAS are required to obtain similar performance to long-chained PFAS (Brendel et al., 2018). The length of chain effects PFAS's physical properties and thus affects the type of remediation method. The physical properties of PFAS make it highly resistant to chemical, biological and thermal degradation.

The molecular structure of PFAS make them thermodynamically stable, requiring a high temperature to dissociate. The hydrophobic and lipophobic properties tend to result in PFAS compounds partitioning to interfaces between air and water. The low vapor pressure and high-water solubility are the main contributors for PFAS partitioning from water to air more readily (Brendel et al., 2018). The physical properties of each form of PFAS can drastically vary as shown in Table 1. The various formations of PFAS causes each compound to behave differently in the environmental. PFOA and PFOS have the same carbon chain length, but PFOA has a stronger hydrophobicity in comparison to PFOS due to the amount of fluorinated carbon bonds.

A research article noted that PFAS compounds with sulfonate head groups showed higher

hydrophobic properties due to the larger size as compared to PFAS compounds with a

carboxylate head group (Meegoda et al., 2020).

Table 1: PFOA and PFOS Properties

Property	PFOA	PFOS
Molecular Formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$
Molecular Weight (g/mol)	414.07	500.13
Color (Room Temperature/Pressure)	White powder	White powder
Melting Point (C°)	189	> 400
Boiling Point (C°)	192.4	Unknown
Density (g/cm³)	1.79	1.79
Water Solubility (mg/l @ 25 C°)	9,500	680
Vapor Pressure (mmHg)	0.53	0.002
Partition Coefficient (Log Kow)	4.81	4.49
Organic Carbon Partition Coefficient (Koc)	2.06	2.57
Acid Dissociation (pKa)	2.8	-3.27

Data taken from: https://pubchem.ncbi.nlm.nih.gov/compound/Perfluorooctanesulfonic-acid#section=Crystal-Structures

2.2   Health Effects

Humans can be exposed to PFAS through inhalation, ingestion and absorption through

the skin. The most common routes of exposure include diet and consumer household products

such as packaged food, nonstick pans, and cleaning products. Recently exposure through

drinking water has become more of a concern due to the discovery of PFAS in groundwater

drinking sources. Epidemiology studies have shown numerous health effects due to PFAS

exposure. Health system affected by PFAS include hepatic, cardiovascular, endocrine, immune,

reproductive, and developmental. Multiple articles have shown PFAS to contain carcinogenic

properties (ASTDR et al., 2021). A study conducted in 2007 showed that an estimated 98% of people have some type of PFAS already in their blood.

A study correlated exposing prenatal rats to different concentrations of PFOS through oral treatment. The exposure was linked to weight loss, specifically in rats exposed to high doses of 25mg/kg/day for a 4-day period (Grasty et al. 2003). One theory is perfluorinated compounds (PFCs) bind to peroxisome proliferator-activated receptors (PPARs) interfering with nuclear receptors in rats responsible for lipid metabolism and adipogenesis (Nelson et al. 2010). The interference with the mechanisms responsible for the formation of fat cells would coincide with the observed weight loss.

Studies performed on rats have noted higher concentrations of PFAS bioaccumulating in the serum and liver (Seacat et al. 2002). A water reservoir contaminated with PFAS from a nearby Armed Forces base in southern Sweden lead to exposing 28,000 people in a municipality. A survey of 3,418 people who drank the contaminated water was conducted and found the average half-life for PFOA was average of 2.7 years, 5.3 years for PFhxS, and 3.4 years for PFOS (Li et al, 2018). The long half-life of PFAS accumulating in the serum and liver correlates to the increase number of liver damage and blood diseases cases. In another study, PFAS was introduced to human hepatoma cells for 24 hours and was reported to cause DNA damage and oxidative stress (Wielsøe et al. 2015). This damage plays a role in the generation of cancer cells, particularly liver cancer in that particular study.

The combination of the PFAS bioaccumulating in blood tissue, the projected long half-life in humans and the potential routine exposure through drinking water raised concern of long-term human exposure. Information on PFAS's health effects on humans is still being generated, but there is enough evidence to raise concern when higher concentrations of PFAS are found in

drinking water sources. The concern of PFAS in drinking water has resulted in regulations being created within the last decade to being to combat the issue.

2.3 History and Regulation

PFAS was first created as waterproof coating as part of the Manhattan project in the 1930's. In the 1940's and 1950's, industries such as 3M and Dupont started to use PFAS in their products. PFAS was utilized in firefighting aqueous film-forming foam (AFFF) around the 1960's since it proved to be an effective flammable-liquid suppressant. It wasn't until the 1980's that people started to became more aware of the health concerns associated with PFAS exposure. These negative health impacts resulted in the production halt of PFOA and PFOS. In the early 2000's, EPA encouraged the phasing out of long-chained PFASs due to the carcinogenic properties and other negative health effects (Andrews et al., 2019).

In 2006, the PFOA Stewardship Program encouraged eight companies to produce ninety-five percent less PFOAs to help phase out the contaminate and its precursors (US EPA, 2006). The EPA included PFAS on the Contaminant Candidate List (CCL 3) in 2009. In 2016, EPA carried PFAS over from CCL 3 to CCL 4 for further evaluation (Humphreys et al., 2019). CCL 4 includes contaminates that are currently not subject to any drinking water regulations, but regulation is anticipated to occur in the near future. There is no established maximum contaminant level (MCL) currently for PFAS, but the Environmental Protection Agency (EPA) issued health advisory in 2016. In 2016, the EPA set a health advisory exposure limit concentration for PFOA and PFOA at 70 part per trillion (ng/L). This value was based on an uncertainty factor of 300, ten for human variability, three for animal to human toxicodynamic differences, and ten for lowest-observed-adverse effect-level (LOAEL). In February 2020, the EPA announced its decision to develop a PFAS action plan under the Safe Drinking Water Act

(SDWA). EPA is required to provide a rule within two years of making a proposed regulation and has eighteen months to start promulgating the regulation. EPA is still conducting research to determine a maximum contaminate level (MCL) and provide feasible treatment methods to meet the MCL.

Individual states within The United States have taken it upon themselves to establish their own MCL's. For example, New York, New Jersey, New Hampshire, California, and Minnesota have proposed and/or enacted stricter MCL's of 15 ng/L or less for the time being. Other states that do not establish a specific MCL will be subject to the current EPA MCL regulation of 70 ng/L. In responses to the HAL, Pennsylvania developed a PFAS action team to develop strategies for managing PFAS in 2019. The action team implemented a drinking water sampling plan in 2020 & 2021 to generate data of contaminated water sources across the state. In June of 2021, the Wolf Administration announced the PFAS sampling results along with a plan to develop an MCL for PFAS. The plan also included several steps addressing remediation of contaminated drinking water sites (PADEP et al., 2021).

The United States appears to be one of the front runners for updating water regulations as more information about PFAS is discovered, however European countries have started to begin setting their own regulations and goals for PFAS contamination as well. PFAS is considered a persistent organic pollutant (POP) and is regulated to discourage the use and production of PFAS. The European Union (EU) is planning to establish a 'group limit' consisting of sixteen individual PFAS types of a concentration no greater than 0.1 ng/L in drinking water. Countries including Denmark, Germany, Netherland and Sweden have set their own national limits for drinking water PFAS concentrations. Countries in the Middle East have minimal regulations for PFAS substances and only include those countries who are a party of the Stockholm Convention

have regulations. The Stockholm Convention is an international environmental treaty that aims to limit the use of POPs (IPEN,2019). Japan has some of the most prominent PFAS manufactures (3M, AGC, Daikin etc.) and, as a result, the country has some of the highest levels of exposure. Japan has some regulations on PFOS, but other forms of PFAS such as PFOA and PFHxs are unregulated (IPEN, 2019). Similar to Japan, China also contains industries that use large amounts of PFAS, but has minimal regulations.

2.4   Treatment Technologies

There are several methods proven to reduce the PFAS concentration from a contaminated water source. Methods include granular activated carbon (GAC), anion exchanged (AIX), reverse osmosis (RO), nanofiltration (NO) and advanced oxidation process (AOP).

Granular activated carbon (GAC) is a common material process used in water treatment to remove organic compounds and to help improve taste and odor. GAC uses a combination of highly porous organic materials such as wood, lignite, coconut and coal. GAC are effective because the material has a large surface area as well micropores to allow adsorption of a wide range of contaminants.

Anion exchange (AIX) relies on separating ions in molecules based on their net surface charge. Anion exchange resin consists of positively charged exchange sites that bind to the negatively charged tail of a PFAS molecule. The size and charge of the most present PFAS molecule determines the best type of resin. From studies, resins can be narrowed down, but bench scaling or pilot scale testing is still performed since there are numerous factors, such as competing ions, that affect the PFAS removal efficiency of resin.

Reverse Osmosis (RO) and Nanofiltration (NF) utilize a pressurized membrane with pores that are permeable to water molecules. This restricts contaminates such as PFAS on the

outer membrane where it is collected as a waste stream. NF has a filter pore size of 0.001 microns while RO has a pore size of 0.0001 microns. Revere osmosis's smaller pore sizes results in removing all organic molecules and viruses as compared to NF which removes most organic molecules and viruses.

Advanced oxidation process (AOP) technology has shown potential to degrade PFOA up to 90% by degrading PFASs into another molecule. The AOP process relies on production of hydroxyl radicals (OH^-) to oxidize the desired compounds in the water. The oxidation of the contaminant breaks it down into smaller inorganic molecules which makes the contaminant easier to remove.

Each treatment method has advantages and disadvantages depending on the treatment objective. The source water characteristics, costs, amount of treatment, size, timeframe and more play into the decision matrix of selecting the best treatment for each particular situation.

GAC is not as effective at removing shorter-chain PFAS. GAC requires a longer empty bed contact time (EBCT) resulting in a larger infrastructure footprint when compared to other treatment methods. The cost of GAC media is less than AIX media, but the typical bed life of GAC is approximately half the bed life of AIX. GAC has a long history of treating PFAS, having been implemented as PFAS treatment removal for over fifteen (15) years now. Spent GAC is more readily disposed of through thermal destruction or reactivated.

Anion exchange resin is greatly affected by the organic content of the treatment water. Organic matter and other anionic compounds will compete with PFAS for the resin's uptake sites thus resulting in a potentially lower PFAS removal efficiency. The molecular weight distribution, charge, and density of organic matter also influences the interaction between PFAS and resin

(Dixit et al. 2019). Due to the high expense of resin, most resins are regenerated using various types of solution (Du et al. 2014). Regeneration solutions are relatively effective, but the waste from the rinse still contains high concentrations of PFAS and which are difficult to dispose of. As a result, most resins are replaced onsite and regenerated by the manufacturer. Anion exchange is a recently emerging technology that needs further research and pilot testing. AIX has a higher capital cost when compared to GAC; As a result GAC is more commonly implemented. Due to the smaller size of the vessels, AIZ typically has a lower total capital cost.

The consequence of reverse osmosis's (RO) small pore size is that it removes essential minerals such as magnesium and calcium. RO and NF require water be pretreated to prevent clogging of the filter. These methods are quite expensive upfront and require routine maintenance to prevent the filters from clogging. Due to the small pore size, RO and NF produce a low yield of clean water compared to the percent wastewater. This results in having numerous filters in order to produce the same quantity of treated water in comparison to other methods. RO and NF creates a high concentration waste of PFAS that make it more difficult to treat and dispose of (Bertanza et al. 2020).

Advanced Oxidation Process (AOP) is still an emerging technology and studies have shown it to not be consistent enough to implement for PFAS treatment. Typically, AOP is used for removing organic materials from the source water, therefore organic materials would compete with PFAS for the oxidant resulting in a lower removal efficiency.

2.5   Granular Activated Carbon Treatment:

2.5.1   Adsorption and Regeneration

Granular activated carbon has been used for over a century in industries to remove organics to help improve water quality. The primary reaction that is responsible for the

adsorption of PFAS and GAC is a hydrophobic interaction. Studies have shown the more hydrophobic the PFAS compound is, the better adsorption rate is. This is specifically true for PFOS which tends to show a higher adsorption rate in comparison to PFOA even though both compounds have a similar tail. PFOS is more hydrophobic than PFOA thus confirming what other studies have shown. The adsorption rate also correlates to the tail length of PFAS compounds. Typically a longer C-F chain correlates to a greater sorption capacity. Generally the length followed by the hydrophobicity of PFAS compounds dictates the order of sorption among PFAS compounds (Deng et al. 2014).

Other studies have shown that PFASs with carboxylic functional groups exhibit a greater electrostatic effect in comparison to sulfonic functional groups. The greater electrostatic effect results in sulfonic compounds being more readily adsorbed in comparison to carboxylic groups. Full scale studies have verified this theory through monitoring of PFBS and PFBA which have the same amount of carbon atoms, but PFBS was adsorbed to a greater extent (Bertanza et al., 2020). Since longer-chained PFAS and other substance may sorb more readily in comparison to short-chained PFAS, this creates a competition for sorption sites. This competition can potentially lead to desorption of short-chained PFAS and explain why short-chained PFAS typically have an earlier breakthrough in comparison to long-chained PFAS (Appleman et al.2014).

The agglomeration process of coal-based material effect the size and consistency of the material's pores (Boone et al. 2019). Understanding the material formation can be used to better predict the pore energy and the total adsorbent characterization under different conditions. The formation process of GAC affects the distribution of flow throughout the vessel that can potentially lead to channels being created. Studies have shown that smaller GAC particles lead to

a greater removal efficiency of PFAS due to having a larger surface area (Liu et al. 2019). Agglomeration produces an even activation through each particle and provides increased kinetic behavior. Though increased surface area leads to a higher removal efficiency, it can also result in more pore blockage.

A comparison study between coal based GAC and coconut based GAC showed that the coal based GAC had fewer high-energy pores relative to the coconut based GAC. At the same time, the coal based GAC has a larger transport pore structures in comparison to the coconut based GAC. Despite having less energy that the coconut based GAC, the coal based GAC has larger transport pore which allows the GAC to be utilized more effectively by creating more sites for adsorption (McNamara et al. 2018).

Another study looked at the formation of hemi-micelles and micelles with long chained PFAS. A micelle is an aggregate of molecules within a liquid that form a colloidal suspension. The micelle structure forms on the surface of the GAC through hydrophobic interactions and acts as an adsorbent for PFAS molecules (Siriwardena et al. 2019). PFOS tends to show a higher tendency to form micelles which yields a higher removal efficiency. At the same time, the formation of micelles can block pathways that has shown to inhibit the sorption of PFOA in certain cases.

GAC systems are normally designed utilizing single vessel or dual vessels. A study compared the amount of bed volumes treated between single and dual vessel arrangements for PFAS treatment. The size of the vessel is dependent on several factors including the desired empty bed contact time (EBCT), the linear velocity, the desired contaminant being removed, type of media, influent water characteristics and more. Typically, GAC systems are installed at the head of the treatment before any other treatment processes occur. This is done because

feeding chemicals upstream of GAC will tend to foul the media faster and reduce the chemical residual in water. In a dual vessel system, the first vessel or "lead" vessel is normally run until the bed effluent exceeds 50% breakthrough of the desired contaminate. Once this occurs, the second or "lag" vessel is switched to become the lead vessel as GAC is replaced in the first vessel. The piping between the lead and the lag vessel is configured to allow either vessel to act as the lead or lag.

Once the GAC media is spent, GAC is typically removed and replaced by a third party working with the manufacturer. GAC vessels are typically equipped with drains to remove the spent media and new media is placed through the influent piping of the vessel. Once the new media is placed, it is common practice to perform a backwash of the vessel and let the vessel sit for twenty-four hours prior to operation. Additional backwashing may be required if the influent water contains higher level of solids, thus, developing a higher head loss through the vessel. GAC vessels used for PFAS treatment normally only require backwashing when media is replaced since additional backwashing decreases the performance efficiency of the media. Since the backwash contains PFAS it also requires the backwash water to be retreated or shipped offsite for disposal.

Spent media removed from the site can be thermally treated for disposal and regeneration purposes. The required PFAS degradation temperature is correlated to the chain length of the PFAS compound, but ultimately required temperatures above 1000 Celsius (Kucharzyk et al. 2017). Heating to this temperature requires a large amount of energy and becomes quite expensive. The reactivation process restores the pore structure of the GAC by eliminating the organic material. Certain studies have shown that regenerated GAC can be more effective at removing certain types of PFAS than virgin GAC.

2.5.2 Evaluation

The selection of an effective material for GAC treatment relies heavily on matching the desired treatment with the best material. Field conditions can be drastically different than bench-scale testing, which can poorly correlate to actual full-scale treatment. Certain types of GAC material are more effective at removing certain types of PFAS due to the length and head group. Due to the high replacement cost of GAC media, research is being conducted to implement a cheaper and more effective material. The most common GAC materials include bituminous coal and coconut-based. Studies have shown that bituminous coal can adsorb a wider range of PFAS compounds and achieve a higher removal efficiency when compared to coconut based GAC. One of the difficulties in selecting a material is that not one material adsorbs all types of PFAS as effective as other materials. This is particularly more evident when it comes to short-chain PFAS. Short-chain PFAS are harder to remove than long-chained PFAS due to the properties of the compounds. Due to the ban of longer-chained PFAS compounds, there has been an increase in use of short-chain PFAS compounds. An increased production has resulted in larger amounts in the environment over time.

Numerous studies and applications of GAC treatment have shown that it to be an effective method for removing various forms of PFAS. Despite this, pilot testing by rapid small-scale column tests (RSSCT) is performed to evaluate the best material for the desired treatment. RSSCT is a common tool for GAC evaluation, this method involves filling small columns with crushed GAC media. A known flow rate and influent PFAS concentration is applied to each column to record the amount of PFAS removed. This data collected is scaled to the needed size based on several parameters. Studies have shown issues can arise when scaling to full-size treatment due to the number of assumptions. RSSCT does not fully consider the competitive

inhibition of seasonal substances that would interfere with the adsorption of PFAS and media pulverization (AWWA et al. 2019). Depending on the number of samples, RSSCT can cost upwards of $5,000 per water sample and media material.

Another common testing method used for determining the GAC media is isotherm testing. Isotherm testing introduces water containing PFAS to a flask with an known amount of media. Sampling is conducted until isotherm equilibrium is achieved. Isotherm equilibrium is achieved when the PFAS adsorption reaches a steady state. Isotherm testing produces fast preliminary adsorption capacities for multiple types of media. Due to the limited scalability this method alone is inadequate to support full scale design (AWWA et al. 2019).

2.5.3 Impact Factors

GAC has proven to be an effective adsorbent technology but can be heavily influenced by multiple parameters. One of the most significant factors that affects GAC removal efficiency of PFAS is the influent water composition. Dissolved organic carbon (DOC) impacts the adsorption and desorption of various contaminants including PFAS. As the amount of DOC fluctuates, it tends to increase pore blockage. It also competes with PFAS for adsorption sites of the GAC media. Other studies have also attributed DOC to reducing the mass transfer surface area and affecting the film mass transfer coefficient (Liu et al. 2019). The natural organic matter (NOM) charge and size also affect PFAS's sorption onto GAC. Another experimental pilot study showed that the sorption of PFOA increased in the presence of co-contaminants by 36-50% due to the coating of coal based GAC making it more hydrophobic (Siriwardena et al. 2019).

PFAS contamination of a drinking water source normally involves a polluted groundwater source. The quality of groundwater sources varies drastically from location to location and can significantly impact the effectiveness of GAC treatment. The pH of the

adsorbent and solution can affect the adsorption of PFAS. The adsorption efficiency has shown to decrease when pH is increased due to the ionic interaction. Decreasing the pH decreases the zeta potentials as well, which makes the interaction slightly more repulsive. The pKa values of PFAS as shown in Table 1 are negative, therefore the electrostatic interaction between the adsorbent and PFAS is slightly repulsive (Deng et al. 2014). Though minimal, if the anions of the PFAS compound are not able to overcome the repulsion, the compound will not be able to be adsorbed by the GAC.

2.5.4 Analytical Methods

There are two current methods accepted by EPA to test for PFAS in finished water sources, Method 537.1 & Method 533. Both methods use solid phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC/MS/MS) to analyze samples. Method 533 was published in December of 2019 to target shorter-chain PFAS that could not be analyzed by Method 537 (Shoemaker et al. 2018). Method 533 can measure a total of twenty-five (25) PFAS including an additional eleven (11) short-chain PFAS.

Sampling can be impacted in several different ways that interfere with accuracy. Co-contaminants and turbidity of the water make quantitation more difficult. Some concentration can be lost through the evaporation of PFAS. There are also thousands of different PFAS forms, the current testing only encompasses twenty-five (25) of those forms.

Testing is not only sensitive but requires a large quantity of sampling. Large amounts of sampling are used to determine the most abundant form and the source of PFAS. Even after the form of PFAS is determined, pilot testing is normally performed with the contaminated water to select the best material for treatment. Each PFAS sample can cost around $300, resulting in a high initial cost on top of the cost of treatment equipment.

3.0 METHODS

3.1 Treatment Sites

This paper focused on two different water systems. Both systems will remain anonymous to protect the identity of the water system. Water System A installed a temporary GAC system at two locations after certain water sources were suspected to be contaminated with PFAS. The two treatment sites will be identified by Treatment Site 1 and Treatment Site 2. The water system responsible for the Treatment Site 1 and 2 will be identified as Water System A. The two GAC vessels at each treatment site were installed in March of 2019. The GAC systems were started in April of 2019 and have been in operation since.

Treatment Site 1 pulls water from two wells for system distribution. Treatment Site 1 now utilizes a lead and lag GAC vessel followed by a chlorine contact pipe as shown in Figure 1. Treatment Site 1 contains two submersible pumps; one Grundfos and one Sulzer. The Grunfos pump has a design flow of 100 gallons per minute (gpm) and the Sulzer pump had a design flow of 140 gpm. The design maximum flow of both wells is 240 gpm. An average flow of 120 gpm was observed from April 2019 to June 2021.
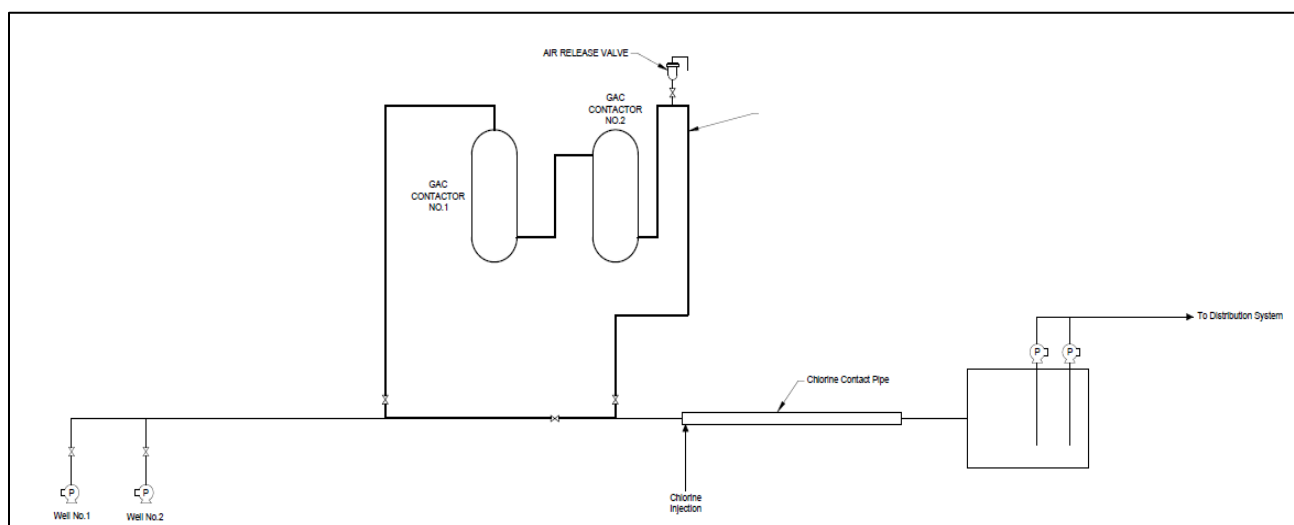

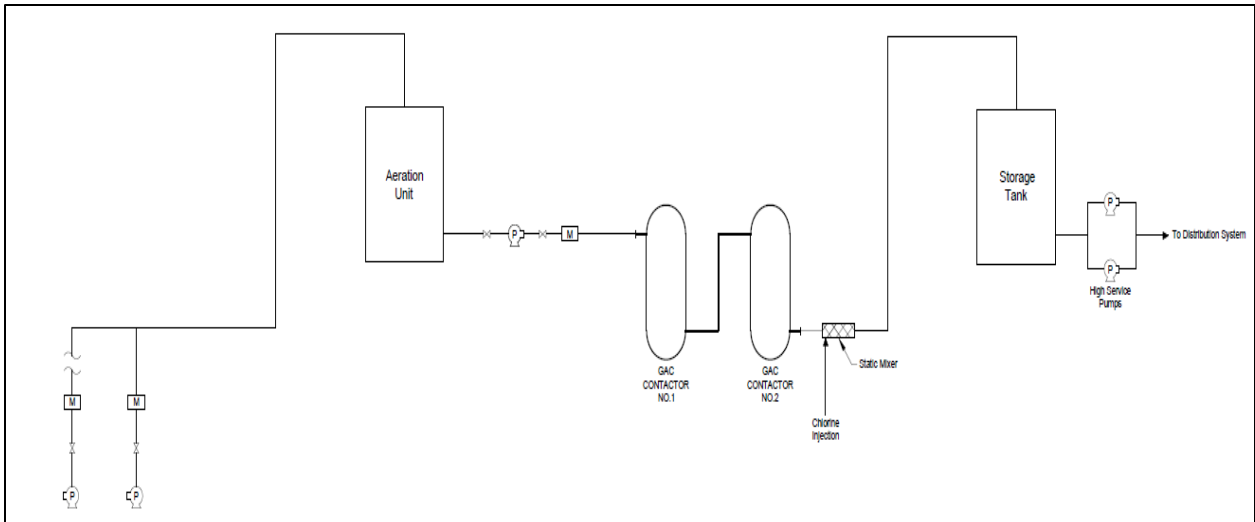**Figure 1: Treatment Site No. 1 Schematic**

Figure 2: Treatment Site No. 2 Schematic

Treatment Site 2 pulls water from two different wells for system distribution. Treatment Site 2 has a shallow tray air stripper operating just prior to the lead and lag GAC system. The air stripper was installed in 1999 to help treat volatile organic compounds (VOCs) such as 1,1,2-Trichloroethane and Trichloroethylene (TCE). The GAC system is followed by chlorine injection and then water stored in a storage tank for distribution as shown in Figure 2. Treatment Site 2 contains two Goulds pumps with a design flow of 95 gpm each. Treatment Site 2 had an average flow of 76 gpm from April 2019 to January 2021.

The third treatment site will be referred as Treatment Site 3 and be associated with Water System B. Water System B has a total of 11 groundwater wells located within a 1 mile radius of one another surrounding the grounds of an airport. Each of the wells was tested in 2014 in response to investigations overseen by EPA for perfluourinated compounds (PFCs). It was discovered that three of the wells were contaminated with PFAS. In response to the detection, Water System B shut down the three wells until further investigation could be conducted. The suspected PFAS source is firefighting foam that had been utilized since approximately 1970's in accordance with FAA requirements.
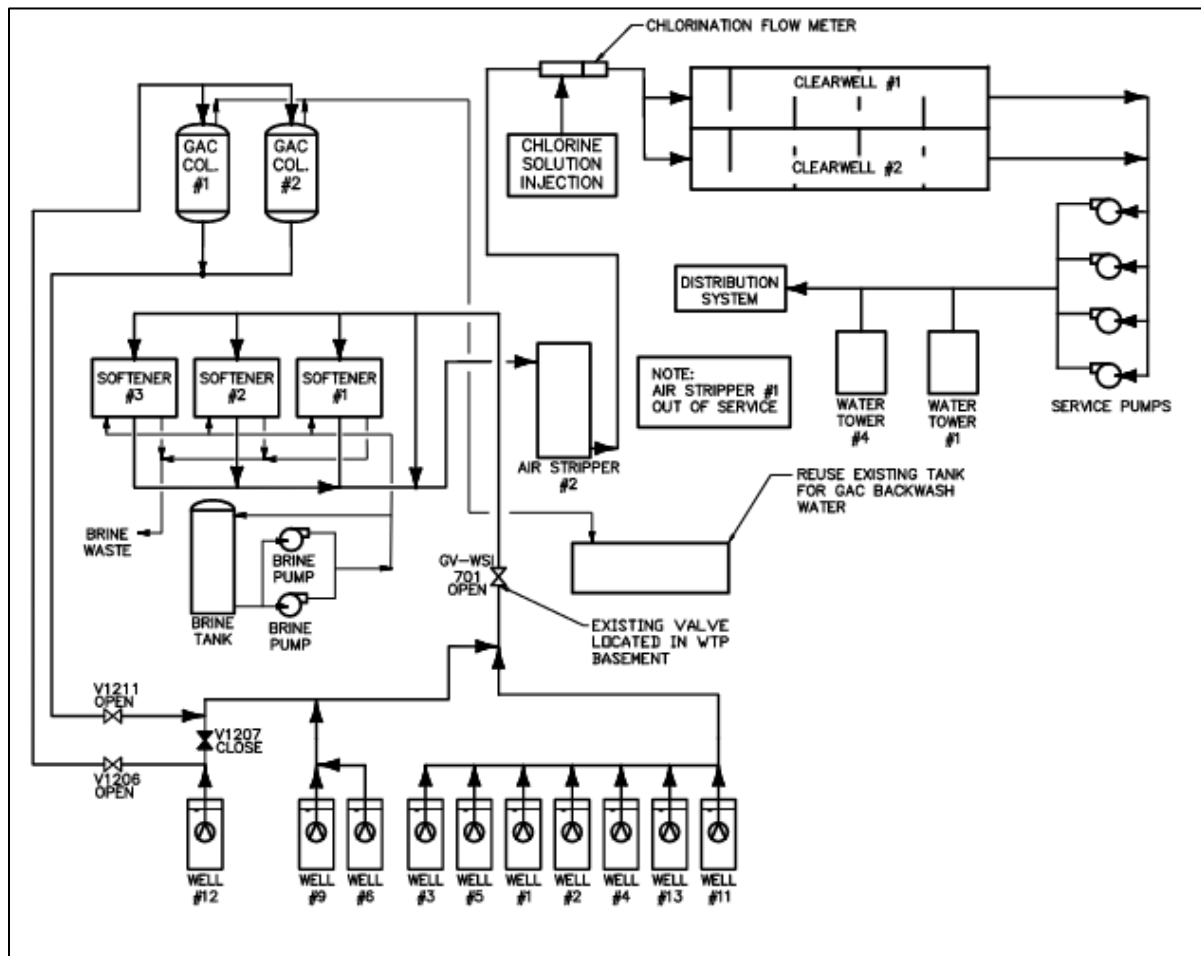
Figure 3 : Water System B Schematic

In 2017, a GAC pilot test was conducted on one of the contaminated wells to develop site specific design criteria for long term use of GAC treatment for PFAS removal. The pilot study revealed that coconut based GAC to be effective at removing PFAS. The pilot study also confirmed that GAC was effective at removing VOC contamination from one of the wells. Water System B currently utilizes an air stripper to treat the VOCs. Once the design criteria was established, a GAC system was designed in 2019 and constructed in 2020. The GAC system was not operated until January of 2020 and has been in operation since. Water System B does not

only utilize one well, but a combination of wells for treatment. Typically, 50% of the water came from a PFAS contaminated well #12 while the remaining 50% came from uncontaminated wells.

3.2   Water Quality

Table 2 shows the raw water quality of each treatment site and the suspected PFAS levels of contamination. Due to the urgency to implement a treatment method at treatment sites 1 & 2, water quality samples were not taken prior to design. This led to the assumption of several parameters as during design. Water quality data shown below was taken form historical water quality sampling. Water quality information for Treatment Site 3 was taken from the pilot study conducted in 2017 and historical water quality sampling.

Table 2: Treatment Site Water Quality

Parameter	Units	Treatment Site 1	Treatment Site 2	Treatment Site 3[4]
pH	Standard Unit	6.5 to 8.5	6.5 to 8.5	6.0 to 9.0
Turbidity	NTU	<1.0	<1.0	<1.0
Temperature Range	°F	50-80	50-80	50-80
TOC	mg/L	<1[1]	<2.4	
Max Perfluorooctane sulfonate (PFOS)	ng/L	15[3]	170[3]	58[3]
Max Perfluorooctanoic acid (PFOA)	ng/L	9[3]	12[3]	14[3]
Nitrate[2]	mg/L	~	1.66-3.5[2]	~
Chloride[2]	mg/L	<250	52.5[2]	<250
Total Dissolved Solids[2]	mg/L	~	215[2]	~
Iron	mg/L	~	0.042	~
Hardness	mg/L	~	~	200
TCE	mg/L	~	0.00096	0.00076

Chlorobenzene	mg/L	~	~	0.00826
Cis-1,2-Dichloroethene	mg/L	~	~	0.00077

(1) TOC was assumed to be < 1 ppm.
(2) Sampling taken in 1987 and 1997.
(3) Raw water samples were taken at each well site every month from April 2019-Jun 2021. The max value was taken from those samples.
(4) The raw water is a blend of different wells. During the operation of the GAC system, 50% of the water came from a PFAS contaminated water and the remaining water came from wells that were not contaminated. The raw water quality is similar among all the wells other than contaminants such as VOCs or PFAS.

3.3   Vessel Information

An emergency GAC system was implemented for Treatment Site 1 and 2, therefore pilot studies were not performed. Treatment Site 3 used a GAC system designed based on a pilot study performed in 2017. The pilot study was conducted over 90 days utilizing two different 5,000 lb sets of vessels at an average flow rate of approximately 95 gpm from one of the contaminated wells. One set of vessels contained a coconut based GAC and the other contained a coal based GAC. Both units contained a secondary set of vessels to remove any remaining PFAS prior to discharging to a storm outlet as shown in Figure 4. The pilot study revealed that the coconut based GAC would have an estimated initial PFOS breakthrough limit of 92 days in comparison to the coal based GAC with 78 days. Due to the longer breakthrough time, the system was designed utilizing the coconut based GAC.
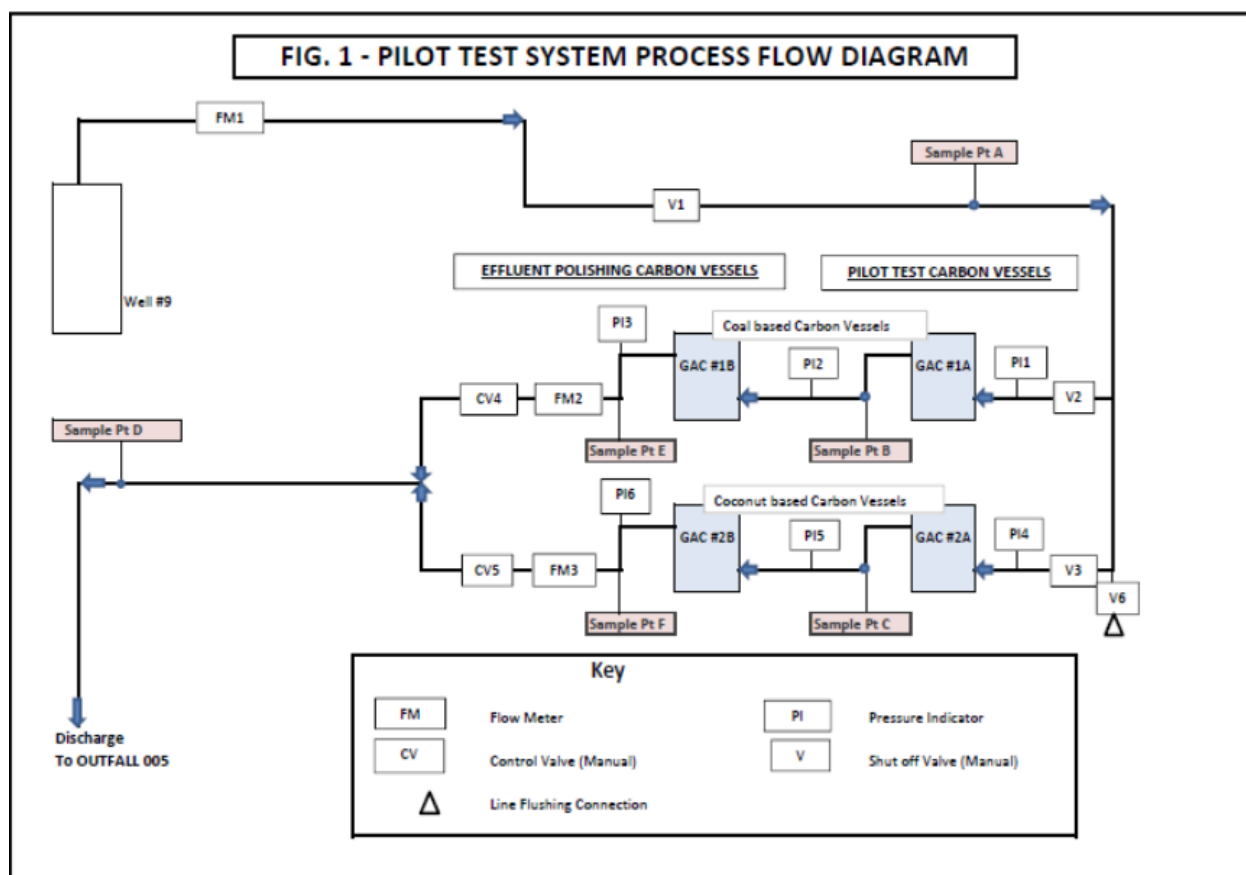
Figure 4: Treatment Site No. 3 Pilot Study Schematic

Information on the GAC systems for each site is provided below. Table 3 provides information on the GAC media provided in each of the vessels. The design criteria of both GAC systems is provided below:

1. Treatment Site 1 and 2 GAC System Design Information
   a. Manufacturer .... Evoqua
   b. Empty Bed Contact Time, min .... $\geq$15
   c. Number of Contactors 2
   d. Treatment Capacity (each), gpm 250
   e. Contactor Diameter, ft 8
   f. GAC Media AC1230CX
   g. Media Quantity (each vessel), cf 285
   h. Design Pressure, psig 100

2. Treatment Site 3 GAC System Design Information

    a. Manufacturer .... TIGG

    b. Empty Bed Contact Time, min .... $\geq$15

    c. Number of Contactors 2

    d. Treatment Capacity (each), gpm 715

    e. Contactor Diameter, ft 10

    f. GAC Media .... TIGG 5DC 1240 NSF

    g. Media Quantity (each vessel), cf 233

Table 3: Properties of GAC Media

Parameter	AquaCarb 1230CX	TIGG 5DC 1240 NSF
Type of GAC	Coconut	Coconut
Mesh Size	12 x 30	12 x 30
Effective Size, mm	0.6-0.85	0.50
Uniformity Coefficient	2.0	~
Iodine, mg/g	1100	1100
Hardness	95	~
Abrasion	85	85
AS, g/cc	0.43-0.46	0.48
Water Soluble Ash, wt %	2	3
Contact pH	9-10	8-10

The carbon used for the GAC vessels at each treatment site is a coconut based GAC designed by Evoqua and Tiggs. As previously discussed, studies have shown that the coal based GAC to be more effective. Recently, manufacturers such as Evoqua and Tiggs have provided data that show the coconut based GAC to just be as effective as coal based GAC. Utilization of coconut-based GAC is more appealing to water systems due to a cheaper cost in comparison to coal based.

3.4   Sampling

Samples were taken weekly from the halfway port of the lead GAC vessels and the port between the lead and lag vessel for Treatment Site 1 & 2. Samples were taken monthly at each well prior to the lead vessel and after the lag vessel. A total of 14 PFASs were sampled at Treatment Site 1 and 2. The types of PFAS's sampled included: N-Ethylperfluorooctanesulfonamido acetic acid (NEtFOSAA), N-Methylperfluorooctane sulfonamidoacetic acid (NMeFOSAA), Perfluorobutanesulfonic acid (PFBS), Perfluorodecanoic acid (PFDA), Perfluorododecanoate acid (PFDOA), Perfluoroheptanoic acid (PHFpA), Perfluorohexanesulfonic acid (PFHxS), Perfluorohexanoic acid (PFHxA), Perfluorononanoic acid (PFNA), Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA), Perfluorotetradecanoic acid (PFTA), Perfluorotridecanoic acid (PFTrDA), and Perfluorouoecanoic acid (PFUnA).

For Treatment Site 3, samples were taken weekly from the influent of the lead vessel and from the 75% lead vessel media depth, 50% depth, 25% depth and the effluent of the lag vessel. A total of 6 PFASs were sampled at Treatment Site 3. The types of PFAS's sampled included: Perfluorobutanesulfonic acid (PFBS), Perfluoroheptanoic acid (PHFpA), Perfluorohexanesulfonic acid (PFHxS), Perfluorononanoic acid (PFNA), Perfluorooctanesulfonic acid (PFOS), and Perfluorooctanoic acid (PFOA)

4.0   RESULTS AND DISCUSSION

4.1   Field Study Results and Discussion

Data collected from Treatment Site 1 and 2 was summarized in Figures 5-10. The percent reduction was based on the amount of bed volumes treated over the length of this study. The amount of bed volumes was calculated using average daily flow and the size of the vessels. Treatment Site 1 and 2 do not have a flow recording device, but the total amount of gallons treated was provided and used to calculate the average flow per day. Due to this assumption and the data collection, the amount of treated bed volumes is expected to be within +/- 10% of the trendlines.
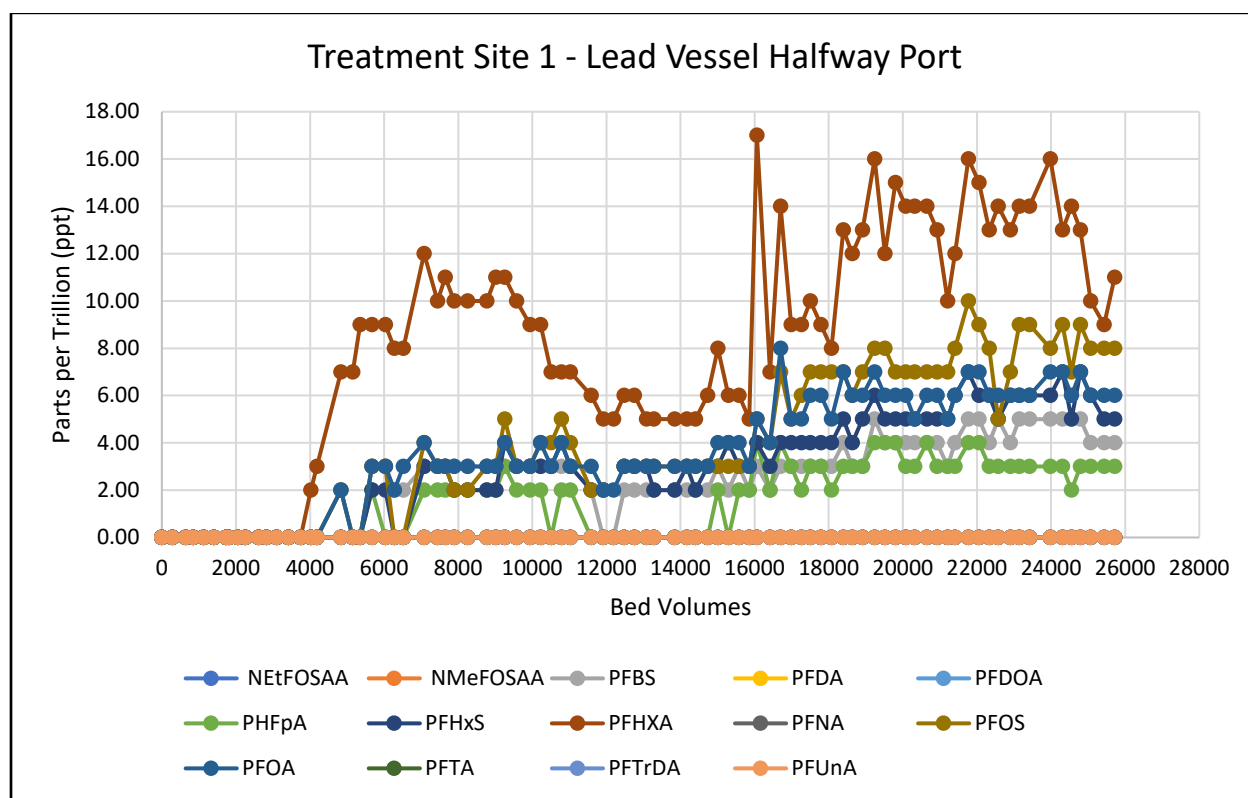

Figure 5: Treatment Site 1 Lead Vessel Halfway Port Sampling

Sampling showed that the influent PFOS and PFOA concentration incoming to Treatment Site 1 remained below the EPA HAL of 70 ng/L. The average concentration of PFOS and PFOA

incoming into the GAC vessels was 18 ng/L and 11 ng/L. The type of PFAS with the highest

concentration entering the GAC vessels was perfluorohexanoic acid (PFHxA). The average

PFHxA concentration coming into the GAC vessels was 21 ng/L and the maximum

concentration was 30 ng/L. PFHxA was also the first PFAS compound to break through the lead

vessel halfway port after approximately 3,700 bed volumes followed by PFOA after
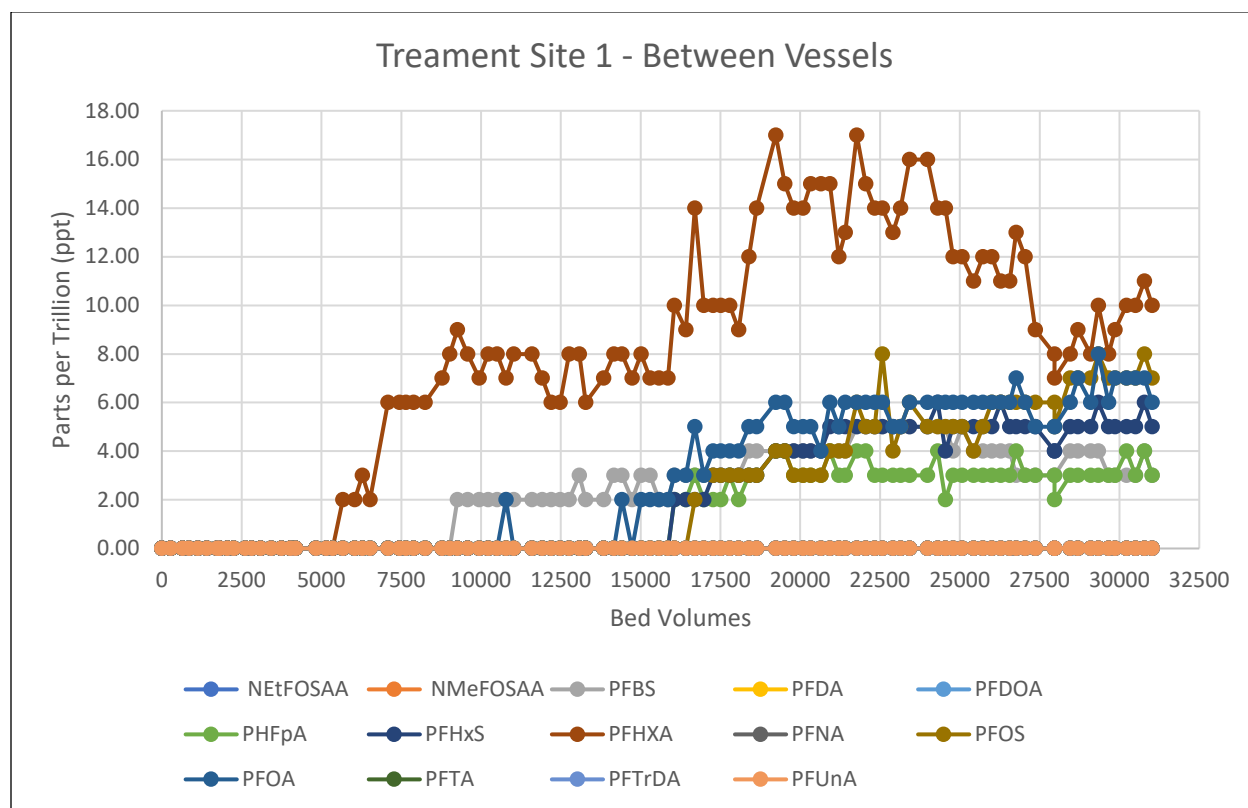
approximately 4,800 bed volumes.

Figure 6: Treatment Site 1 Between Vessels Port Sampling

Sampling between the vessels showed a similar trend to the lead vessel sampling in

which PFHxA was the first PFAS compound to breakthrough the lead vessel after approximately

5,600 bed volumes. PFBS was the second compound to breakthrough the lead vessel after

approximately 9,000 bed volumes which differentiated from the breakthrough order of the lead

vessel. This was likely because sulfonates have a slightly higher affinity for GAC in comparison

to carboxylates. PFBS also has a smaller average concentration of 6 ng/L. The trends above supports that GAC treatment is not as effective at treating short-chain PFAS compounds as it is for long-chain PFAS compounds.
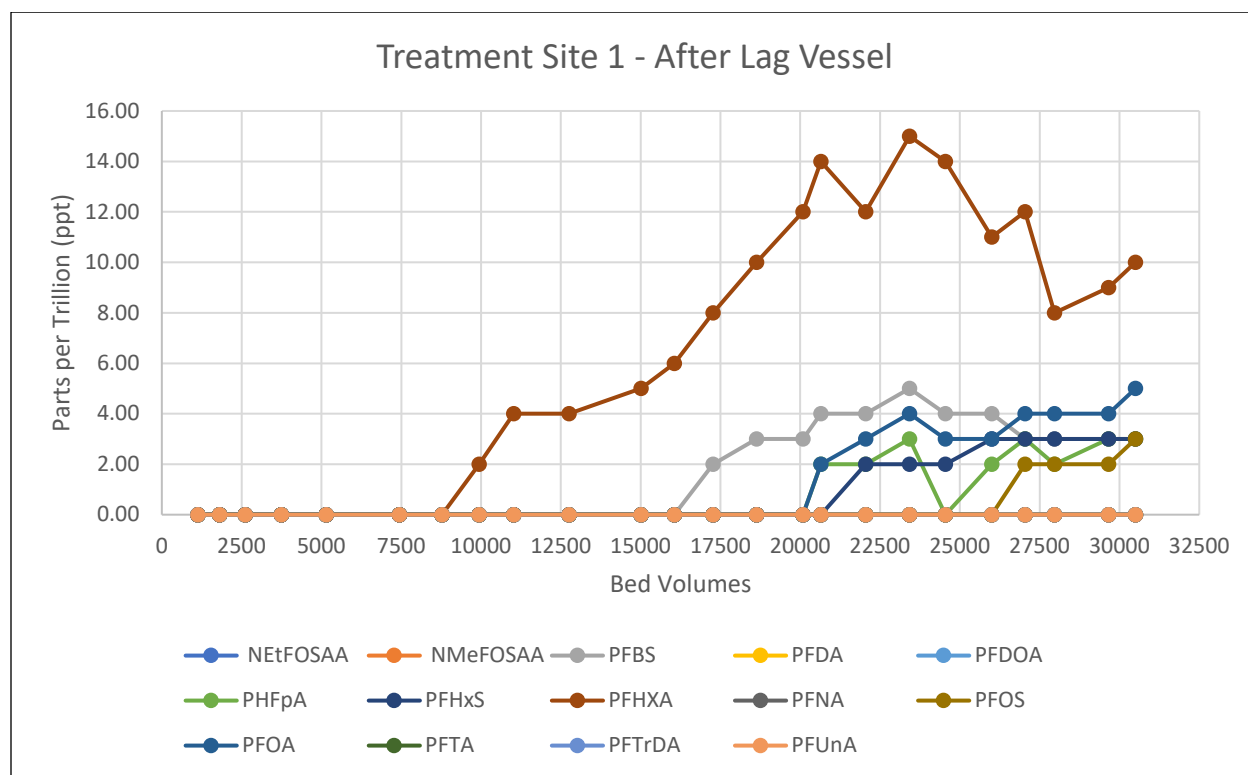

Figure 7: Treatment Site 1 After Lag Vessel Port Sampling

Sampling after the lag vessel showed a similar trend to sampling between the vessel in which PFHxA was the first PFAS compound to breakthrough the lag vessel after approximately 8,700 bed volumes. PFBS was the second compound to breakthrough the lag vessel after approximately 16,000 bed volumes which differentiated from the breakthrough order of the lead vessel. PFOA and PFOS had a breakthrough volume of approximately 20,000 and 26,000 bed volumes. Other studies have typically shown PFBS to be the first PFAS compound to breakthrough the lag vessel. PFHxA breakthrough prior to PFBS was likely due to the higher

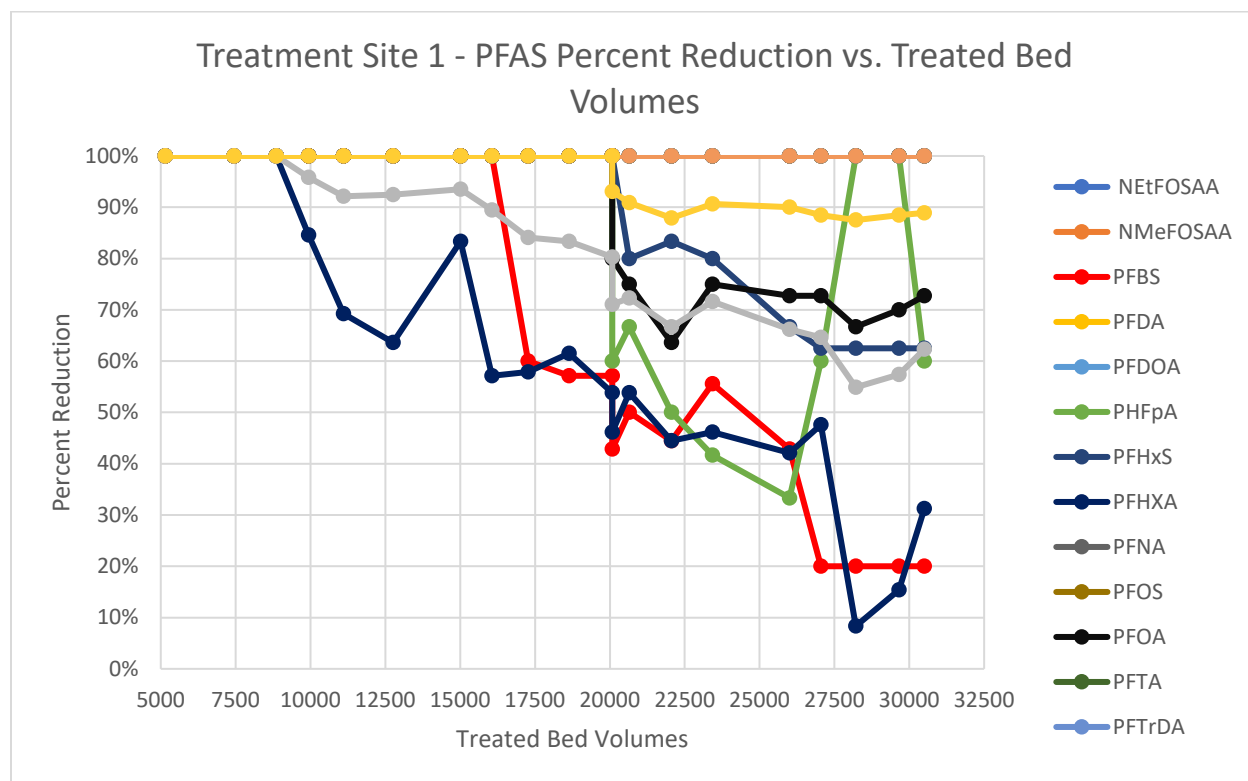concentration and the sulfonates have a slightly higher affinity for GAC in comparison to carboxylates.

Figure 8 : Treatment Site 1 Percent Reduction vs Treated Bed Volumes

For each treatment site, the percent reduction was calculated by taking the difference in concentration between the influent port and after the lag vessel port as shown. The purpose of these figures is to show the adsorption behavior of each form of PFAS over the life of the GAC media. The percent reduction efficiency of PFOS and PFOA was approximately 90% over the span of the media life as shown in Figure 8. The combined PFOS and PFOA after the lag vessel was nearly reduced to 0 during the duration of this study. The media was replaced on November 5th, 2020 due to the increase of PFOS and PFOA concentration between the vessels and the breakthrough of the lag vessel. After approximately 30,000 treated bed volumes, the percent reduction for PFBS and PFHxA was reduced to 20%. When dealing with small influent

concentrations, the percent reduction is more likely to vary, but still presents a data trend for interpretation. The percent reduction is also highly specific to the treatment site since a number of factors affect the adsorption performances.
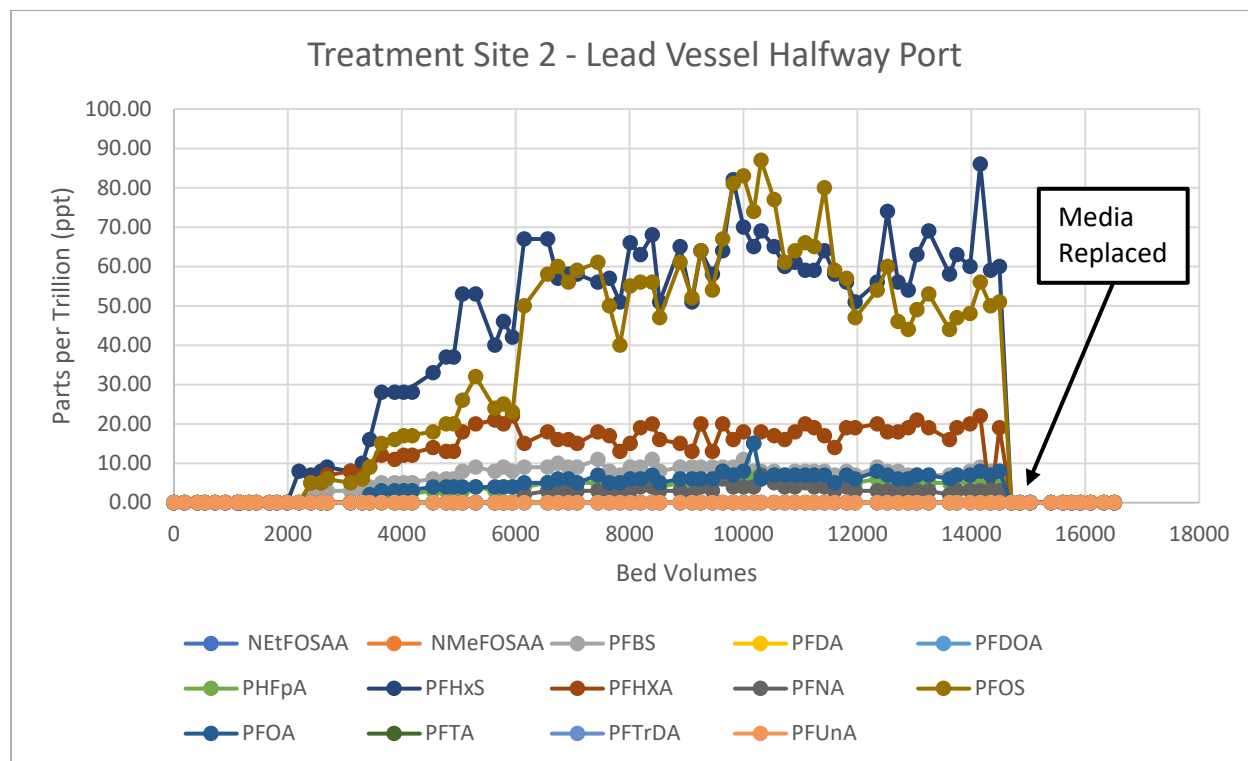

Figure 9: Treatment Site 2 Lead Vessel Halfway Port Sampling

Sampling for Treatment Site 2 showed that combined average PFOS and PFOA concentration incoming to the GAC vessels was above EPA standards at approximately 186 ng/L. PFOS was the major raw water PFAS containment averaging at 172 ng/L and having a max concentration of 300 ng/L. The type of PFAS with the highest concentration entering the GAC vessels was PFOS followed by PFHxS. The average PFHxS concentration coming into the GAC vessels was 158 ng/L and the max concentration was 230 ng/L. PFHxS was the first PFAS compound to break through the lead vessel halfway port after approximately 2,000 bed volumes followed by PFOS and PFHxA after approximately 2,200 bed volumes. The GAC media was

replaced in both vessels at Treatment Site 2 on November 5 2020 after approximately 14,500 treated bed volumes.
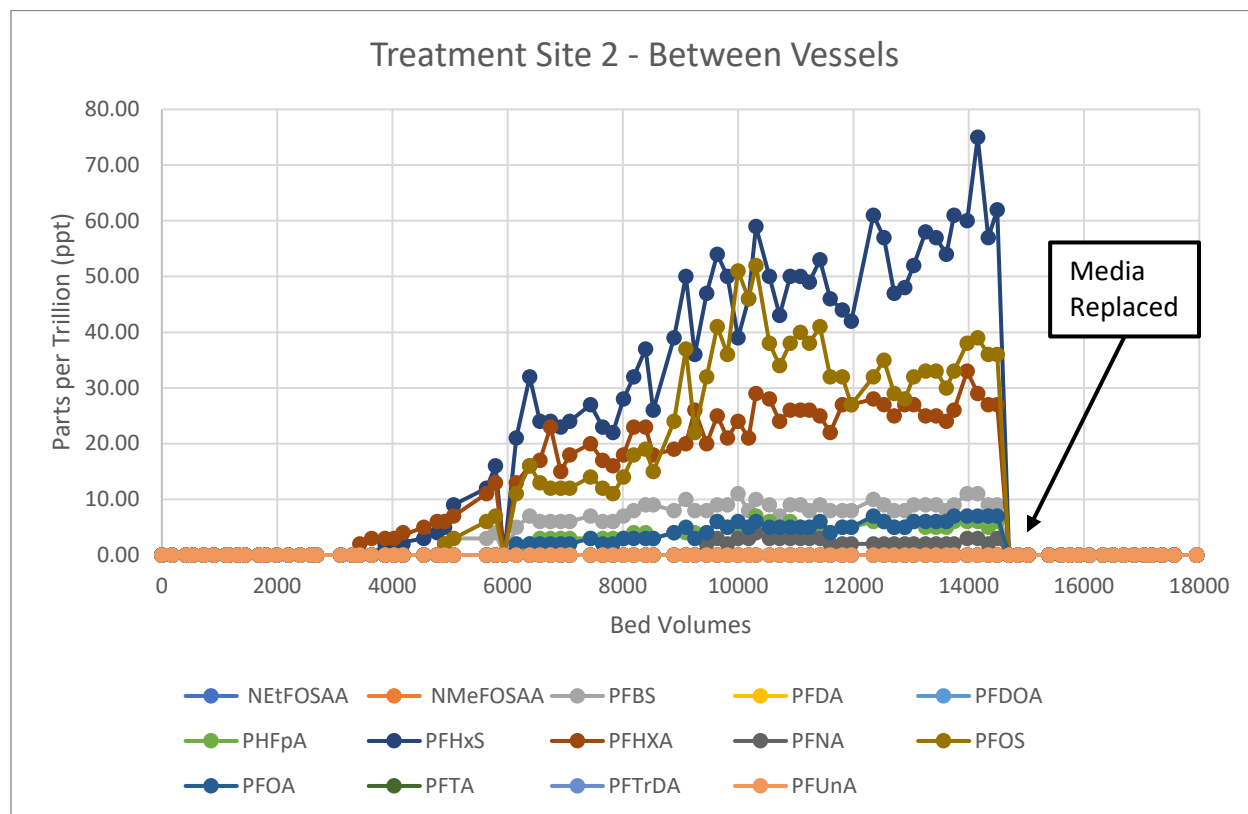
Figure 10: Treatment Site 2 Between Vessels Port Sampling

Sampling between the vessels showed a similar trend to the lead vessel sampling in with exception to PFHxA was the first PFAS compound to breakthrough the lead vessel after prior to PFBS. PFHxA breakthrough was approximately after 3,300 bed volumes followed shortly after by PFBS with 3,600 bed volumes. The average PFHxA concentration coming into the lead vessel was 22 ng/L in comparison to PFBS concentration of 158 ng/L. In comparison, the concentration of PFHxA is much less that PFBS thus supporting two theories. One being that sulfonates have a slightly higher affinity for GAC in comparison to carboxylates. The second being that PFBS and

PFOA have similar sorption behavior and thus have similar breakthrough volumes despite having drastically different influent concentrations.
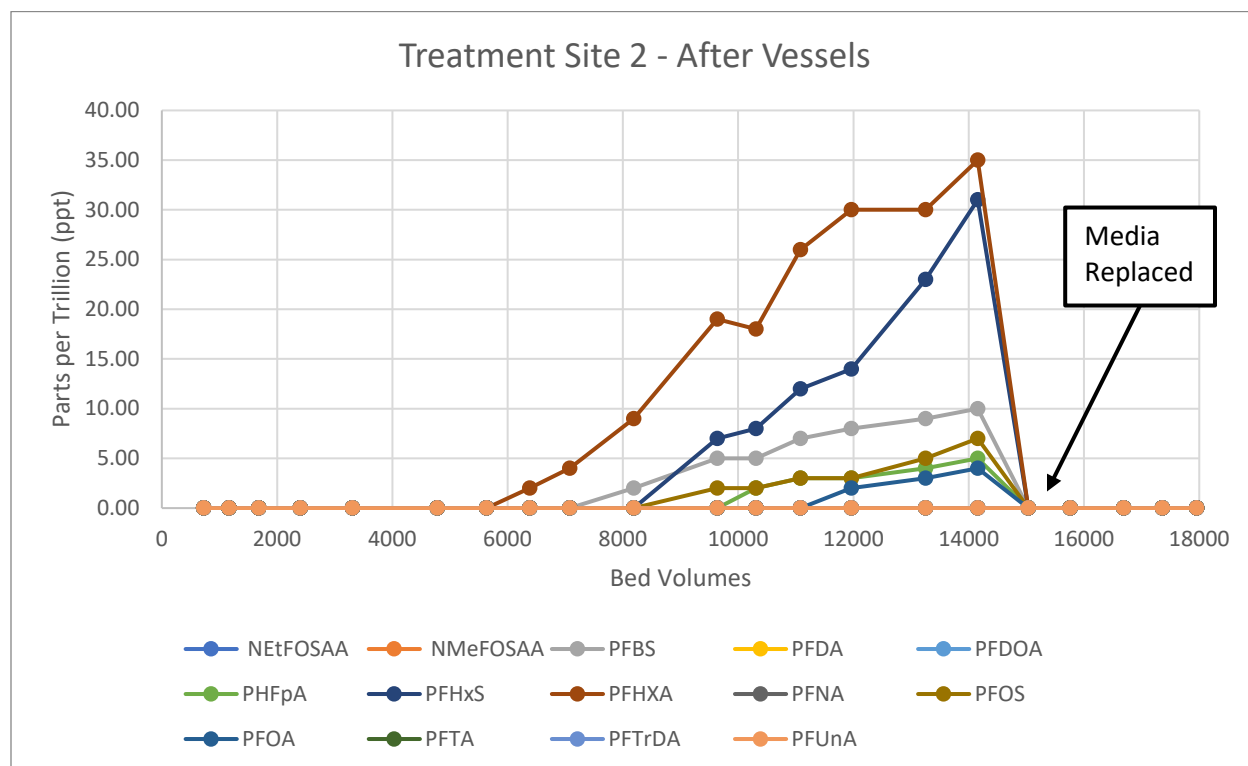
Figure 11: Treatment Site 2 After Lag Vessel Port Sampling

Sampling after the lag vessel showed a similar trend to sampling between the vessel in which PFHxA was the first PFAS compound to breakthrough the lag vessel after approximately 5,600 bed volumes. PFBS was the second compound to breakthrough the lag vessel after approximately 7,100 bed volumes. PFOA and PFOS had a breakthrough volume of approximately 12,000 and 9,600 bed volumes. Treatment Site 2 showed a similar breakthrough behavior to Treatment Site 1 with PFHxA's breakthrough occurring prior to PFBS. As theorized before, PFBS and PFOA have similar sorption behavior causing similar breakthrough volumes. The difference in breakthrough bed volumes was more slightly more between PFBS and PFOA than through the lead vessel. This was likely due to the GAC having a higher affinity for sulfonates and the media having treated a larger quantity of water over time.
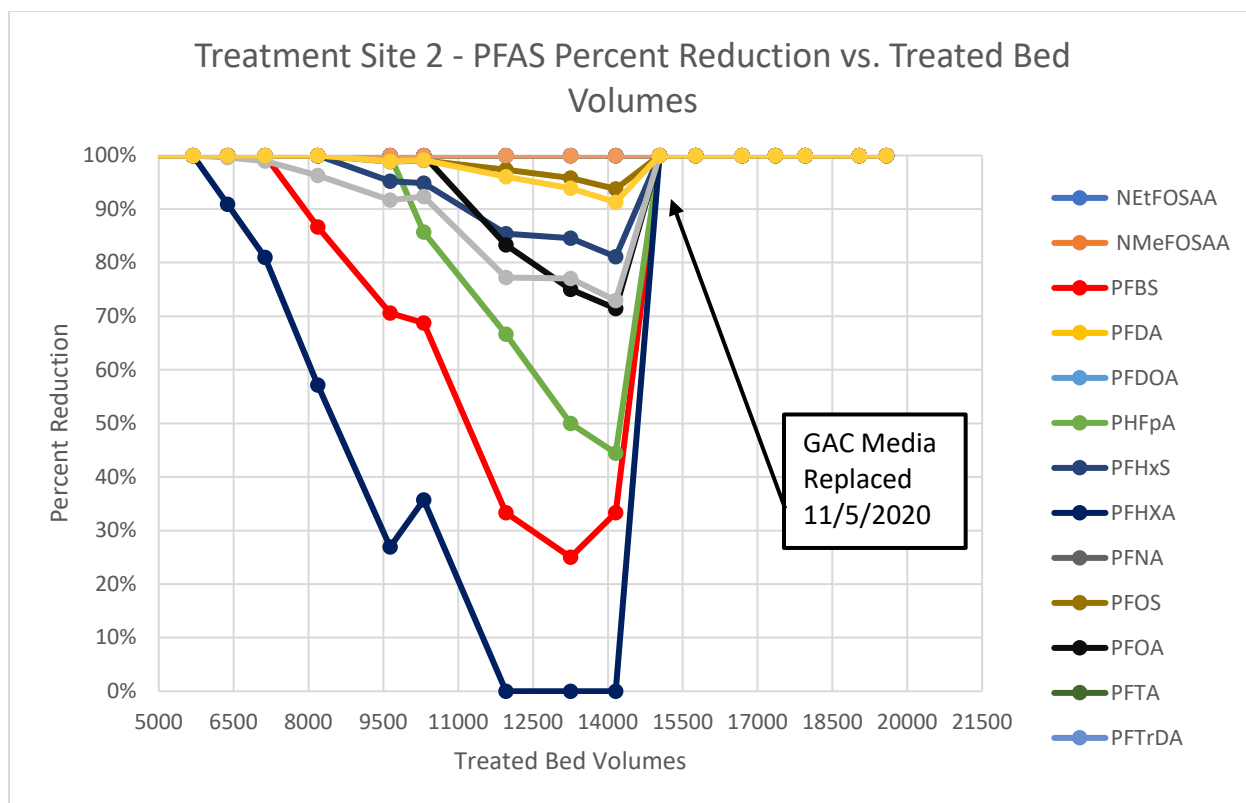
Figure 12: Treatment Site 2 Percent Reduction vs Treated Bed Volumes

Figure 12 shows the percent reduction based on the amount of bed volumes treated over the length of this study for Treatment Site 2. After approximately 14,000 bed volumes, the PFOS and PFOA reduction was 91%.

After the initial breakthrough, PFHxA reduction percentage decreased drastically until 12,000 bed volumes where the concentration leaving the lag vessel was higher than the influent concentration. This trend first initially occurred after approximately 12,000 treated bed volumes tuntil approximately 15,000 treated bed volumes when the media was replaced in both vessels. During this time, the concentration of PFHxA leaving the lag vessel was on average 44% greater than the concentration coming into the lead vessel. This suggests that PFHxA had fully saturated the media and desorbing from the media. The desorption of PFHxA is likely to adsorption competition with another form of PFAS or organics within the water.

Perfluoroheptanoic acid (PHFpA) and PFBS saw a percent reduction of 44% and 22% breakthrough after approximately 15,000 treated bed volumes. The influent concentration of PHFpA and PFHxA was much smaller in comparison to PFBS, yet the two short-chain carboxylates had a earlier breakthrough and lower percent reduction over time.
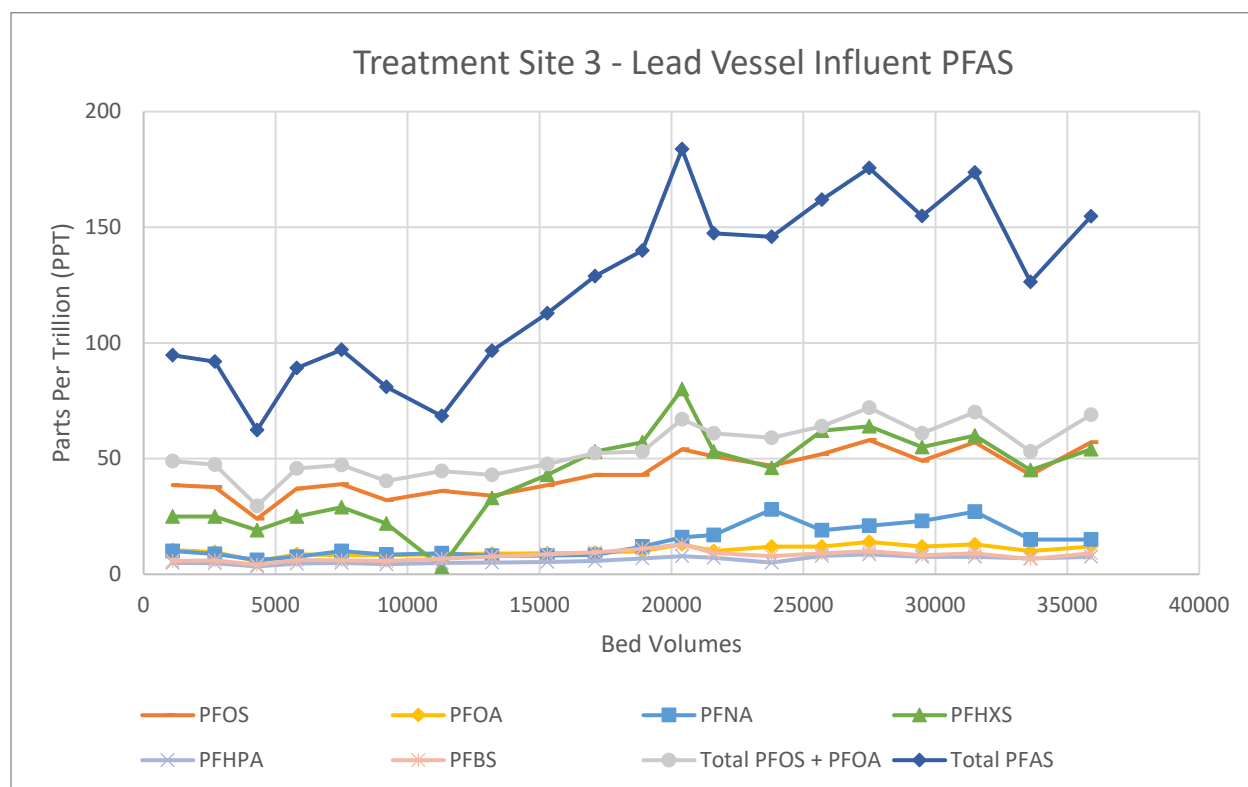
Figure 13: Treatment Site 3 Influent Lead Vessel Port Sampling

Data was collected from January of 2020 to August of 2021 as shown in Figures 13-15. The media was replaced in the original lead vessel (Vessel 1) in January of 2021. At the same time, the lag vessel (Vessel 2) was switched to be the lead vessel to optimize a longer GAC life expectancy. Sampling for Treatment Site 3 showed that combined average PFOS and PFOA concentration incoming to the GAC vessels was an average of 52 ng/L. PFOS was the major raw water PFAS containment, averaging 43 ng/L and a max concentration of 58 ng/L. As shown in Figure 13, the total concentration of PFAS has been on a linear increase from approximately 95

ng/L in the beginning to 150 ng/L in August of 2021. Since no forms of PFAS broke through the

lag vessel, the behavior of PFAS was studied through the lead vessel.
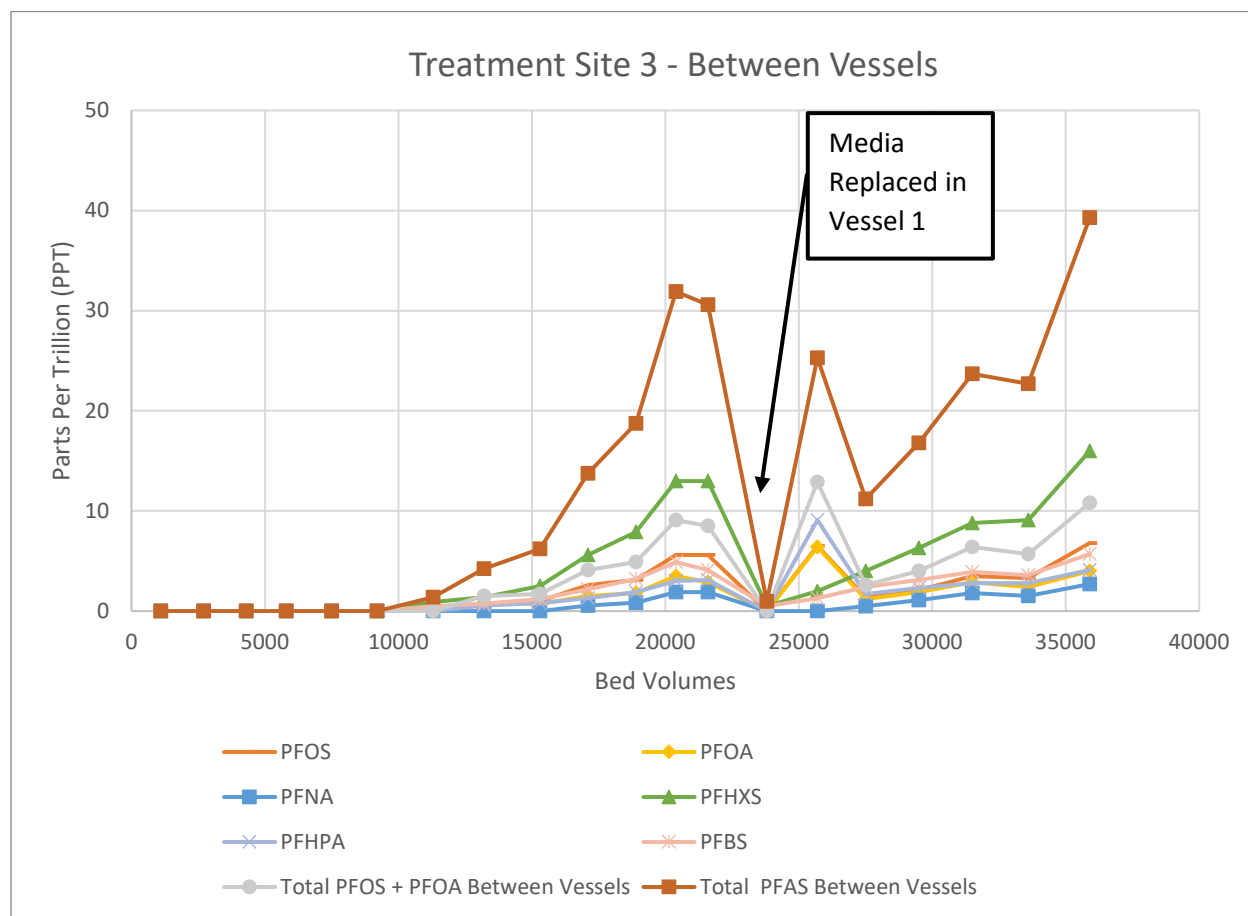
Figure 14: Treatment Site 3 Between Vessel Port Sampling

As shown in Figure 14, the vessels order was switched and the media was replaced in

Vessel 1 after approximately 23,000 bed volumes. The switching caused an initial decrease in

concentration for PFAS between the vessels followed by a slight spike increase in concentration.

PFHxS was the second major raw water PFAS containment, averaging 42 ng/L and a max

concentration of 80 ng/L. This was almost identical to the PFOS raw water concentrations, yet

the concentration for PFHxS and PFOS between the vessels was 13 ng/L and 5 ng/L prior to the

media replacement. After the media replacements, both contaminants saw a decrease in

concentration for a small amount of treated bed volumes followed by an increasing linear trend similar to the trend prior to the media replacement.

The initial decrease in concentration was expected due to Vessel 2 becoming the lead vessel and having available adsorption sites since it had previously served as the lag vessels. After this decrease, there is a spike increase in PFAS concentration which was attributed to media still becoming stabilized and that Vessel 2 was more heavily influenced by organics after becoming the lead vessel. This spike does not fit the trend of the PFAS concentration after 26,000 treated bed volumes, so this may have been also due to a higher influent PFAS concentration on that sampling date. After the spike increase, it was assumed that the media was stabilized regarding adsorption due to the slight increasing linear trend in PFAS concentration.
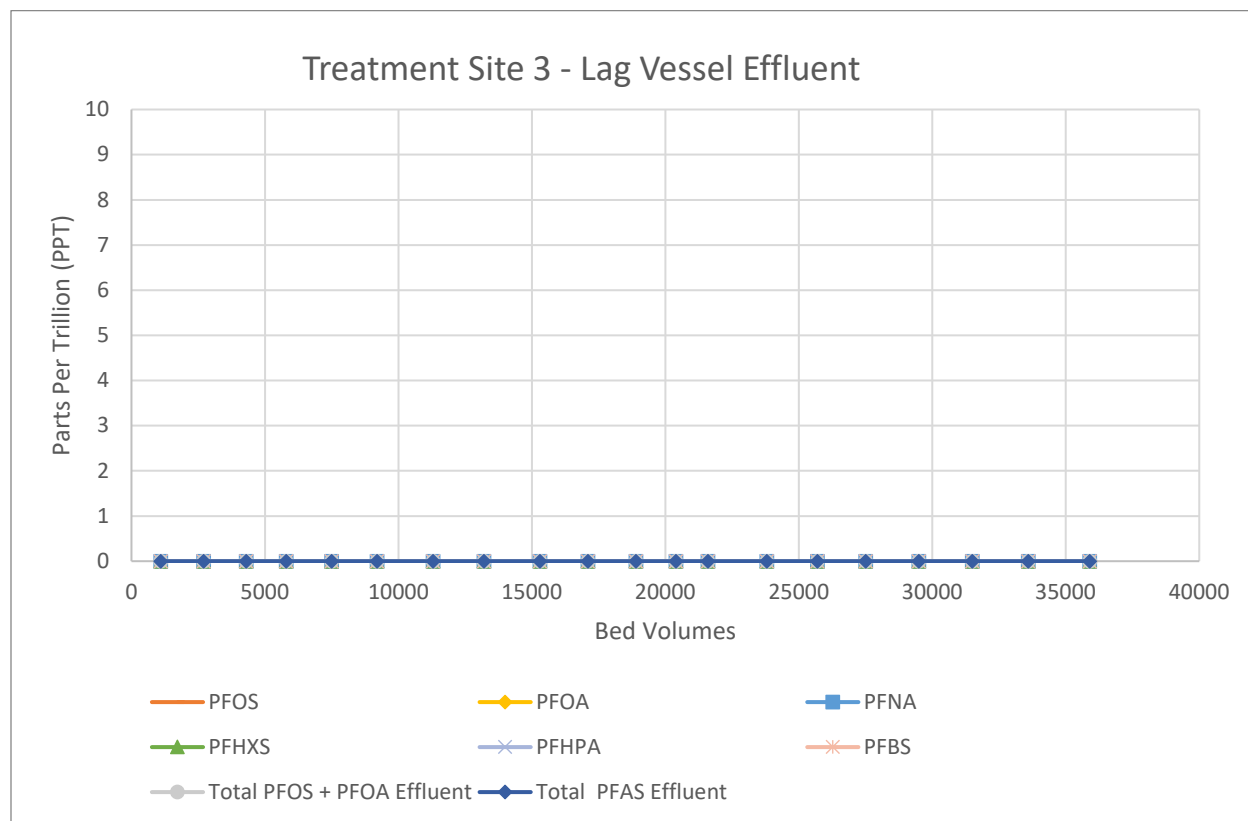
Figure 15: Treatment Site 3 Lag Vessel Effluent Port Sampling

Sampling for Treatment Site 3 showed that combined PFOS and PFOA leaving the effluent GAC vessel remained at 0 ng/L after a total of 36,000 bed volumes thus meeting the EPA HAL of 70 ng/L.
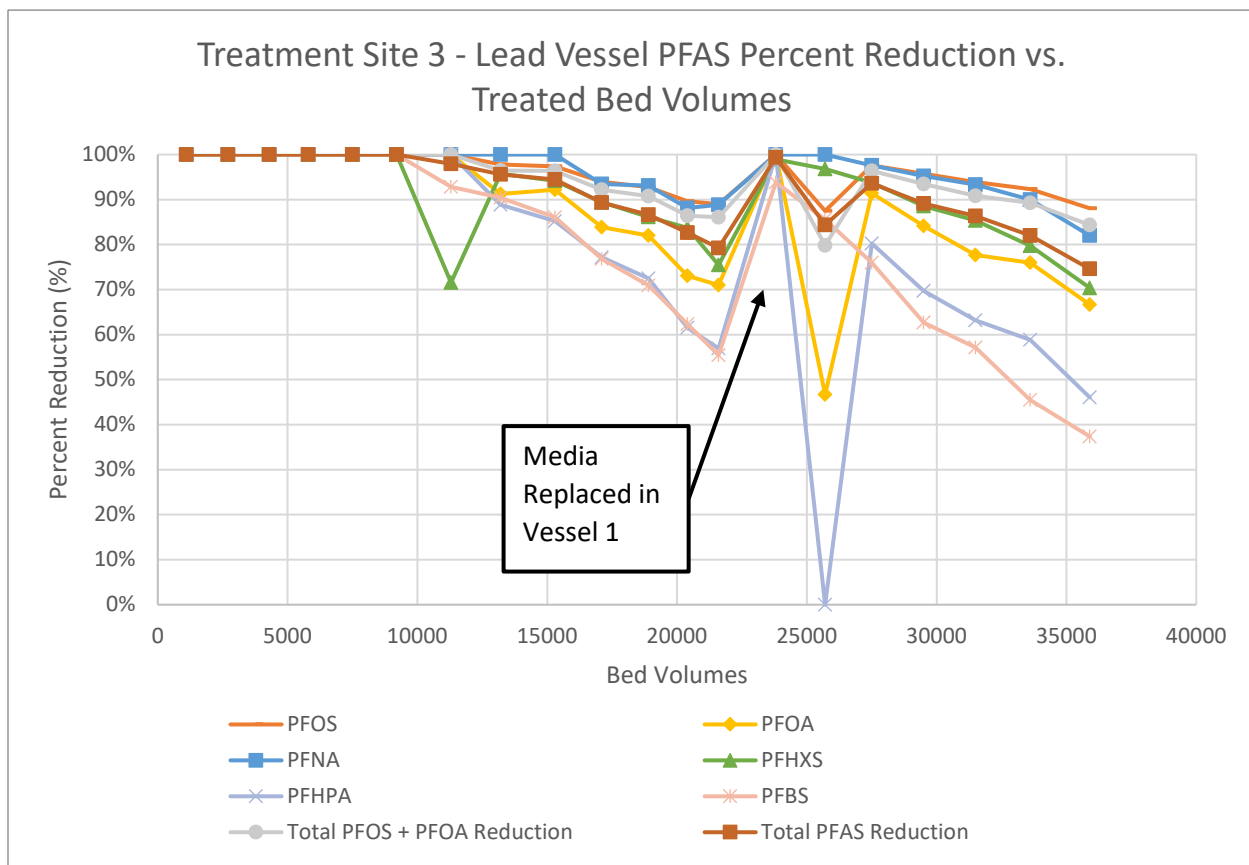
Figure 16: Treatment Site 3 Lead Vessel Percent Reduction vs Treated Bed Volumes

As shown in Figure 16, Vessel 2 was switched to the lead vessel at approximately 22,000 bed volumes. After the switch, there was a slight decrease in percent reduction of PFAS followed by a spike increase in percent reduction. This spike initially latest approximately 1,800 bed volumes before declining in reduction efficiency. Followed by the slight decline was another spike increase in reduction efficiency that lasted approximately 1,900 bed volumes. Though the increase in reduction efficiency occurred in a shorter amount of bed volumes, the percent

reduction is greater than before Vessel 1's GAC media was changed and switched to the lag vessel.

The declining reduction efficiency of PFBS and PFHpA continued even after the switch of the lead and lag vessel. The original lead vessel saw a reduction efficiency of about 55% for PFBS and PFHPA after approximately 22,000 treated bed volumes. When Vessel 2 was switch to the lead vessel, a reduction efficiency of about 55% for PFBS an PFHPA occurred after 10,000 treated bed volumes. After the vessel arrangement was switched, there was an drastic drop in percent reduction for PFOA and PFHpA. As discussed for Treatment Site 1 and 2, sulfonates such as PFOS and PFBS have a slightly higher affinity for GAC in comparison to carboxylates like PFOA and PFHpA. The spike is attributed to the desorption of carboxylates due to competition with other forms of PFAS or organics within the water.

As previously discussed, studies have shown that GAC is not as effective at removing short-chained PFAS. One form of PFAS to break through the lag vessel first at each treatment site was PFHxA. PFHxA is a short chained 6 carbon perfluorinated carboxylic acids (PFCAs) with high mobility through groundwater. A study collected PFAS samples over a 5-year period for several treatment sites. A site with an identical setup (Site 20) exhibited similar behavior to Treatment Site 1. This study noted a similar breakthrough of PFHxA and percent reduction of 68% after a year of treatment (Appleman et al. 2013).

Other studies have noted that PFBS was the first to breakthrough due to having the shortest chain length of four carbon. For Treatment Site 1 & 2, PFBS was second to breakthrough which was likely partially attributed to the lower initial concentration. The breakthrough characteristics of PFHxA, PFBS, PFHxS, and PHFpA at both treatment sites were correlated to the desorption behavior of these substances. A study showed that that these

substances reach saturation more rapidly and desorb shortly after the GAC media is saturated (Bertanza et al 2020). Part of the reason to why PFHxA broke through before PFBS may be due to the type of GAC used. A study noted that the same coconut based GAC that was used for Treatment Sites 1 and 2 (AX1230CX) removed PFOS more quickly than PFOA, showing a preference to perfluoroalkane sulfonic acids (PFSA) over perfluorocarboxylic acids (PFCA) (Holliday, 2020). The breakthrough and percent reduction at the treatment sites supports this hypothesis since PFHxA broke through prior to PFBS despite have similar quantities and chemical properties.

Treatment Site 2 experienced breakthrough trends significantly earlier in some cases. One hypothesized contribution to this was air stripper upstream of the lead GAC vessel. The air stripper was installed to treat VOC's such as 1,1,2-Trichloroethane & Trichloroethylene (TCE). Having the air stripper upstream of the GAC vessels could be beneficial since it will reduce the amount of VOC adsorption onto the GAC media. On the other hand, the air stripper increases the amount of O_2 in the water thus fouling the media at a faster rate due to increased formation of calcium carbonate. In conducting research, no research was discovered to conclude that VOC's have any interactions with PFAS compounds other than competition for adsorption sites.

One study noted that the concentration of PFCAs and PFSAs was consistently higher following oxidation treatment, which is a similar trend to what was observed at Treatment Site 2 (Bertanza et al 2020). The air stripper does not fully eliminate the concentration of the VOC's, therefore the remaining VOC's are absorbed by the GAC media. This adsorption is assumed to take up potential absorption sites that could contribute to an earlier PFAS breakthrough specifically related to short-chained PFAS. There are notable property differences between 1,1,2-Trichloroethane & TCE and short chained PFAS such as PFBS and PFHxA that affect

adsorption. TCE and 1,1,2-Trichloroethane have a higher solubility which means it is more likely to have a stronger adsorption to GAC in comparison to short-chained PFAS.

Looking at Figure 16 for Treatment Site 3, the increased concentration of PFAS and the GAC media being already saturated with PFAS is likely the reasoning to the more drastic decline in PFAS reduction after the vessel's order was switched. Similar to Treatment Site 1 & 2, the nature of the data trend for Treatment Site 3 confirms that short chained PFAS such as PFBS and PFHPA had saturated the lag vessel prior to vessels being switched.

With the regulation of long-chained PFAS, the use of short chained PFAS concentrations are likely to increase in the future. The regulation has also caused more research to be conducted on long-chained PFAS and minimal information on short-chained PFAS. This may pose a problem for GAC in the future since short chained PFAS such as PFBS and PFBA's saturate the GAC media more readily and thus result in desorption faster. If regulations change to include short-chain PFAS, then this will require more frequent filter media replacement. Or the addition of alternate treatments that are proven more effective at reducing short-chain PFAS. An increased frequency of media replacement will result in a higher cost for the owner and change the operation of the system. It will also create an issue with an increased demand to disposal and/or treat spent GAC media.

4.2   Modeling

The theoretical amount of bed volumes until breakthrough was calculated using the Freundlich equation. The Freundlich equation provides a relationship between the sorption of liquid solutes to a solid surface. The Freundlich equation relies on two constants; Freundlich adsorption constant (Kf) and sorption intensity (n). The constants are determined by correlating

$$(q_e)_0 = KC_e^{1/n}$$

q_e = Quantity of adsorbate per unit of adsorbant (mg/g)

C_e = Equilibrium concentration of adsorbate in solution (mg/L)

K and n = Freundlich adsorption isotherm constants for a given adsorbate at a given temperature

experimental adsorption data to a linear isotherm model. Since several factors affect adsorption, the constants have been found to be highly site specific. Even sites that have similar parameters have shown to produce different Freundlich constants. Therefore, sampling and testing is normally recommended at each site to develop accurate adsorption capacities. The third parameter of the equation is the equilibrium concentration in the solution (Ce), which in this case is the PFAS concentration.

Sampling for developing the Freundlich constant was not conducted in this study. As previously discussed, no piloting had been conducted for Treatment Site 1 & 2. Sampling was conducted in 2017 for Treatment Site 3, but constants for the Freundlich equation were not developed. As a result, constants were taken from other treatment sites of similar water quality to calculate the theoretical breakthrough. The theoretically calculated breakthrough was compared to the actual breakthrough as shown in Table 4. This calculation considered the average influent PFAS concentration over the duration of the study.

Table 4: Theoretical vs Actual Breakthrough

	Treatment Site 1								
PFAS Compound	**Average PFAS Conc. (Ce)**	**Kf[2]**	**1/n[2]**	**Qe**	**GAC Mass per Bed**	**Total Amount of PFAS removed per Bed**	**Amount of PFAS Absorbed by Carbon**	**Theoretical Breakthrough**	**Actual Breakthrough**
Units:	**(ng/l) PFAS**	**(ng/mg)/ (ng/L)^(-1/n)**		**(ng PFAS/ mg GAC)**	**Grams**	**ng PFAS**	**ng PFAS**	**Bed Volumes**	**Bed Volumes**
PFBS	67	0.60	0.54	5.811	5,558,770	9.57E+08	1,081,159	885	16,000
PFHxA	20	0.87	0.43	3.155	5,558,770	1.76E+09	322,734	5,460	8,700
PFOS	18	2.43	0.23	4.724	5,558,770	1.18E+09	290,461	4,051	26,000
PFOA	10	2.20	0.33	4.704	5,558,770	1.18E+09	161,367	7,324	20,000
PFHxS	9	1.74	0.45	4.677	5,558,770	1.19E+09	145,230	8,184	21,000
	Treatment Site 2								
PFAS Compound	**Average PFAS Conc. (Ce)**	**Kf[2]**	**1/n[2]**	**Qe**	**GAC Mass per Bed**	**Total Amount of PFAS removed per Bed**	**Amount of PFAS Absorbed by Carbon**	**Theoretical Breakthrough**	**Actual Breakthrough**
Units:	**ng/l PFAS**	**(ng/mg)/ (ng/L)^(-1/n)**		**(ng PFAS/ mg GAC)**	**Grams**	**ng PFAS**	**Bed Volume/ng PFAS**	**Bed Volumes**	**Bed Volumes**
PFBS	16	0.60	0.54	2.68	5,558,770	2.07E+09	258,187	8,029	16,000
PFHxA	22	0.87	0.43	3.29	5,558,770	1.69E+09	355,007	4,764	8,700

PFAS Compound	Average PFAS Conc. (Ce)	Kf[2]	1/n[2]	Qe	GAC Mass per Bed	Total Amount of PFAS removed per Bed	Amount of PFAS Absorbed by Carbon	Theoretical Breakthrough[3]	Actual Breakthrough
PFOS	172	2.43	0.23	7.94	5,558,770	7.00E+08	2,775,512	252	26,000
PFOA	15	2.20	0.33	5.38	5,558,770	1.03E+09	242,051	4,271	20,000
PFHxS	157	1.74	0.45	16.93	5,558,770	3.28E+08	2,533,462	130	21,000
Treatment Site 3									
PFAS Compound	Average PFAS Conc. (Ce)	Kf[2]	1/n[2]	Qe	GAC Mass per Bed	Total Amount of PFAS removed per Bed	Amount of PFAS Absorbed by Carbon	Theoretical Breakthrough[3]	Actual Breakthrough
Units:	ng/l PFAS	(ng/mg)/ (ng/L)^(-1/n)		(ng PFAS/ mg GAC)	Grams	ng PFAS	Bed Volume/ng PFAS	Bed Volumes	Bed Volumes
PFBS	8	0.60	0.54	1.84	2,272,269	1.23E+09	52,770	23,348	11,000
PFOS	44	2.43	0.23	5.80	2,272,269	3.92E+08	290,234	1,349	13,000
PFOA	11	2.20	0.33	4.85	2,272,269	4.68E+08	72,559	6,452	13,000
PFHxS	43	1.74	0.45	9.45	2,272,269	2.40E+08	283,638	847	11,000

(1) Half of the average flow for Treatment Site 3 was used since 50% of the influent water was from the contaminated well.
(2) Adsorption constants taken from Table 3 of (Cantoni et al., 2021).
(3) Based on breakthrough of lead vessel.

Major differences between the theoretical and actual breakthrough can be attributed to several factors. The biggest factor being that the Freundlich equation assumes that contaminate is the only contaminate being adsorbed by the GAC. The Freundlich does not account for the concentrations of other contaminants and the water quality parameters that are affect adsorption as well. The competition for absorption is key to the breakthrough observed for each of the contaminants, specifically short-chained PFAS. As shown in Table 4, the theoretical breakthrough bed volume for short-chained PFAS was greater than the long-chained PFAS. This differentiates from the actual breakthrough since short-chained PFAS had less bed volumes than the long-chained PFAS. As discussed before, this difference is believed to be due to short-chained PFAS compounds competing with long-chained PFAS compounds and other organics for adsorption sites.

The theoretical breakthrough is believed to be less than the actual breakthrough for certain compounds due to the safety factor implemented with design. Due to uncertainty, manufacturers supply a larger vessel to account for possible unforeseen circumstance. GAC systems are designed normally using a max concentration of each PFAS compound. This results in a larger amount of bed volumes.

4.3   Cost Analysis

Table 5 provides a cost comparison between PFOS and PFOA treatment based on the amount of bed volumes treated until breakthrough for Treatment Site 2 & 3. Table 5 assumes that once PFAS breaks through the vessel that the media would be replaced. The cost to replace the media for Treatment Site 2 and 3 was supplied by the water systems.

Table 5: PFAS Treatment Cost

Treatment Site #	PFAS Type	Average Concentration (ng/L)	Average Flow (MGD)	Amount of PFAS Per Day (mg/day)	Time to Breakthrough (Days)	Total amount of PFAS treated (mg)	Media Replacement Cost ($)	Cost to Treat per gram PFAS ($/mg)
2	PFOS	172	0.11	71.6	373	26745	$60,000	$2.25
2	PFOA	15	0.11	6.2	463	2895	$60,000	$20.75
3	PFOS	44	0.11	18.0	233[1]	7778	$43,428[2]	$10.36
3	PFOA	11	0.11	4.5	233[1]	1852	$43,428[2]	$41.45
3	PFOS	44	0.11	18.0	433[3]	14455	$86,856[4]	$11.15
3	PFOA	11	0.11	4.5	433[3]	3442	$86,856[4]	$44.61

(1) Amount of days to break through lead vessel.
(2) Cost to replace the media in one vessel.
(3) Amount of days to break through lead vessel after Vessel 2 was switched to lead vessel.
(4) Total cost to replace media in both vessels.

The media was not immediately replaced upon breakthrough for each of the treatment sites, therefore the cost will be slightly less than what is provided in Table 5. Operating the vessels after the initial lead vessel breakthrough provides a more efficient use of media. Once breakthrough has occurred though, it will begin to utilize the adsorption capacity of the lag vessel. If influent PFAS concentration and flow is similar before the breakthrough of the lead vessel, then the same amount of time to breakthrough for the lag vessel can be assumed. Though this can be assumed, it is normally encouraged to schedule the media replacement after the breakthrough of the lead vessel. Several small changes can reduce the amount of bed volumes prior to breakthrough and coordinating media replacement takes time.

Treatment Site 3 was considered as two different parts since the media was only replaced in Vessel 1 and Vessel 2 was switched to the lead vessel. By operating the GAC vessels in this manner, the system was able to add another 200 days of treatment before seeing significant

breakthrough of PFAS through Vessel 2 (Lead Vessel). If the media had been replaced in both vessels, the cost to treat PFAS per pound would have essentially doubled.

The variation in cost from each PFAS compound was likely due to influent concentration and the competition for adsorption sites. For example, PFOA is approximately shown to be ten times more expensive than PFOS in Table 5. The competition for adsorption sites between PFOA and PFOS has been shown to be fairly similar. Since PFOA had a lower initial concentration, this resulted in a lower amount of PFOA being treated thus ultimately costing more. If PFOA had been independent of the PFOS concentration, the cost per milligram would be much lower.

It is important to consider the raw water quality since other contaminants and organics can compete with PFAS for adsorption onto GAC media. The major factors that affect cost include the factors that influence the adsorption of GAC such as the influent organic concentration, PFAS concentration, and volume of water. Several of the factors are out of the control of the system, therefore, understanding the behavior of PFAS and GAC adsorption is important. Optimizing the full potential of the GAC treatment effectiveness ultimately coincides with reducing the cost. If GAC is replaced prior to being full saturated, then the full potential of the media is not being utilized. As research advances over time, more methods and materials will be implemented to improve the adsorption of PFAS. It is critical with GAC systems that adequate bed volume is provided to maintain a proper EBCT accounting for the factors discussed above.

4.4   Possible Treatment Improvements

Based on the raw water quality data collected for each treatment site, it does not appear that nitrate, total organic carbon, or hardness appear to be affecting the life of the GAC media

due to the low concentrations. The pH remained consistent throughout the study and the temperature ranged within normal limits that these parameters would not affect the GAC media life expectancy. The concentration of the VOC's is relatively small for Treatment Site 2 that minor competition for adsorption is suspected. The design of the vessels meet the AWWA recommendations of having 10-20 minutes of EBCT. Therefore, it was concluded that the raw water quality and vessel arrangement are not hindering the effectiveness of the GAC media in reducing PFAS.

One item for consideration in the future for each treatment site is to perform a pilot utilizing different types of GAC media. Multiple studies have stated that coal-based GAC is more effective at removing PFAS. Other studies have shown coconut based GAC to just be as effective at removing PFAS. The cost of GAC may lead to new variations of media enhancement being discovered that may be more effective that the medias that are currently utilized. By having more effective media, it will ultimately lead to the cost reduction which is one of the major implications of GAC treatment. One study suggested the use of two different types of media for GAC in a series configuration to optimize the treatment of long and short-chained PFAS. The study suggests leading with a mesoporous GAC, which has shown data to be more effective at treating long-chained PFAS and DOM. The lead vessel would be followed by a microporous activated carbon, which has shown to be more effective at treating short-chained PFAS (Cantoni et al. 2021).

For Treatment Site 1 & 2, it would be encouraged to modify replacement of GAC media within the vessels. By replacing the media in one vessel and switching the lead/lag vessel, the media can be optimized to reduce costs drastically as discussed in Section 4.3. This assumes that the replacement cost is the same and does not account for additional fees.

5.0   CONCLUSION

Based on the data that was collected the research gathered from various sources, the following conclusions were gathered.

- The data provided has shown that GAC to be effective at removing long-chained PFAS. 90% of PFOA and PFOS was removed at each of the three treatment sites over the duration of this study.

- The data provided has shown that GAC is not as effective at removing short-chained PFAS. Over the duration of the study, less than 50% of the PFHxA and PFBS was removed.

- Due to the number of variables that affect the absorptivity of GAC, piloting utilizing to the contaminated source is recommended. Parameters that affect the absorption of PFAS the greatest include the water quality, contaminant properties, and the absorbent characteristics.

- Switching the lag vessel to the lead vessel prior to media replacement has shown to utilize the media more efficiently thus reducing the cost of treatment.

To further expand upon the data and research conducted within this paper, the following is recommended:

1. Collect further data on the operation of switching the lead and lag vessel to optimize media replacement.

2. Collect information on the various Langmuir and Freundlich constants for different forms of PFAS to develop modeling behavior of PFAS adsorption.

3. Investigate the transportation of PFAS in groundwater to better understanding the behavior.

4. Conduct further research into the behavior of short-chained PFAS after breakthrough.

5. Investigate incorporating different processes with GAC media to enhance PFAS removal.

References

Anderson, J. K., Luz, A. L., Goodrum, P., & Durda, J. (2019). Perfluorohexanoic acid toxicity, part II: Application of human health toxicity value for risk characterization. *Regulatory Toxicology and Pharmacology*, *103*, 10–20. https://doi.org/10.1016/j.yrtph.2019.01.020

Andrews, D., Faber, S., & Hayes, J. (2019, March 6). *Mapping PFAS Chemical Contamination at 206 U.S. Military Sites | Environmental Working Group*. EWG. https://www.ewg.org/research/mapping-pfas-chemical-contamination-206-us-military-sites

Appleman, T. D., Higgins, C. P., Quiñones, O., Vanderford, B. J., Kolstad, C., Zeigler-Holady, J. C., & Dickenson, E. R. V. (2014). Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems. *Water Research*, *51*, 246–255. https://doi.org/10.1016/j.watres.2013.10.067

ATSDR. (2021). *Toxicological Profile for Perfluoroalkyls*. 993.

AWWA. (2019). *Drinking Water Treatment for PFAS Selection Guide Technical Support on Per- and Polyfluoroalkyl Substances Policy*.

Bertanza, G., Capoferri, G. U., Carmagnani, M., Icarelli, F., Sorlini, S., & Pedrazzani, R. (2020). Long-term investigation on the removal of perfluoroalkyl substances in a full-scale drinking water treatment plant in the Veneto Region, Italy. *Science of The Total Environment*, *734*, 139154. https://doi.org/10.1016/j.scitotenv.2020.139154

Boone, J. S., Vigo, C., Boone, T., Byrne, C., Ferrario, J., Benson, R., Donohue, J., Simmons, J. E., Kolpin, D. W., Furlong, E. T., & Glassmeyer, S. T. (2019). Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States. *Science of The Total Environment*, *653*, 359–369. https://doi.org/10.1016/j.scitotenv.2018.10.245

Brendel, S., Fetter, É., Staude, C., Vierke, L., & Biegel-Engler, A. (2018). Short-chain perfluoroalkyl acids: Environmental concerns and a regulatory strategy under REACH. *Environmental Sciences Europe*, *30*(1). https://doi.org/10.1186/s12302-018-0134-4

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., de Voogt, P., Jensen, A. A., Kannan, K., Mabury, S. A., & van Leeuwen, S. P. (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management*, *7*(4), 513–541. https://doi.org/10.1002/ieam.258

Cantoni, B., Turolla, A., Wellmitz, J., Ruhl, A. S., & Antonelli, M. (2021). Perfluoroalkyl substances (PFAS) adsorption in drinking water by granular activated carbon: Influence of activated carbon and PFAS characteristics. *Science of The Total Environment*, *795*, 148821. https://doi.org/10.1016/j.scitotenv.2021.148821

Challenges of PFAS in Groundwater: Lessons Learned from Michigan's Survey of Community Water. (n.d.). Retrieved April 4, 2021, from https://regenesis.com/en/webinars/2-thank-you-

challenges-of-pfas-in-groundwater-lessons-learned-from-michigans-survey-of-community-water/

Challenges of PFAS in Groundwater: Lessons Learned from Michigan's Survey of Community Water. (n.d.). *REGENESIS Remediation Solutions*. Retrieved April 4, 2021, from https://regenesis.com/en/webinars/2-thank-you-challenges-of-pfas-in-groundwater-lessons-learned-from-michigans-survey-of-community-water/

Crimi, M., Holsen, T., Bellona, C., Divine, C., & Dickenson, E. (2017). In Situ Treatment Train for Remediation of Perfluoroalkyl Contaminated Groundwater: In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC). SERDP, 148.

Deng, S., Zhang, Q., Nie, Y., Wei, H., Wang, B., Huang, J., Yu, G., & Xing, B. (2012). Sorption mechanisms of perfluorinated compounds on carbon nanotubes. *Environmental Pollution*, *168*, 138–144. https://doi.org/10.1016/j.envpol.2012.03.048

Dixit, F., Barbeau, B., Mostafavi, S. G., & Mohseni, M. (2019). PFOA and PFOS removal by ion exchange for water reuse and drinking applications: Role of organic matter characteristics. *Environmental Science: Water Research & Technology*, *5*(10), 1782–1795. https://doi.org/10.1039/C9EW00409B

Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., & Yu, G. (2014). Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *Journal of Hazardous Materials*, *274*, 443–454. https://doi.org/10.1016/j.jhazmat.2014.04.038

Emerging chemical risks in Europe—'PFAS'—European Environment Agency. (n.d.). [Briefing]. Retrieved April 4, 2021, from https://www.eea.europa.eu/publications/emerging-chemical-risks-in-europe/emerging-chemical-risks-in-europe

Grasty, R. C., Grey, B. E., Lau, C. S., & Rogers, J. M. (2003). Prenatal window of susceptibility to perfluorooctane sulfonate-induced neonatal mortality in the Sprague-Dawley rat. *Birth Defects Research Part B: Developmental and Reproductive Toxicology*, *68*(6), 465–471. https://doi.org/10.1002/bdrb.10046

Holliday, M. D. (2020). Comparison of the PFAS Adsorption Capabilities of a Coconut Shell Based Granular Activated Carbon and a Bituminous Coal Based Granular Activated Carbon. *Air Force Institute of Technology*, 94.

Humphreys, E. H., & Tiemann, M. (2019). PFAS and Drinking Water: Selected EPA and Congressional Actions. *Congressional Research Service*, 23.

IPEN. (2019). PFAS Pollution Across The Middle East And Asia. *IPEN*. What is the outlook for pfass in asia

Jackson, A. (2020, March 25). *Feature: What is the outlook for PFASs in Asia?* Chemical Watch. https://chemicalwatch.com/102583/feature-what-is-the-outlook-for-pfass-in-asia

Kothawala, D. N., Köhler, S. J., Östlund, A., Wiberg, K., & Ahrens, L. (2017). Influence of dissolved organic matter concentration and composition on the removal efficiency of perfluoroalkyl substances (PFASs) during drinking water treatment. *Water Research*, *121*, 320–328. https://doi.org/10.1016/j.watres.2017.05.047

Kucharzyk, K. H., Darlington, R., Benotti, M., Deeb, R., & Hawley, E. (2017). Novel treatment technologies for PFAS compounds: A critical review. *Journal of Environmental Management*, *204*, 757–764. https://doi.org/10.1016/j.jenvman.2017.08.016

Li, Y., Fletcher, T., Mucs, D., Scott, K., Lindh, C. H., Tallving, P., & Jakobsson, K. (2018). Half-lives of PFOS, PFHxS and PFOA after end of exposure to contaminated drinking water. *Occupational and Environmental Medicine*, *75*(1), 46–51. https://doi.org/10.1136/oemed-2017-104651

Liu, C. J., Werner, D., & Bellona, C. (2019). Removal of per- and polyfluoroalkyl substances (PFASs) from contaminated groundwater using granular activated carbon: A pilot-scale study with breakthrough modeling. *Environmental Science: Water Research & Technology*, *5*(11), 1844–1853. https://doi.org/10.1039/C9EW00349E

McNamara, J. D., Franco, R., Mimna, R., & Zappa, L. (2018). Comparison of Activated Carbons for Removal of Perfluorinated Compounds From Drinking Water. *Journal AWWA*, *110*(1), E2–E14. https://doi.org/10.5942/jawwa.2018.110.0003

Meegoda, J. N., Kewalraman, J. A., Li, B., & Marsh, R. W. (2020). A Review of the Applications, Environmental Release, and Remediation Technologies of Per- and Polyfluoroalkyl Substances. *International Journal of Environmental Research and Public Health*. https://pubmed.ncbi.nlm.nih.gov/33153160/

Naming_conventions_508_2020Aug_Final.pdf. (n.d.). Retrieved April 4, 2021, from https://pfas-1.itrcweb.org/wp-content/uploads/2020/10/naming_conventions_508_2020Aug_Final.pdf

Nelson Jessica W., Hatch Elizabeth E., & Webster Thomas F. (2010). Exposure to Polyfluoroalkyl Chemicals and Cholesterol, Body Weight, and Insulin Resistance in the General U.S. Population. *Environmental Health Perspectives*, *118*(2), 197–202. https://doi.org/10.1289/ehp.0901165

Pelch, K. E., Reade, A., Wolffe, T. A. M., & Kwiatkowski, C. F. (2019). PFAS health effects database: Protocol for a systematic evidence map. *Environment International*, *130*, 104851. https://doi.org/10.1016/j.envint.2019.05.045

Per-andPolyfluoroalkylSubstances(PFAS)-Treatment.pdf. (n.d.). Retrieved April 4, 2021, from https://www.awwa.org/Portals/0/AWWA/ETS/Resources/Per-andPolyfluoroalkylSubstances(PFAS)-Treatment.pdf?ver=2019-08-14-090249-580

PFAS in Pennsylvania. (n.d.). Department of Environmental Protection. Retrieved November 8, 2021, from https://www.dep.pa.gov:443/Citizens/My-Water/drinking_water/PFAS/Pages/default.aspx

PubChem. (n.d.). *Perfluorooctanesulfonic acid*. PubChem. Retrieved April 4, 2021, from https://pubchem.ncbi.nlm.nih.gov/compound/74483

Seacat, A. M., Thomford, P. J., Hansen, K. J., Olsen, G. W., Case, M. T., & Butenhoff, J. L. (2002). Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys. *Toxicological Sciences*, *68*(1), 249–264. https://doi.org/10.1093/toxsci/68.1.249

Shoemaker, J. A., Boutin, B. K., & Tettenhorst, D. R. (2018, November 2). *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)*.
USEPA. https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL

Siriwardena, D. P., Crimi, M., Holsen, T. M., Bellona, C., Divine, C., & Dickenson, E. (2019). Influence of groundwater conditions and co-contaminants on sorption of perfluoroalkyl compounds on granular activated carbon. *Remediation Journal*, *29*(3), 5–15. https://doi.org/10.1002/rem.21603

Wielsøe, M., Long, M., Ghisari, M., & Bonefeld-Jørgensen, E. C. (2015). Perfluoroalkylated substances (PFAS) affect oxidative stress biomarkers in vitro. *Chemosphere*, *129*, 239–245. https://doi.org/10.1016/j.chemosphere.2014.10.014

Woodard, S., Berry, J., & Newman, B. (2017a). Ion exchange resin for PFAS removal and pilot test comparison to GAC. *Remediation Journal*, *27*(3), 19–27. https://doi.org/10.1002/rem.21515