Effect of Anion Exchange Resin
Properties on the Adsorption
of PFAAs and NOM

by

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ABSTRACT

Humans are exposed up to thousands of per- and polyfluoroalkyl substances (PFAS) in the environment, but most of the research and action has been directed towards only two PFAS compounds. These two compounds are part of a subcategory of PFAS called perfluoroalkyl acids (PFAAs). It has been a challenge for the environmental community to mitigate risks caused by PFAAs due to their high persistence and lack of effective measures to remove them from the environment, especially in heavily impacted areas like fire-training sites. The goal of this work was to further answer some questions regarding the removal of PFAAs in the environment by looking at anion exchange resin characteristics and presence of a competing compound, natural organic matter (NOM), in the adsorption of environmentally relevant PFAS compounds including the two often monitored 8-carbon chain PFAAs. Two different resins were tested with two forms of counterions, in both groundwater and NOM impacted groundwater. Resin polymer matrix was the most important property in the adsorption of PFAAs, the two resins used A520E and A860 had similar properties except for their matrices polystyrene (PS) and polyacrylic (PA), respectively. The PS base is most effective at PFAAs adsorption, while the PA is most effective at NOM adsorption. The change in the counterion did not negatively affect adsorption of PFAAs and is therefore a viable alternative for future studies that include regeneration and destruction of PFAAs. The presence of NOM also did not significantly affect the adsorption of PFAAs in the PS resin A520E, although for some PFAAs compounds it did affect adsorption for the PA resin. Ultimately, PS macroporous resins with a strong Type I or Type II base work best in PFAAs removal.

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LIST OF ACRONYMS MENTIONED IN THIS WORK

AFFF	Aqueous Film Forming Foam
AIX	Anion Exchange
DI	Deionized Water
DOC	Dissolved Organic Carbon
DP,EP,CE,CXP	Voltage Settings: Declustering Potential, Entrance Potential, Collision Energy, & Collision Exit Potential
DVB	Divinyl Benzene
ESI	Electrospray Ionization
G	Gel
GAC	Granular Activated Carbon
GW	Groundwater
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
LOQ	Limits of Quantitation
MP	Macroporous
MRM	Multiple Reaction Monitoring
NOM	Natural Organic Matter (Interchangeable With SRNOM)
NPOC	Non-Purgeable Organic Carbon
PA	Polyacrylic
PFAA	Perfluoroalkyl Acid
PFAS	Per- And Poly- Fluoroalkyl Substances
PFBA	Perfluorobutyrate/ Perfluorobutyric Acid
PFBS	Perfluorobutane Sulfonate/Perfluorobutane Sulfonic Acid
PFHxA	Perfluorohexanoate/Perfluorohexanoic Acid
PFHxS	Perfluorohexane Sulfonate/Perfluorohexane Sulfonic Acid
PFOA	Perfluorooctanoate/Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate/Perfluorooctane Sulfonic Acid
POP	Persistent Organic Pollutant
PS	Polystyrenic
RO	Reverse Osmosis
SRNOM	Suwanee River Natural Organic Matter (Interchangeable With Nom)
TOC	Total Organic Carbon
UV	Ultraviolet Visible Spectroscopy
WTP	Water Treatment Plant (Drinking Water)
WWTP	Waste Water Treatment Plant

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CHAPTER 1

INTRODUCTION

1.1. Defining perfluoroalkyl and polyfluoroalkyl substances

1.1.1. Chemical behavior, uses, & fate

Per- and polyfluoroalkylated substances (PFAS) are a group of over 3,000 anthropogenic organic compounds with similar chemical properties desirable for consumer products (Wang, DeWitt, Higgins, & Cousins, 2017). The first of these substances was invented as early as the 1930s (Yingling, 2018). PFAS have an aliphatic carbon backbone in which hydrogen atoms have been entirely (prefix: per-) or partially (prefix: poly-) replaced by fluorine. Fluorine, when bound to carbon, is the strongest bond in organic chemistry and its strength increases with every replacement of hydrogen with fluorine in an alkane (Rahman, Peldszus, & Anderson, 2014). There are numerous PFAS compounds in use, for example phosphorus-containing PFAS which have only very recently been detected in surface, drinking, and waste waters (Rahman et al., 2014).

This work focused on a specific class of PFAS, perfluoryl alkyl acids (PFAAs), due to their environmental importance. For clarity, all PFAAs are PFAS but not all PFAS are PFAAs. PFAAs are found at larger quantities in the environment relative to other PFAS which have been labeled as a persistent organic pollutant (POP) by the USEPA. PFAAs are carbon chains saturated with fluorine atoms with a sulfonic or carboxylic terminal acid group. In Figure 1.1, a section of the PFAS family is shown to illustrate groupings of subcategories with similar chemical structures and properties. The six chemical structures shown are the ones that will be discussed in this work. These were chosen because the 8-carbon chain PFAS were the first to attract the attention of regulatory committees worldwide but are being phased out by shorter chain analogues like the ones shown (Wang et al., 2017). The impacts of which are not fully understood, and research shows that these analogues may be even harder to remove from the environment (Conte L., 2015; Maimaiti et al., 2018; Zaggia, Conte, Falletti, Fant, & Chiorboli, 2016).

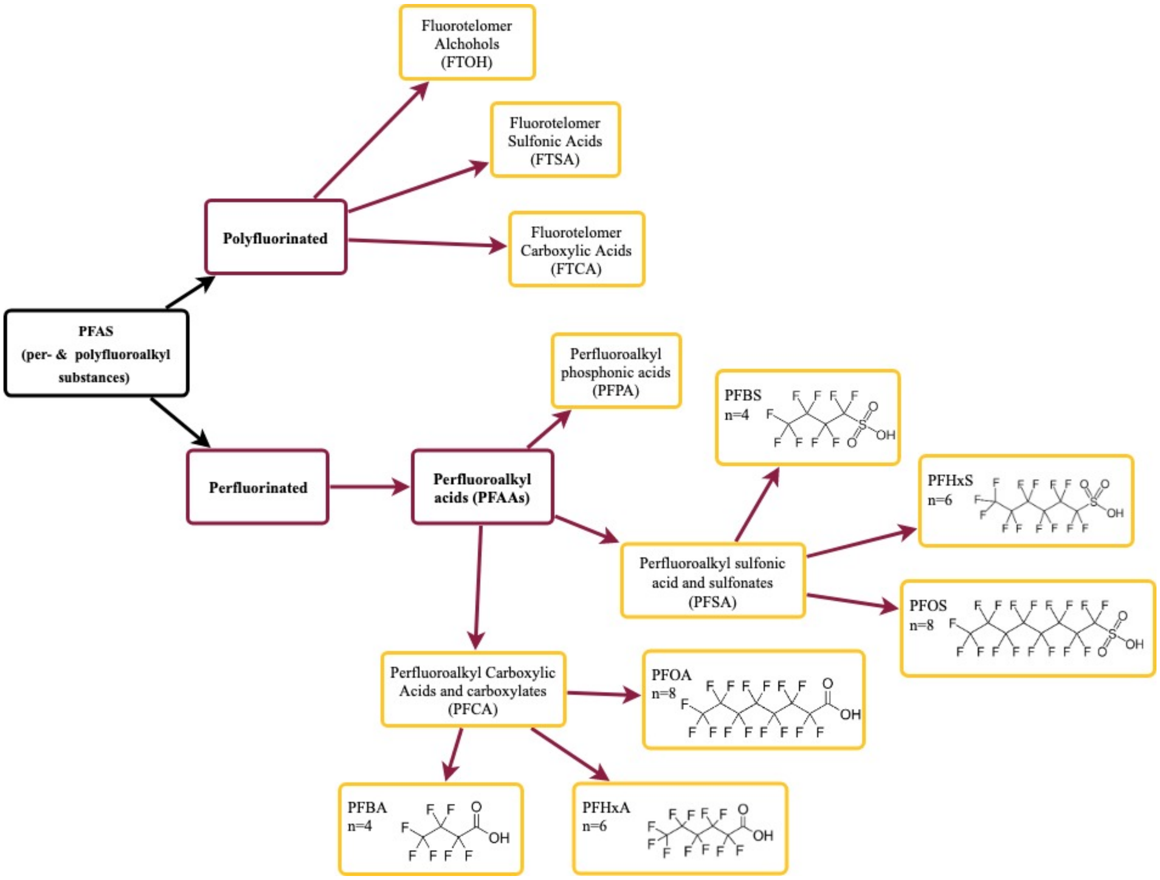

Figure 1.1 PFAS family tree with selected PFAAs Perfluoroalkyl acids discussed in this work shown with their structural formula, where "n" signifies the number of carbons in the alkyl.

PFAS, due to their unique chemical properties, are used as a coating material for materials such as textiles, metal plating, and even cookware thanks to their hydrophobicity, lipophobicity, temperature resistance, and low friction – but unfortunately these characteristics also allow them to persist in the environment (Rahman et al., 2014; Yingling, 2018). Industrial sites that may be sources of PFAS releases to the environment include metal finishing and plating, wire manufacturers, textile/leather industries, and any facilities using surfactants, resins, molds, plastics, photolithography, and semiconductors – mostly through waste products, but also through leaching, spills, and exhaust. Landfills are the ultimate reservoir for PFAS-laden consumer products, sewage sludge, and industrial waste products which can contaminate waste water treatment plants (WWTP) during leachate treatment, as well as the soil/groundwater below the landfill (Maimaiti et al., 2018; Yingling, 2018).

The fluorocarbon chains found in PFAAs are by nature larger and more rigid than hydrocarbon chains because fluorine is a larger, more electronegative element than hydrogen. Consequently, fluorocarbon chains tend to have low polarizability, and weak Van der Waals forces (Kovalchuk, Trybala, Starov, Matar, & Ivanova, 2014). The stability of fluorocarbons makes PFAS more stable and less reactive, thereby withstanding heat, acids, bases, reducing agents, oxidants, photolytic, microbial, and metabolic degradation. Partitioning and transport in the environment is directed by several factors including electrostatic interactions of their polar functional group with environmental matrices, sorption which usually increases with increasing C-F tail length, and their ability to function as surfactants – which is what makes them such popular commercial products – allows them to aggregate at the interface of water and octanol (Higgins & Luthy, 2006; Rahman et al., 2014)

PFAAs also have an acidic terminal group. Sulfonic acids are commonly cited as magnitudes more acidic than carboxylic acids which have a low pK_a already, PFAAs are therefore considered strong acids for this reason as well as the dipole effects from the highly electronegative fluorine atoms (Yingling, 2018). Specific pK_a values for PFAAs are generally not available, but perfluorooctanoic acid (PFOA) pK_as are predicted to range from -0.5 to 3.8, due to their acidity (Burns, Ellis, Li, McMurdo, & Webster, 2008). Strong acids will readily dissociate in water and other environmental matrices, therefore PFAAs are often found in their anionic form, unless in very rare extreme conditions of very low pH (Guelfo & Higgins, 2013). This is important to note because the acid and anionic forms have very different physical and chemical properties. At high enough concentrations, PFAS will aggregate and form micelles which could enhance, or in some cases reduce, sorption on carbon and minerals in the environment (Du et al., 2014; Gao, Deng, Du, Liu, & Yu, 2017; Yingling, 2018).

The global use of PFAS in industry has led to a concern for the global community because of its persistence in the environment and ability to bioaccumulate, with implications for public health. The impact of several PFAS (especially PFAAs) are being monitored by environmental and health organizations across the world, including in the United States. The USEPA has a combined health advisory level of 70 parts per trillion in drinking water for perfluorooctanoic acid (PFOA) or perfluorooctanoate in anion form and perfluorooctane sulfonic acid (PFOS) or perfluorooctane sulfonate in the anion form; 8-carbon chain PFAAs are most commonly found in drinking water (EPA 2019). EPA's health advisories are non-enforceable and non-regulatory and provide information to states agencies and other public health officials on contaminants that can cause human health effects and occur in drinking water (EPA 2019). At both more regional and global levels however there are more stringent regulations that even include some of the other PFAAs discussed in this work.

1.1.2. Environmental point sources & human toxicity

There are four major point sources for PFAS found in the environment: fire training or response sites, industrial sites, landfills, and wastewater treatment plants/biosolids. Typical PFAS concentrations in environmental waters range from pg/L to ng/L. However, higher concentrations (µg/L to even mg/L) have been detected in surface water and groundwater following fire-fighting activities or explosions, and in some waters adjacent to fluorochemical manufacturing facilities (Rahman et al., 2014). Fire training and response sites for military and civilian airports, and other facilities employ aqueous film-forming foams (AFFFs) to extinguish fuel fires. AFFFs are a commercial surfactant solution that is by nature a variable mixture of PFAS. AFFF can contaminate soil, surface and groundwaters once released into the environment and can co-locate with the petroleum hydrocarbons that are also commonly found at sites where AFFFs are used. Because of the variability of AFFF makeup, and geochemical makeup of soils and groundwater, the fate and transport of these AFFF derived PFAS are variable and uncertain. This work used concentrations nearing those of AFFF impacted sites for the six chosen PFAAs because these sites are some of the most heavily impacted and the concentrations would be environmentally relevant.

The large variability in structure and function of PFAS makes them difficult environmental contaminants to remediate, but furthermore PFAS have been found in human serum and have been shown in epidemiological and animal studies to cause health effects of varying degrees. PFOA, for example, one of the most commonly occurring PFAS, has a human serum half-life of 3.8 years and in animal studies has been associated with tumor development in prostate, bladder, liver, and/or kidneys, immunotoxicity, and developmental and hormonal effects (Rand & Mabury, 2017). The large number of different PFAS makes it difficult to study effects of each one, and animal models cannot always predict how chemicals will interact in humans. Most of the focus has been on the traditional 8-carbon chain PFAAs because they are most commonly detected at high levels relative to other PFAS, however shorter chain analogues and precursors to these PFAAs also pose health concerns. A hallmark response of most PFAA exposure is hepatoxicity, despite the variable kinetics and levels of toxicity (Wang et al., 2017). The shorter chain PFAS or the precursor compounds have also been shown to interact with metabolites in the body, causing conformational chemical changes, as well as bonding to glutathione, an important antioxidant that helps to prevent DNA damage (Rand & Mabury, 2017). In laboratory animal studies, exposure to high levels of the 4-carbon chain PFAA, perfluorobutanoate (PFBA) resulted in thyroid and liver effects, such as increased thyroid and liver weight, changes in thyroid hormones, decreased cholesterol, and cellular changes in both organs. Other effects of PFBA exposure included delayed development and decreased red blood cells and hemoglobin. Like other shorter chain PFAAs (less than 8 carbons) studies of PFBA in people are lacking and while these shorter chain analogues have been detected in the blood of people exposed to PFAS, it is less common than other PFAAs (Ehlinger, 2017).

1.1.3. PFAAs in drinking & waste water treatment & removal methods

In traditional water treatment there is very poor removal of PFAS. In several instances, detected concentrations of PFOA and PFOS in treated drinking water were higher than in raw water prior to treatment (Rahman et al., 2014). It is believed that breakdown of larger compounds to PFOS and PFOA during treatment may be possible or that leaching from Teflon®-coated treatment equipment components and desorption from GAC filters that had been in service for long periods without reactivation may be responsible (Rahman et al., 2014). Shorter chain PFAAs concentrations, in particular, may be higher after treatment as a result of desorption from GAC due to competition for active sorption sites with longer chain PFAAs or natural organic matter (NOM) constituents (Rahman et al., 2014). Standard treatment processes such as coagulation, flocculation, sedimentation and filtration, as well as more advanced processes like UV, chlorine disinfection, ozonation and sand filtration showed ineffectiveness in the removal of PFAAs (Pan, Liu, & Ying, 2016). In full scale water-treatment systems reverse osmosis (RO), granular activated carbon (GAC), and anion exchange (AIX) were the most effective at reducing PFAS concentrations at a full scale, although RO worked best with the shorter chain PFAS (Appleman et al., 2014). However, there is the need to consider that RO is expensive, energy intensive, and susceptible to fouling. With all the aforementioned methods, disposal of the PFAS once it has been removed from water also becomes a factor and would ultimately lead to higher operating costs. There is no one size fits all and the treatment chosen would have to be chosen considering the circumstances. Several other studies that have compared GAC to AIX have found that AIX is more efficient at PFAS removal in comparison to GAC (Chularueangaksorn, Tanaka, Fujii, & Kunacheva, 2014; McCleaf et al., 2017; S. T. Senevirathna et al., 2010; S. T. M. L. D. Senevirathna et al., 2010; Woodard, Berry, & Newman, 2017; Yu, Zhang, Deng, Huang, & Yu, 2009). Regenerable AIX media offers sustainability benefits because the media can be reused, but the process for regenerating requires chemicals and creates a concentrated waste stream which must be managed (Yingling, 2018).

The research lacks comprehensive look at the most effective resins and regeneration methods for all PFAAs including the short chain PFAAs which pose a risk to the environment. Furthermore, treatment is dependent on what the source of impact is, for example in AFFF impacted sites the main area affected is the soil and groundwater directly near the site, this would require a separate approach to treatment of an industrial waste stream feeding into a WWTP.

Sorption and retardation generally increase with increasing perfluoroalkyl tail length (Guelfo & Higgins, 2013), indicating that the short-chain PFAAs (for example, perfluorobutane sulfonic acid [PFBS] and perfluorohexanoic acid [PFHxA]) are retarded less than their long-chain counterparts. In addition, sulfonic acid PFAAs tend to sorb more strongly than those with a carboxylic acid terminal group of equal chain length, and branched isomers have less sorption than linear (Yingling, 2018). PFAAs are, in general, far less volatile than many other groundwater contaminants (Yingling, 2018). This adds a level complexity to attempts to remove PFAAs from water systems. In environmental waters with a combination of PFAS, inorganic, and organic matter, the question still remains as to what treatment may be most effective. This work focuses on illuminating some of the questions remaining with AIX since it is a versatile and relatively inexpensive method of remediation and would be most relevant for AFFF impacted groundwaters.

1.2. Anion Exchange Resins

AIX resins are created using a base monomer (e.g., styrene) mixed with a catalyst and a crosslinking monomer such as divinyl benzene (DVB). The amount of crosslinking monomer used affects porosity and water retention (W. S. Miller & Pieper, 1981). There are two main types of porosity: gel or macroporous. Standard anion exchange resins are prepared by causing amines to react with the copolymer intermediate. The type of amine used determines whether the final product is a weak-base or strong base. Weak-base resins are in a free-base form; strong-base resins are in a chloride form. Strong base resins are highly ionized and can be used over the entire pH range (W. S. Miller & Pieper, 1981). In the literature there are two main types of polymer backbone used, either polyacrylic (PA) crosslinked with DVB or polystyrenic (PS) crosslinked with DVB, then there are two porosities either macroporous (MP) or gel (G), there are different base types used as terminal groups and usually associated with a chloride ion. The chloride ion is then exchanged for the desired anion, be it PFAS or some other anion. The chloride ion can be exchanged for a different ion as well to lessen environmental burden when managing waste solutions or to enhance destruction of waste post resin regeneration (Hu, Foster, & Boyer, 2016).

1.2.1 Anion Exchange Resins Used for Removal of PFAAs

In the literature before 2015 anion exchange resins were only compared in the removal of PFOS. Looking at only the papers that compared two or more anion exchange resins some conclusions can be drawn, however with the wide range of PFAS compounds and resin characteristics there are still questions that have not been answered by the literature. In Appendix A Table A8 summarize the findings of research looking at 2 or more anion exchange resins for the removal of PFAS. To summarize for the removal of PFOS polyacrylic resins were shown to exhibit faster uptake kinetics and higher capacity compared to polystyrene resins, regardless of whether the resins were tested in gel-type or macroporous form (Deng, Yu, Huang, & Yu, 2010). The faster uptake kinetics and higher capacity were attributed to the more hydrophilic properties of the polyacrylic resin (Deng et al., 2010). The hydrophilic properties of the resin aid in the movement of water into the pores. However in later studies, that included some of the shorter chain analogues polystyrenic resins were used exclusively and the hydrophobicity of the bases played an important role in PFAA adsorption (Conte L., 2015; Maimaiti et al., 2018; Zaggia et al., 2016). Polyacrylic resins therefore have only mainly been researched in the removal of PFOS and polystyrenic in the removal of the remaining PFAAs. It is unclear if polyacrylic would perform well in the removal of the shorter chain analogues as well as it does with the 8-carbon chain PFOS. It has been reported with PFOS that the presence of one hydroxyl group close to the quaternary nitrogen can make macroporous strong base polystyrene resin more hydrophilic and provide a more open structure (Deng et al., 2010). A macroporous strong base polystyrene resin containing a hydroxyl group close to the ammonium nitrogen was used in one study for the removal of 6-carbon PFHxS and co-removal of other PFAS with success. However, PFASs decreased in the order of PFOS > PFHxS > PFOA > PFBS>PFHxA > PFBA, closely related to the hydrophobicity and functional groups of PFAAs (Maimaiti et al., 2018).

The hydrophobicity of the terminal base and copolymer structure are important because of the chemical structure of PFAAs. Longer chain PFAAs are more hydrophobic and therefore it is thought that hydrophobic interactions are the predominant sorption mechanism for long chain PFAAs, whereas electrostatic effects may be more significant for cationic precursors and short chain PFAAs (Kucharzyk, Darlington, Benotti, Deeb, & Hawley, 2017). From the literature Type II bases, which have dimethyl ethanol amine groups making them slightly less basic than Type I, tend to perform slightly better and have higher capacity than Type I bases.

Macroporous resins when all other characteristics are the same work better than their gel counterparts (Conte L., 2015; Deng et al., 2010) Polyacrylic resins have not been explored outside of PFOS and generally all the research concludes that treatment train approaches that allow for decentralized remediation may be more promising than a single technology. Based on these results from previous studies, this work focuses on looking at resins that are macroporous with the same terminal base group but with alternating polymer structures, to compare PS and PA resins for the removal of a larger variety of PFAAs. Furthermore, due to promising results with some destruction technologies it would be beneficial to have a different exchangeable ion form for the resins, so that after resin regeneration the waste stream with the brine can be used for destruction of the PFAAs (Ross et al., 2018), for this a comparison between the native chloride ion form and a sulfate ion form will be explored.

1.3. Natural Organic Matter

Natural organic matter (NOM) is a catch-all term for carbon-based compounds found in natural aquatic and terrestrial environments (Tan & Kilduff, 2007). They are complex molecules varying in size with charged and uncharged portions, much like PFAAs. NOM is found in larger quantities in surface waters but may also be found to varying degrees in groundwater as well (Bolto, Dixon, & Eldridge, 2004). The amount of

NOM present in water is another factor in the removal of PFAAs. PFAAs are present as organic anions and are therefore relatively mobile in groundwater but tend to associate with the organic carbon fraction that may be present in soil or sediment (Guelfo et al., 2018; Higgins & Luthy, 2006). In one study, perfluorohexane sulfonic acid (PFHxS) sorption decreased with the addition of organic and inorganic carbon sources (Maimaiti et al., 2018), however a comprehensive look at sorption effect with several PFAAs in environmental waters has not been thoroughly studied. Drinking water sources typically contain around 5 mg/L of NOM, of which only 10–30% has been identified, NOM already poses several problems for the water treatment industry, among them the formation of potentially carcinogenic chlorinated hydrocarbons such as trihalomethanes (THMs) during the disinfection process (Bolto et al., 2004). The make-up of the organic compounds in NOM are a large part of fulvic acids and humic acids, but also include hydrophilic acids, carbohydrates, carboxylic acids, and amino acids. Humic substances (encompassing fulvic and humic acids) are have variable properties, in terms of acidity (pKa 3–5), MW (several hundred to ten thousand) and molecular structure. They behave as anions and can interact via their hydrophobic aromatic and aliphatic regions with non-polar pollutants (Bolto et al., 2004).

Resin properties are also important in the removal of NOM, although this has been largely studied, resin pore size is very important in the uptake of NOM because size-exclusion can limit adsorption. Macroporous resins (100-3500 nm pore size) work better than smaller pore sized resins (Tan & Kilduff, 2007). It has also been shown that hydrophilic acrylate resins are highly effective at NOM removal (Bolto et al., 2004).

This thesis set out to fill gaps in the literature by looking at polyacrylic and polystyrene macroporous resins with varying counterions, in the removal of PFAAs. There is a lot of literature to show how anion exchange resins perform in the presence of NOM, therefore NOM impacted groundwater will be used to confirm known resin trends and characterize the impact of changing the counterion. It is expected that the polyacrylic resin will outperform the polystyrenic resin in NOM removal as has been shown in the literature. However, it is unclear how PFAAs removal will be impacted with the difference in polymer base, the difference in counterion form, or the addition of NOM as a competitive ion. The purpose of this work is to provide relevant information for AFFF impacted groundwater treatment. Due to the variability of groundwater composition it is important to test how NOM concentration affects PFAAs removal.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

2.1.1. Anion Exchange Resins

The two anion exchange resins used in this work were strong base resins A520E and A860. A520E has a macroporous polystyrene structure while A860 has a macroporous polyacrylic structure. As mentioned previously, macroporous resins have been shown to work better than their gel counterparts for both PFAAs and NOM. The resins were supplied by Purolite, USA. The composition and properties of the resins used are listed in Table A1 in Appendix A, as reported by the supplier. The resins were received in chloride form and had to be converted to sulfate form by mixing resins in a highly concentrated sodium sulfate solution (CAS 7757-82-6). Mixing occurred in a jar test apparatus at 200 rpm for 24 h. Resins were filtered from solution and rinsed with deionized (DI) water and placed to dry in a desiccator. Ion chromatography was used to confirm the exchange from sulfate to chloride ion in brine solution. Resin density was calculated in quintuplet by measuring 1 mL wet resin in a graduated cylinder and then dried at room temperature in a desiccator for both the chloride and sulfate forms. Densities are reported in appendix A Table A9. Dry mass was measured and used for determination of dry resin doses for all experiments.

2.1.2. Test Water

Groundwater was collected from a single Tempe groundwater well. The composition of which is reported by the city of Tempe in Table A2 in appendix A. Groundwater was used as the main solvent for all experiments. Groundwater was chosen because of the interest in AFFF impacted sites, which largely affect groundwater sources. There was no detectable background PFAS in this water and under 2 mg/L of dissolved organic carbon as measured by the total organic carbon analyzer (TOC).

2.1.3. Perfluoroalkyl acids (PFAAs)

The PFAS used in this work were perfluorooctanesulfonic acid (PFOS) (CAS# 1763-23-1, ACS grade, Sigma Aldrich), perfluorooctonoic acid (PFOA) (CAS# 335-67-1, ACS grade, Sigma Aldrich) potassium nonafluoro-1-butanesulfonate (PFBS potassium salt) (CAS# 29420-49-3, ACS grade, Sigma Aldrich), heptafluorobutyric acid (PFBA) (CAS# 375-22-4, ACS grade, Sigma Aldrich), tridecafluorohexane -1- sulfonic acid potassium salt (PFHxS potassium salt) (CAS# 3871-99-6, ACS grade, Sigma Aldrich), and undecafluorohexanoic acid (PFHxA) (CAS# 307-24-4, ACS grade, Sigma Aldrich). The PFAS solutions were prepared by creating concentrated stock solutions in 10% by volume methanol (MeOH) in DI water due to the surfactant properties of PFAS, MeOH aids in homogenizing the solution. These six separate stock solutions were then further diluted in groundwater for each batch experiment into one working solution containing all PFAAs at the concentrations shown in Table 2.1 below.

Table 2.1

Working Solution PFAAs Concentrations

PFAS	Stock Concentration in 10% MeOH *(μg/L)*	Concentration in Batch Experiment in Groundwater *(μg/L)*
PFOA	4.75×10^6	500
PFOS	4.40×10^6	500
PFBS	8.67×10^6	250
PFHxA	8.80×10^6	500
PFBA	4.90×10^6	250
PFHxS	5.00×10^6	500

2.1.4. Natural Organic Matter (NOM) solutions

Suwannee River NOM (SRNOM, 2R101N, International Humic Substances Society) was the dissolved organic carbon source used in this work. Solutions were prepared in groundwater at 20 mg/L, which is 50.7% elemental composition of carbon in %(w/w) of a dry, ash-free sample, therefore it is expected to have about 10 mg/L of carbon per solution.

2.2. Experimental methods

Batch tests were conducted with various resin doses for both resins in 125 mL amber glass bottles. The experimental schematic is shown in Table 2.2. All samples were run in triplicate and tests were conducted on Thermo Scientific™ MaxQ™ 2000 and 3000 Benchtop Orbital Shakers at 200 rpm for 24 h at room temperature (approx. 22 °C). Controls of untreated test waters were run with each test in triplicates. Afterwards, all samples without PFAS were filtered through 0.45 µm membrane filters and those containing PFAS were centrifuged at 5000 rpm for 30 min, due to the nature of PFAS to form films on membranes leading to fouling (Lath, Knight, Navarro, Kookana, & McLaughlin, 2019).

Table 2.2

Experimental Schematic for Batch Studies

Batch Experiment	Test Water	Resin Form	Resin Dose[a] *(mL/L)*
1	Groundwater	Chloride	0.25, 0.5, 1, 2, 4
2	Groundwater + SRNOM	Chloride	0.25, 0.5, 1, 2, 4
3	Groundwater + PFAAs	Chloride	0.25, 0.5, 1, 2, 4
4	Groundwater + SRNOM + PFAAs	Chloride	0.25, 0.5, 1, 2, 4
5	Groundwater	Sulfate	0.25, 0.5, 1, 2, 4
6	Groundwater + SRNOM	Sulfate	0.25, 0.5, 1, 2, 4
7	Groundwater + PFAAs	Sulfate	0.25, 0.5, 1, 2, 4
8	Groundwater + SRNOM + PFAAs	Sulfate	0.25, 0.5, 1, 2, 4

[a] Dose for each resin measured in dry weight using calculated density
(SRNOM) Suwanee River Natural Organic Matter. (PFAAs) Perfluoroalkyl Acids.

2.3. Analytical methods

Baseline measurements of groundwater and groundwater with NOM were taken in duplicates before the start of batch experiments. These are reported in Table A3 in appendix A and they include pH, conductivity, UV254 on 0.45 µm filtered sample, UV254 on centrifuged sample, TOC, DOC on 0.45 µm filtered sample, DOC on centrifuged sample, inorganic anions by IC, and inorganic cations by IC. Samples were filtered using 0.45 µm filters (Environmental Express, SC,USA) before being measured for pH and conductivity using an Orion Versastar Pro-advanced Electrochemistry meter. The meter was calibrated for pH with pH 4, 7, and 10 buffer solutions and for conductivity with 100 µScm^{-1}, 1413 µScm^{-1}, 12000 µScm^{-1}, 50000 µScm^{-1} and 100000 μScm^{-1} standards prior to use. Ion chromatography (IC) (Dionex ICS 5000+) was used for analysis of fluoride, chloride, nitrate, nitrite, sulfate, phosphate, lithium, sodium, potassium, magnesium, calcium, and ammonium. The IC method followed U.S. EPA method 300.1. Check standards for anion and cations (Dionex, CA, USA) were added every 10 samples. Peaks were analyzed using Chromeleon Peak Analysis software. A total organic carbon (TOC) analyzer (Shimadzu TOC- VCH) was used for analyzing TOC and DOC, using the non-purgeable organic carbon (NPOC) method. Dissolved organic carbon standards (Ricca) were run as checks every 15 samples for the TOC analyzer with relative difference less than 15%. Experimental batch samples were filtered on 0.45 μm filters if they did not contain PFAS (batch experiments 1,2,5 and 6) while PFAS containing samples were centrifuged at 5000 rpm for 30 min (batch experiments 3,4,7, and 8) due to possible loss of PFAS on filters (Lath et al., 2019). Filtered samples were compared with filtered samples for analysis and centrifuged samples were only compared with centrifuged samples. Experimental samples were analyzed using the TOC analyzer and UV DR6000 Laboratory Spectrophotometer (HACH) using EPA method 415.3 for measuring organic carbon at 254 nm. All samples were measured in triplicate.

PFAS quantification analysis was performed by collaborators at the Colorado School of Mines on an Agilent high pressure liquid chromatography (HPLC) system using gradient elution and a Phenomenex Gemini C18 column (110Å, 100×3 mm, 5 μm) equipped with a C18 guard column and Agiment Diol guard column (12.5×4.6 mm, 6 μm) coupled to a Sciex 3200 triple quadruple spectrometry in multiple reaction monitoring (MRM) and negative electrospray ionization (ESI) mode. Injection volumes were 20 μL and a delay column (Luna C18,100Å, 30×3 mm, 5 μm) was placed between the pump and autosampler. The flow rate was 0.8 mL/min, and the gradient mobile phase consisted of 20 mM of Ammonium acetate in water (A) and in methanol (B) starting at 5% B, increased to 60% B in 0.75 min, increased to 100% B for 4 min, and maintained for 3 min, decreased to 5% B in 1 min, and maintained at 5% B for 2 min. Tandem mass spectrometry (MS-MS) transitions, limits of quantitation (LOQ), surrogates, voltage settings (DP, EP, CE, CXP) , internal standards, and % recoveries for each PFAA are in Table 2.3 below.

Table 2.3

Tandem mass spectrometry conditions for each PFAAs

Parent Mass (Da)	Product Mass (Da)	Retention time (min)	Name	DP (V)	EP (V)	CE (V)	CXP (V)	LOQ (µg/L)	R^2
212.8	168.9	3.6	PFBA	-10	-4.5	-12	0	5	0.9924
216.9	171.8	3.6	MPFBA	-10	-4.5	-16	0		
298.9	80.0	4.2	PFBS(1)	-45	-8	-50	-2	1	0.9931
298.9	98.9	4.2	PFBS(2)	-45	-8	-42	0	0.5	0.9918
301.9	79.9	4.2	M3PFBS	-40	-11	-50	-2		
312.9	118.8	4.53	PFHxA(1)	-10	-6	-30	-4	5	0.9964
312.9	269.0	4.53	PFHxA(2)	-10	-6	-12	0	5	0.9864
315.0	270.0	4.53	M2PFHxA	-10	-6	-12	-2		
398.8	79.9	4.8	PFHxS(1)	-65	-8	-56	-6	0.5	0.9970
398.8	98.9	4.8	PFHxS(2)	-65	-8	-50	0	1	0.9947
402.9	83.9	4.8	MPFHxS	-60	-10	-64	-6		
412.9	168.9	5.2	PFOA(1)	-10	-4.5	-24	-4	1	0.9928
412.9	369.0	5.2	PFOA(2)	-10	-4.5	-14	-2	0.5	0.9854
416.9	372.1	5.2	M4PFOA	-10	-4	-14	0		
498.9	98.9	5.45	PFOS(1)	-70	-7.5	-54	0	5	0.9982
498.9	79.9	5.45	PFOS(2)	-70	-7.5	-86	-6	0.5	0.9874
503.0	79.9	5.45	MPFOS	-70	-7	-74	-6		

(1) Transition for quantification, (2) transition for confirmation

Sample composition was 1:1 MeOH and water.
DP: declustering potential. EP: entrance potential. CE: collision energy. CXP: collision exit potential.
R^2: Coefficient of determination

2.3.1 Statistical Analysis

Paired two tailed t-tests were conducted to determine if the change between exchangeable ion forms was statistically significant and if the addition of NOM had any significant effect on adsorption. Table 2.4 shows how data was pooled and compared. All data was paired by resin dose, and each resin, A520E and A860, was analyzed separately. Each PFAA compound was also analyzed separately and then as a total amount, both values are reported. Data was all normalized by C/C0 removal of NOM and PFAA separately. UV measurements were used for calculations of C/C0 NOM removal. For MS-MS measurements the LOQ for the compound was used when the reading was below LOQ. One tailed paired t-test were then conducted if the two-tailed t-test showed a rejection of the null hypothesis, in order to determine which condition was more successful at removal.

Table 2.4
Data Grouping for T-Test Analysis

Chloride and Sulfate form Comparison				GW and SRNOM Comparison		
Experiments:	2,6	3,7	4,8	Experiments:	3,4	7,8

CHAPTER 3

RESULTS AND DISCCUSSION

Results are discussed on the basis of NOM and/or PFAAs removal for each of the experimental conditions. The resin properties that were being compared were polymer base: PA or PS, and exchangeable ion form: chloride or sulfate. Otherwise both resins were Type I strong base macroporous resins, their capacities as given by the manufacturer differed slightly due to difference in structure. A520E is the PS resin and A860 is the PA resin. The error bars depict standard deviation between triplicates, for PFAA measurements the LOQ was used if the result was below LOQ.

3.1. NOM removal in Groundwater with Chloride and Sulfate Resins

The resins were initially tested with the Tempe groundwater, the ground water already contains within 1-2 mg/L of DOC. These results were inconclusive due to a high standard deviation between triplicates, this may be due to the low amount of background NOM present to interact with resin, this figure is presented in Appendix B as Figure B1. In experiments 2 and 6 SRNOM was added to the groundwater at a concentration of 20 mg/L. Figure 3.1 shows NOM removal measured with both UV 254 method of detection for organic carbon and TOC analyzer for non-purgeable organic carbon, the GW control is the untreated groundwater without the addition of NOM and the zero-resin dose is the untreated groundwater with NOM. These results confirmed the expectation that the polyacrylic A860 resin would be better suited for DOC removal at lower concentrations relative to the polystyrenic A520E. Even in these studies though it is seen that the resin removes NOM only as much as the background NOM present in the GW, which further explains why the initial study with groundwater alone proved inconclusive. The background NOM may not be in anionic form or it may not be removed by anion exchange due to other properties of its makeup.

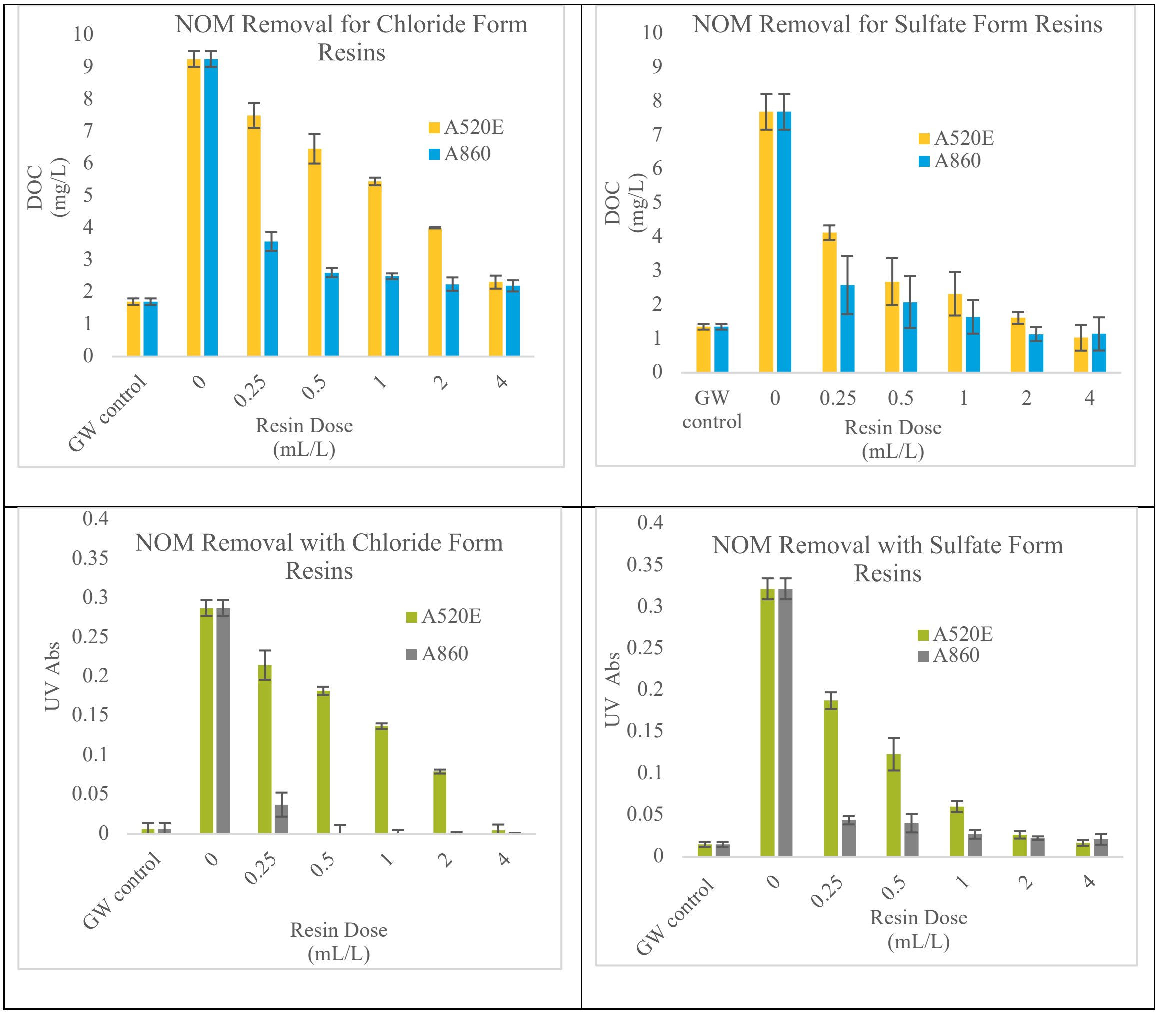

Figure 3.1 NOM impacted groundwater batch studies with chloride (experiment 2) and sulfate resins (experiment 6): top left: DOC for experiment 2; top right: DOC for experiment 6; bottom left: UV for experiment 2 ; bottom right: UV for experiment 6. GW control signifies untreated GW without addition of NOM. Resin dose 0 is untreated NOM impacted GW

3.2. NOM removal in PFAA impacted water

NOM removal efficiency was measured by UV 254 and TOC analyzer, as before. PFAA removal is depicted in a stacked bar chart showing concentrations for each individual PFAA, the raw values for PFAA removal are in Tables A4-A7 in appendix A. Figures 3.2 and 3.3 display the NOM removal for experiments 3 and 4 (top half) and 6 and 7 (bottom half) from the TOC analyzer and UV at 254 nm. In the PFAA impacted groundwater without the addition of NOM (left half of the figures) there is an increase in DOC measured by the instrument for the PA resin A860, the mechanism for what is occurring here is unknown, but it may be PFAA breakdown causing the increase in DOC. This increase is not seen on the UV data which points to the possibility of it originating from PFAAs. The UV254 method is reliable at detecting organic compounds but specifically those that contain aromatic rings or unsaturated carbon bonds in their molecular structure, since these absorb a portion of the UV light as it passes through the water (EPA method 415.3). Since the intensity of the light source is known and constant at 254 nm, a detector at the opposite end of the cell is used to measure the amount of light absorbed by the unsaturated carbons in organic compounds, thus a good method for NOM detection but not for PFAAs since these are by nature saturated carbon bonds. The polyacrylic resin in PFAA impacted water loses its ability to effectively remove any quantity of NOM, in PFAA impacted GW, however as discussed previously in the groundwater alone batch studies, there was poor removal of NOM from both resins. The polystyrene A520E resin does seem to remove more DOC than in the groundwater alone, this may be due to co-removal happening with PFAA. On the right side of the figures when the GW is impacted with both NOM and PFAAs, a more familiar trend is seen of increasing NOM removal with increasing resin dose. The polystyrene resin in this situation performs almost as well as the polyacrylic and even better than the polyacrylic when the counterion is in sulfate form, however when compared to the left side graphs that show untreated PFAA impacted GW it is seen that total removal would be below 2 mg/L and in the chloride-form both PA and PS resins only remove NOM to 2 mg/L. In the sulfate form the PS resin removes to 1.06 mg/L which is less than the 1.58 mg/L of untreated PFAA impacted groundwater, the PA resin does not achieve this it's lowest concentration of DOC is 1.75 mg/L. The UV results showed similar trends, but elucidates some more as to what is being measured in the NOM and PFAA impacted water treated with chloride form resins, from the DOC measurements of the TOC it seems that PA and PS resin are almost identical, but the UV absorbance measurements show that the PA resin is removing more NOM however some of the organic carbon being measured by the TOC may be coming from the PFAAs.

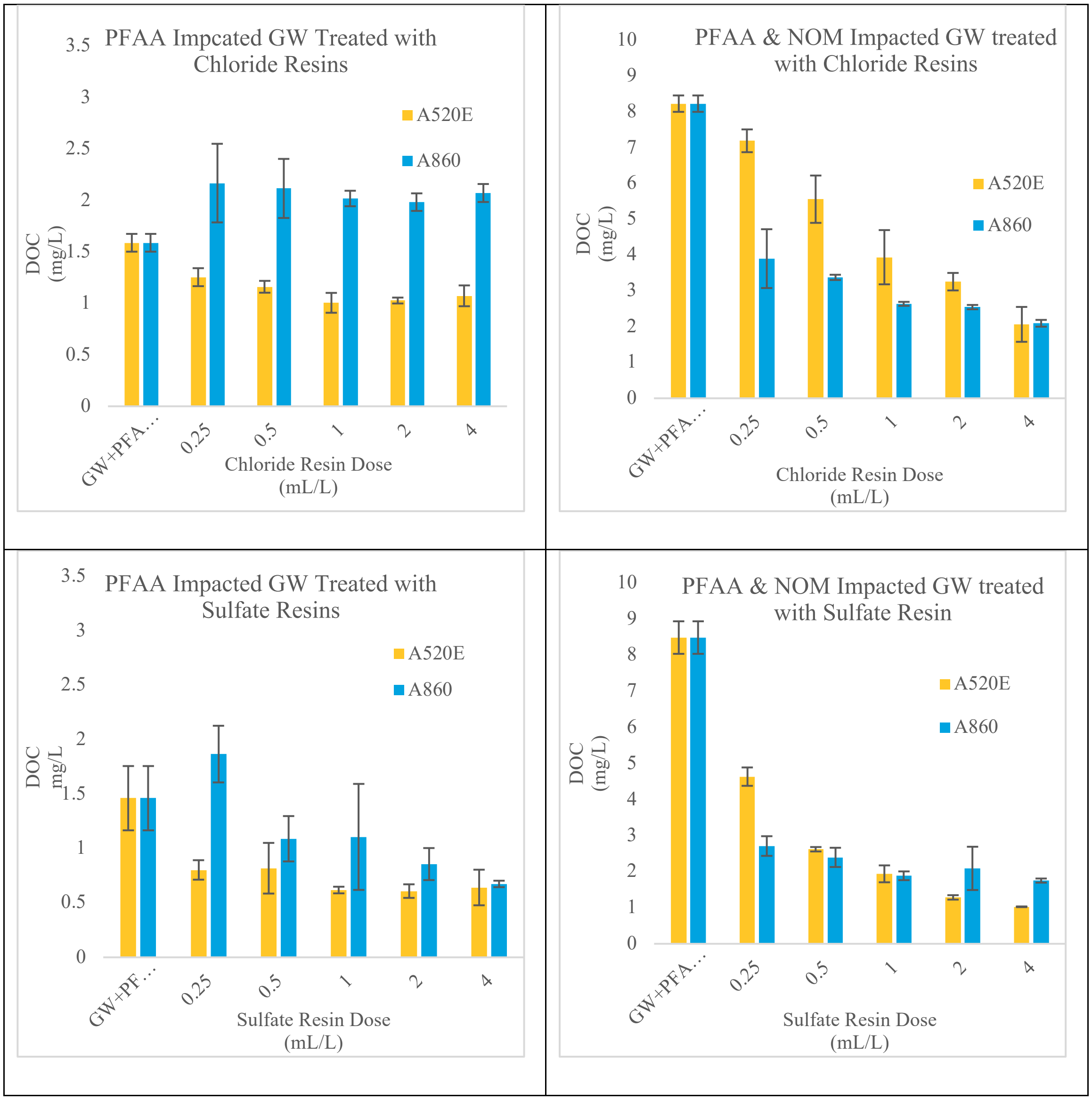

Figure 2.2 PFAAs impacted GW NOM removal measured by the TOC analyzer top left: experiment 3; top right: experiment 4; bottom left: experiment 7; bottom right: experiment 8. Resin dose titled GW+… is the untreated water for that condition.

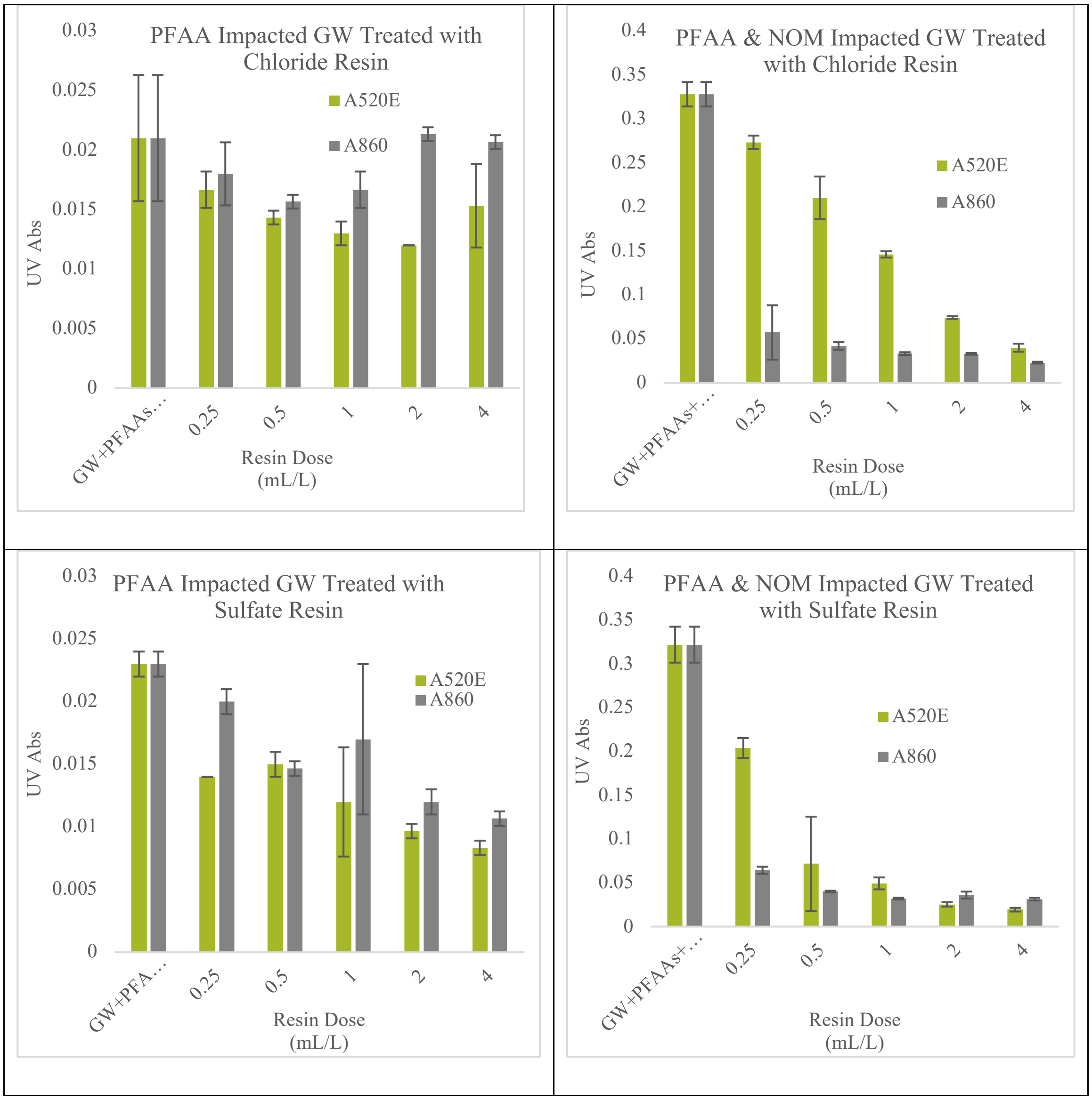

Figure 3.3 PFAAs impacted GW NOM removal measured by UV vis at 254 nm top left: experiment 3; top right: experiment 4; bottom left: experiment 7; bottom right: experiment 8. Resin dose titled GW+… is the untreated water for that condition.

3.3 PFAA removal with chloride and sulfate form resins

PFAA removal is depicted in a stacked bar chart showing concentrations for each individual PFAA adding up to the total amount of PFAAs in the water. The raw values for PFAA removal are in Tables A4-A7 in appendix A. Although all experiments were run in triplicate these results are only for single sample measurements, the triplicate samples are still being analyzed by MS-MS. Therefore, there may be some unseen errors in the samples analyzed due to lack of comparison with the remaining two samples in the set of triplicates. In Figure 3.1 the PS resin is on the top, with experiment 3 on the right-hand side and 4 on the left-hand side; and the PA resin on the right, with experiment 7 on the right and 8 on the left. The PS resin significantly outperforms the PA resin when it comes to PFAA removal. The total PFAAs left over after treatment with the PS resin in a low concentration of NOM groundwater was 36.48 µg/L, and in a high NOM groundwater was 51.01 µg/L, since this work has been done for the treatment of groundwater remediation not drinking water the EPA health advisory is not pertinent but it is worth noting that for both PFOS and PFOA the amounts were below LOQ, therefore below 1µg/L for PFOA and 5 µg/L for PFOS. This would give a combined 6 µg/L if we assign the LOQ as the value which still exceeds EPA health advisory of 70 ppt combined.

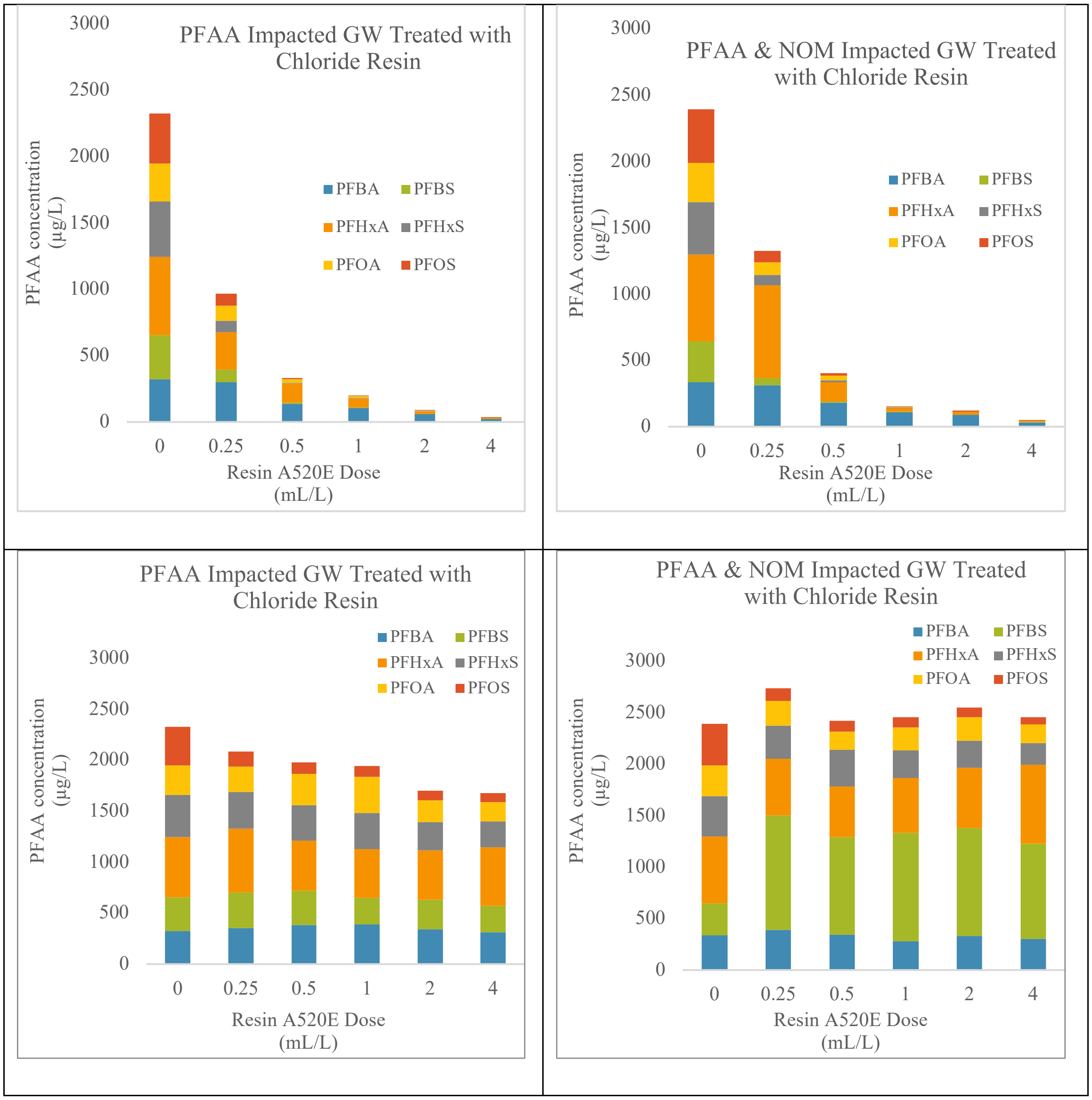

Figure 3.4 PFAAs impacted GW treated with chloride form Resins top left: experiment 3 with PS resin ; top right: experiment 4 with PS; bottom left: experiment 3 with PA resin; bottom right: experiment 4 with PA resin. Zero resin dose signifies untreated test water

Figure 3.5 is similarly organized but for the sulfate form of the PA and PS resins. Again, the PS resin outperformed the PA resin in PFAAs removal. In the PA resin there even seems to be more PFAAs present in resin dose 0.25 mL/L and 0.5 mL/L than in the untreated water this may be due to standard deviation between samples unaccounted for due to lack of replicate measurements. In the sulfate form the lowest total PFAA concentration for the PS resin was 29.34 µg/L and 34.07 µg/L, for experiments 7 and 8 respectively. Slightly lower than the totals for the chloride resin dose, however the initial concentrations were also different. Figure 3.6 shows removal in C/C0 plots which allows for better comparison across experiments.

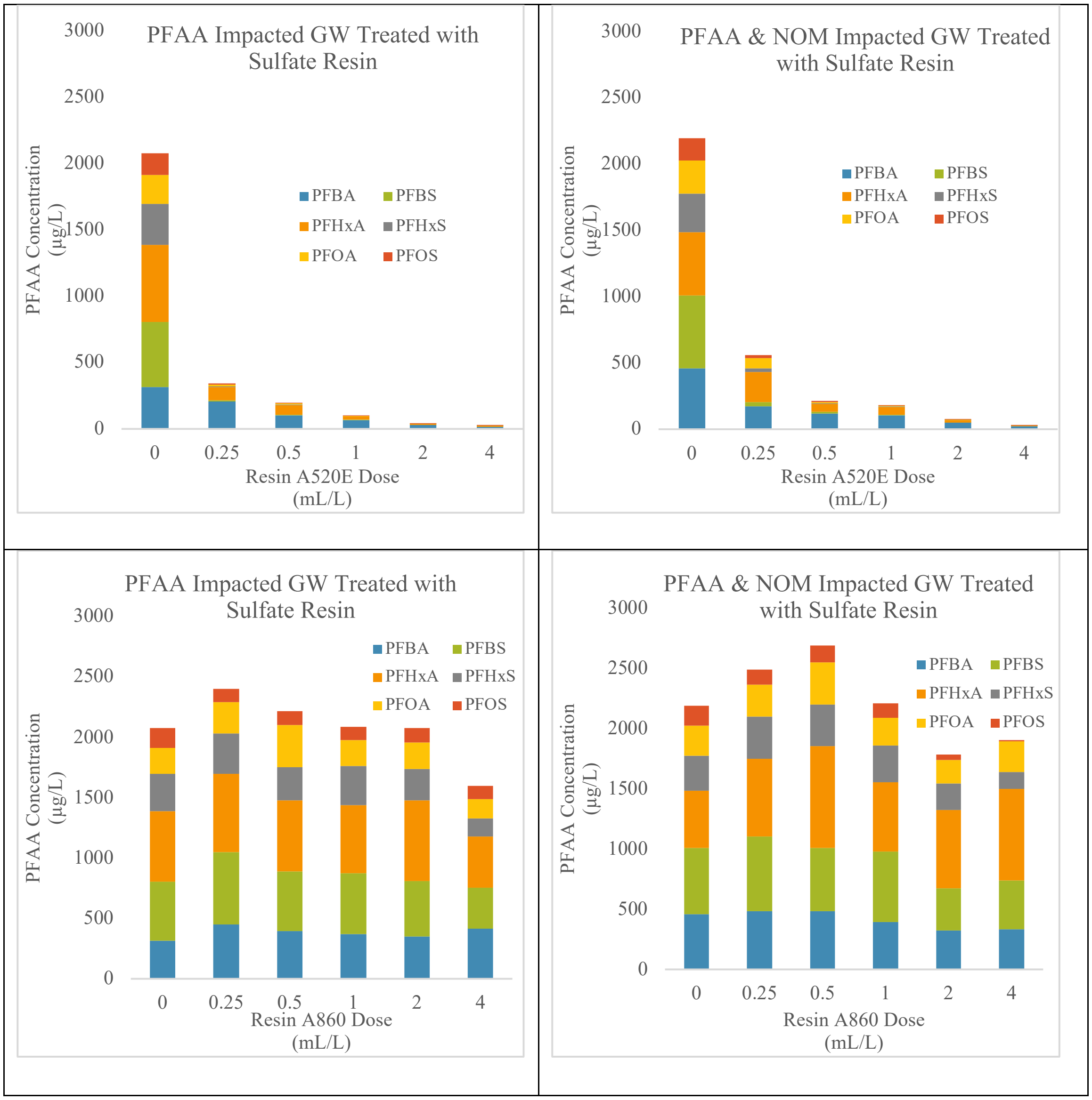

Figure 3.5 PFAAs impacted GW treated with sulfate form Resins top left: PFAA removal in PFAA impacted GW with PS resin; top right: PFAA removal in PFAA and NOM impacted GW with PS resin; bottom left: PFAA removal in PFAA impacted GW with PA resin; bottom right: PFAA removal in PFAA and NOM impacted GW with PA resin

3.3.1 Trends in PFAA removal for PS Resin

Figure 3.6 below is only for the PS resin since it outperformed the PA resin in PFAA removal, in this figure trends about specific PFAA removal are better depicted and the experiments can be compared. The trend of PFAA removal shown here are consistent with the data in the chloride form resins PFOS is removed first followed by the shorter chain sulfonic acid PFAAs and then the carboxylic acids PFOA>PFHxA>PFBA. With PFBA being the least removed by the resin. The sulfate form is even more selective for PFAAs with a sulfonic acid terminal group, the addition of NOM does seem to dampen some of the resin efficiency based on the bar graphs, however it would be important to see the standard deviation between triplicates to be able to determine for sure.

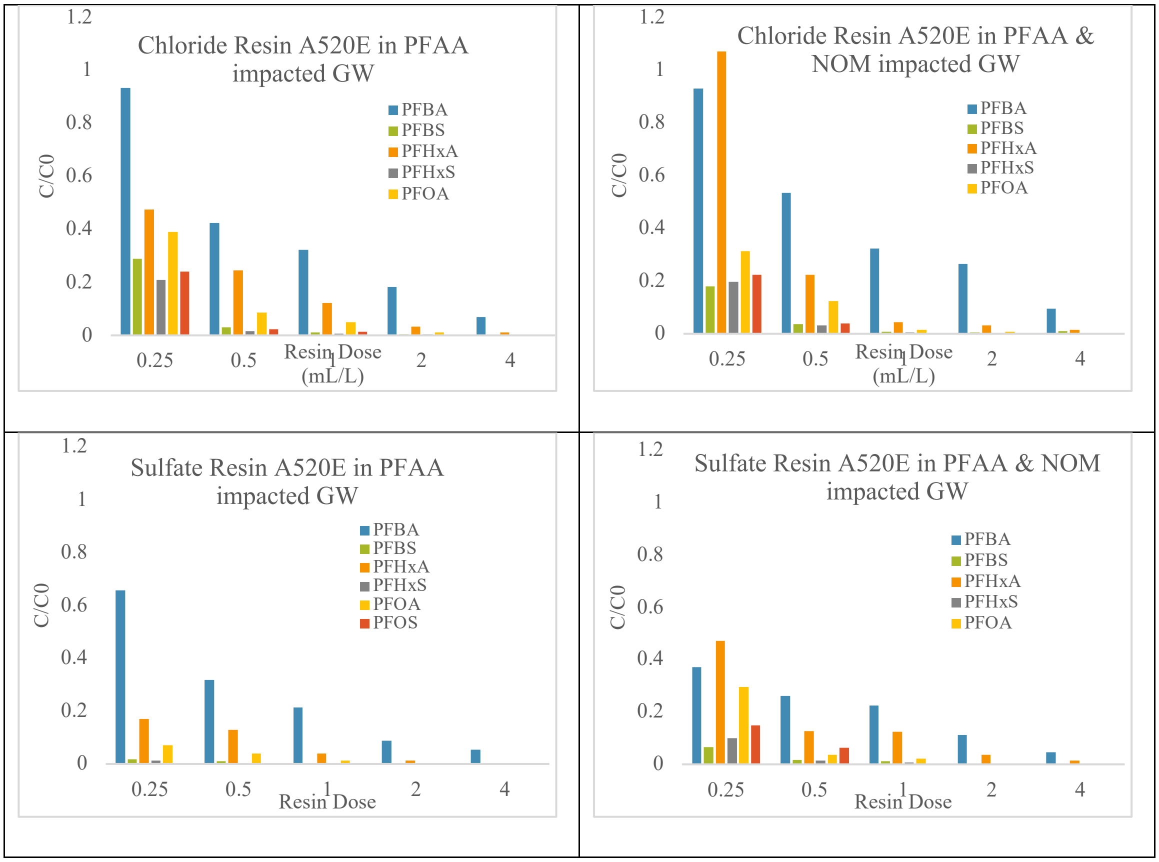

Figure 3.6 PFAA removal plots for both Sulfate and Chloride Resins in PFAA impacted GW and NOM + PFAA impacted GW

3.4. Statistical Analysis

Paired t-tests were conducted to determine the statistical significance of the results. Tables 3.1 and 3.2 depicts the p-values for each of the conditions analyzed. Highlighted values are less than the α=0.05 therefore we reject the null hypothesis that says there is no change between samples. Full statistical analysis tables for conditions with p-values ≤ 0.05 are found in Appendix A Tables A10-25. The t-test data in Table 3.1 showed that for NOM removal in the PS resin the sulfate form was significantly better at NOM removal than the chloride form. In the comparison between experiments 2 and 6 the chloride form resin was better for A860, this is NOM impacted GW without any PFAAs, in these experiments the PA A860 resin was better than the PS, however in experiments 3 and 7 when the GW was impacted with PFAAs the sulfate form of A860 was slightly better than the chloride form. In those experiments (3,7, 4,& 8) however the PS resin performed better overall in comparison to the PA.

Table 3.1
p-Values for NOM removal

	Chloride and Sulfate form Comparison		
Experiments:	2,6	3,7	4,8
p-Value for A520E	$8.97\text{x}10^{-5}$	$1.04\text{x}10^{-3}$	$6.24\text{x}10^{-5}$
p-Value for A860	$1.23\ \text{x}10^{-5}$	$5.87\text{x}10^{-3}$	$2.32\text{x}10^{-1}$

Table 3.2 shows the p-values for PFAA removal in experiments 3,4,7 and 8 compared by exchangeable ion form and presence of added NOM in the PFAA impacted GW. The PS A520E resin was better at PFAA removal overall in comparison to A860, when compared

to itself with differing counterions there was not much difference except in the removal of PFBA in which the sulfate form was superior. There was no significant change in the PS resin efficiency in the presence of NOM. For the PA A860 resin sulfate form was more effective at removing some of the shorter chain PFAAs in NOM+PFAA impacted water but the chloride form was better at removing PFOS in just PFAA impacted GW. Even though the A860 resin performed poorly at removing PFAAs in comparison to eh PS resin, in some instances the presence of NOM may have slightly increased its efficiency in the removal of PFBA, PFBS, PFHxA, and PFOS. This may be due to co-removal occurring with the NOM into the resin. Overall the removal of PFAAs did not suffer significantly for most of the compounds when conditions were changed from chloride to sulfate or low NOM to high NOM.

Table 3.2
p-Values for PFAA Removal

Chloride and Sulfate form Comparison				GW and SRNOM Comparison			
Experiments:		3,7	4,8	Experiments:		3,4	7,8
p-Values for A520E	PFBA	0.055	0.072	p-Values for A520E	PFBA	0.124	0.324
	PFBS	0.306	0.257		PFBS	0.421	0.232
	PFHxA	0.123	0.363		PFHxA	0.459	0.214
	PFHxS	0.313	0.276		PFHxS	0.989	0.285
	PFOA	0.240	0.294		PFOA	0.455	0.355
	PFOS	0.520	0.977		PFOS	0.864	0.250
	Combined	0.001	0.019		Combined	0.404	0.212
p-Values for A860	PFBA	0.149	0.150	p-Values for A860	PFBA	0.161	0.013
	PFBS	0.202	0.005		PFBS	0.005	0.270
	PFHxA	0.409	0.017		PFHxA	0.941	0.039
	PFHxS	0.171	0.067		PFHxS	0.321	0.325
	PFOA	0.184	0.078		PFOA	0.134	0.392
	PFOS	0.006	0.099		PFOS	0.012	0.388
	Combined	0.001	0.346		Combined	0.071	0.698

CHAPTER 4

CONCLUSION

The results have shown that the most important factor in PFAA adsorption was the polymer base of the resin, PS resin A520E was more efficient at PFAA removal than PA resin A860. PFAAs were also removed in accordance with the literature for the most part the perfluoroalkyl sulfonates have greater adsorption than the perfluoroalkyl carboxylates, and longer chains adsorb better than shorter chain PFAAs. While the purpose was to look at removal of PFAA in different conditions, it was also seen that the removal of NOM was affected by the presence of PFAAs. This may inform the treatment train conducted in a pilot study or field test in the future, AIX may not be the best method if NOM is to be removed first as the PFAAs outcompete the NOM for active sites. The counterion form did not affect the removal of PFAAs in a negative matter, and for some PFAAs there was a positive effect, meaning this is a viable counterion when thinking about waste management alternatives. The presence of NOM did not significantly affect PFAA removal, therefore for a pump and treat situation there wouldn’t need to be a pretreatment for NOM removal. The proposed mechanisms for each of these conclusions are discussed.

4.1. Adsorption Effects of Resin Polymer Base

The A520E resin has a polystyrene-DVB crosslinked polymer base, polystyrenes have a chain of aromatic compounds that may stabilize the PFAA molecules within resin matrix. Aromatic compounds are very stable and not very reactive when compared to other double bonded compounds, this increases their hydrophobicity. Hydrophilicity is a compounds likelihood of interacting with water, and because of the conformation of the atoms in water there is a dipole created that imparts polarity to the molecule, therefore the more electronegative oxygen will interact more readily with more positively charged molecules, whereas the hydrogens will interact with more negatively charged molecules. In comparison to polyacrylates, polystyrenes have more hydrophobic, less reactive groups, therefore the fluorocarbon chains, which are also hydrophobic can weakly interact with these groups through Van Der Waals forces. Polyacrylates on the other hand contain amides which interact more with water and water partitioning groups. In principle, two mechanisms are possible for the removal of organic anions by anion-exchange resins: (1) ion exchange, involving counterion displacement from the resin phase and electrostatic interaction between ionic functional groups, and (2) physical adsorption, involving van der Waals interactions between non-ionic (hydrophobic) moieties present on the molecule of interest and the resin polymer backbone. The differences in preferential adsorption for PFAAs by the PS resin and for NOM by the PA resins can be mostly explained by these factors. The hydrophobicity of PFAAs and the tendency of hydrophobic molecules to interact with one another is part of the reason it has such good surfactant properties, but it is also why it interacts with the PS resin more favorably than the PA resin.

4.2. PFAAs Removal Trends

The trends observed match knowledge about PFAAs sorption preferences. With some minor differences, however it is unclear if this is because these are single samples and given the triplicate data these may not be observed or if this is actual phenomena happening due to the resin properties. The data seems to indicate it is sample variance, for example the 6-carbon sulfonate PFAA in one experiment was not adsorbed as quickly as expected but in all the other experiments it did, given the variance between experiments though it cannot be ascertained what the cause of that was until more data is collected. If this was an actual result that is replicated with other samples it may be due to the smaller PFAA molecules having weaker steric effect and quicker diffusion in the porous resins, leading to faster adsorption kinetics (Du et al., 2014).

Longer chain PFAAs are more hydrophobic due to the stability of the fluorocarbon chains, therefore they can have better interactions with the hydrophobic resins (Du et al., 2014). Longer chain PFAAs are also known to at times create micelles and hemimicelles, which may allow for greater mass transfer in to the resin than the shorter chain PFAAs (Yingling, 2018). In organic chemistry chain length is usually determined by number of carbons, however the carboxylate PFAAs are in fact smaller molecules than their carbon-length counterpart sulfonate PFAAs. For example, in the 8-carbon chain PFOA and PFOS, the 8th carbon in PFOA is not saturated with fluorine but is actually the functional carboxylate group whereas in PFOS it is saturated with fluorine and then the chain continues to the sulfonate functional group. This means that PFOS is slightly more hydrophobic than PFOA. According to Pearson's concept of soft- and hard-acids or bases, the sulfonate group is considered as a hard base while the carboxylate group is a relatively soft base (Du et al., 2014). This may help sulfonate groups preferentially interact with the strong base, it may also be why in the literature Type II bases had slightly better removal of carboxylate PFAAs, because softer bases preferentially interact with softer bases.

4.3. NOM Effects on PFAAs adsorption and PFAAs Effects on NOM adsorption

NOM was tested at 20 mg/L in each batch experiment, this would be an inordinately high amount of NOM for groundwater. This was chosen to test extremes, but even at this quantity no significant effect was seen in the removal of PFAAs. However, the NOM adsorption did suffer in PFAA impacted water, and the PS had greater efficiency at times than the PA which previously had been the most effective at NOM removal. This may be because the PFAAs interacted with the functional groups exchanging with the counterion but were not transferred into the pores, creating a barrier for NOM to interact with the resin and transfer into the pores. The PA resin preferentially adsorbed NOM because structurally NOM can have quite large and variable compounds, but they tend to be hydrophilic or amphipathic therefore more favorably interacting with water and PA resin. PA resins also have a more open, water solvated structure, NOM, having larger compounds, may have encountered some size exclusion effects with the PS resin.

4.4. Counterion Effect on PFAAs and NOM adsorption

While overall there was no significant counterion effect observed for PFBA the sulfate counterion was more effective at adsorption than the chloride. Again this may be single sample effect or it may be that a sulfate ion is more easily exchanged due to its 2- charge, in comparison to the 1- charge of chloride.

The chloride form worked better on the whole for NOM adsorption and this may be because it is well known that sulfate can compete with NOM for ion-exchange sites (Tan & Kilduff, 2007).

The matter of regeneration was outside the scope of this work but should be the next step in future studies. Regeneration is a concern with AIX resins but especially when the waste stream will contain PFAA, taking the waste stream to a landfill is not a removal of the current environmental problem we are facing. The salts and chemicals required for regeneration include concentrated brine and alcohols, such as methanol or ethanol. The management of waste brine is a major challenge to implementation. With the promising outlook of the sulfate form resin, it would be interesting to explore regeneration methods with sulfate and possibly other functional groups that may have a regeneration waste stream that is less damaging to the environment than the current known methods with chloride.

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APPENDIX A

SUPPLEMENTARY TABLES

Table A1

Anion Exchange Resin Properties

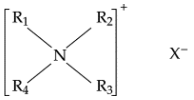
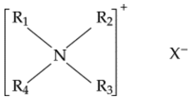
Resin Name	Type	Polymer Structure	Porosity	Functional Group	Capacity	Ion Form
A520E	Strong Base	Polystyrene crosslinked with divinylbenzene	Macroporous	Type I Quaternary ammonium 	0.9 eq/L	Cl-
A860	Strong Base	Polyacrylic crosslinked with divinylbenzene	Macroporous	Type I Quaternary ammonium 	0.8 eq/L	Cl-

Table A2

Tempe Groundwater Composition Maricopa County Well: AZ0407100 provided by the County

Analyte Name	Reporting Level *(mg/L)*	Concentration *(mg/L)*	MCL *(mg/L)*
Antimony, Total	.003		.006
Arsenic		.0044	.01
Barium		.080	2
Beryllium, Total	.001		.004
Cadmium	.001		.005
Chromium		.0028	.1
Fluoride		.4	4.0
Mercury	.0002		.002
Selenium		.0011	.05
Sodium		270.0	3,000
Thallium, Total	.001		.002
1-1-1 Trichloroethane	.0005		.2
1-1-2 Trichloroethane	.0005		.005
1-1 Dichloroethylene	.0005		.007
1-2-4 Trichlorobenzene	.0005		.07
1-2 Dichloroethane	.0005		.005
1-2 Dichloropropane	.0005		.005
Benzene	.0005		.005
Carbon tetrachloride	.0005		.005
Chlorobenzene	.0005		.1
cis-1-2 dichloroethylene	.0005		.07
Dichloromethane	.0005		.005
Ethylbenzene	.0005		.7
O-dichlorobenzene	.0005		.6
P-dichlorobenzene	.0005		.075
Styrene	.0005		.1
Tetrachloroethylene	.0005		.005
Toluene	.0005		1
Trans-1-2 dechloroethylene	.0005		.1
Trichloroethylene	.0005		.005
Final chloride	.0005		.002
Xylenes, Total	.0015		10

Table A3

Analysis of Groundwater and NOM Solution

Water and processing type	pH	Conductivity *(μScm^{-1})*	TOC/DOC *(mg/L)*	UV254 *(cm^{-1})*
Groundwater (GW)	8.127	1797	2.321	0.015
Filtered GW	8.030	1797	.0870	0.013
Centrifuged GW	8.224	1798	1.152	0.014
GW + NOM	8.012	1698	8.248	0.332
GW + NOM filtered	7.975	1697	9.068	0.325
GW + NOM centrifuged	7.937	1698	8.666	0.333

Table A4

PFAA impacted groundwater treated with chloride form A520E & A860 resin

	A520E						*A860*					
Resin Dose *(mL/L)*	0	0.25	0.5	1	2	4	0	0.25	0.5	1	2	4
PFBA *(μg/L)*	321.16	299.66	136.14	103.48	58.33	21.96	321.16	351.79	382.35	390.76	339.46	312.47
PFBS *(μg/L)*	333.4	96.1	10.31	3.51	1.57	<LOQ	333.4	348.75	339.33	256.23	288.69	257.03
PFHxA *(μg/L)*	587.46	279.29	144.12	72.06	19.37	6.89	587.46	627.95	485.77	478.9	488.38	575.52
PFHxS *(μg/L)*	417.36	87.67	6.61	3.08	1.57	0.63	417.36	356.34	353.24	353.91	275.36	253.79
PFOA *(μg/L)*	288.71	112.56	24.92	14.15	3.32	<LOQ	288.71	253.64	302.87	354.48	211.34	185.63
PFOS *(μg/L)*	374.67	90.25	8.37	5.17	<LOQ	<LOQ	374.67	146.43	113.7	108.08	98.41	90.38

Table A5

PFAA & NOM impacted groundwater treated with chloride form A520E & A860 resin

	A520E						*A860*					
Resin Dose *(mL/L)*	0	0.25	0.5	1	2	4	0	0.25	0.5	1	2	4
PFBA *(µg/L)*	336.9	313.44	179.79	109.23	89.53	32.04	336.9	390.79	344.41	280.52	330.06	304.53
PFBS *(µg/L)*	308.7	55.6	11.44	2.57	1.67	2.96	308.7	1110.06	948.47	1050.7	1048.15	925.44
PFHxA *(µg/L)*	652.05	697.66	146.26	29.5	20.17	9.26	652.05	554.88	489.54	532.4	587.49	766.97
PFHxS *(µg/L)*	394.6	77.63	12.15	2.44	1.04	0.75	394.6	322.23	357.89	269.9	264.26	207.32
PFOA *(µg/L)*	298.19	93.11	36.91	4.77	2.32	<LOQ	298.19	234.95	178.39	224.65	228.61	182.42
PFOS *(µg/L)*	403.91	89.83	15.84	<LOQ	<LOQ	<LOQ	403.91	124.75	102.29	97.9	94.55	69.35

Table A6

PFAA impacted groundwater treated with sulfate form A520E & A860 resin

	A520E						*A860*					
Resin Dose *(mL/L)*	0	0.25	0.5	1	2	4	0	0.25	0.5	1	2	4
PFBA *(µg/L)*	317.35	208.31	100.92	67.55	28.1	16.84	317.35	449.25	393.46	368.23	352.29	413.36
PFBS *(µg/L)*	486.5	8.5	5.3	1.4	<LOQ	<LOQ	486.5	601.16	494.69	508.01	458.05	341.12
PFHxA *(µg/L)*	585.13	99.78	75.34	23.45	7.88	<LOQ	585.13	646.85	589.7	562.04	670.5	426.42
PFHxS *(µg/L)*	308.17	4.06	1.26	0.64	0.28	<LOQ	308.17	333.02	276.68	323.38	257.17	149.94
PFOA *(µg/L)*	214.61	15.3	8.43	3	<LOQ	<LOQ	214.61	263.38	348.64	215.34	218.04	156.19
PFOS *(µg/L)*	167.32	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	167.32	109.27	113.98	110.43	119.91	110.84

Table A7

PFAA & NOM impacted groundwater treated with sulfate form A520E & A860 resin

	A520E						*A860*					
Resin Dose *(mL/L)*	0	0.25	0.5	1	2	4	0	0.25	0.5	1	2	4
PFBA *(µg/L)*	460.23	171.1	120.66	102.96	51.53	20.96	460.23	481.61	483.87	393.56	324.14	331.42
PFBS *(µg/L)*	548.04	35.71	9.54	7.1	0.84	<LOQ	548.04	623.58	527.59	587.67	347.45	405.38
PFHxA *(µg/L)*	478.54	225.47	60.97	59.61	17.48	6.41	478.54	642.89	844.27	575.17	655.21	764.65
PFHxS *(µg/L)*	288.94	28.8	4.44	1.8	0.23	<LOQ	288.94	353.22	344.83	304.86	217.8	140.68
PFOA *(µg/L)*	249.81	73.52	8.93	5.66	<LOQ	<LOQ	249.81	264.2	351.61	227.33	194.55	250.88
PFOS *(µg/L)*	167.32	24.91	10.53	<LOQ	<LOQ	<LOQ	167.32	124.17	138.91	121.16	48.44	10.86

Table A8

Resin Capabilities from the Literature

PFAA	*Resins*	*Polymer type*	*Porosity*	*Results*	*References*
PFOS	Ira67 ira96 ira400 ira410 ira900 ira958 DowmarathonA and AMB-IRA400	PA PS PS PS PS PA PS PS	G MP G G MP MP G G	Polyacrylic resins had faster sorption and higher capacity due to their hydrophilic matrix. The macroporous polystyrene resins had much faster sorption and higher sorption capacity for pfos than the gel-type polystyrene resins Amblra400 best filter material to eliminate pfos at >1ug/l. Dowmarathona better for pfos removal at ng/l concentrations	Deng et al 2010 Senevirathna et al 2010
PFOS & PFBS	PFA444<PFA400<GAC<IRA400< DowmarathonA< PFA300	PS<PS<GAC<S<S<PS	G	Adsorption decreased in order of pfa300, dowmarathona, ira400, gac, pfa400, pfa444. The functional groups of resins have influence on adsorption capacity. Adsorption of pfbs (c4) onto pfa400 and pfa444 were conducted under the same experimental conditions as pfos (c8) adsorption. Both resins showed higher kf values for pfbs than pfos	Chularueangaksorn et al 2014
PFOS PFOA PFBS PFBA (8 & 4 C)	A600E<A520E< A532E A600E, PAD500, PAD428, A520E MN102	PS PS PS PS PS PS	G<MP<G G MP MP MP MP	More hydrophobic resins work better hydrophobic macroporous resin A520E showed greater equilibrium capacities indicating that its porous structure speeds up the mass transfer phenomena.	Zaggia et al 2016 Conte et al 2015
4 or more PFAA	IRA 400 < IRA 96 < IRA 67 < IRA 910	PS<PS<PA<PS	G<MP<G<MP	IRA910 had high adsorption capacity for all six PFAS. When PFHxS co-existed with other PFASs in bisolute system, it replaced the adsorbed PFASs with shorter C-F chains on the IRA910. adsorbed amounts of PFHxS on the anion-exchange resins increased with increasing exchange capacity of resins indicating that mechanism was mainly through anion exchange	Maimaiti et al 2018

Table A9

Resin Densities Calculated for each Resin

Chloride Resins		Sulfate Resins	
A520E	A860	A520E	A860
0.44028 g/mL	0.6218 g/mL	0.4912 g/mL	0.828 g/mL

Table A10

t-Test: Paired Two Sample for Means for NOM Removal

Experiments 2 and 6 Resin A520E

	Sulfate	*Chloride*
Mean	0.303377329	0.466245645
Variance	0.074980027	0.08873924
Observations	16	16
Pearson Correlation	0.91101219	
Hypothesized Mean Difference	0	
df	15	
t Stat	-5.30219807	
P(T<=t) one-tail	4.4339E-05	
t Critical one-tail	1.753050356	
P(T<=t) two-tail	8.8678E-05	
t Critical two-tail	2.131449546	

Table A11

t-Test: Paired Two Sample for Means for NOM Removal

Experiments 4 & 8: Resin A520E

	Sulfate	*chloride*
Mean	0.27775621	0.48780488
Variance	0.08518957	0.08769706
Observations	16	16
Pearson Correlation	0.86454972	
Hypothesized Mean Difference	0	
df	15	
t Stat	-5.4886246	
P(T<=t) one-tail	3.1185E-05	
t Critical one-tail	1.75305036	
P(T<=t) two-tail	6.237E-05	
t Critical two-tail	2.13144955	

Table A12

t-Test: Paired Two Sample for Means for NOM removal

Experiments 3 & 7: Resin A520E

	chloride	*Sulfate*
Mean	0.69940476	0.54347826
Variance	0.01745087	0.03201008
Observations	16	16
Pearson Correlation	0.54603602	
Hypothesized Mean Difference	0	
df	15	
t Stat	4.05568223	
P(T<=t) one-tail	0.00051764	
t Critical one-tail	1.75305036	
P(T<=t) two-tail	0.00103528	
t Critical two-tail	2.13144955	

Table A13

t-Test: Paired Two Sample for Means for NOM removal

Experiments 2,6 Resin A860

	chloride	*Sulfate*
Mean	0.018292683	0.151185015
Variance	0.078376574	0.052300085
Observations	16	16
Pearson Correlation	0.966393849	
Hypothesized Mean Difference	0	
df	15	
t Stat	-6.38482082	
P(T<=t) one-tail	6.1319E-06	
t Critical one-tail	1.753050356	
P(T<=t) two-tail	1.22638E-05	
t Critical two-tail	2.131449546	

Table A14

t-Test: Paired Two Sample for Means for NOM Removal

Experiments 3,7 Resin A860

	Sulfate	*chloride*
Mean	0.66847826	0.88690476
Variance	0.03903592	0.01507937
Observations	16	16
Pearson Correlation	-0.4138766	
Hypothesized Mean Difference	0	
df	15	
t Stat	-3.2075168	
P(T<=t) one-tail	0.00293638	
t Critical one-tail	1.75305036	
P(T<=t) two-tail	0.00587276	
t Critical two-tail	2.13144955	

Table A15

t-Test: Paired Two Sample for Means for combined PFAA removal

Experiments 3,7 A520E Resin

	sulfate	*chloride*
Mean	0.223076754	0.28436369
Variance	0.138742005	0.14093942
Observations	36	36
Pearson Correlation	0.964251367	
Hypothesized Mean Difference	0	
df	35	
t Stat	-3.676011947	
P(T<=t) one-tail	0.000393987	
t Critical one-tail	1.689572458	
P(T<=t) two-tail	0.000787973	
t Critical two-tail	2.030107928	

Table A16

t-Test: Paired Two Sample for Means for combined PFAA removal

Experiments 4,8 A520E

	sulfate	*chloride*
Mean	0.24086458	0.29928825
Variance	0.13058485	0.15848956
Observations	36	36
Pearson Correlation	0.93401809	
Hypothesized Mean Difference	0	
df	35	
t Stat	-2.458229	
P(T<=t) one-tail	0.00952766	
t Critical one-tail	1.68957246	
P(T<=t) two-tail	0.01905531	
t Critical two-tail	2.03010793	

Table A17

t-Test: Paired Two Sample for Means for Combined PFAA Removal

Experiments 3,7 A860 Resin

	sulfate	*chloride*
Mean	0.98437519	0.84324349
Variance	0.05620608	0.07210445
Observations	36	36
Pearson Correlation	0.71465495	
Hypothesized Mean Difference	0	
df	35	
t Stat	4.38337389	
P(T<=t) one-tail	5.0809E-05	
t Critical one-tail	1.68957246	
P(T<=t) two-tail	0.00010162	
t Critical two-tail	2.03010793	

Table A18

t-Test: Paired Two Sample for Means for PFBA Removal

Experiments 3,7 Resin A520E

	sulfate	*chloride*
Mean	0.38814663	0.48819384
Variance	0.13680273	0.15235284
Observations	6	6
Pearson Correlation	0.96782174	
Hypothesized Mean Difference	0	
df	5	
t Stat	-2.4870383	
P(T<=t) one-tail	0.02768077	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.05536154	
t Critical two-tail	2.57058184	

Table A19

t-Test: Paired Two Sample for Means for PFBS Removal

Experiments 4,8 Resin A860

	sulfate	*chloride*
Mean	0.92441853	2.91087356
Variance	0.03861438	0.92638892
Observations	6	6
Pearson Correlation	-0.0803116	
Hypothesized Mean Difference	0	
df	5	
t Stat	-4.8770736	
P(T<=t) one-tail	0.00228231	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.00456463	
t Critical two-tail	2.57058184	

Table A20

t-Test: Paired Two Sample for Means for PFHxA Removal

Experiments 4,8 Resin A860

	sulfate	*chloride*
Mean	1.3794493	0.91591391
Variance	0.07453828	0.02328737
Observations	6	6
Pearson Correlation	-0.0885771	
Hypothesized Mean Difference	0	
df	5	
t Stat	3.50055924	
P(T<=t) one-tail	0.00863705	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.0172741	
t Critical two-tail	2.57058184	

Table A21

t-Test: Paired Two Sample for Means for PFOS Removal

Experiments 3,7 Resin A860

	sulfate	*chloride*
Mean	0.72889274	0.41444026
Variance	0.01816721	0.08493269
Observations	6	6
Pearson Correlation	0.95659513	
Hypothesized Mean Difference	0	
df	5	
t Stat	4.60738944	
P(T<=t) one-tail	0.00290065	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.0058013	
t Critical two-tail	2.57058184	

Table A22

t-Test: Paired Two Sample for Means for PFBA Removal

Experiments 7,8 A860 Resin

	GW	*NOM*
Mean	1.20473715	0.89622942
Variance	0.02162352	0.02538878
Observations	6	6
Pearson Correlation	0.15915012	
Hypothesized Mean Difference	0	
df	5	
t Stat	3.7996595	
P(T<=t) one-tail	0.00631644	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.01263288	
t Critical two-tail	2.57058184	

Table A23

t-Test: Paired Two Sample for Means for PFBS Removal

Experiments 3,4 A860 Resin

	NOM	*GW*
Mean	2.91087356	0.91153269
Variance	0.92638892	0.01590137
Observations	6	6
Pearson Correlation	-0.2711343	
Hypothesized Mean Difference	0	
df	5	
t Stat	4.87763626	
P(T<=t) one-tail	0.00228119	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.00456239	
t Critical two-tail	2.57058184	

Table A24

t-Test: Paired Two Sample for Means for PFHxA Removal

Experiments 7,8 A860

	GW	*NOM*
Mean	0.99141501	1.3794493
Variance	0.02143186	0.07453828
Observations	6	6
Pearson Correlation	-0.2728746	
Hypothesized Mean Difference	0	
df	5	
t Stat	-2.7695195	
P(T<=t) one-tail	0.01969387	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.03938773	
t Critical two-tail	2.57058184	

Table A25

t-Test: Paired Two Sample for Means for PFOS Removal

Experiment 3,4 A860 Resin

	GW	*NOM*
Mean	0.41444026	0.36837827
Variance	0.08493269	0.09766736
Observations	6	6
Pearson Correlation	0.99773619	
Hypothesized Mean Difference	0	
df	5	
t Stat	3.85421158	
P(T<=t) one-tail	0.00597497	
t Critical one-tail	2.01504837	
P(T<=t) two-tail	0.01194994	
t Critical two-tail	2.57058184	

APPENDIX B

SUPPLEMENTARY FIGURES

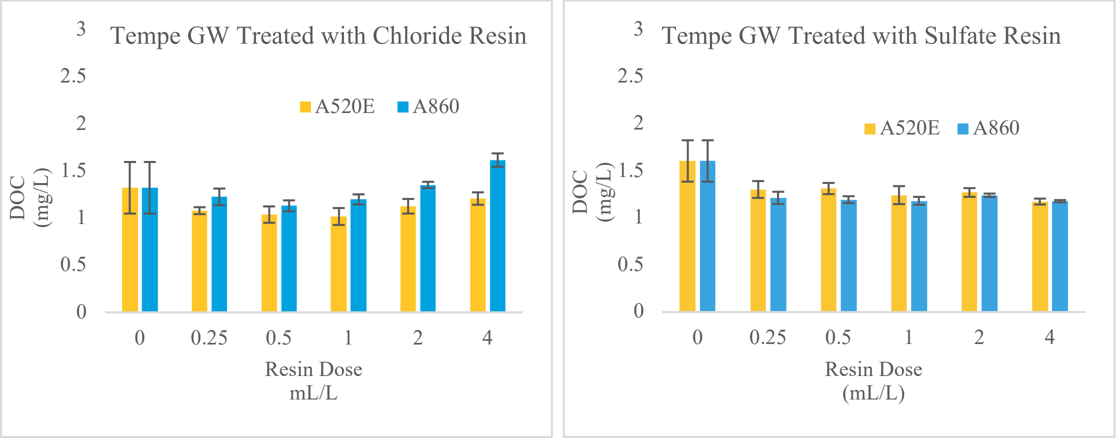


Figure B1. Tempe groundwater batch studies 1 with chloride resin (left) and 5 with sulfate form resin (right). DOC removal is plotted against increasing resin dose. Resin dose 0 indicates untreated groundwater. Error bars show SD between triplicates