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Removal Of Emerging Poly- And Per-Fluoroalkyl Substances By Water Treatment

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REMOVAL OF EMERGING
POLY- AND PER-FLUOROALKYL SUBSTANCES BY WATER TREATMENT

by

Ryan Alexander Hanson

Bachelor of Science, Civil Engineering, University of North Dakota, 2016

A Thesis

Submitted to the Graduate Faculty

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for the degree of

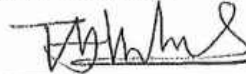Master of Science, Civil Engineering
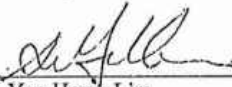

Grand Forks, North Dakota

May 2018

This thesis, submitted by Ryan Hanson in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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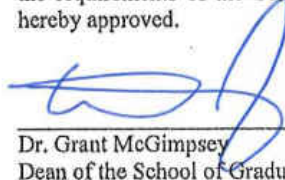Dr. Feng Xiao (Chair)

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This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the School of Graduate Studies at the University of North Dakota and is hereby approved.

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Dean of the School of Graduate Studies

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Title	Removal of Emerging Poly- and Per-fluoroalkyl Substances by Water Treatment
Department	Civil Engineering
Degree	Master of Science in Civil Engineering

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ABSTRACT

Per- and poly-fluoroalkyl substances (per- and poly-PFASs) are emerging contaminants that have raised great concern in recent years. Two anionic per-PFASs in particular, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), has received worldwide attention for their persistence in the natural environment, resistance to typical environmental degradation, bioaccumulation potential, and adverse health effects in humans. The stable chemical characteristics have enabled these chemicals to be used in many industrial and consumer products over the past 50 years. They have been detected all over the world in various environmental matrices.

The water treatment removal of per-PFASs has been well documented, but the full classification of PFASs has yet to be determined and new compounds are being discovered and tested. Recent studies have identified numerous cationic and zwitterionic poly-PFASs whose fate and removal during drinking-water and municipal wastewater treatment remain unclear. However, there is limited knowledge on the fate of these emerging PFASs in water treatment processes. Studies on the removal mechanisms of cationic and zwitterionic poly-PFASs are needed to select the efficient treatment approaches while limiting the secondary formation of PFOS and PFOA. Furthermore, a few recently manufactured poly-PFASs as PFOS/PFOA alternatives have been found in drinking water and environmental samples. As the use of certain PFASs are being phased out of major manufacturers to reduce emissions, alternative PFAS compounds may start to become more detected in aquatic environments, which creates many unknowns for removal methods.

The goal of this project is to examine the removal of PFOS/PFOA alternatives and precursors and to model cationic and zwitterionic poly-PFAS compounds during conventional, enhanced, and advanced drinking-water treatment systems. Various water treatment technologies were investigated with regard to the removal and transformation of cationic and zwitterionic PFASs and PFOS/PFOA alternative compounds, including, enhanced coagulation, filtration, advanced carbon adsorption, chlorination, and ozone treatment to determine removal possibilities. These cationic and zwitterionic poly-PFASs have similar chemical structures as PFOS and PFOA, and our data as shown below indicate that certain cationic and zwitterionic poly-PFASs can convert to PFOS and PFOA during water disinfection processes with chlorine or ozone. The results of this work will shed light on the overall contribution of precursor compounds to the formation of PFOS and PFOA in engineered environmental systems.

It was determined that the removal of the target PFASs during conventional techniques, coagulation, and sand filtration was low. As for filtration by activated carbon, the concentrations immediately were almost below detectable ranges proving its wide known effectiveness against the removal of longer chained PFASs. Disinfection technique, chlorination, was found to be effective for the removal of PFOAB and PFOAAmS. Alternatively, ozone was found to be more effective at removing PFOSB and PFOSAmS at high ozone concentrations. Remarkably, in certain experiments, we observed the generation of PFOA and PFOS from cationic and zwitterionic precursor PFAS compounds during disinfection with either chlorine or ozone. Supported by some of the results, it was concluded that PFOAB and PFOAAmS degrade to form PFOA and, PFOSB and PFOSAmS degrade to form PFOS. PFOA was generated as high >4000% of their initial concentrations under certain conditions. These results will shed light on

the degradation and removal behaviors of emerging PFASs during engineered systems and their

contribution to the secondary formation of PFOS and PFOA.

1. INTRODUCTION

1.1. Polyfluoroalkyl and Perfluoroalkyl Substances (PFASs)

"Emerging contaminants" are substances that are not routinely included in water quality tests. They can broadly be defined as "any synthetic or naturally occurring chemical or microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and human health effects" (USGS, 2009). Per- and poly-fluoroalkyl substances (PFASs) or perfluorinated chemicals (PFCs) constitute a major subgroup of these contaminants. With any emerging contaminant, especially ones that are potentially hazardous to humans, studies should be conducted to discover the threats and treatment methods. Hence, strong concerted global regulatory initiatives are highly desirable to address PFAS emissions on a global scale.

The compounds comprise of a family of manmade organic chemicals that have a completely (per-) or partially (poly-) fluorinated carbon chain connected to different functional groups. PFASs have received global public attention in recent years due to their persistence and resistance to typical environmental degradation (Appleman et al., 2014; ATSDR, 2009), bioaccumulation potential (Martin et al., 2003; Xu et al., 2014; Houde et al., 2011), and possible adverse effects on living organisms and autotrophic and heterotrophic food webs (Peng et al., 2010; Martin et al., 2003), and capability for long-range transport through the atmosphere and water (Shoeib et al., 2006; Houde et al., 2011).

A recent report estimates "that there are probably at least 3000 PFASs currently on the global market" (Wang et al., 2017). Two groups, perfluoroalkyl carboxylic acids [$C_nF_{2n+1}COOH$;

$n \geq 7$ (PFCAs)] and perfluoroalkyl sulfonic acids [$C_nF_{2n+1}SO_3H$; $n \geq 6$ (PFSAs)], have been the focus of many studies. These groups have been shown to be very persistent and their longer chained compounds have shown to bioaccumulate and biomagnify in food webs (Buck et al., 2011; Butt et al., 2010). In particular, one PFSA, perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$), and one PFCA, perfluorooctanoic acid (PFOA, $C_7F_{15}COO^-$), have been measured in many components of the biosphere and aroused the attention among the scientific and regulatory communities and the public. These compounds have been measured in drinking water at numerous sites in the United States and in other parts of the world at concentrations ranging from a few to several tens of ng/L (Eschauzier et al., 2012; Ericson et al., 2009; Hölzer et al., 2008; Quinones and Snyder, 2009). PFOS and PFOA have been included into the EPA's Contaminant Candidate List 3 of chemicals under consideration for future drinking water regulation in the U.S. (USEPA, 2009). These two chemicals as well as perfluoroheptanoic acid (PFHpA), perfluorononanoate (PFNA), perfluorobutane sulfonic acid (PFBS), and perfluorohexanesulfonate (PFHxS) have been also added to the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR 3), which requires nationwide monitoring by public water suppliers to provide occurrence data needed for regulatory decision making (Post et al., 2012; US EPA, 2012).

1.1.1. Production

The stable chemical characteristics and water solubility have enabled these chemicals to be used over the past 50 years in many industrial and consumer products, including fabric surface protectants, upholstery, carpets, polishes, shampoos, fire-fighting foams, non-stick cookware, electrical wire casings, and pesticide formulations (Brooke et al., 2004; Kissa, 2001;

Yamashita et al., 2008). With ineffective pretreatment, these compounds directly release from industries to natural waterways or wastewater treatment plants. In addition, the indirect release of PFCAs and PFSAs are dominated by the abiotic and biotic degradation of precursors that can form PFCAs and PFSAs (Labadie & Chevreuil, 2011; Buck et al., 2011). Some of these precursors are semi-volatile and contribute to the spreading of the stable non-volatile PFAS to distant regions far from pollution sources (Buck et al., 2011; Butt et al., 2010).

1.1.2. Transportation

The physical transport and directional partitioning of PFASs are highly dependent on their physicochemical properties that which vary depending on their chain length and functional group. In some cases, many PFASs have been found in drinking water wells far from the point source, suggesting that multiple transportation mechanisms may be present (Post et al., 2012). In groundwater, PFASs can span long aquifer distances via the well-established pathway of migration of a contaminated groundwater plume (Xiao et al., 2015). However, it has been suggested that air emissions from nearby industrial facilities may result in a deposition to the groundwater (Post et al., 2012). These two pathways of transport of PFAS have been suggested to be the main contributors: hydrosphere and atmospheric. The atmospheric process is described as long-range atmospheric transport of volatile to semi-volatile precursors followed by oxidation to PFOA and other PFASs which are then deposited onto the land or the water (Li et al., 2011; Shoeib et al., 2006). This is the governing hypothesis for how they are transported from densely populated use areas to remote places. The transport process following these final degradation products proceeds mainly in the aqueous phase. At a global level, PFASs have been estimated to travel higher in the water phase as compared with transport in the atmosphere (Shoeib et al.,

2006; Yamashita et al., 2005). However, it is still under dispute whether the water phase transport or the atmospheric transport is the dominant pathway for ionizable PFASs.

1.1.3. Exposure and Toxicity

Some PFASs are extremely resistant to degradation and have therefore been frequently detected ubiquitously in the aquatic environment, including finished drinking water at pg/L to µg/L (Rahman et al., 2014). The contaminated drinking water has been suggested to be a major exposure pathway (Xiao et al, 2013). Low-level concentrations have been detected in human tissue and blood serum worldwide (ATSDR, 2009). In a Nation Health and Nutrition Examination Survey (NHANES), PFOA was found at > 0.1 ng/mL in the serum of 99.9% of 2100 U.S. participants aged 12 or older; with a geometric mean of 4.13 ng/L (Post et al., 2012). PFASs are proteinophilic and are found in living organisms in protein-rich tissues such as liver, blood, kidney, and eggs and do not accumulate in fat tissue like POPs and other hydrophobic contaminants (Ladadie and Chevreuil, 2011, Butt et al., 2010). Some PFASs have a very low rate of elimination from serum with half-lives of several years (ATSDR, 2009; Seals et al., 2010). In addition, consumption of lower food web species fish with levels of PFASs showed the potential for concentration to significantly biomagnify through the process of bioaccumulation (Xu et al., 2014). The prolonged half-life and bioaccumulation potential creates the potential for longstanding body burdens that could result in adverse outcomes.

The studies of the toxic effects of PFASs are still not fully understood and are quite limited. In a study done in Ohio on residents that were exposed to contaminated drinking water or had worked at the DuPont Washington Works chemical plant found that thyroid, kidney, and testicular cancer risk increased with an increase of estimated cumulative PFOA serum

concentration (Vaugh et al., 2013). Other studies have suggested a link between other PFASs in blood serum and elevated cholesterol, increase in uric acid (Steenland et al., 2010), low birth weight and infertility measured as longer waiting time to pregnancy (Fei et al., 2007; Fei et al., 2009), delayed puberty in children (Lopez-Espinosa et al., 2011), onset of early menopause in women (Knox et al., 2011), and low semen quality in men (Joensen et al., 2009). Much of the research out there on direct human effects is still progressing and being disputed, but the possible health effects from PFASs and their accumulation in humans, together with the detection of the compounds in drinking water, stress the importance of effective removal techniques of PFASs in water treatment plants.

1.1.4. Treatment

Wastewater and water treatment plants are considered a key factor in the elimination of water-borne contaminants. In May 2016, the U.S. EPA released an updated drinking water advisory on PFOA and PFOS specifying a maximum combined level of 70 ng/L. To accomplish this, removal processes need to be implemented at the municipal level (EPA, 2016). The removal and treatment of PFOA and PFOS have been highly researched, but many PFASs are still being discovered have little to no removal strategies established. It is generally believed that PFOA and PFOS are difficult to remove during conventional water and wastewater treatment (Xiao et al., 2013; Xiao et al., 2012). At 130 kcal/mol, the C-F bond is the strongest covalent bond (Lemal, 2004) and extremely difficult to destroy. These chemicals can be removed by advanced but expensive or energy-intensive technologies, such as activated carbon, reverse osmosis, and ion exchange (Appleman et al., 2014). These treatments simply transfer the contaminants from one phase to another. However, the total mass of PFOA/PFOS does not decrease, it is just collected.

To reduce the mass of these compounds, a chemical reaction and transformation would be necessary. However, in certain conditions, PFOA and PFOS are generated during biological and chemical treatment, possibly from their precursor compounds (Xiao et al., 2012).

1.1.5. Alternatives, Precursors, and Undocumented PFASs

The removal of per-PFASs has been well documented, but the full classification of PFASs has yet to be determined and new compounds are being discovered and tested. The primary manufacturers of PFOA/PFOS and related chemicals include 3M and DuPont. Since the phase-out in 2015 of PFOA/PFOS production by the manufacturers including the two companies, the production of fluoropolymer compounds has been shifted towards 1) shorter-chained PFASs, which has proven to have shorter half-life in the human body (Butt et al., 2010), and 2) alternative compound, many of which have limited toxicity and removal data (Oliaei et al., 2013).

With advancements in analytical methods, recent studies have identified numerous cationic and zwitterionic poly-PFASs whose fate and removal during drinking-water and municipal wastewater treatment remain unclear. Some of these, being precursor compounds, may degrade to PFOA and PFOS during water treatment. However, their fate and transformation pathways during the treatment are poorly understood. In this work, we focus on four potential cationic and zwitterionic precursor compounds, in terms of their removal and transformation behaviors during water treatment. Furthermore, a few recently manufactured poly-PFASs as PFOA alternatives, GenX and ADONA, have been found in drinking water and environmental samples (Strynar et al., 2015; Sun et al., 2016; Xiao, 2017). In addition to the precursor compounds, GenX and ADONA were also studied for removal during water treatment. The

treatment technologies include conventional coagulation, enhanced coagulation, sand filtration, activated carbon adsorption, chlorination, and ozonation.

1.2. Conventional Drinking-water Treatment

Although many of the already classified PFASs are being researched, there is little to no research on the unclassified emerging PFASs that could produce the same effects as the common types. The following treatment techniques are some of the most widely used strategies for organic contaminant removal. It is important to determine if removal is possible with these methods before moving to more advanced methods.

1.2.1. Coagulation and Flocculation

Coagulation, using hydrolysable metal salts, is a long-standing technology in drinking water treatment plants for removing suspended particulates and NOM (Edzwald, 1993; Matilainen & Sillanpää, 2010). Dissolved and suspended particles are present in most of the natural waters. To separate the particles from the water, coagulation and flocculation processes are used. The purpose of wastewater flocculation is to form aggregates or flocculants from finely divided particles and from chemically destabilized particles. Flocculation is a transport step that brings about the collisions between the destabilized particles needed to form larger particles that can be removed readily by settling or filtration. Most of these destabilized particles suspended in water possess a negative charge, mainly due to an adsorbed layer of natural organic matter (Hunter & Liss, 1982). Coagulants with charges opposite to those of the suspended solids are added to neutralize the particles. Once neutralized, the suspended particles are capable of sticking together to form flocculants. These flocculants attract other organic compounds

suspended in the water and then settle out. Enhanced coagulation is loosely defined by the EPA as the addition of an excess coagulant to improve removal of TOC. This enhanced technique has been seen to have a small amount of removal of PFOS and PFOA (Xiao et al., 2013). It is expected that there could be a possibility for the cationic and zwitterionic precursor PFASs to attach to the negatively charged flocculants and settle out

1.2.2. Media Filtration

Filtration is often the next treatment step after coagulation/flocculation and sedimentation to remove remaining colloidal particles. There are many types of filtration media that can remove compounds and suspended particles. The most common filtration process employs a granular medium of a certain size and depth. The pretreated water slowly percolates through the porous material to remove particulate and other impurities, including floc, from the water being treated. The particulate matter is collected by a series of collisions and forces throughout a porous media. This is generally used after coagulation to assist in the removal of colloidal particles, bacteria and viruses, organic matter, and heavy metals (Kawamura, 2000; Huisman & Wood, 1974; Collins et al., 1992; Aziz et al., 2008). For small soluble organic compounds, minuet forces are the cause of any collection or partitioning effects.

There are three main types of filters: rapid (gravity) sand filters, upward flow sand filters and slow sand filters. All of these methods are used extensively in the water industry throughout the world. Sand bed filters work by providing the particulate solids with many opportunities to be captured on the surface of a sand grain. As fluid flows through the porous sand along a tortuous route, the particulates come close to sand grains. They can be captured by direct collision with the sand particles or an attraction causing adsorption. This is due to either Van der

Waals forces or a strong surface to chemical charge attraction. There could also be electrostatic attraction or repulsion depending on the charge of the target contaminants. In a study done by Nakada et al., 2007, they found up to >80% removal of several selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration. Much like coagulation, it is expected that the positively charged precursor PFASs could have an attraction to the negatively charged sand particles.

1.2.3. Activated Carbon Filtration

Active carbon is a manufactured type of charcoal with strong sorption properties and a large surface area, up to 1000 m^2/g. The AC has been shown to be an effective water cleaning agent for different pollutants. Recent studies have also documented its remediation capacity for soil and sediment (Hansen et al., 2010). Adsorption of organic contaminants by carbonaceous sorbents are influenced by many factors, and sorbent-specific factors including sorbent surface chemistry (e.g., elemental compositions, surface acidity and basicity, and point of zero charge) and physical properties (e.g., pore size distribution, pore volume, and shape) are often examined and used for selecting proper sorbents for a specific application (Zhi & Liu, 2015).

In addition to sorbent properties, molecular structure and water chemistry play an important role in sorption of PFASs at the solid-liquid interface. Previous studies PFAAs have found sorption to increase with increasing carbon chain length of the molecules when the carbon chain length is more than six (Pignatello & Xing, 1995; Ahrens et al., 2011; Higgins & Luthy, 2006). Ochoa-Herrera & Sierra-Alvarez (2008) compared the sorption of PFOS, PFOA and PFBS to granular active carbon (GAC). The study showed that sorption was stronger for PFOS than for PFOA, and PFBS, reflecting the influence of an increasing carbon chain length and the

substitution of a carboxylic group by a sulfonic group. Due to their toxic effects and resistant

nature, much of the literature, including this research, focus on these larger chain PFAS.

Granular activated carbon adsorption can be used together with sand filtration to form a

dual filtration system or individually after conventional sand filtration. Powdered activated

carbon (PAC) can also be added together with coagulants during coagulation as a slurry

(Chowdhury et al., 2013). In the adsorption process of a compound, bonds are formed of

intermolecular attraction energies, which are much weaker than the covalent bonds involved in a

chemical reaction. If the bonds are instead formed between a compound and the interface of a

specific phase it is called *adsorption* (Schwarzenbach et al., 2003). The term *sorption* can be

used when both adsorption and absorption are involved. It is often suggested that the

"hydrophobic effect" plays a dominant role for PFAS sorption in many instances despite the

ionizable functional groups (Higgins & Luthy, 2006), which can be entirely ascribed to van der

Waals interactions; the most well established intermolecular attractions involved in the

partitioning process. Once the occurrence of the compounds is balanced between the different

phases and as long as the external factors such as temperature and pressure remain unchanged,

the equilibrium has been reached.

1.2.4. Disinfection

The purpose of the disinfection process is to kill the growing form of pathogenic

microorganisms. Disinfection can be attained by means of physical or chemical

disinfectants. There are many methods to disinfect wastewater, but none are universally

applicable. The disinfection of pathogens takes place because of cell wall corrosion in the

microorganisms, or changes in cell permeability, protoplasm or enzyme activity. For resistant

organic compounds, specific organic chemical reactions are necessary to take place in order to cause degradation.

For the most part, chlorine and ozone are the most widely used oxidants used in water treatment disinfection. The presence of functional groups with high electron density such as double bonds, activated aromatic systems, and amino groups generally increase the reactivity of a compound with ozone (E0 ¼ 2.07 V), while the presence of electron withdrawing groups (e.g. $-Cl$, $-NO_2$, $-COOH$) lowers their reactivity (Von Gunten, 2003). PFAAs do not contain aromatic bonds or phenolic structures. Thus, the presence of the strong C-F bond together with the electron withdrawing functional groups -COOH and -SO3H in the structures of PFCAs and PFSAs, respectively, indicate that these compounds will likely be resistant to oxidation (Rahman et al., 2014). However, the polyfluorinated compounds containing C-H bonds may be oxidizable, which could cause noticeable degradation for those compounds.

Chlorine

As a halogen, chlorine is a highly efficient disinfectant and is added to public water supplies to kill disease-causing pathogens, such as bacteria, viruses, and protozoans, that commonly grow in water supply reservoirs, on the walls of water mains and in storage tanks (Calderon, 2000). Although this procedure removes pathogens, the chlorine can also react with compounds in the water. As a chemical oxidant, though less reactive than ozone, chlorine can transform numerous inorganic and organic compounds found in water (pharmaceuticals, estrogenic compounds, antibiotics, etc.) (Adams et al., 2002; Alum et al., 2004; Chamberlain & Adams, 2006; Benotti et al., 2008).

Chlorination can be achieved by using liquefied chlorine gas (Cl_2), sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$), and chlorine dioxide (ClO_2). Many large cities have switched from chlorine gas to sodium hypochlorite because of the safety concerns and regulatory requirements related to the handling and storage of pressurized liquid chlorine.

To ensure that there is enough chlorine available for disinfection (free chlorine), breakpoint disinfection is usually applied. The term *breakpoint chlorination* refers to the process whereby enough chlorine is added to react with all oxidizable substances and ammonia such that if additional chlorine is added it will remain as free chlorine. To assure effective disinfection, enough chlorine to obtain free chlorine needs to be added. After the chlorine demand has been met and the breakpoint has been achieved, combined chloramines are present as free chlorine which is a mixture at normal pH values of hypochlorous acid (HOCl) and hypochlorite (OCl^-).

Ozone

Ozone (O_3) is a slightly bluish unstable gas produced by electrical discharge in a gas phase when oxygen molecules are dissociated into atomic oxygen and subsequently collide with another oxygen molecule (Spellman, 1999). Ozone is often produced by ultraviolet light and lightning during a thunderstorm. Design engineers in the US began to evaluate ozone for wastewater disinfection in the early 1970s. Since then, ozone has been proved to be one of the most effective disinfectants and is widely used to inactivate pathogens in drinking water (Langlais et al., 1991).

Ozone is very unstable and decomposes in water very fast, which can generate hydroxyl radicals ($\bullet OH$) in water by the following pathways (Staehelin & Hoigne, 1985):

$$O_3 + H_2O \rightleftharpoons HO_3^+ + OH^-$$

$$HO_3^+ + OH^- \rightleftharpoons 2HO_2$$

$$O_3 + HO_2 \rightleftharpoons HO\bullet + 2O_2$$

$$HO\bullet + HO_2 \rightleftharpoons H_2O + O_2$$
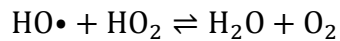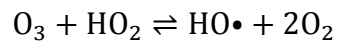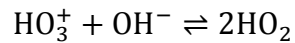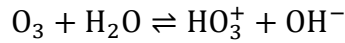
The dot ($\bullet$) that appears next to the hydroxyl and other radicals is used to denote the fact that these species have an unpaired electron. Since OH is an extremely reactive radical, it reacts as soon as it is formed. The half-life of the OH radical is very short at only about 10^{-9} (Sies, 1993), which means that these radicals are highly reactive and can be assumed to have great oxidizing power. These free radicals also possess the oxidizing power to react with other impurities in aqueous solutions that ozone may not be able to convert. While ozone is considered the dominant primary disinfectant, oxidation processes may occur through both oxidants. Therefore, the assessment of ozone processes as oxidation always involves the two species: ozone (O_3) and OH radicals (Langlais & Reckrow, 1991).

Much like chlorination, ozone effectiveness is usually related to contact time (Ct) and disinfectant concentration. Ozone demand can be caused by certain inorganics, organics, and suspended solids. That is why the samples done in distilled water, may create the better understanding of the effect of ozone on the PFASs. Comparison of batch contact reactors (where the ozone gas is added at the start of the reaction) with continuous-flow reactors is made more difficult because of the simultaneous increase of dissolved ozone and decrease of oxidizable species as well as microorganisms. If Ct values are used, the assumption is that concentration remains constant throughout the contact time and that the kinetics (order and rate constant) are also constant.

1.3. Objective and Hypotheses

The main objective of this master thesis was to examine the removal of PFOS/PFOA alternatives and model cationic and zwitterionic poly-PFASs during conventional, enhanced, and advanced drinking-water treatment systems (i.e., conventional and enhanced coagulation/flocculation, sand filtration, activated carbon adsorption, chlorine disinfection, ozone disinfection). These PFOS/PFOA precursors may be affected by these conventional techniques due to their positive electrical charges. These charges may cause the chemicals to be more inclined to sorb onto surfaces easier or have their chains broken by enhanced oxidation. Because of broken chains, the possibility of creating PFOS and PFOA as byproducts will be studied. As for the alternative compounds, it is expected that the fluorinated ether structure may have the possibility to break during advanced treatment, but it is unlikely. The results of this study will be useful for identifying effective treatment strategies dealing with these emerging organic contaminants.

2. MATERIALS AND METHODS

2.1. Test Water

All batch experiments that were performed using surface water or distilled water with the purpose to give ideal conditions for treatment. The surface water was extracted from the Red River (Figure 1) at location at 47.942170, -97.048374. This site was initially chosen due to it not freezing in the winter. The samples were extracted into 5-gallon pales, as needed. The removal mechanics were studied for each of the techniques and there was no investigation on a micro scale level. The intention of this study was not to optimize the removal efficiency of these techniques but to investigate their successfulness for a range of different PFASs. In addition, this master thesis did not include an investigation of the influence of different water types on the removal efficiency of PFASs in water, which could play an important role.

Figure 1: Sampling Location of Red River Surface Water (47.942170, -97.048374)

The batch experiments were performed at the College of Engineering and Mines, UND. The quantification of PFASs in solution was conducted with an Acquity Ultra Performance Liquid Chromatography (Figure 2) and SYNAPT G2-S High Definition Mass Spectrometer. The quantification was done based via external standards based on the peak areas at specific m/z values (Figure 3). This was then converted to concentration as available using the calibration standards in Appendix A.

Figure 2: The Acquity Ultra Performance Liquid Chromatography
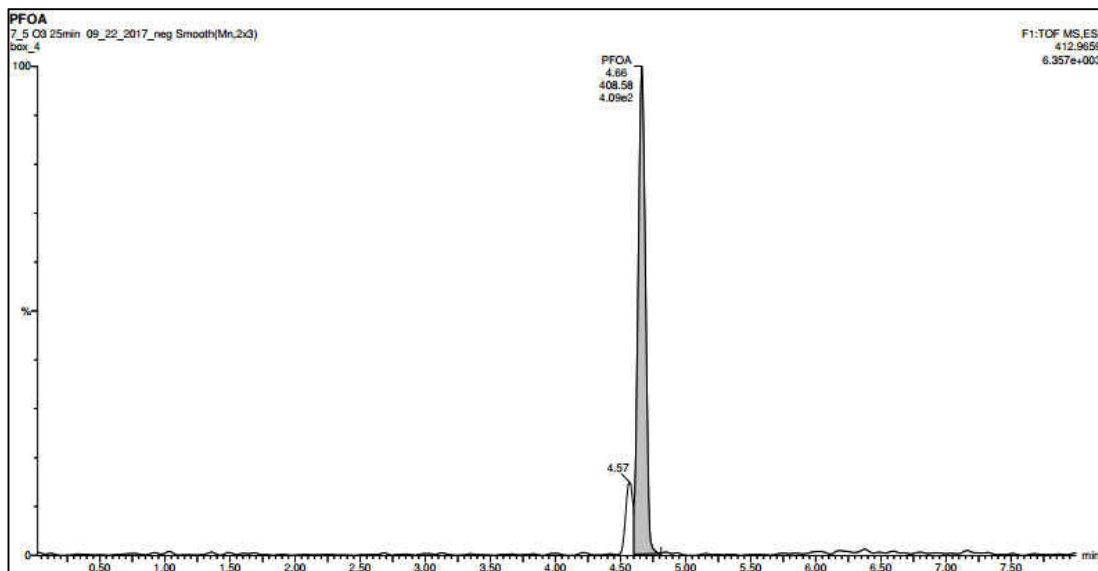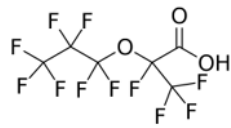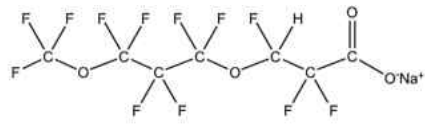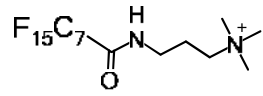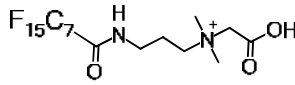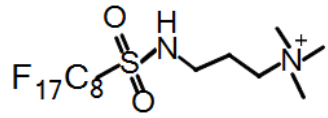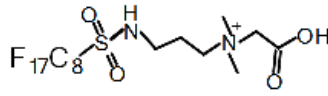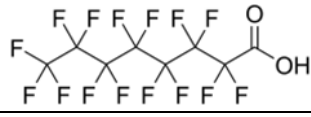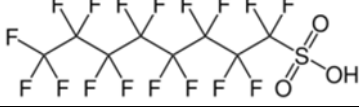
Figure 3: Example of UPLC—ESI⁻—ToF—MS Spectrum for a PFOA Sample

2.2. Chemicals

In this study, we focus on four cationic and zwitterionic compounds including perfluorooctaneamido ammonium salt (PFOAAmS), perfluorooctanesulfonamido ammonium salt (PFOSAmS) and their corresponding zwitterionic counterparts — perfluorooctaneamido betaine (PFOAB) and perfluorooctanesulfonamido betaine (PFOSB). PFOAB (pK_{a1} = -0.48, pK_{a2} = 2.27), PFOSB (pK_{a1} = 1.91, pK_{a2} = 3.30), PFOAAmS (pK_a = -0.53), and PFOSAmS (pK_a = 3.28) were purchased from Fluobon Surfactant Institute (China) (purity: PFOAB, 95%; PFOSB, 95%; PFOAAmS, 98%; PFOSAmS, 98%). Their pK_a values were estimated by a freeware (Marvin 15.10.26, ChemAxon, Cambridge, MA). It is notable that all the newly identified PFASs are polyfluoroalkyl compounds, which have perfluoroalkyl of varying carbon chain lengths and contain either tertiary amine, or quaternary ammonium groups. In addition, PFOS (potassium salt) (>98%) and PFOA (96%) were purchased from Sigma–Aldrich. HFPO-DA (GenX) and Sodium Dodecafluoro-3H-4,8-dioxanonanoate (NaDONA) were also a focus of this study along with any indirect sources of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). The molecular makeup of these compounds can be seen in Table 1.

Table 1: PFASs examined in this study

Compound	Chemical Formula	Molecular Formula	MW
GenX	$C_6H_4F_{11}NO_3$		347.084
NaDONA	$C_7H_5F_{12}NO_4$		395.01
PFOAAmS	$C_{14}F_{15}N_2OH_{16}$		513.27
PFOAB	$C_{15}F_{15}N_2O_3H_{15}$		556.27
PFOSAmS	$C_{14}F_{17}SN_2O_2H_{16}$		599.33
PFOSB	$C_{15}F_{17}SN_2O_4H_{15}$		642.33
PFOA	$C_8HF_{15}O_2$		414.07
PFOS	$C_8HF_{17}O_3S$		500.13

2.3. Water Treatment Procedures

2.3.1. Coagulation/Flocculation

The coagulation was performed by regular jar tests that simulate similar settling processes by drinking water treatment plants for estimating the optimum coagulant dosage (Xiao et al., 2008). Coagulation of surface water spiked with PFAS compounds was performed in a series of jar tests at different dosages of coagulant using the Phipps & Bird PB-700 Jar Tester (Figure 4) with alum (aluminum sulfate (Al2(SO$_4$)$_3$ · 18H$_2$O)) as the coagulant. A known volume of alum stock solution was added to the jars to reach the required aluminum sulfate

Figure 4: Phipps & Bird PB-700 Jar Tester

concentration. The stir rods were immediately activated following the coagulant spike and were rapidly mixed for 1 min at 140 rpm. During this stage, the particles come in contact with hydrolyzed aluminum species and are neutralized. The rapid mix is to promote particle collision. After 1 min, the solution is slowly mixed for 20 min at 40 rpm to ensure sufficient mixing and allow for the precipitated aluminum species to slump together into amorphous flocs. After coagulation, the solution was allowed to settle for at least 20 min so that the flocs can precipitate. The supernatant was extracted and assumed to be the final concentration of coagulation tests to be analyzed for compound removal.

2.3.2. Sand Filtration Procedure

Sand filtration was also conducted to remove target PFASs. One of the important parameters of sand filtration is the flow rate. A typical ordinary slow sand filter and rapid sand filter have filtration rates of 0.05 gpm/ft^2 and 2 gpm/ft^2 respectively (Kawamura, 2000), or with a 3" diameter base for the column, the flow range is between 0.05 gpm/ft^2 and 2 gpm/ft^2. Contrary to popular belief, the filtration rate of high-rate filters does not significantly affect the quality of the filtered water for flow rates up to 10 gpm/ft^2 (Kawamura, 2000). In this study, a filtration rate of 70 mL/min (0.094 gpm/ft^2) was chosen. The filter was Ottawa standard sand (Fisher Sci) with the size of 20−30

Figure 5: Sand filter design

mesh (0.595-0.841 mm). The flow rate was controlled with a Masterflex Easy-Load II peristaltic pump (filter shown above in Figure 5). The sand filter was first run with a nitrate tracer to determine the breakthrough time (Figure 6). After this was done, the filter was purged with clean tap water before running a PFASs solution through to see if any removal in the effluent was present.
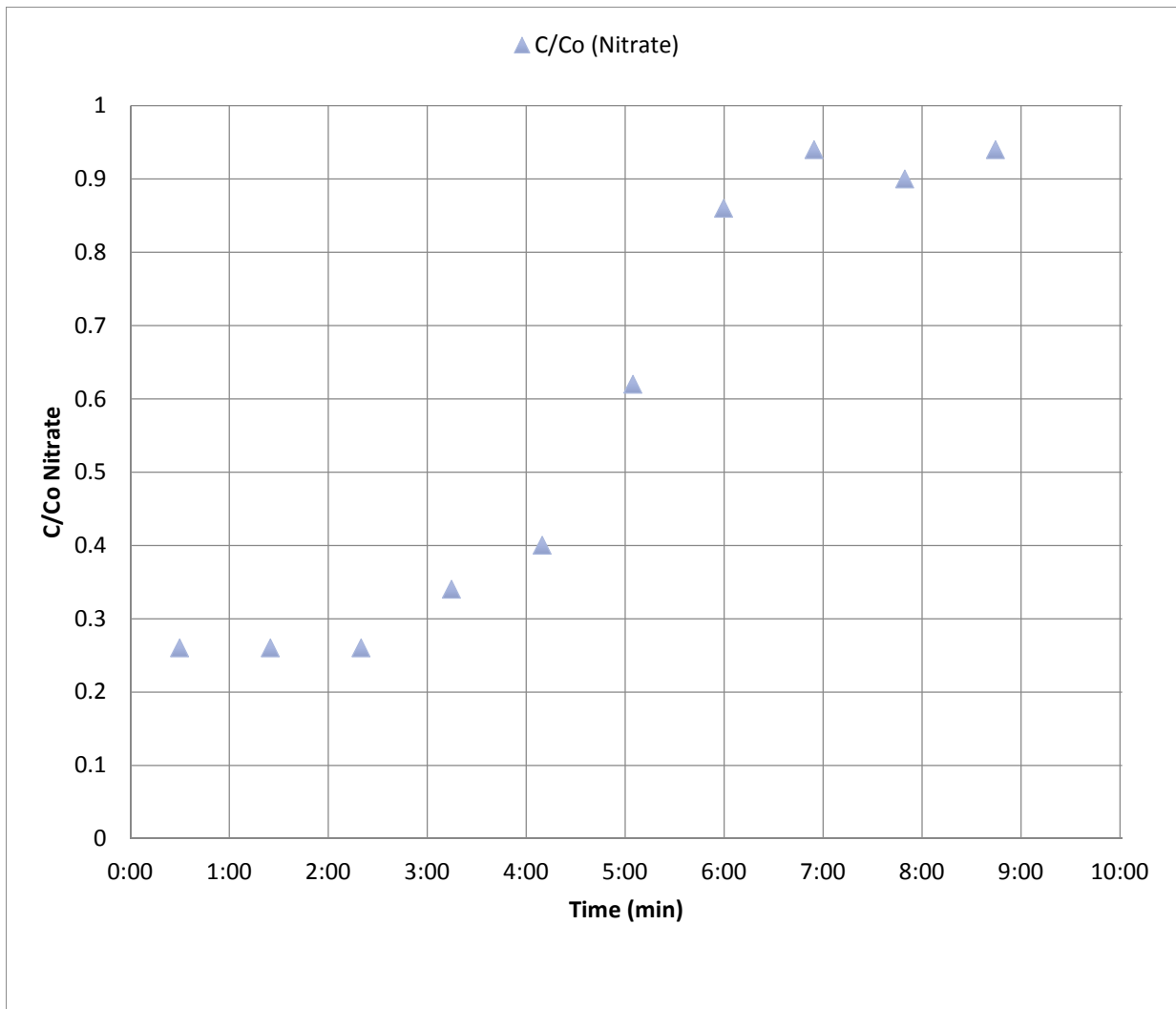
Figure 6: Nitrate tracer test for sand filter

2.3.3. Activated Carbon Adsorption

The activated carbon adsorption experiments were performed using bituminous coal-based activated carbons*:* Calgon Filtrasorb 200, which is a granular activated carbon (GAC), and Calgon WPL, a powdered activated carbon (PAC). Experiments were conducted on 50 mL of filtered surface water spiked with PFASs in 50 mL polypropylene centrifuge tubes. The surface water was coagulated and paper filtered Red River water. The samples
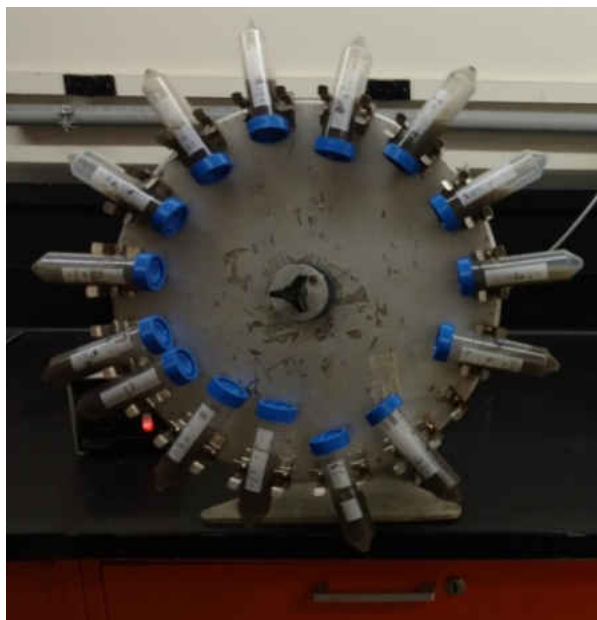
Figure 7: Tube rotator used to keep samples under constant agitation

were kept under constant agitation in order to provide optimum surface area contact (Figure 7). This process was run for 10 days to ensure that equilibrium was met.

After this, the adsorption isomers could be created for applicable use. The adsorption isotherms are the functions between the aqueous-phase concentration and the amount of adsorbate adsorbed. The most widely used methods for finding the adsorption isotherms for a specific system are the Freundlich and Langmuir isotherm equations. PFASs' adsorption isotherms can be described by the Langmuir and Freundlich models (Du et al., 2014). Using Freundlich model in Equation 1, the mass of compound adsorbed per mass of activated carbon can be found. These values are commonly used to compare adsorption capabilities that can be applied to advance filter designs for full-scale and lab-scale implementation.

$$C_S = \frac{(C_0 - C_W) * V}{m}$$

(1)

where C_s: mass compound uptake per mass of activated carbon

C_0: initial concentration

C_w: final concentration

V: volume of sample

m: mass of activated carbon in sample

Once the adsorption isotherm is created it can be applied to Equation 2. The log C_S is plotted versus log C_W for each of the influent concentration to determine the degree of removal achieved by adsorption processes and the adsorptive capacity of the carbon.

$$C_S = K_F C_W^n$$

(2)

where K_F: Freundlich adsorption coefficient

C_w: final concentration

n: Freundlich exponent indicating nonlinearity

m: mass of activated carbon in sample

2.3.4. Chlorination

Free chlorine stock solutions were prepared by dilution from purchased 5% sodium hypochlorite solution (NaOCl) into distilled water. Stock solution concentrations were checked using the free chlorine test with the HACH Pocket Colorimeter II unit. Experiments were conducted on 25-mL with either laboratory water or filtered surface water spiked with individual PFASs or combined PFASs in a 60-mL amber vial. The laboratory water was distilled water to which sodium bicarbonate (NaHCO$_3$) buffer was added to mimic the pH of surface water. The surface water was coagulated and paper filtered Red River water. The residual free chlorine (Cl$_2$)

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was monitored using the HACH Pocket Colorimeter II to regulate the available chlorine for disinfection after the breakpoint. The initial reading of free chlorine, prior to spiking, was about 5 mg/L. After spiking, the residual chlorine measured at a range of 0.8-2.8 mg/L for surface water and 4-5 mg/L for buffered distilled water after 2 hours of contact time (Ct). After the set contact time was achieved, the samples were quenched with a stock solution of 0.1 mol/L sodium thiosulfate ($Na_2S_2O_3 \cdot H_2O$) at about a 5:1 ratio to free chlorine to ensure adequate neutralization. The objective of this experiment was to hopefully achieve breakpoint chlorination by representing dosages similar to water treatment concentrations. An ideal system supplies free chlorine at a concentration of 0.3-0.5 mg/L.

2.3.5. Ozone

Like chlorination, two types of degradation experiments were performed containing the studied PFASs: combined PFASs, individual PFAS. This was to examine more clearly which PFASs were being directly oxidized by the ozone. The individual PFAS or batch experiment PFASs were dissolved into 500 mL of pure or buffered distilled water or filtered surface water from the Red River. The PFAS solution was then transferred to a 750mL flask for ozone diffusion. Ozone (O_3) was bubbled in using a diffuser stone at various lengths of time. Ozone was generated initially with an Aqua-6 Multi-Purpose ozone generator (A2Z Ozone

Figure 8: A_2Z Model Z-7G Ozone Generator

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Inc., Louisville, KY), but was found to be inefficient to generate enough ozone to oxidize the compounds. To correct this, a more powerful generator A_2Z Model Z-7G (A2Z Ozone Inc., Louisville, KY) was purchased (Figure 8). The input gas for the generator was wet ambient air for the initial stage of experiments, but was still unable to supply high O_3 concentration (0.5 mg/L). Fortunately, pure oxygen (O_2) became available for a short period of experiments, which allowed for higher generation of ozone concentration (5.0 mg/L). The input of O_3 concentration was measured in distilled water with an Evolution 220 UV-Visible Spectrophotometer at $\lambda = 254$ nm (UV_{254}) in a quartz cuvette (L = 1 cm). After the sample was tested in the UV Spectrophotometer, the samples were quenched with a stock solution of 0.1 mol/L sodium thiosulfate ($Na_2S_2O_3 \cdot H_2O$) at about a 5:1 ratio to expected ozone residual concentration using Beer's Law and a molar absorptivity of $\varepsilon_{260} = 3150$ L/(mol·cm)to ensure adequate neutralization. For samples in surface water, this UV_{254} cannot be assumed to be the accurate concentration after converting due to the fact UV_{254} can pick up other organics in the water. For that reason, the expected concentration was assumed by experiments run in distilled water.

Based on the degradation results, the thesis advisor, Dr. Feng Xiao at the University of North Dakota, did additional experiments with individual PFAS compounds using the same approach. The results can be found in a paper from us to be published at a later date.

3. RESULTS AND DISCUSSIONS

The initial abstract of this research was to focus on the removal aspects of the studied

compounds, which will be the discussed below firstly. It was assumed that the focus, like much

other research, would be driven towards the removal by carbon adsorption. After several initial

tests using oxidation, the conversion of PFSA precursors to PFOS/PFOA occurred. This will be

discussed in more detail below after providing the initial conventional treatment techniques that

were studied.

3.1. Coagulation

To determine the optimal coagulant dosage for future experiments, an experiment was conducted. Table 2 shows the optimal coagulant dosage during conventional and enhanced coagulation. It can be seen that a coagulant dosage between 40 and 80 mg/L reduces the turbidity the most while maintaining adequate pH.

Table 2: Optimal coagulant dosage results.

Concentration of Aluminum Sulfate	pH	Turbidity	
mg/L		FTU	NTU
0	7.8		6.92
5	7.64	7	4.71
10	7.63	6	3.95
20	7.56	12	8.79
20	7.64	4	1.14
40	7.41	8	4.75
40	7.49	3	1.05
60	7.2	7	1.17
80	7.11	6	1.28
80	7.14	3	1.65
100	7.07	3	1.51
120	7.01	2	0.836
140	6.98	4	2.35

While coagulation can effectively remove turbidity particles, this process does not result in

significant removal of the tested PFASs. Figure 9 and Figure 10 show two different tests using

GenX, and GenX & NaDONA together. Figure 9 shows that the removal of GenX during

coagulation is minimal. However, in another group of experiments (Figure 10), there were 33%

and 17% GenX removal for 100 mg/L and 40 mg/L alum dosages respectively. This, however, could be due to the differing suspending solids in treatment water or sampling and detection errors. If it is true, being that GenX has been a forefront of the PFAS news lately, this is promising for pretreatment removal. Same goes for NaDONA with removal at 49% and 20% for 100 mg/L and 40 mg/L respectively (Figure 10). In this case, 100 mg/L appeared to be the optimal coagulant dosage for both substances.
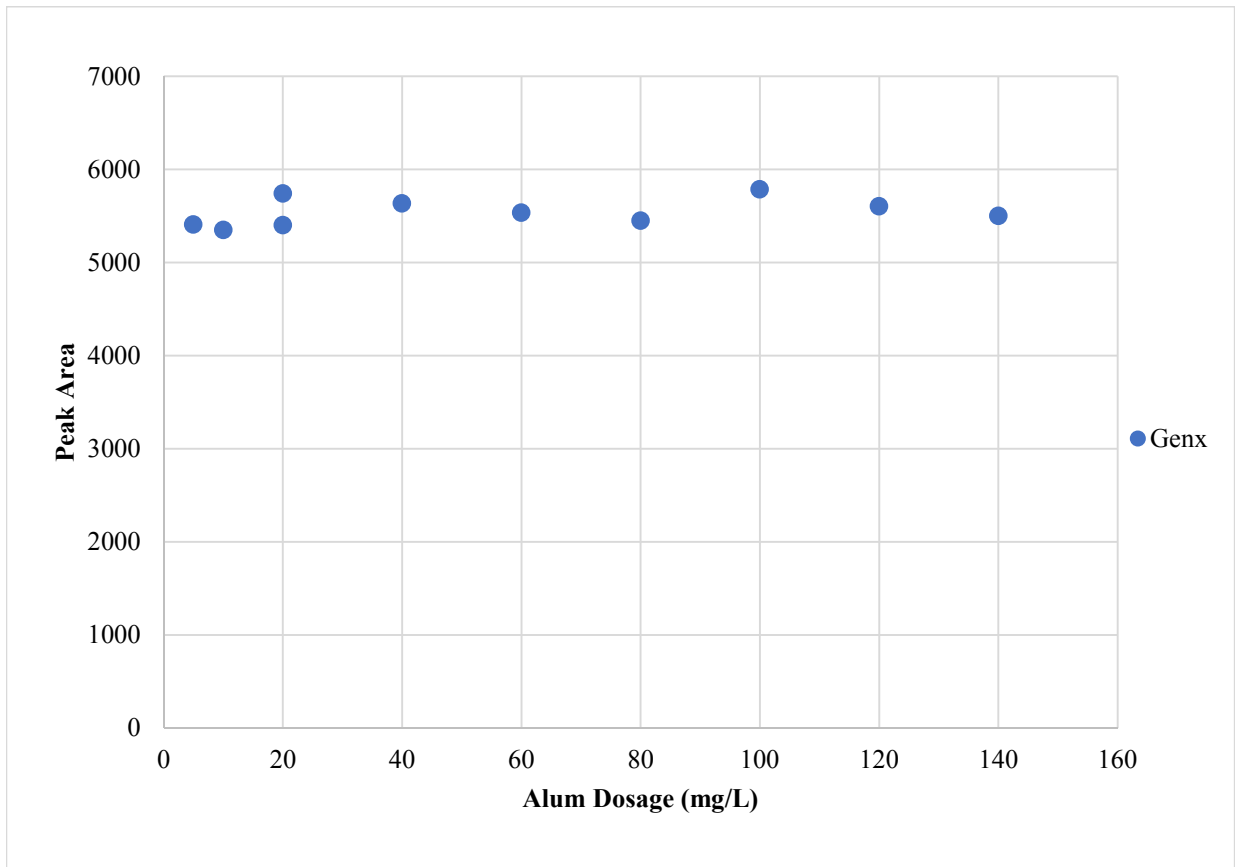
Figure 9: Coagulation experiment of GenX and varying alum dosages (mg/L).
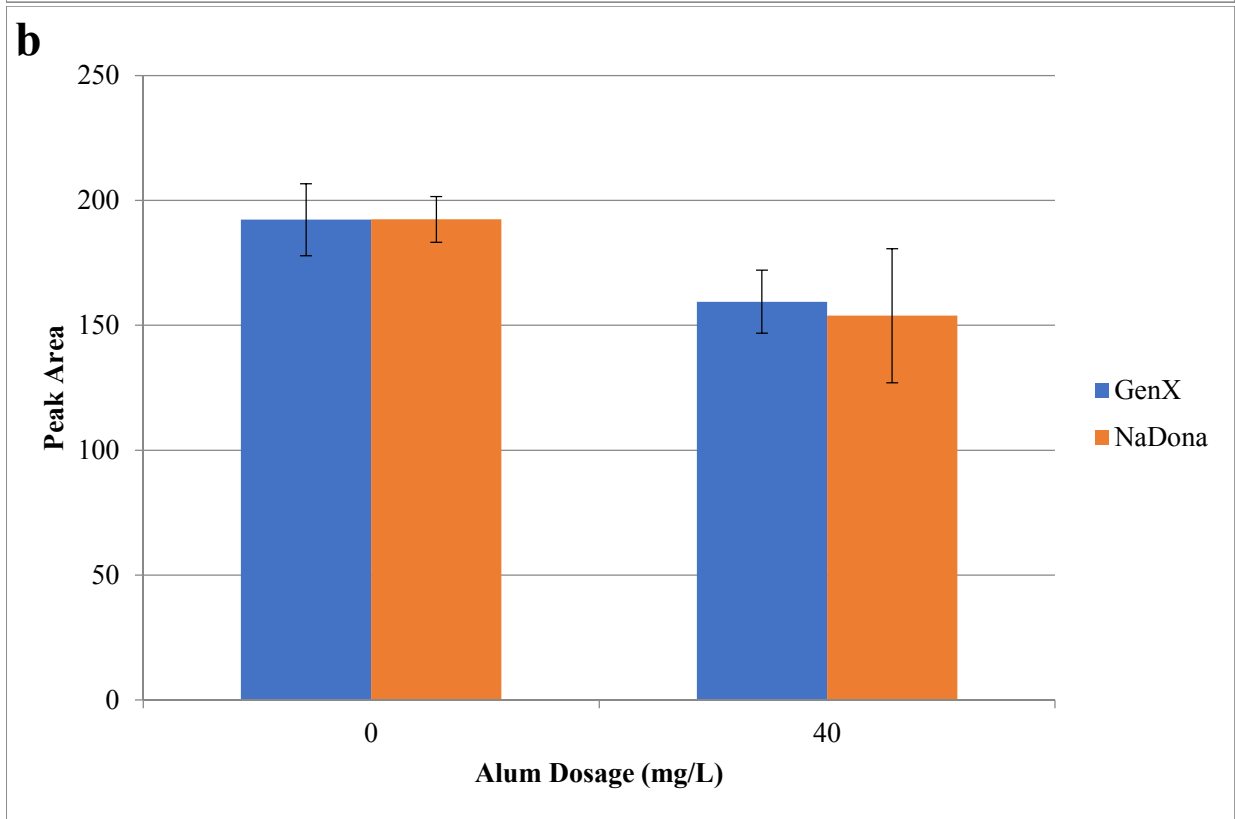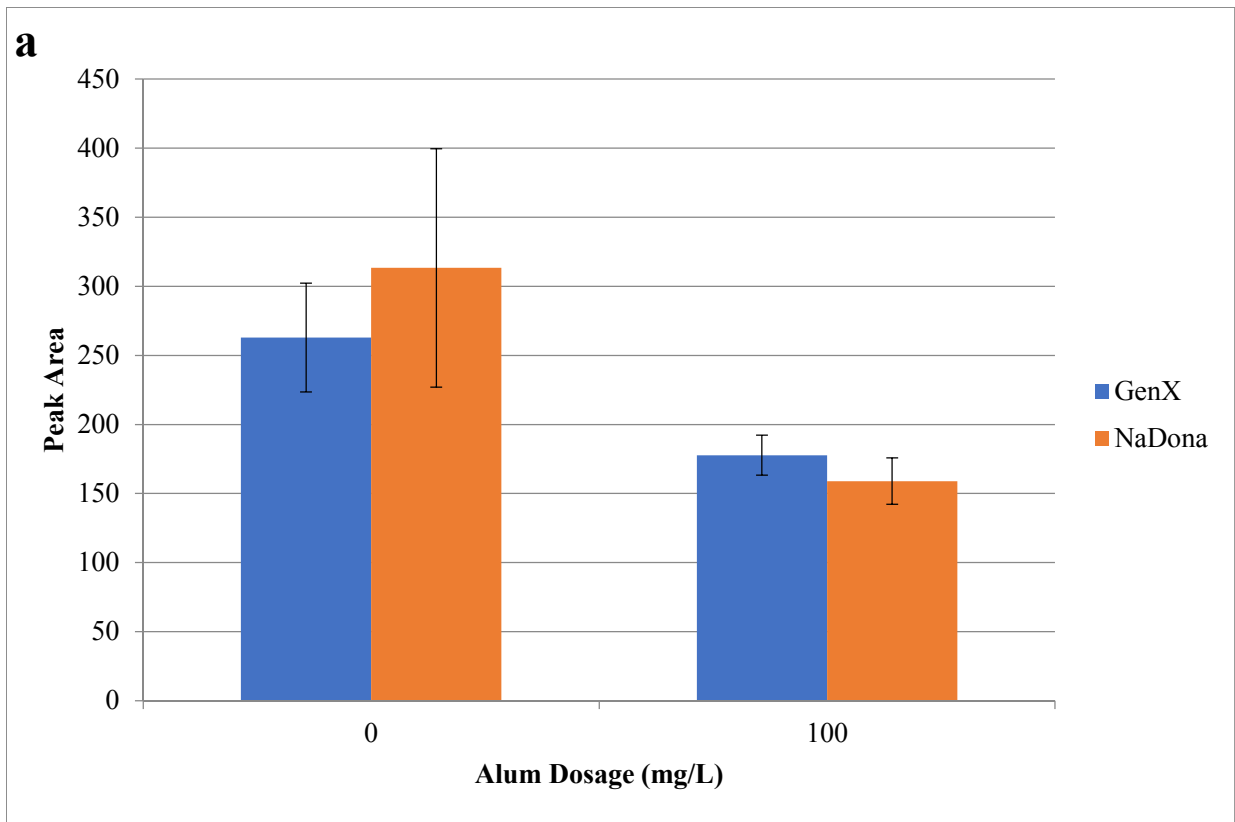
Figure 10: Coagulation experiment of combined compounds, GenX and NaDONA, for alum dosages of 40 mg/L and 100 mg/L.

As for the other PFASs (PFOAAmS, PFOAB, PFOSAmS, PFOSB), the PFSAs (PFOSAmS, PFOSB) were below detection limits in one of the experiments (Figure 11). As for the second experiment, they were nearly undetectable (Figure 12). The compounds might have precipitated in the stock solution due to their higher pKa values or had an extremely high affinity to the suspended particles due to their high tendency to be hydrophobic. The PFCAs (PFOAAmS, PFOAB) were still able to be detected and the results showed that there is no quantifiable amount of consistent reduction in concentration. The two experiments below were not from the same batch of surface water, so they do not have the same amount of TOC, NOM or total suspended solids (TSS). This concept would play an important role in the amount of flocculants created, however, both tests were not absent of flocculants masses capable of removing organic compounds. It appears, from the results, that enhanced coagulation is not efficient to remove PFOAAmS, PFOAB, PFOSAmS, and PFOSB.

Figure 11: Coagulation experiment of combined compounds (PFOAB, PFOAAmS, PFOSB, PFOSAmS). PFOSB and PFOSAmS were below the detection limit.
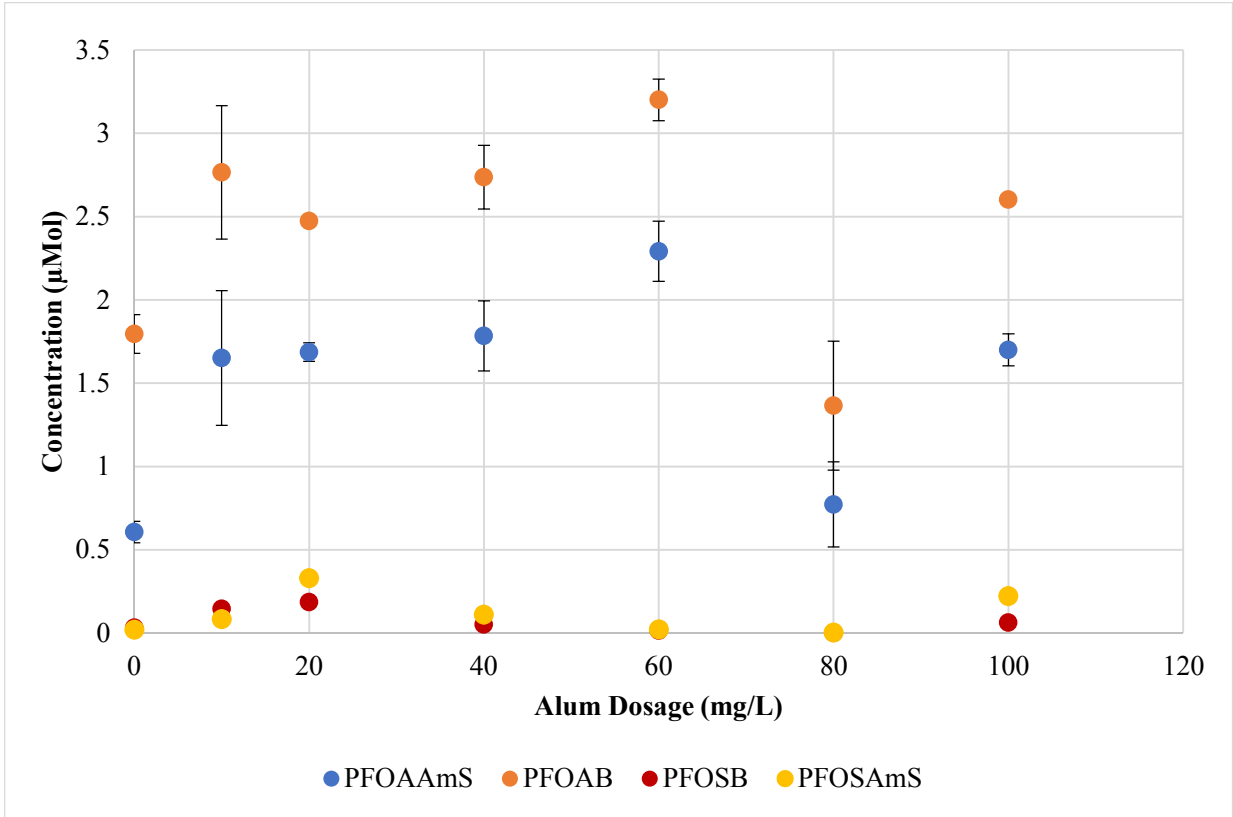
Figure 12: Coagulation experiment of combined compounds (PFOAB, PFOAAmS, PFOSB, PFOSAmS).

3.2. Sand Filtration

Sand filtration was expected to follow similar results as coagulation. This did prove true for GenX and NaDONA (Figure 13). Both compounds had no significant removal as compared to the nitrate tracer. If there was any sorption, the curve should have been delayed by a specific factor indicating a time-lag from adsorption effects. Being that they followed the nitrate tracer directly, sand filtration is inefficient at all to remove GenX and NaDONA.
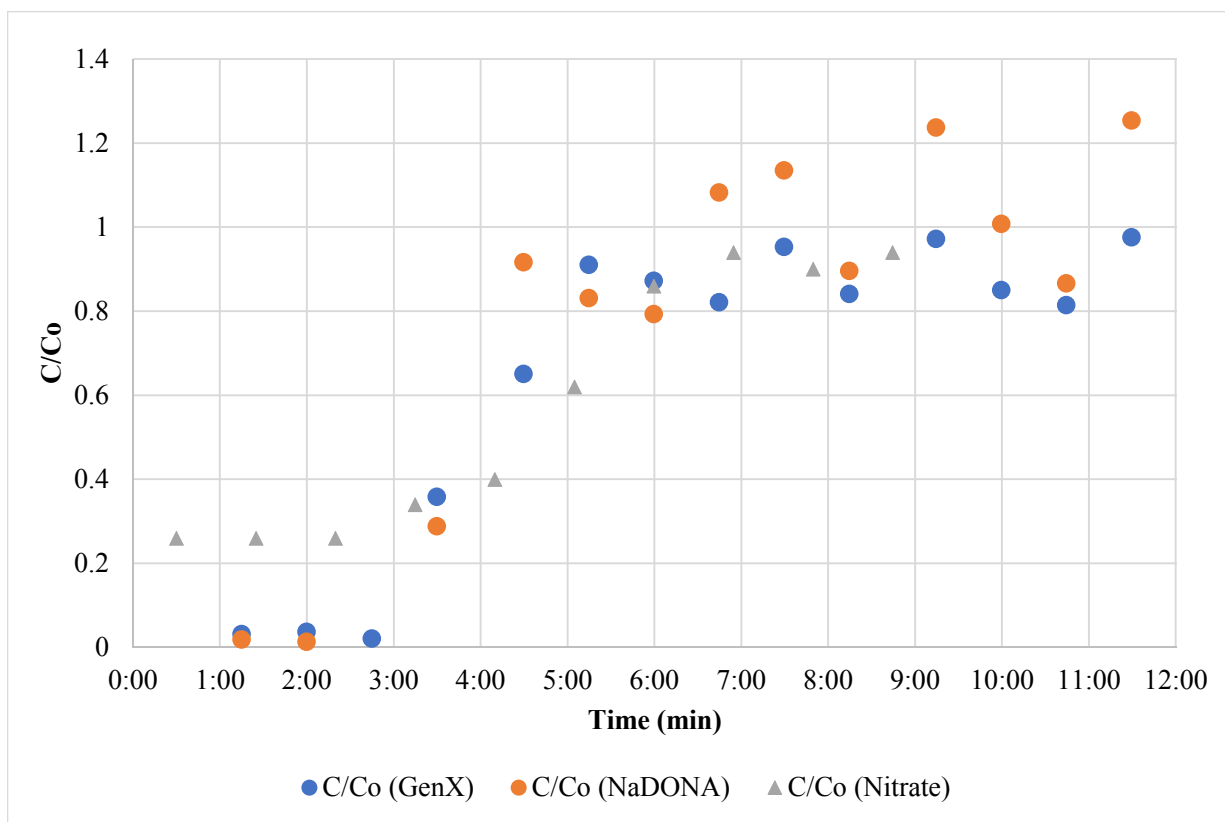
Figure 13: Sand filtration experiment of combined compounds(GenX and NaDONA).

As for the precursor compounds, PFOSB and PFOSAmS were not detected again in any of the samples. Like before, they will have to be ignored for this section and will need additional research regarding their fate through a sand filter. PFOAAmS and PFOAB were detected. However, from Figure 14, it can be seen that the results are inconclusive for PFOAB. In general, it looks to follow the nitrate tracer. Controversially, PFOAAmS appeared to not have any variation in the data spread. From the results, PFOAAmS did appear to have a time-lag confirming some sorption onto the sand particles as they passed through the media filter. In other experiments done by the groupmates, PFOAAmS has a much stronger adsorption towards soil particles than PFOAB, which may explain the stronger attachment to sand and the longer time-lag. Nevertheless, based on our results, sand filtration cannot be suggested as a successful removal for any of the studied PFASs, at this time.
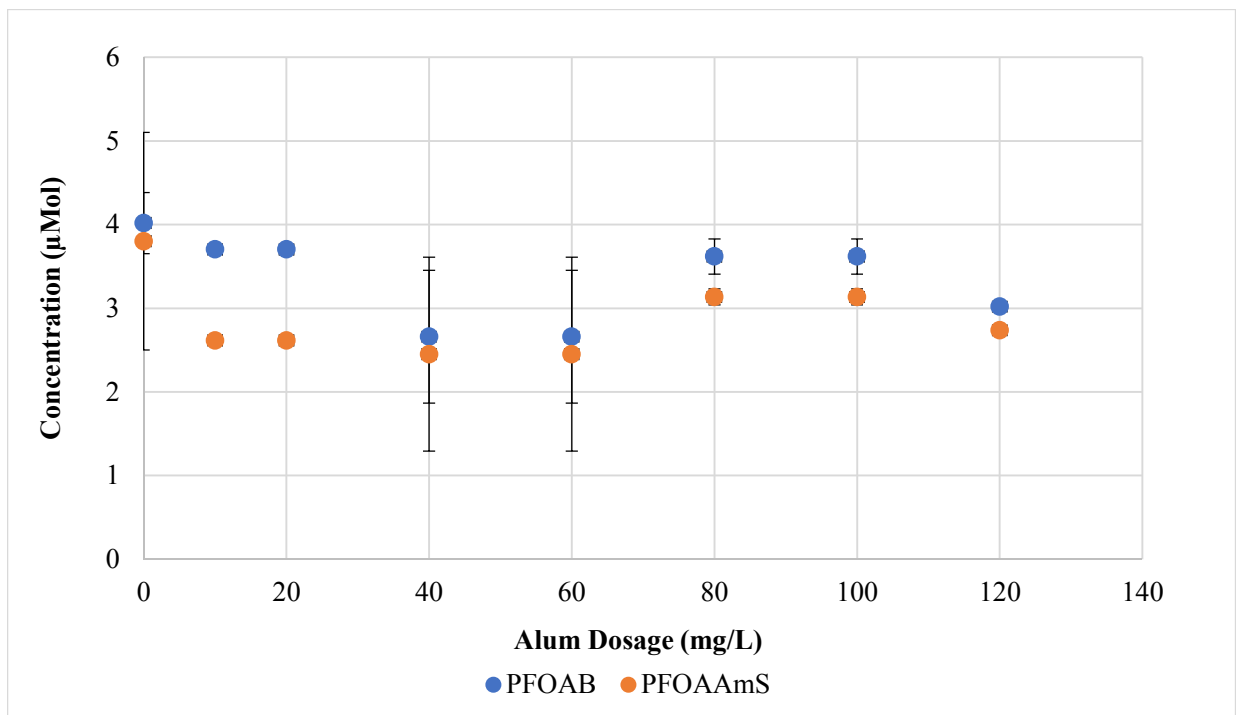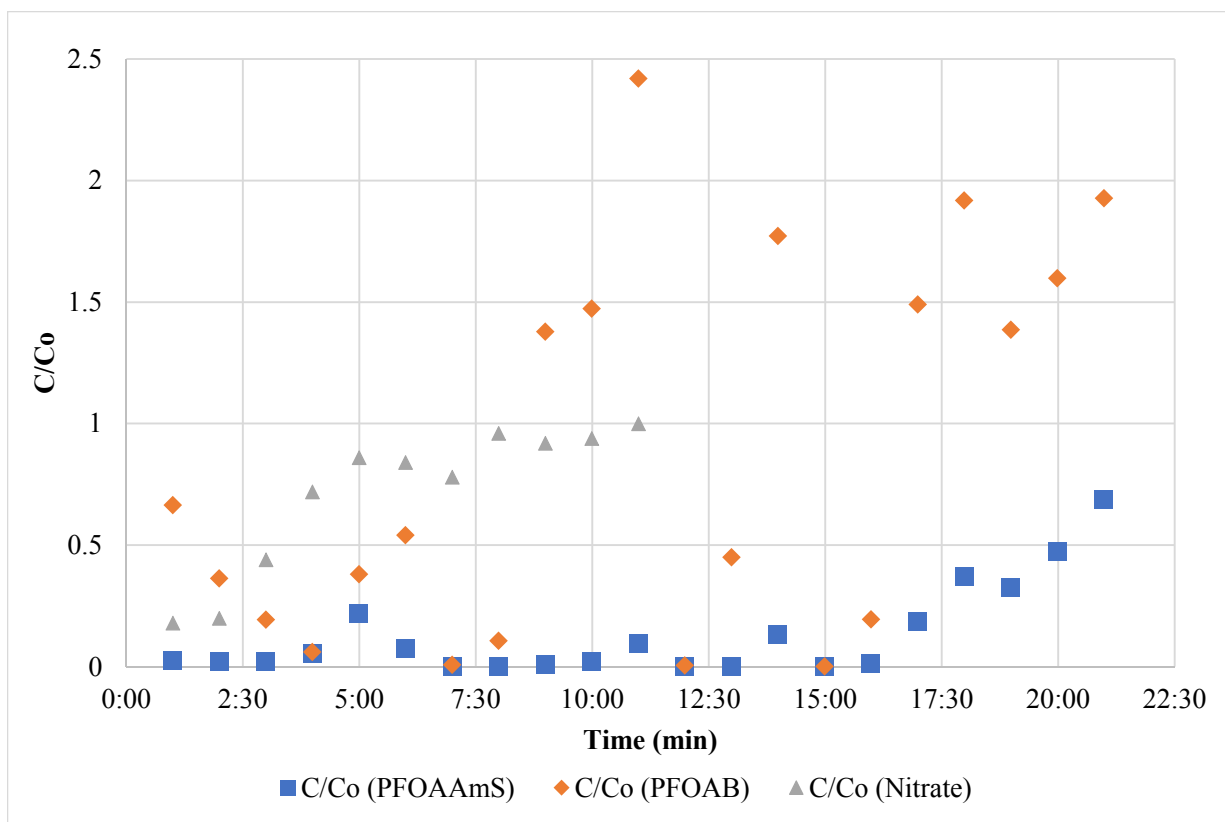
Figure 14: Sand filtration experiment of combined compounds (PFOAB, PFOAAmS, PFOSB, PFOSAmS). PFOSB and PFOSAmS were below the detection limit.

3.3. Activated Carbon

Using Freundlich model, the amount of impurity in solution to the amount that was adsorbed was empirically derived. This data can be used for future analysis of packed bed activated carbon filters. However, isotherm data is developed by achieving equilibrium conditions, while field adsorption systems operate in a dynamic environment that is not necessarily in equilibrium, isotherm data overestimate the capacity of operating systems. In Figure 15, the GenX isotherm and empirical values were able to be generated for GAC and PAC experiments. In Figure 16, using GAC, and isotherm and empirical values for the other four precursor compounds was able to be generated. In the PAC tests, the concentration of the precursor PFASs, after adsorption, was below the detection limit immediately. Even for the

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GAC, concentrations were below detection limits faster than expected. This could be due to the cationic effects creating a larger attraction to the surface of the carbon or higher adsorption due to the increased carbon-fluorine chain length. However, with the current results, it can be observed that adsorptive capacity did not appear to increase with increasing chain length for the four compounds, which is common throughout literature. Compared to the chain length of GenX, the results show a decrease in adsorption with increasing carbon-fluorine chain length.

From the results, a pilot study was expected to be continued for pressure filtration with this research, but time did not permit.
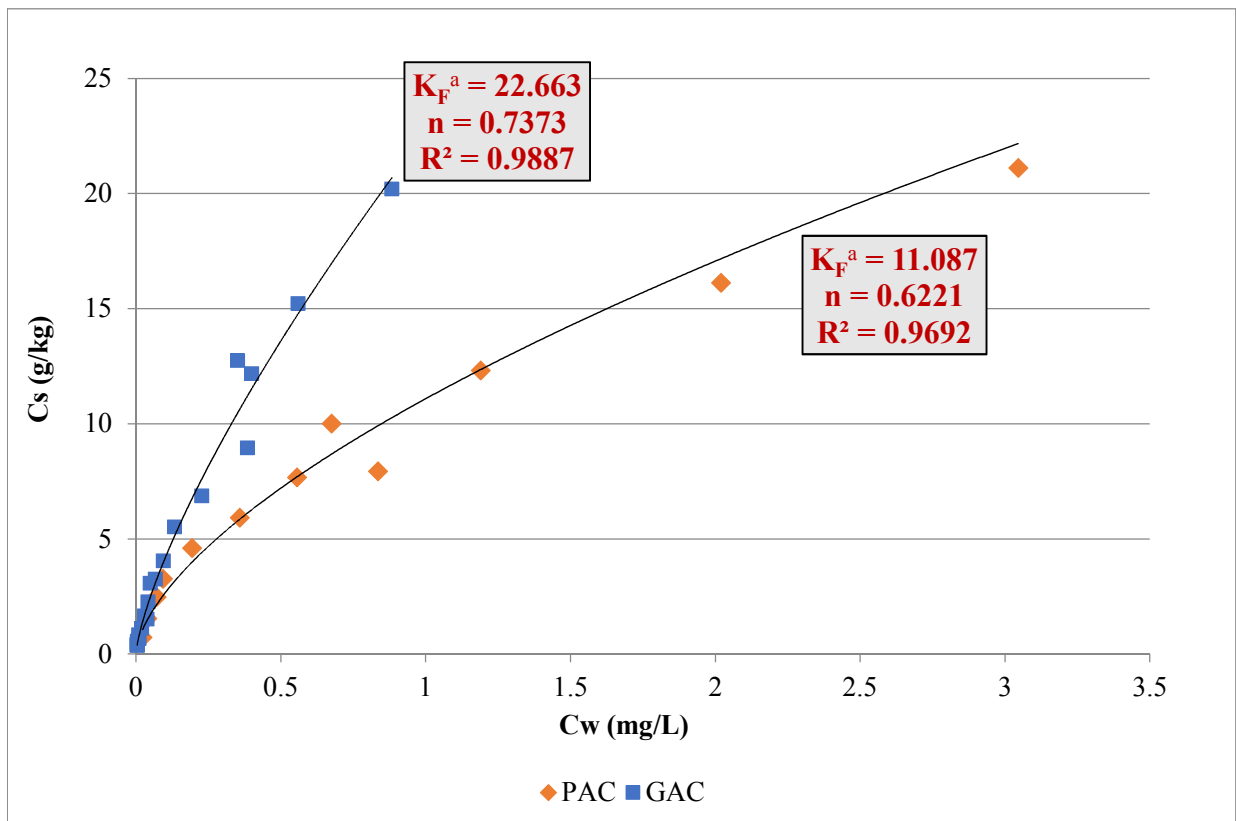
Figure 15: Activated carbon experiment isotherm for GenX.
[a]Units for K_F $(mg/g)(L/mg)^{1/n}$
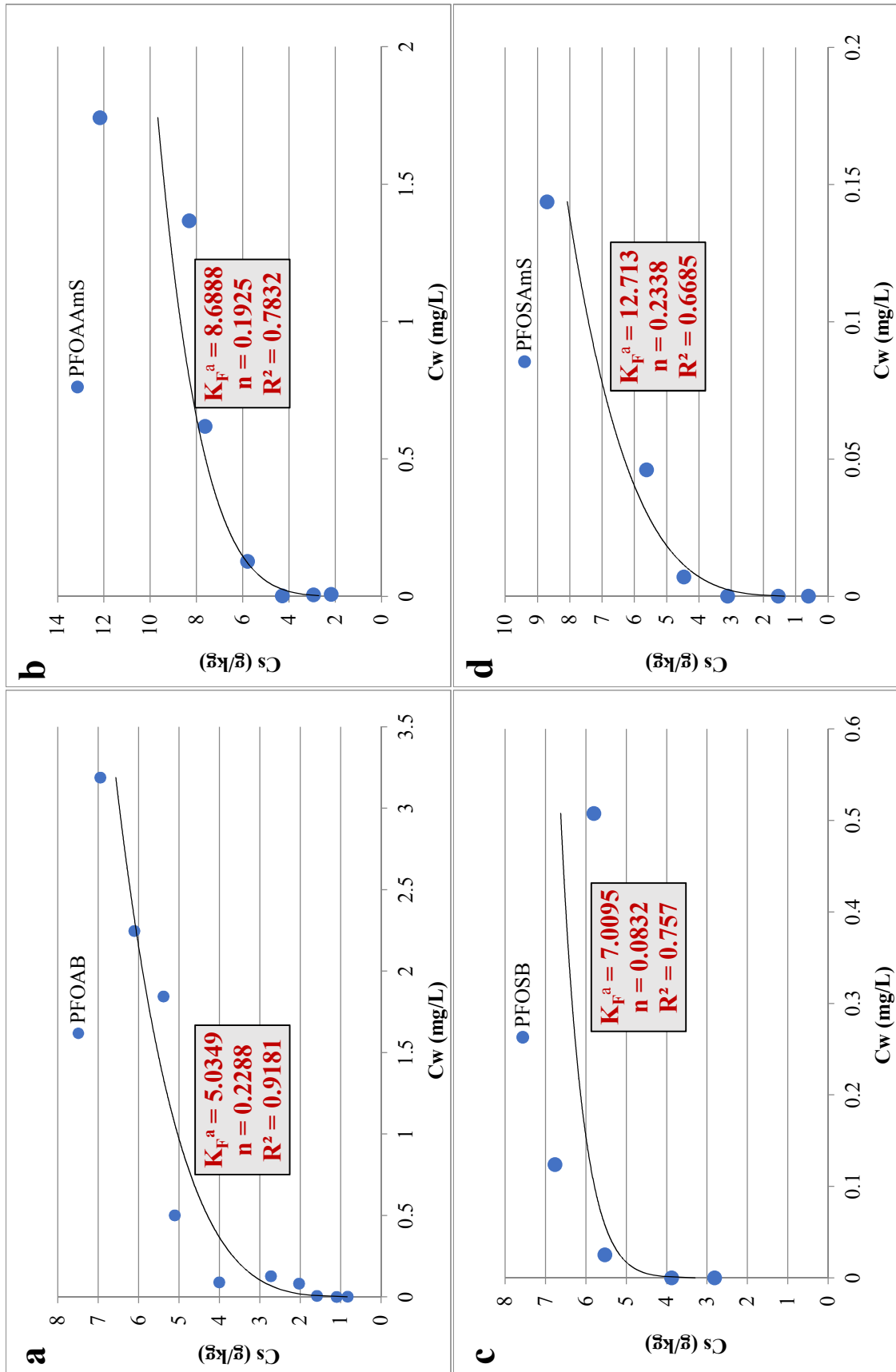
Figure 16: Granular activated carbon experiment isotherms of combined compounds: (a) PFOAB, (b) PFOAAmS, (c) PFOSB, (d) PFOSAmS.

[a]Units for K_F $(mg/g)(L/mg)^{1/n}$

3.4.   Chlorination

As stated earlier, chlorination became one of the major scopes of this project halfway through for the compounds other than GenX and NaDONA. As expected, GenX and NaDONA did not degrade during chlorination disinfection. Figure 17 shows two tests that are clear to see no measurable decrease in concentration. In distilled water, the free chlorine concentration did not decrease much, reaffirming no reaction occurred in the solution to use up substation available free chlorine. These results show that disinfection with chlorination should not be expected to result in any removal on GenX or NaDONA.

On the other hand, the other four precursor compounds produced interesting results. Figure 18 and Figure 19 display the results of the first chlorination trial in buffered distilled water and surface water respectively. For both tests, the compounds were combined in the solution and then chlorinated. The distilled water samples can be analyzed for a very clear decrease in concentration for PFOAAmS and PFOAB at 98% and 94% respectively. The available free chlorine supports that reactions occurred in the solution. It can be expected that the reactions were first with the sodium bicarbonate and then the PFCAs (PFOAAmS, PFOAB). Supporting this claim, the surface water experiment displayed removal of PFOAAmS and PFOAB at 23% and 31% respectively, assuming that there was no error in the initial samples. For the PFSAs (PFOSAmS, PFOSB), chlorination disinfection did not have any noticeable decrease in the concentration in either distilled or surface water or had inconclusive results. For the surface water experiment, it appears that the initial samples could have been spoiled.
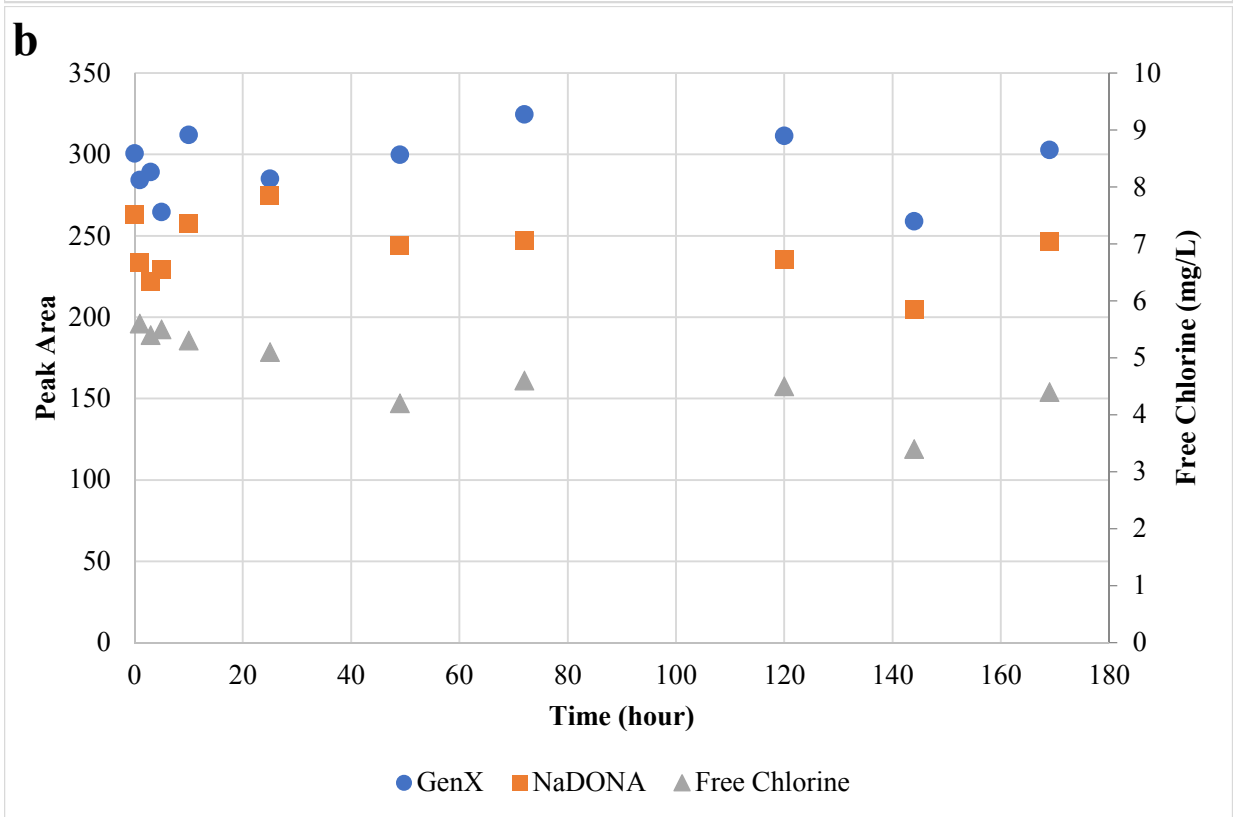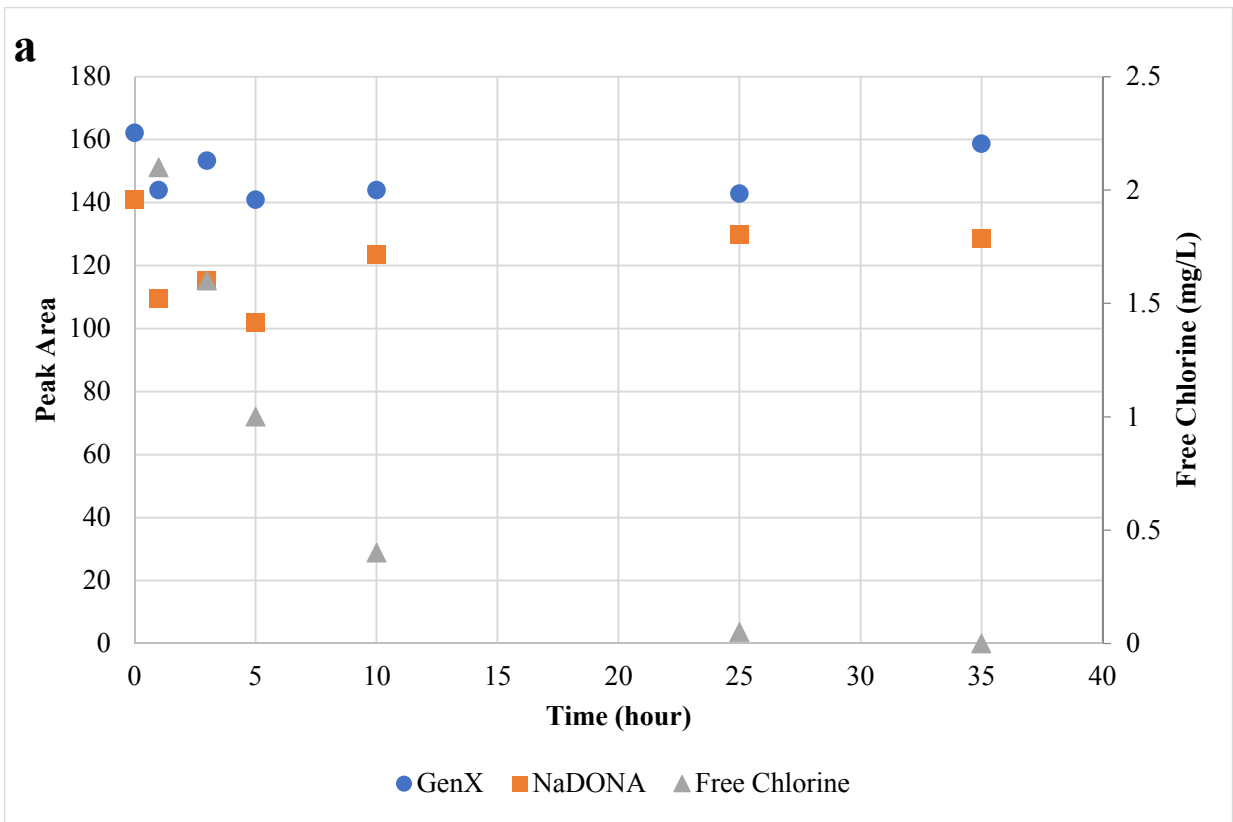
Figure 17: Chlorine disinfection experiment of combined compounds (Genx, NaDONA) in (a) coagulated and filtered surface water and (b) buffered distilled water.

Figure 18: Chlorine disinfection experiment in buffered distilled water of combined compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.

Figure 19: Chlorine disinfection experiment in surface water of combined compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.

The most interesting part of this first experiment was the concentration change of PFOA and PFOS. In Figure 20, it is very clear to see that PFOA, a concerning PFCA, increased dramatically, especially in the distilled water experiment. In addition to PFOA's increase in concentration, PFOS appeared to increase as well by a very small fraction. In the distilled water experiment, PFOA and PFOS increased by 2336% and 67% respectively and in the surface water experiment, PFOA and PFOS increased by 411% and 2755% respectively. This means that there must be a source that converted to these compounds to increase their concentrations. Comparing the molecular structures, a second hypothesis was made that the PFSAs precursors (PFOSAmS, PFOSB) should be responsible for any PFOS generation and the PFCAs (PFOAAmS, PFOAB) should be responsible for any PFOA generation. The following experiments were to examine this idea as a plausible side effect of using these compounds.

Figure 20: PFOS/PFOA generation in chlorine disinfection experiment in (a) buffered distilled water and (b) surface water.

This experiment was run again in Figure 21 for distilled water to confirm the results. This experiment was done in parallel for each compound and then combined at the end for analysis. This was done so that the competition for free chlorine would be substantially less. The results for the decrease in PFOAB and PFOAAmS were confirmed along with a contradicting decrease in PFOSAmS and PFOSB. However, the initial samples do appear to be major outliers for each of the graphs. If the initial samples were taken out of all of the graphs, the perfluoroalkyl carboxylates would display decreasing results at 98% for both, and the perfluoroalkyl sulfonates (PFOSAmS, PFOSB) would be 68% for both. In the surface water samples in Figure 22, which were done combined like the first experiment, similar results were found. Following the same issue with the initials, they were thrown out and the results showed PFOAAmS and PFOAB decreasing by 88% and 49% respectively, and PFOSB and PFOSAmS with no quantifiable decrease. As predicted, Figure 23 shows that PFOA was generated again from the experiment at 485% and 1633% for distilled and surface water respectively. There was no PFOS generation in either of the two experiments. Mistakenly, no samples were extracted prior to the combination. This information would have allowed us to see what portions of the PFCAs were generated by which compound.
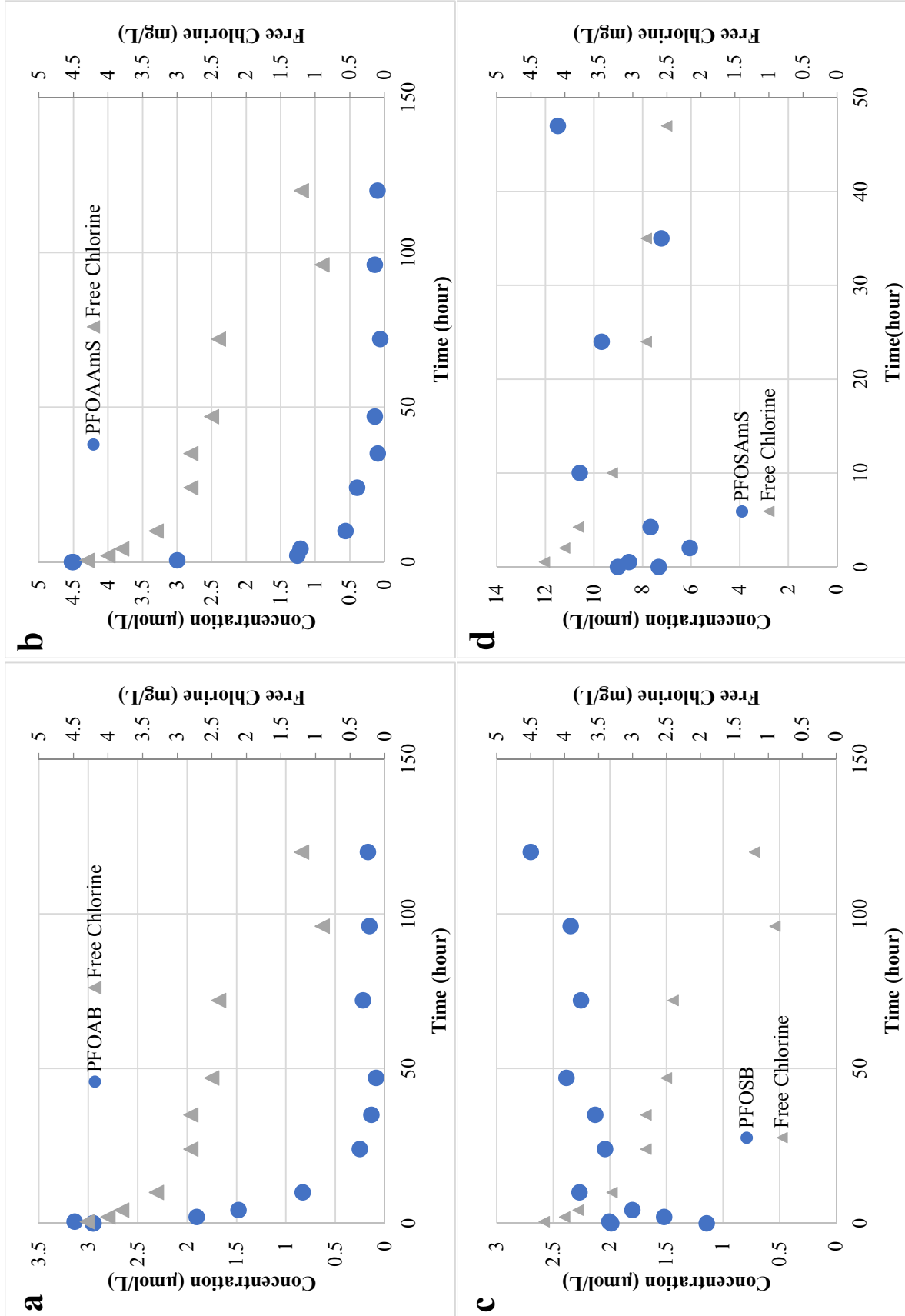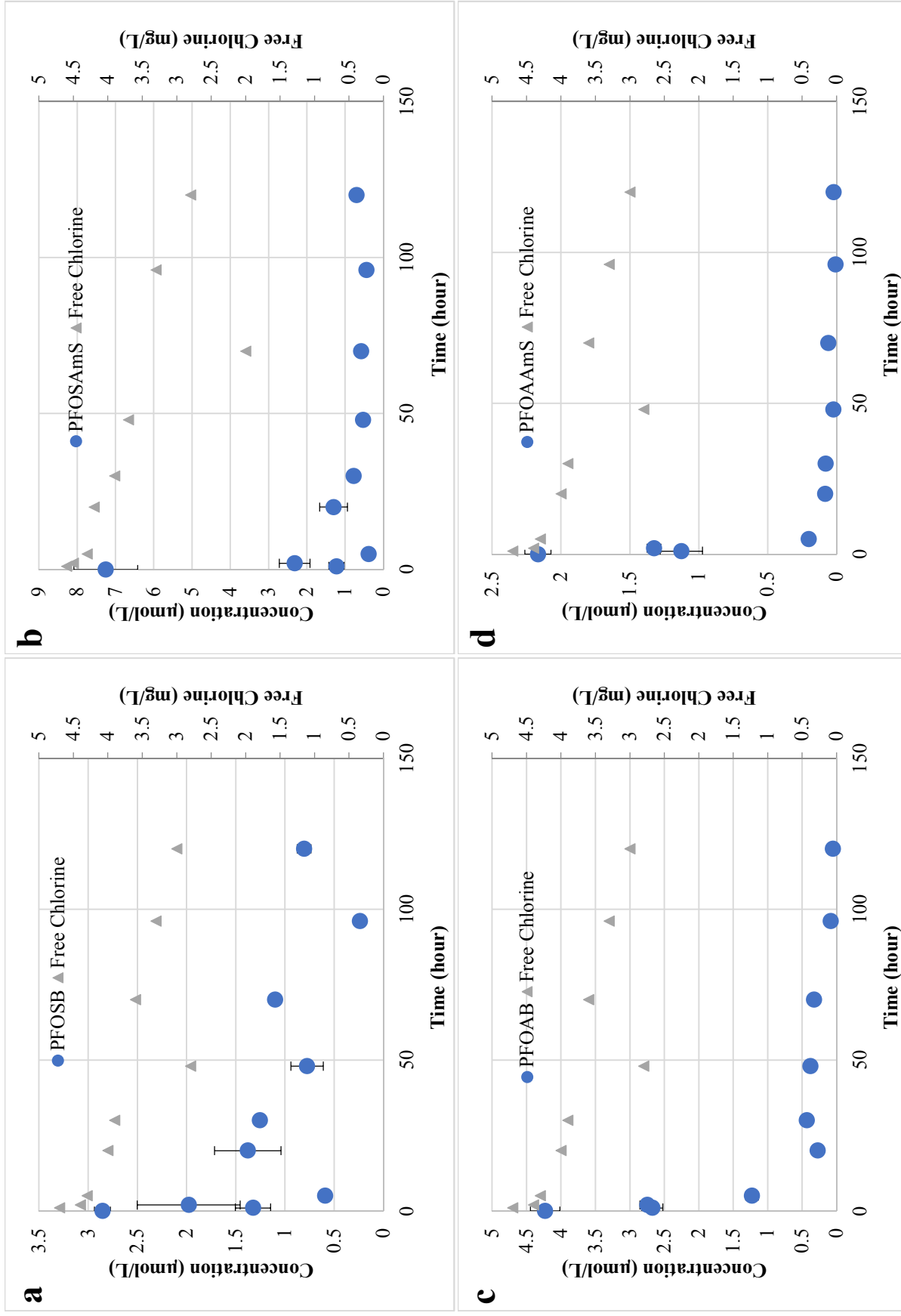
Figure 21: Chlorine disinfection experiment in buffered distilled water of parallel compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.
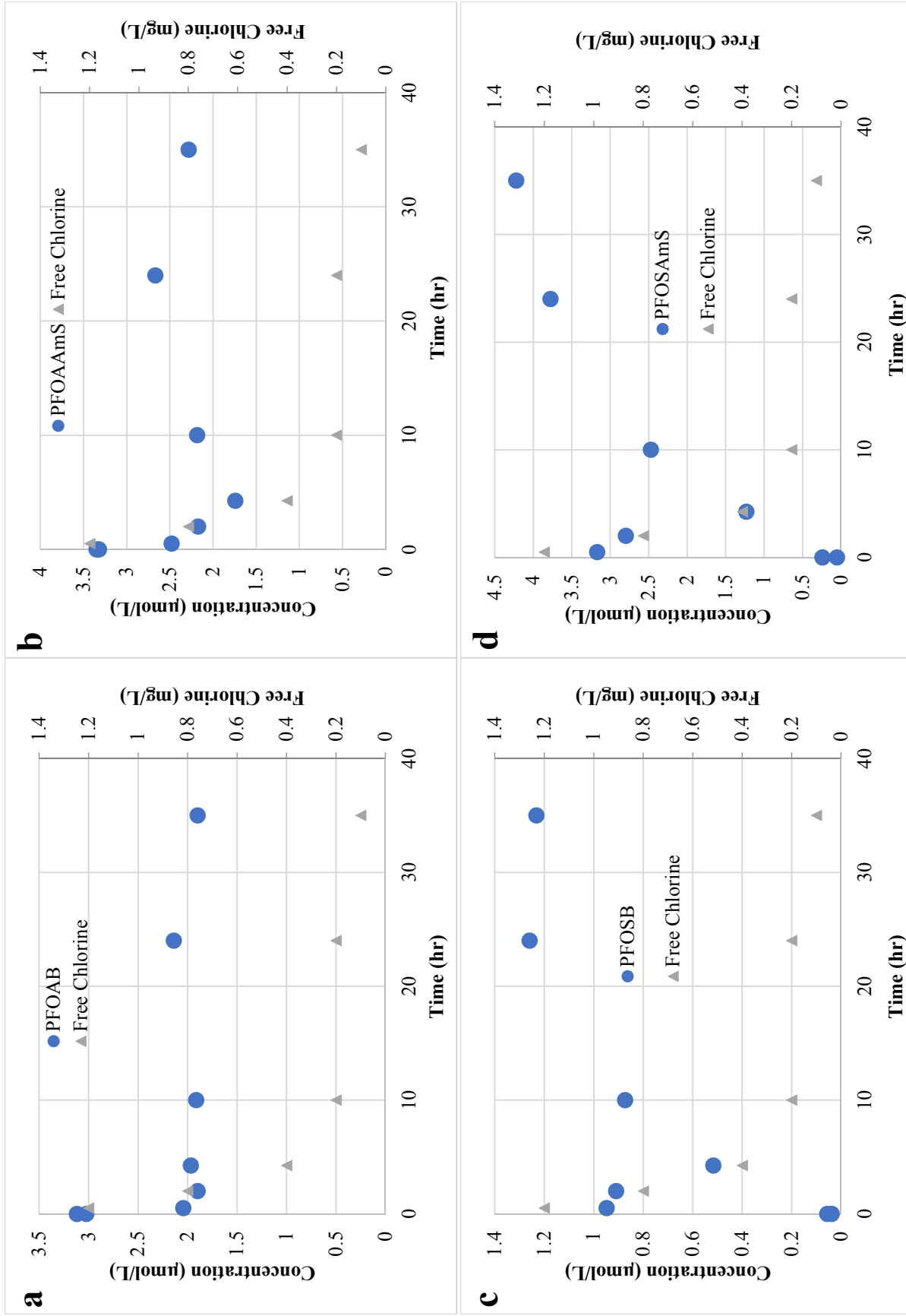
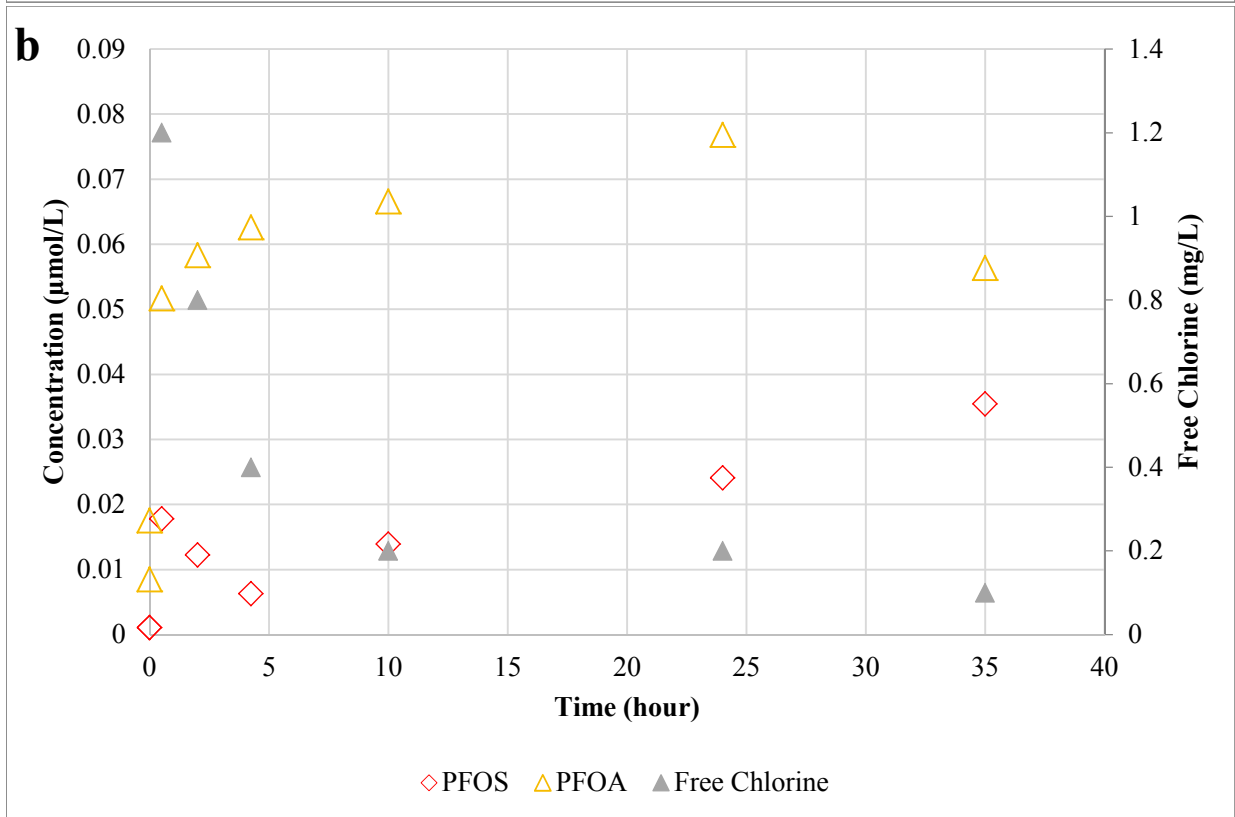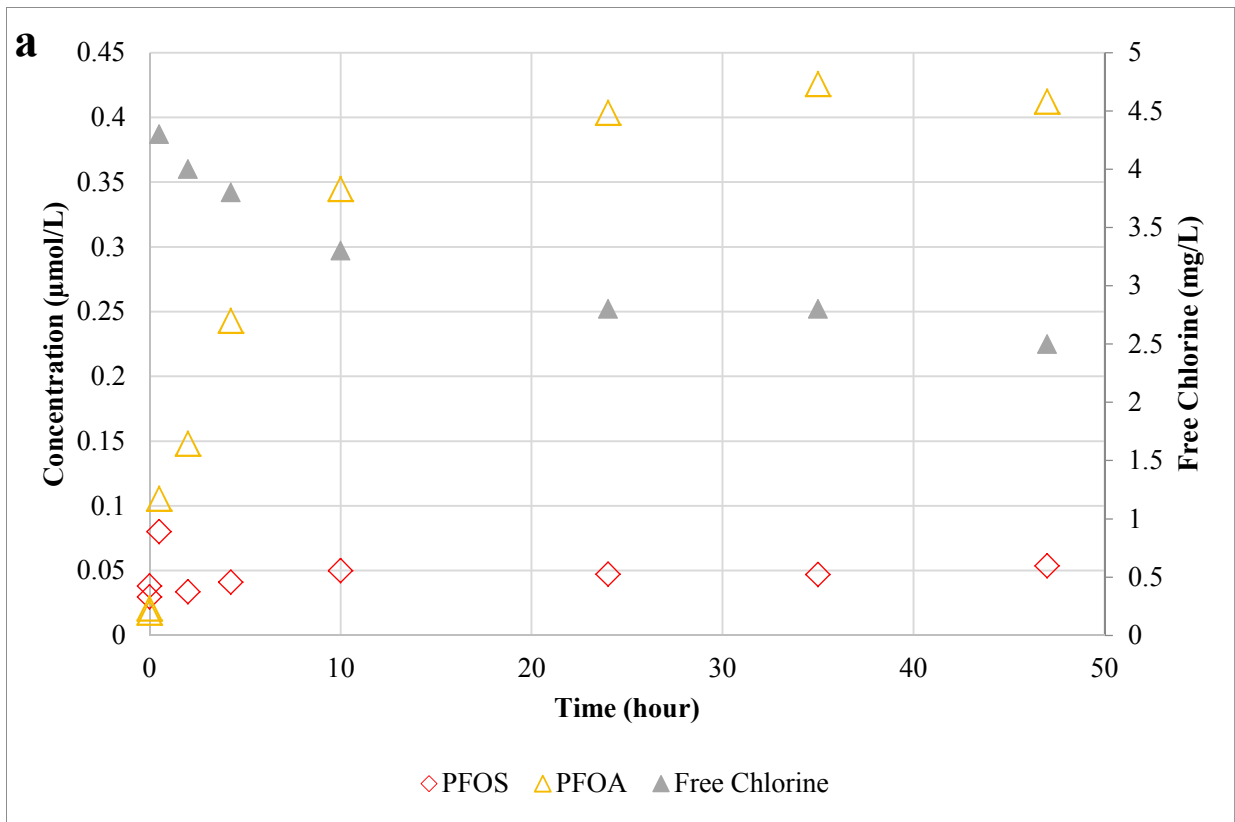Figure 22: Chlorine disinfection experiment in surface water of parallel compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.
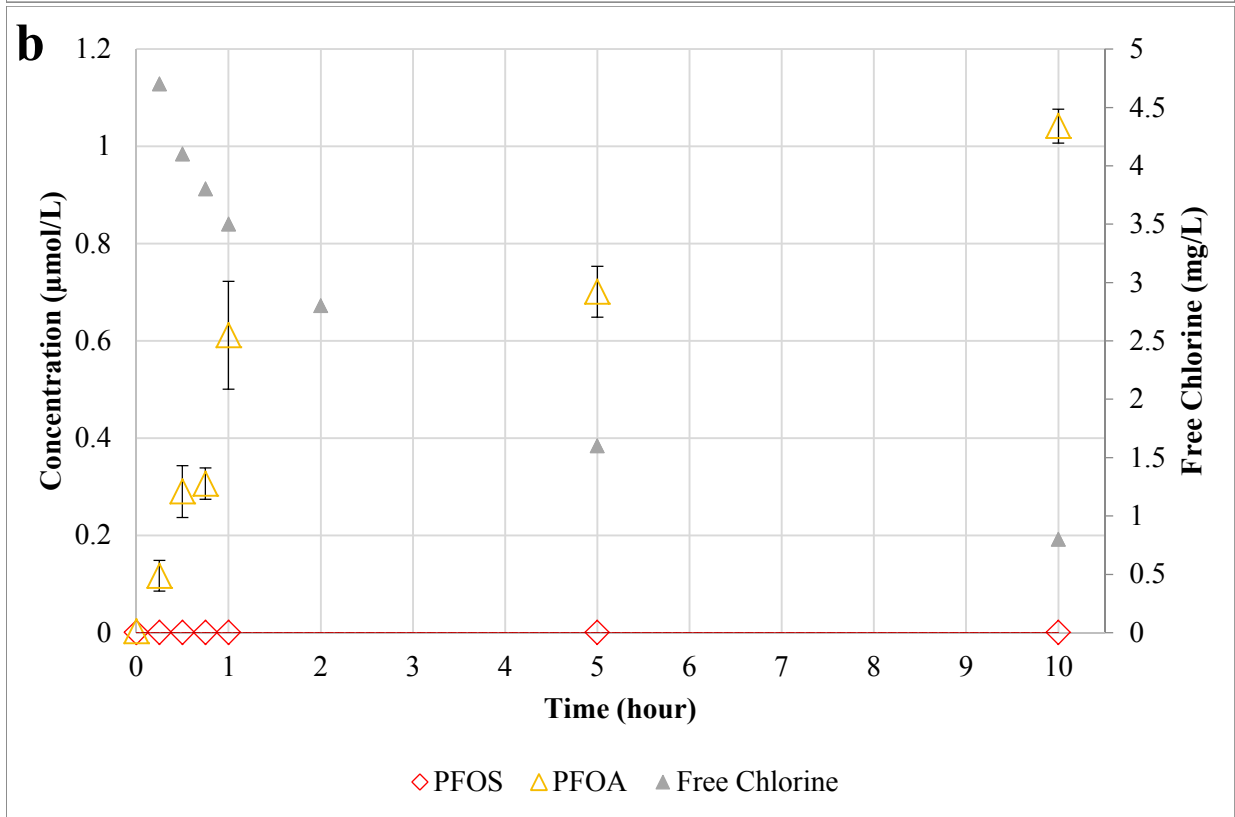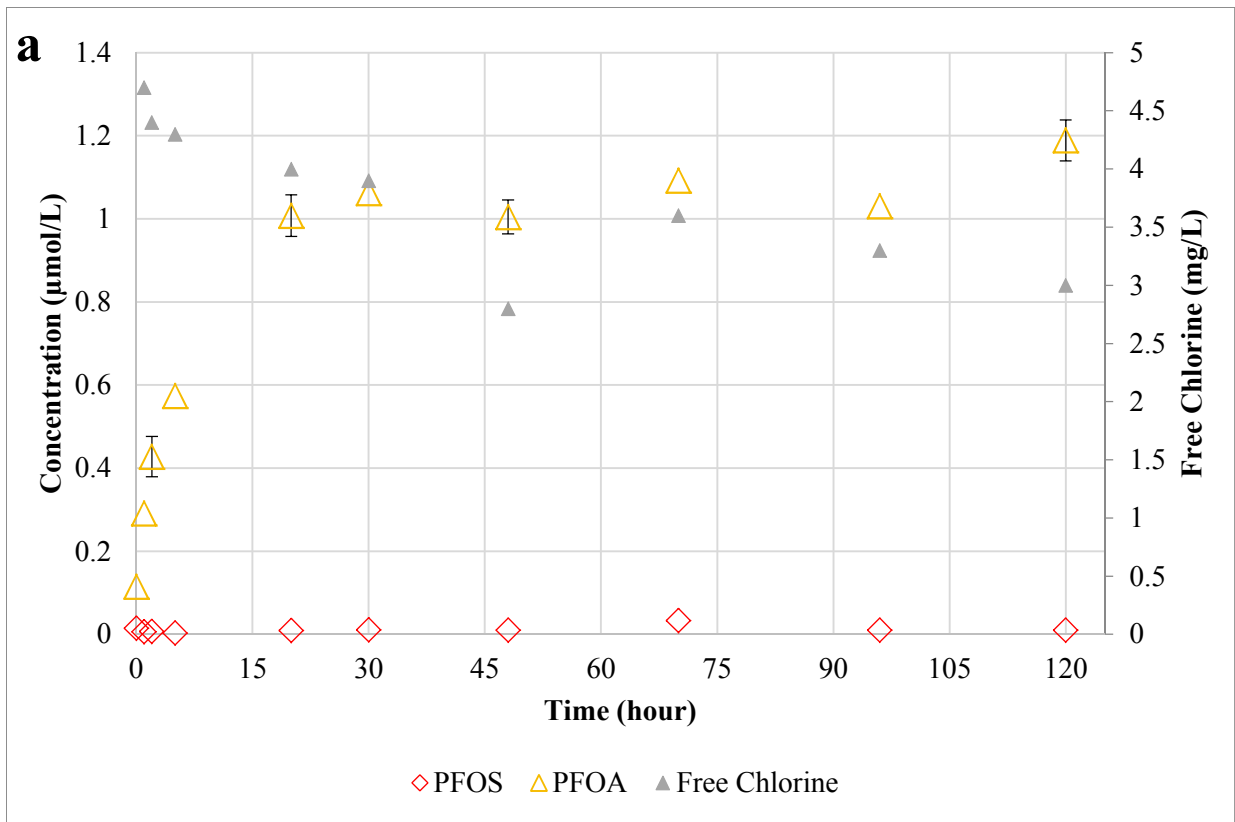
Figure 23: PFOS/PFOA generation in chlorine disinfection experiment in (a) distilled water and (b)surface water.

To make up for this mistake, an experiment with individual compounds was conducted and kept separate. Figure 24 shows the results of the 3-day chlorination of each compound. The results were found to follow, for the most part, our previous results. PFOAAmS, PFOAB, PFOSB decreased by 99.98%, 94% and 50% respectively. PFOSAmS did not have any decrease for this experiment. The generation of PFOA is most noticeable for the PFOAAmS and PFOAB, as expected, at 5860% and 907% respectively. As for PFOS, a 134% and 239% generation for PFOSAmS and PFOSB experiments is observed.

These results show that the perfluoroalkyl carboxylate (PFCA) precursor compounds have no problem degrading during chlorination as a preliminary method of removal. For the perfluoroalkyl sulfonates (PFSA) precursor compounds, it appeared that both may degrade at a small portion, if used as a preliminary method. However, if used as a preliminary method for treatment and removal of these PFASs, the creation of PFOA and PFOS may be observed and should be monitored.
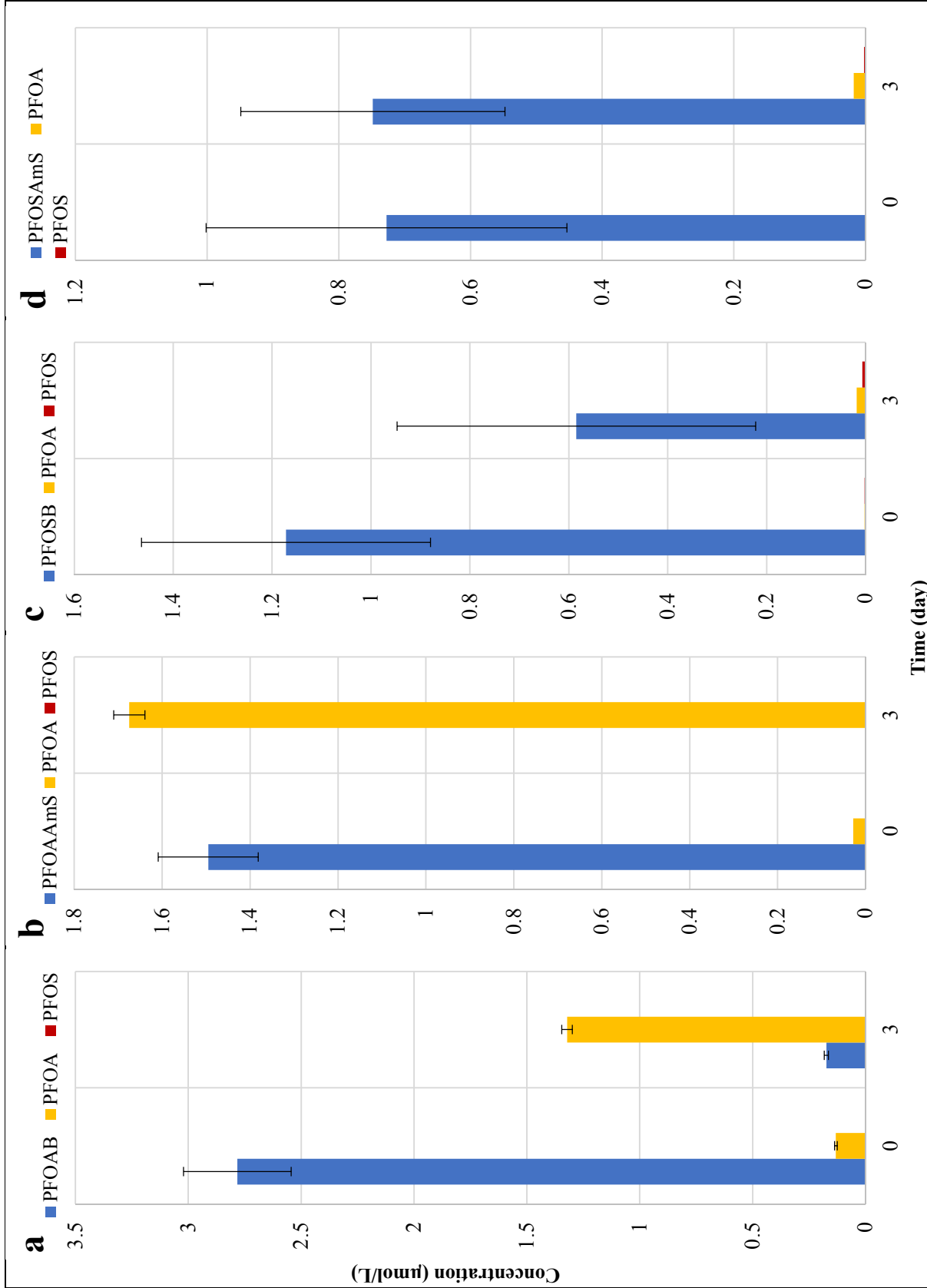
Figure 24: Chlorine disinfection experiment in surface water of individual compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.

3.5. Ozone

As another disinfection method, ozone was hoped to create the same results as chlorination. The first experiment was done with GenX and NaDONA in combination with the other four precursor PFASs using the A2Z Aqua-6 Ozone Generator, which outputs a lower ozone dosage as a model that was purchased later on. Figure 25 shows the concentration over 36 minutes of continuous input of ozone. Unfortunately, the initial samples were unable to be tested. In addition, it can be seen that the 2-min samples may have also been spoiled since they do not match the theoretical concentration. If those are thrown out, there still may be a slight decrease in concentration over the 36-min. Therefore, no conclusions can be made for degradation of GenX and NaDONA at the applied ozone dosage. Throwing out the initials and the 2-min samples for the other four precursor samples, Figure 26 shows that there looks to be a noticeable slight decrease in PFOAB only. As for PFOA and PFOS, Figure 27 shows that no generation occurred. If anything PFOA was shown to decrease by a fraction.
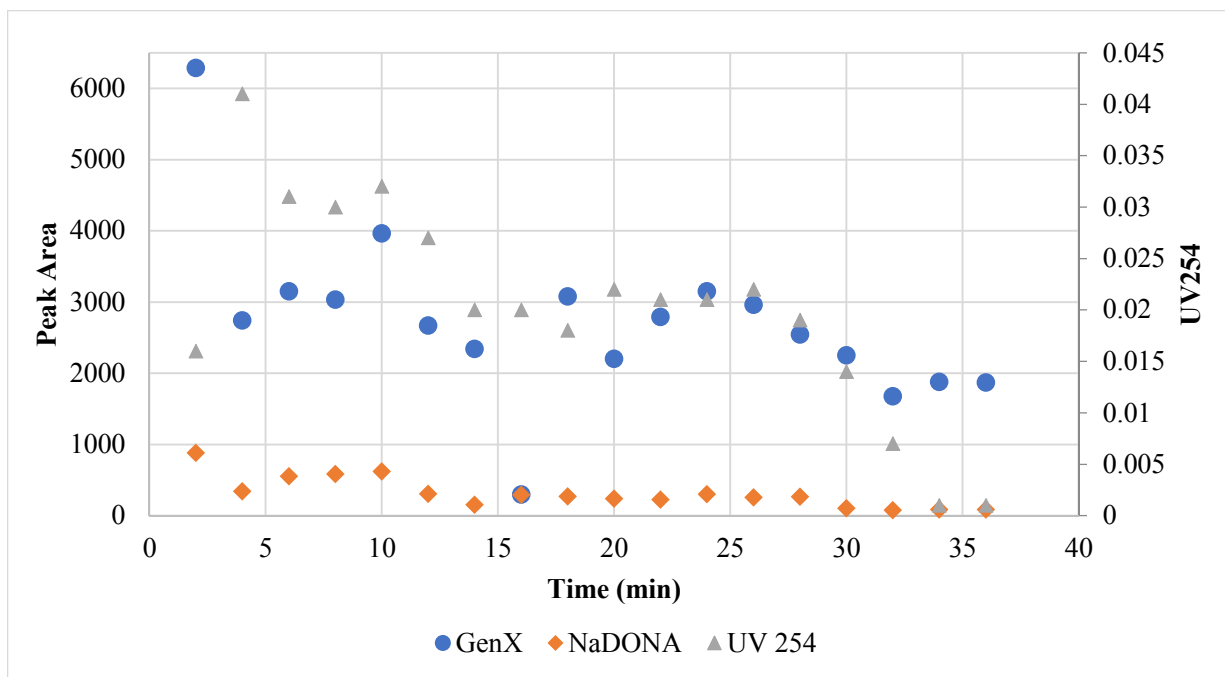
Figure 25: Ozone disinfection experiment of combined compounds (Genx, NaDONA, PFOAB, PFOAAmS, PFOSB, and PFOSAmS) in pure distilled water.
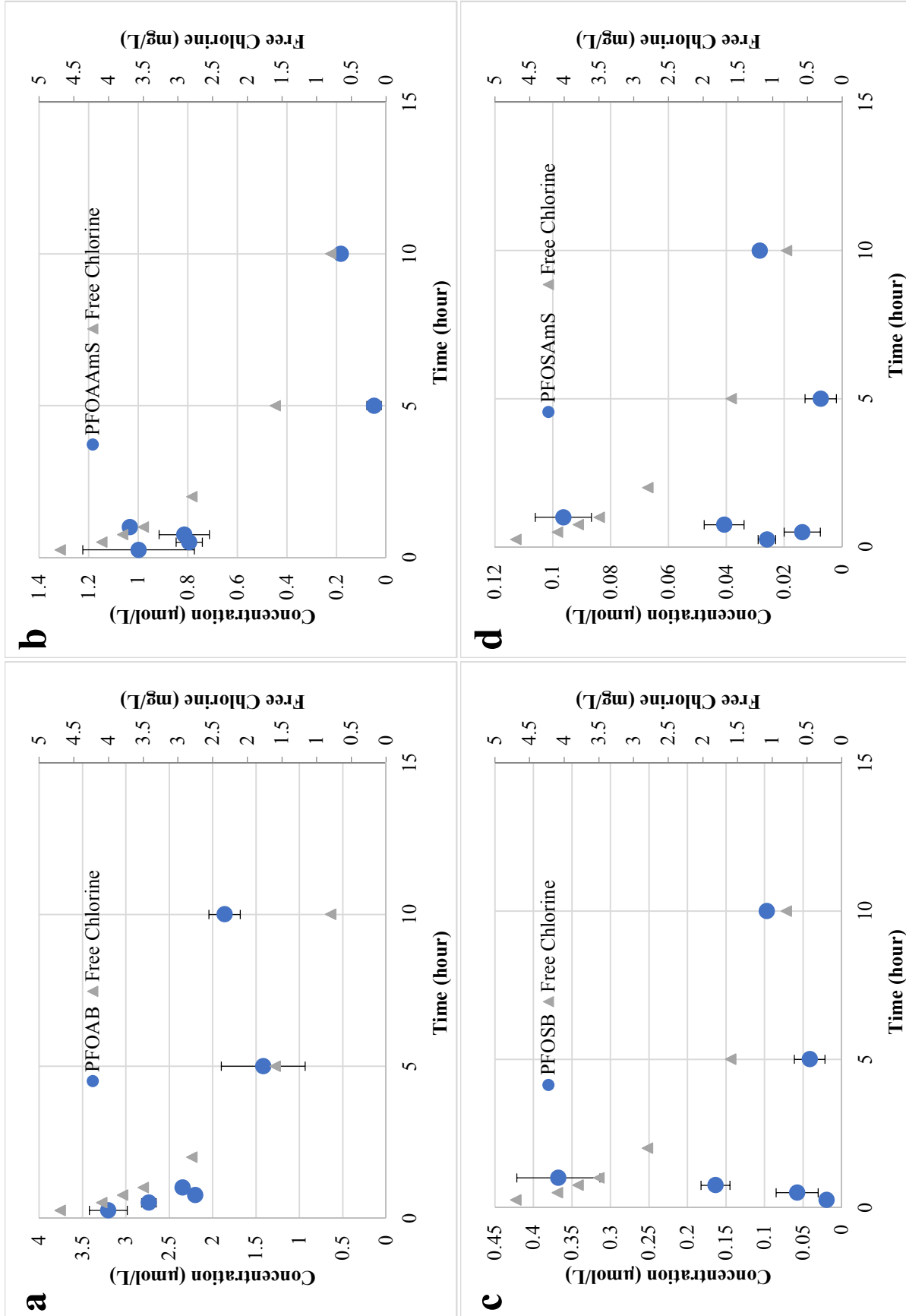
Figure 26: Ozone disinfection experiment in pure distilled water of combined samples: GenX, NaDONA, (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.
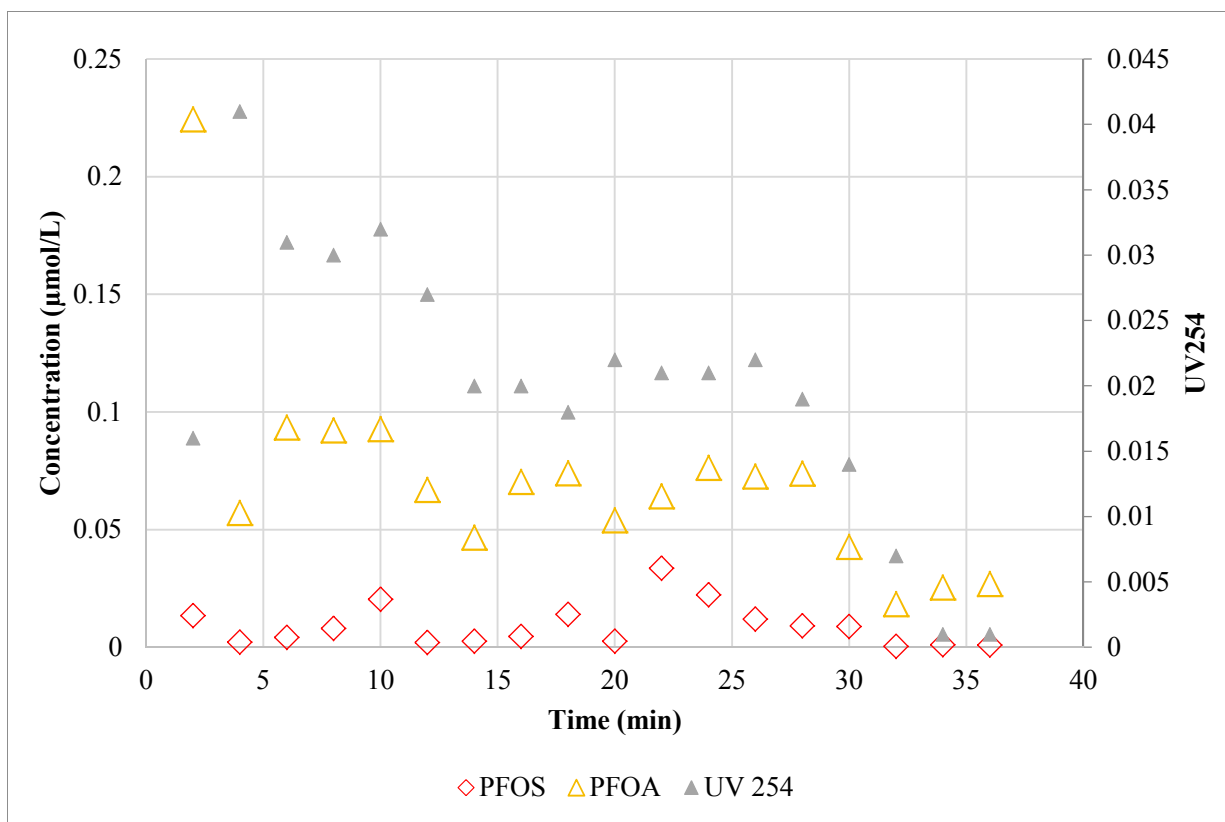
Figure 27: PFOS/PFOA generation in ozone disinfection experiment in pure distilled of combined compounds (GenX, NaDONA, PFOAB, PFOAAmS, PFOSB, PFOSAmS).

Using the same ozone generator, PFOAB was chosen to study individually to confirm its' decrease in concentration. To be compared to this, PFOSB was chosen as the opposite perfluoroalkyl sulfonate PFAS. Both compounds were run independently from each other, so that there would be no competition for disinfectant. This was done in pure distilled water. Figure 28 shows the PFOAB was shown to decrease slightly again (18.5%), as shown in the previous experiment. PFOA seemed to be generated initially, but is unable to be quantified. As for PFOSB in Figure 29, no noticeable decrease can be seen. As for PFOA and PFOS generation, a slight generation can be seen at about 400% and 18% respectively.
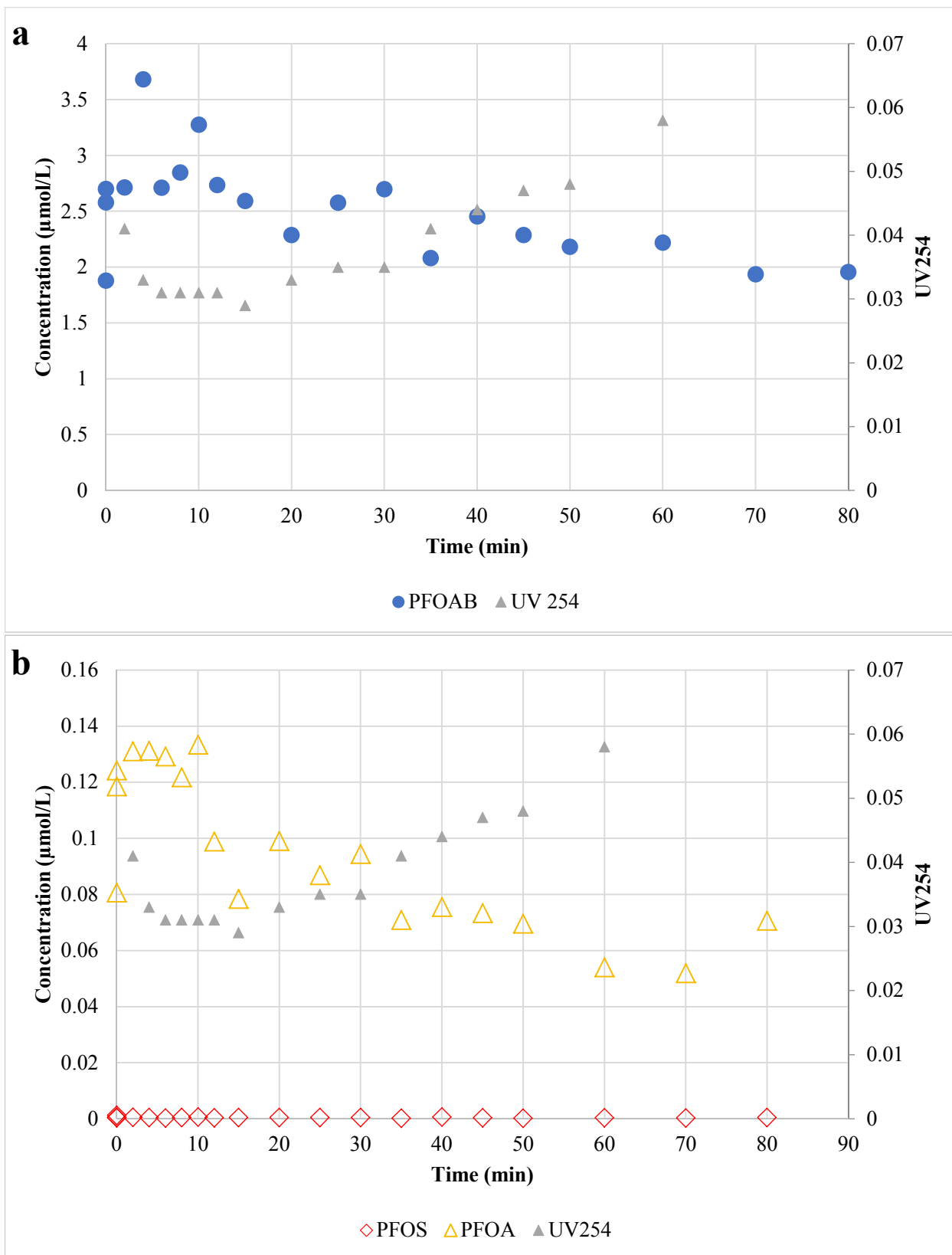
Figure 28: Ozone disinfection experiment in pure distilled water of individual compound (a) PFOAB and the corresponding (b) PFOS/PFOA generation.

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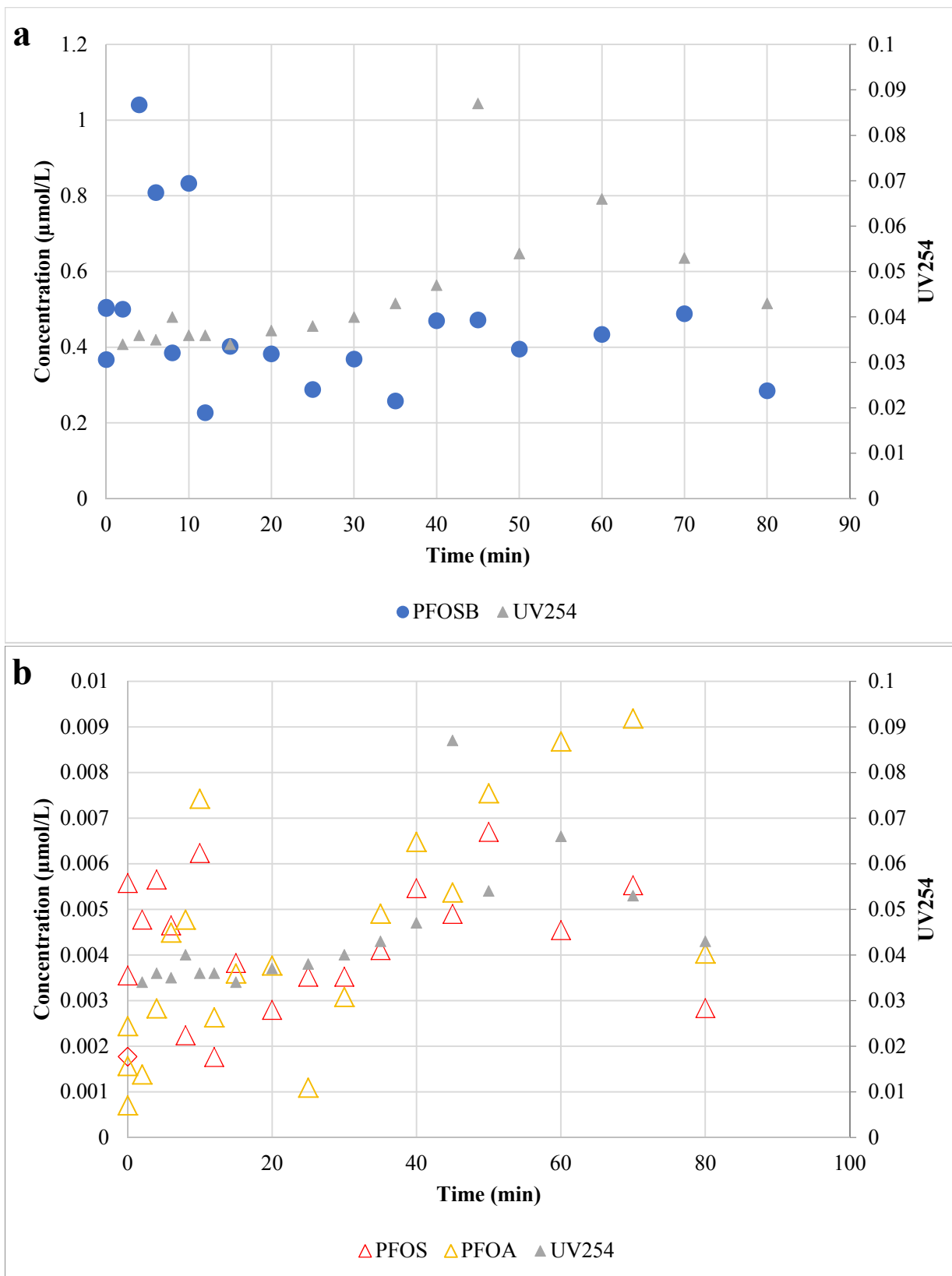
Figure 29: Ozone disinfection experiment in pure distilled water of individual compound PFOSB and the corresponding (b) PFOS/PFOA generation.

Using the same approach and the new A$_2$Z Model Z-7G (A2Z Ozone Inc., Louisville, KY) coupled with pure oxygen input, another set of parallel experiments were conducted for each of the four PFASs in distilled and surface water individually. After the experiment, the samples were combined for analysis. Figure 30 shows that each of the compounds were found to decrease in distilled water, except for PFOAAmS. PFOSAmS appeared to decrease the most at 98.5%, assuming the initials are correct. PFOAB and PFOSB also decreased at 46% and 92% respectively. As for surface water in Figure 31, the results were successful for all four compounds. PFOAB, PFOAAmS, PFOSB, PFOSAmS decreased at 45%, 52%, 96%, and 95% respectively. Figure 32 shows that PFOA and PFOS was not generated for distilled water with higher ozone levels and actually seemed to have a decrease in levels. This would mean that the initial samples were probably spoiled with an unforeseen and unaccounted for addition on PFOA and PFOS or that PFOA was generated very quickly right away and decreased throughout the contact time. The surface water experiment, on the other hand, displayed the results that were expected. PFOA and PFOS increased by 263% and 4317% respectively.

To determine if this could be replicated with less competition, another individual compound experiment was run using the A$_2$Z Model Z-7G (A2Z Ozone Inc., Louisville, KY) without oxygen in pure distilled water. This was to determine if the competition from the other compounds was conflicting with degradation and PFOA/PFOS generation. Figure 33 shows the results of this experiment. It can be seen that PFOSB and PFOSAmS were the only two to degrade at 43.7% and 96.4%. As for generation of PFOS, PFOSB and PFOSAmS were the only two to generate at 44.89% and 1712% respectively. For PFOSAmS, a generation of 1336% PFOA was also found.
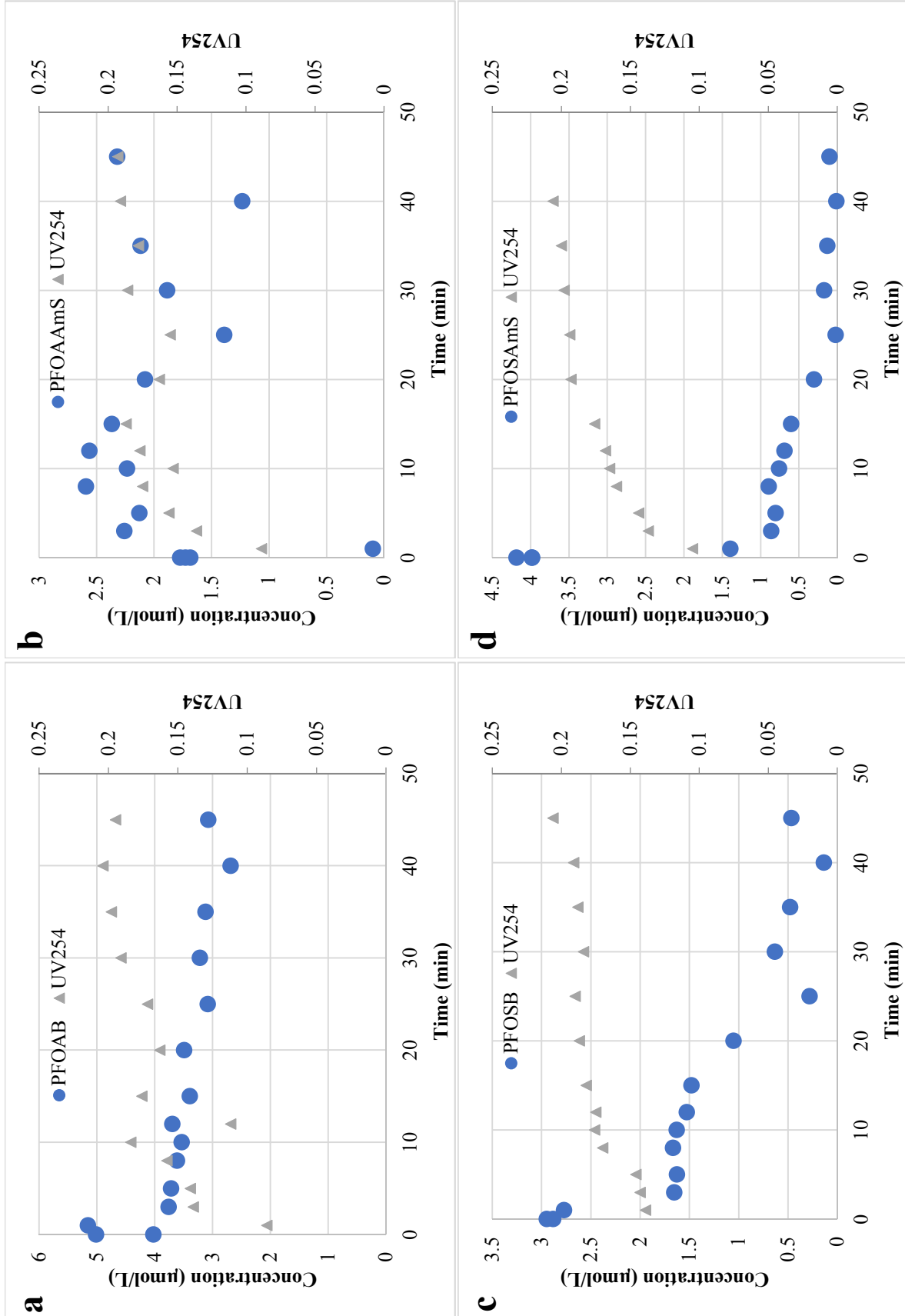
Figure 30: Ozone disinfection with pure O₂ input experiment in pure distilled water of combined samples: (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.
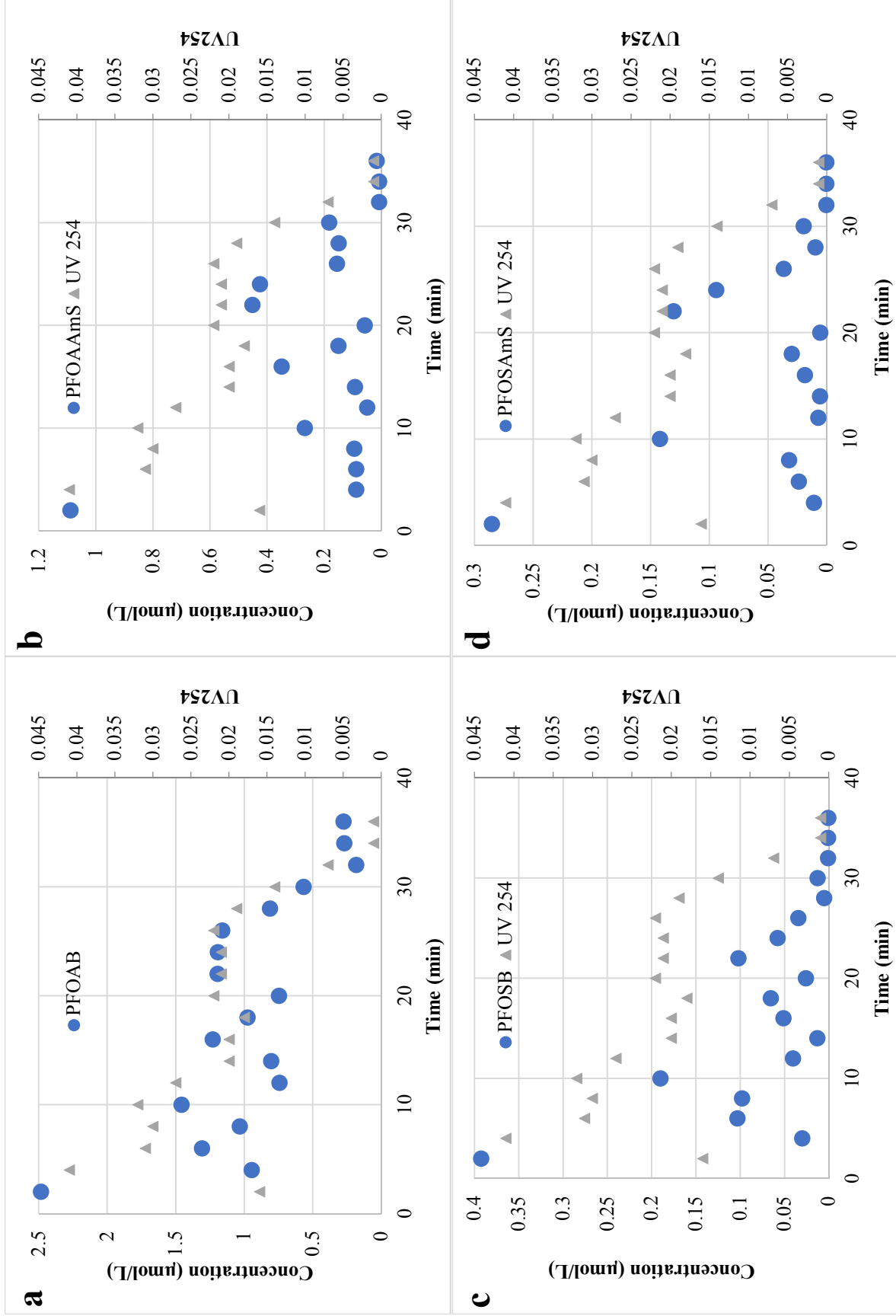
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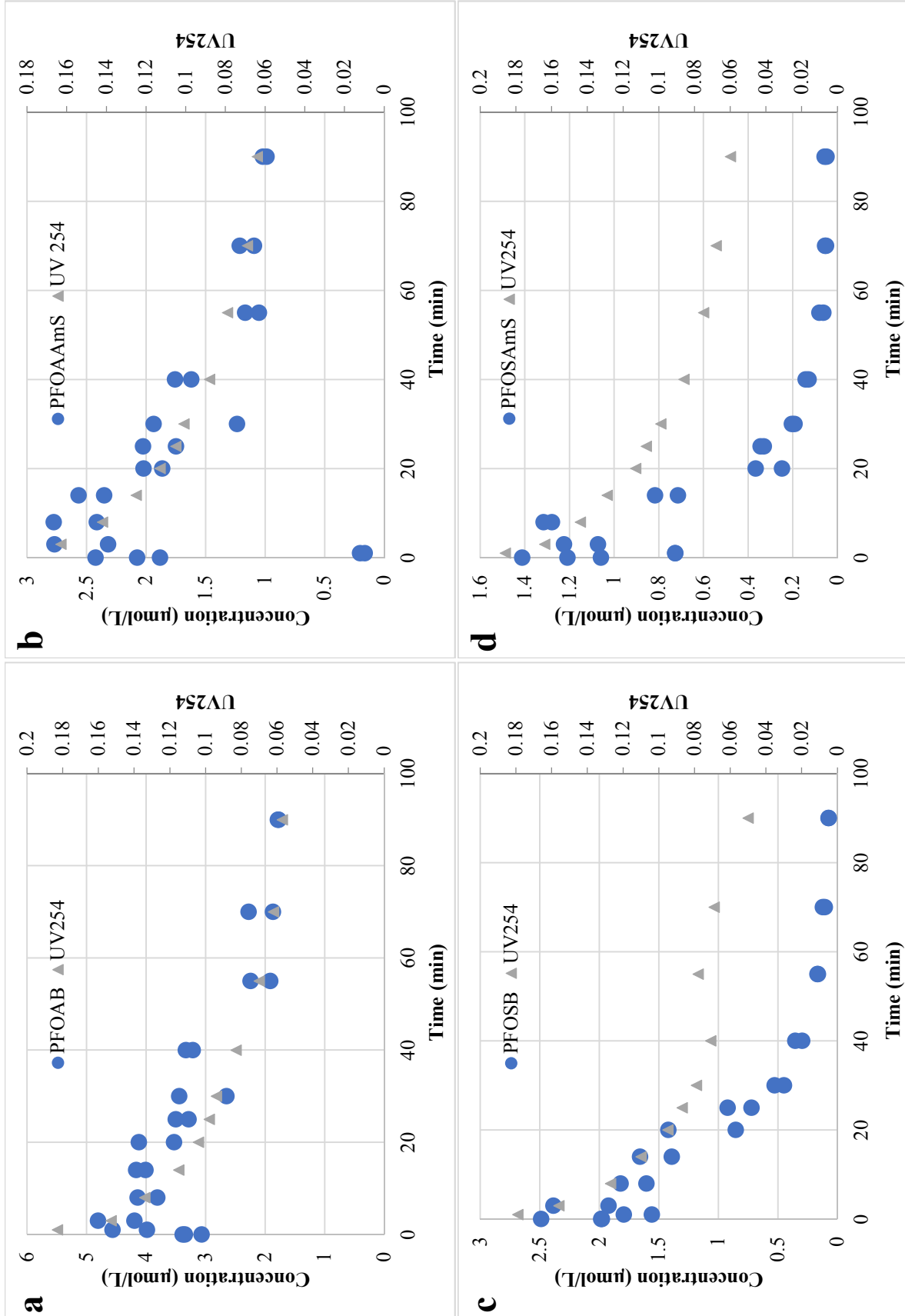
Figure 31: Ozone disinfection experiment with pure O$_2$ in surface water of combined samples: (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.
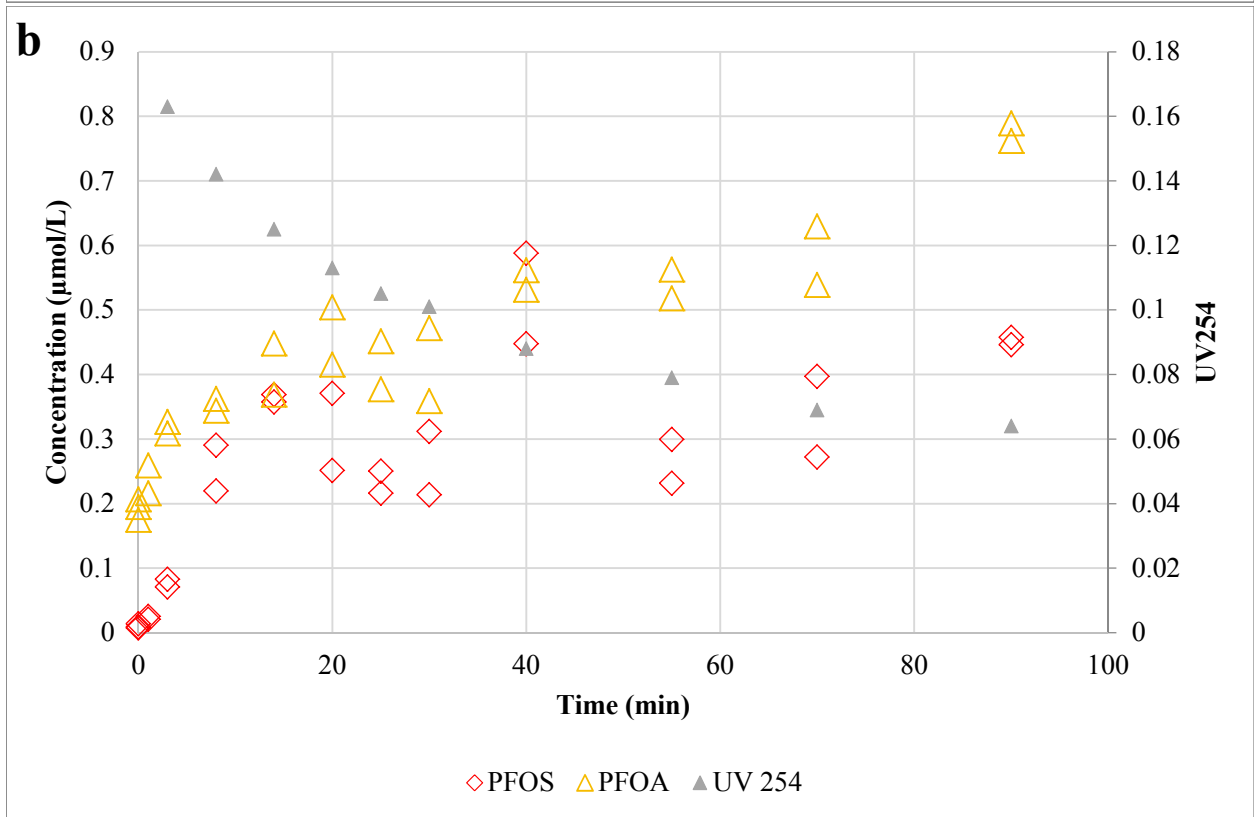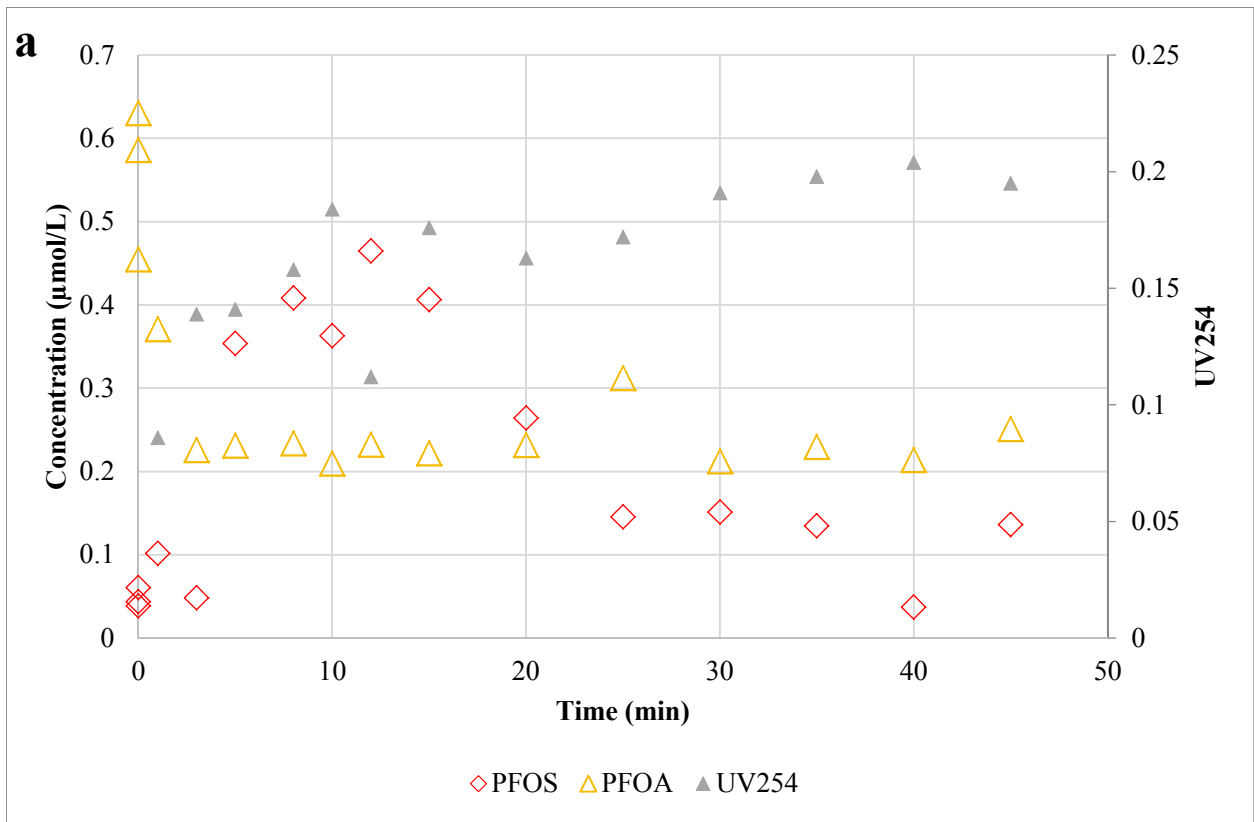
Figure 32: Ozone disinfection experiment with pure O_2 in (a) pure distilled water and (b) surface water of combined samples (PFOAB, PFOAAmS, PFOSB, and PFOSAmS).
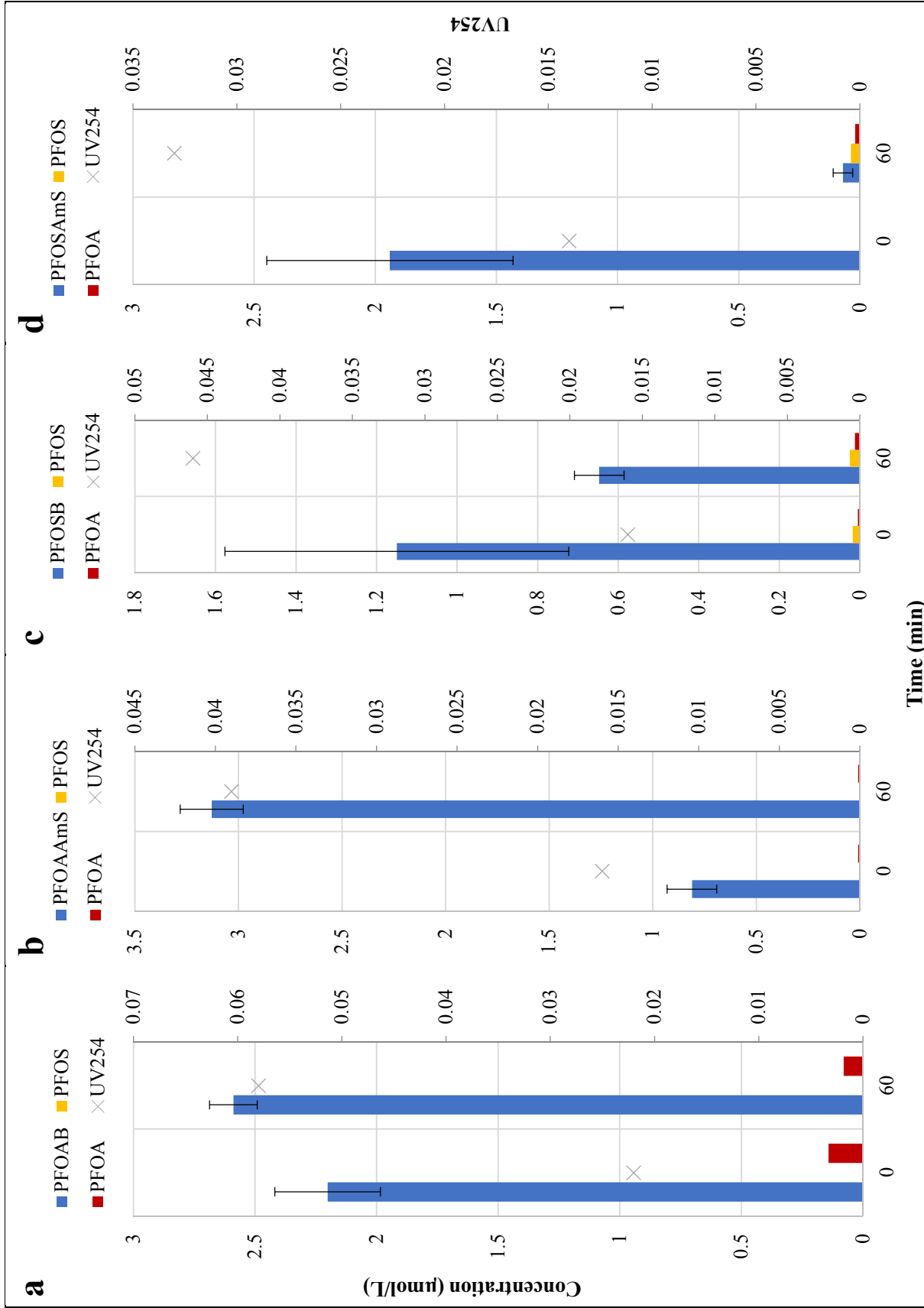
Figure 33: Ozone disinfection experiment in distilled water of individual compounds (a)PFOAB, (b)PFOAAmS, (c) PFOSB, and (d) PFOSAmS.

The stability of ozone largely depends on the water matrix, especially its pH, the type and content of natural organic matter (NOM) and its alkalinity (Hoigne, 1998). It would be expected that the NOM in the surface water samples would cause competition for the free ozone and less decomposition would occur; this was not the case. One hypothesis is that the additional NOM, promote an accelerated transformation from O_3 to the OH radicals (OH•), which have a much stronger oxidation potential, which has been supported by multiple studies (Staehelin & Hoigne, 1985; Vaughan & Blough, 1998; Von Gunten, 2003). Hydroxyl radicals are a non-selective, potent oxidant and being electron-thirsty they are prone to attack the perfluoro-anion and become quenched into hydroxide ions, leaving perfluorinated radicals for continuing chain reactions that lead to further decomposition (Lin et al., 2012). These added OH radicals could potentially be the source of the added biodegradation and PFOA/PFOS generation.

3.6. Discussions

Table 3 is a summary of the range of values that were found for disinfection throughout these experiments. The four newly discovered compounds are qualified as polyfluorinated compounds thereby containing C-H bonds that may be oxidizable. Thus, if ozone or chlorination were able to oxidize polyfluorinated precursors present in the raw water, the concentration of terminal compounds such as PFOS or PFOA may actually increase in finished water. Previous studies have shown indirectly shown similar results of the formation of PFOA and PFOS in various oxidation, aeration, disinfection treatment trains (Appleman et al., 2014; Tagaki et al., 2011, Rahman et al., 2014). Being that it is very unlikely the chemicals generated naturally, the only logical explanation would be a partial degradation of other compounds in the system.

Table 3: Maximum degradation/generation for disinfection experiments.

Experiment	Chlorine		Ozone	
	Distilled	Surface Water	Distilled	Surface Water
Compound	Maximum Degradation	Maximum Degradation	Maximum Degradation	Maximum Degradation
PFOAAmS	99.98	88	ND	52
PFOAB	98	49	46	45
PFOSB	68	ND	92	96
PFOSAmS	68	ND	98.5	95
Compound	Maximum Generation	Maximum Generation	Maximum Generation	Maximum Generation
PFOA	5860	1633	1336	263
PFOS	239	2755	1712	4317

Multiple studies have shown that the oxidation of difficult-to-measure and unidentified PFAA precursors and alternatives has shown to generate stable, easily measured PFCAs (Anumol et al., 2016; Mejia-Avendaño et al., 2016; Mejia-Avendaño et al., 2015; Houtz & Sedlak, 2012; Plumlee et al., 2009; Dinglasan et al., 2004; Wang et al., 2009). These studies consistently provide enough information to determine a rapid transformation from the n:2 fluorotelomer unsaturated carboxylic acids (FTUCA) and n:2 fluorotelomer alcohols (FTOH) to the n-C PFCA during the treatment process. In most of the cases, it was shown that 8:2 FTOH and 8:2 FTUCA, transformed to 8-C PFCAs, namely PFOA. A proposed biodegradation scheme (Figure 34) is based upon results of this laboratory study and built on earlier results presented by (Hagen et al., 1981).
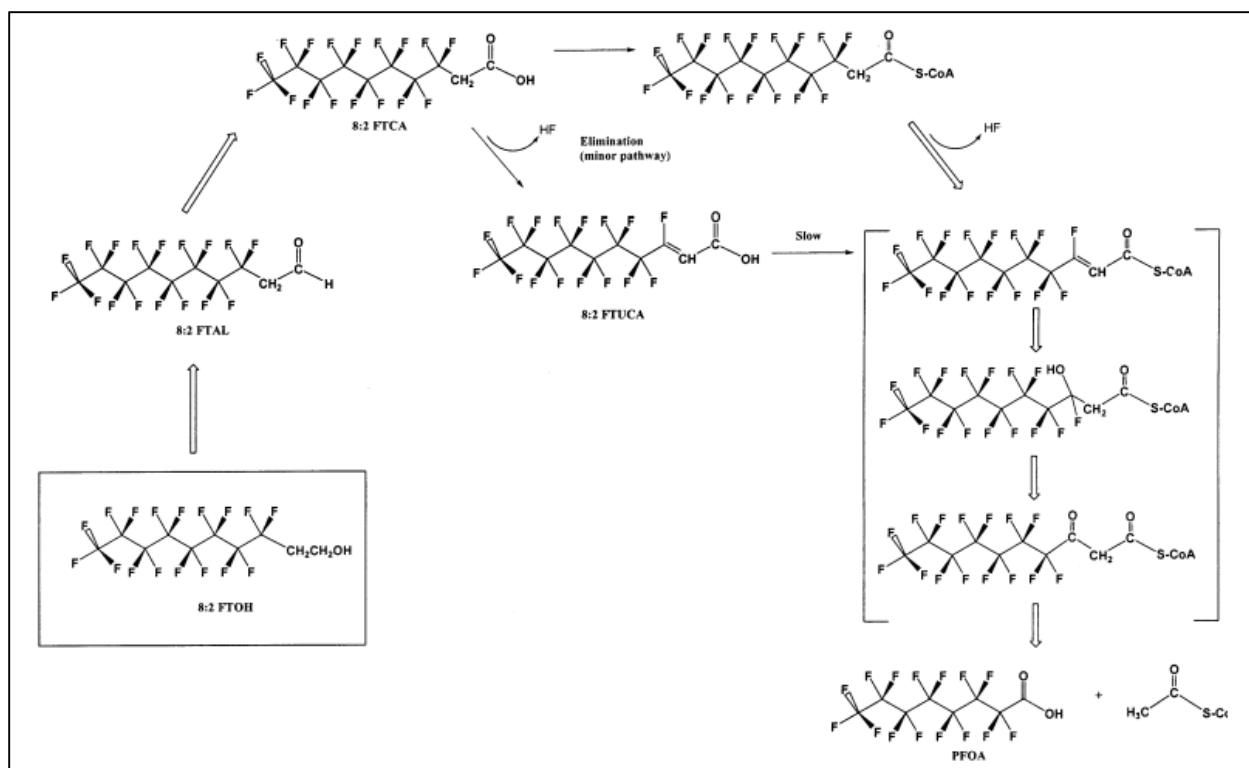
Figure 34: Proposed biodegradation pathway and products of 8:2 FTOH.

Using the same approach, a proposed degradation pathway may be proposed for the
compounds studied in this research. From our results, it was seen that for the parent compound
PFOAAmS and PFOAB were more capable of converting to PFOA than PFOSAmS and PFOSB.
The direct pathways are shown below in Table 4 as well as well as the predicted
biotransformation pathways of PFOSAmS and PFOAAmS presented by Mejia-Avendaño et al.,
2016 in Figure 35.

Table 4: Proposed byproduct (PFOA/PFOS) for each compound.

PFOAAmS		**PFOA**
$F(CF_2)_7CONH(CH_2)_3N(CH_3)_3^+$	→	$F(CF_2)_7COOH$
PFOAB		**PFOA**
$F(CF_2)_7CONH(CH_2)_3N(CH_3)_2(CH_2)CO_2^+$	→	$F(CF_2)_7COOH$
PFOSAmS		**PFOS**
$F(CF_2)_8SO_2NH(CH_2)_3N(CH_3)_3^+$	→	$F(CF_2)_8SO_3H$
PFOSB		**PFOS**
$F(CF_2)_8SO_2NH(CH_2)_3N(CH_3)_2(CH_2)CO_2^+$	→	$F(CF_2)_8SO_3H$
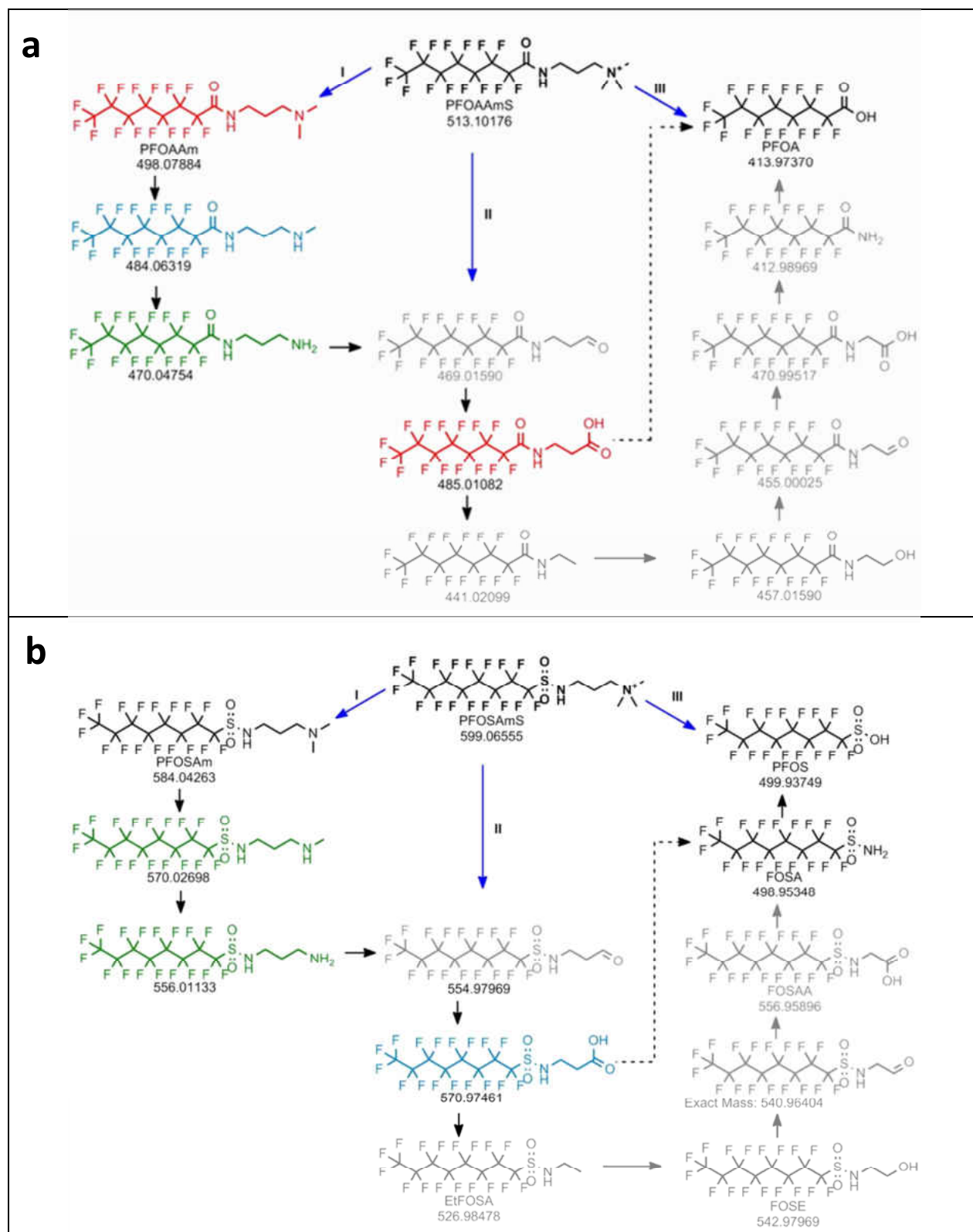
Figure 35: Proposed biodegradation pathway and products of (a) PFOAAmS and (b) PFOSAmS.

It can be seen that both compounds were eventually oxidized prior to the N-H bond and replaced by a hydroxyl found readily in water. From there, oxidation, even by molecular ozone and hydroxyl radicals (Eo = 2.8V), has been reported to have a limited capacity to break down PFOA or PFOS alone (Atkinson et al., 2008; Quinones and Snyder, 2009; Takagi et al., 2011).

It was expected that the PFSAs (PFOSAmS, PFOSB) were expected to produce the same level of PFOS as the PFCAs (PFOAAmS, PFOAB) to PFOA, but this was not observed. This conclusion has been observed previously in a biotransformation study in aerobic soil, in which, PFOA increased to 30.1 mol% of the original PFOAAmS dosed and PFOS reached only 0.3 mol% of the initial mass of PFOSAmS (Mejia-Avendaño et al., 2016). It was hypothesized that one reason for the higher persistence of PFOSAmS is its higher hydrophobicity than PFOAAmS or a high resistance to aerobic microbial degradation. Relating this to a high persistence seen for the case of chlorination, it can be implied that the oxidation and type of oxidant play an important role in the difference of degradation of n≥8 PFSAs and n≥6 PFCAs. This longer chain length and higher molecular weight has been known to cause higher persistence to degradation (Prevedouros et al., 2006). This would be the same assumption for comparing PFOSB and PFOAB.

4. CONCLUSIONS

The extent to which these PFAS precursors play a role in human or environmental exposure to PFOA/PFOS is not well characterized. Drinking water quality leaving the effluent of a water treatment plant may, in some cases, go directly to consumers. This is why it is directly important to study emerging contaminants that may be of concern to the health of the general public. Poly- and per-fluoroalkyl substances have all the necessary components to warrant environmental and health concern. As stated previously; they are toxic, have a bio-accumulative potential and are highly persistent.

Water is one of the most important reserves of PFASs in the environment due to their high solubility. Since most PFASs are extremely resistant to degradation and have therefore been detected ubiquitously in the aquatic environment, the chance for direct use by humans for drinking, agriculture, municipal services and industry is almost inevitable in certain areas. In 2009, PFOA and its precursors were added to Annex B of the International Stockholm Convention Treaty on Persistent Organic Pollutants. However, many municipalities utilize the blending of treated wastewater with freshwater sources to augment water supplies along with urban runoff, which creates a major avenue for PFASs to enter drinking water. This could be especially true for downstream runoff sites of AFFF impacted soil sites. Some widely used treatment methods have been shown to be effective to remove PFASs from water, but new technologies have been tested showing a range of outcomes. That being said, there is still a great need for the expansion of knowledge in treating and removing to nontoxic levels for consumption.

Many water and wastewater treatment plants utilize the methods that were tested in this research. For the PFOA alternatives, it can be seen that the treatment techniques tested in this thesis may are not successful at removing high percentages of GenX and NaDONA. As for the cationic precursor compounds, the results suggest that the possible sorption may be present on the NOM in coagulation and sand filtration, but does not result in significant removal. In advance filtration using activated carbon, the results are conclusive with the hypothesis and the isotherms generated may be used for continuing research into activated carbon efficiency on the PFASs studied. Most interestingly, chlorine disinfection proved to be highly effective against the removal of the PFCA precursor compound, which ended up resulting in a conversion to more persistent and toxic PFASs. The significant generation of PFOA from the PFCA precursors demonstrated that PFAS-based cationic surfactants could be very important PFAA precursors in the environment and through treatment trains. However, this result was not seen for the PFSA precursor compounds. Although the PFSA precursors did not convert to PFOS as readily as the PFCA precursors, they did, however, still degrade in specific ozone trials and a few chlorination trials. This could prove that under the right oxidant and correct conditions, which PFOSAmS and PFOSB could degrade in treatment.

The companies that are attempting to phase-out these compounds may not be successful in their efforts if their unregulated additional PFASs convert to the ones they were trying to phase-out. PFOA and PFOS have been on the radar for many years and were part of the phase-out by major contributors. If these PFCAs (PFOAAmS, PFOAB) are truly capable of converting to PFOA, a strong PFCA, by chlorination, which is a major disinfectant process in water treatment, then these compounds should be seriously considered to be rejected as a

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plausible addition for any PFAS-based manufacturing process and should be avoided at all costs.

PFASs are a proven hazard to environmental and human health and present an important target for environmental chemistry research. This project is a small step towards developing important technologies for the viable and effective treatment of water contaminated with PFOA alternatives, PFAS precursors and other persistent organic pollutants. It also brings to light the continued debated practice of advanced oxidation processes (AOPs) that have been proven to create highly toxic disinfection by-products (DBPs) in finished treated water systems.
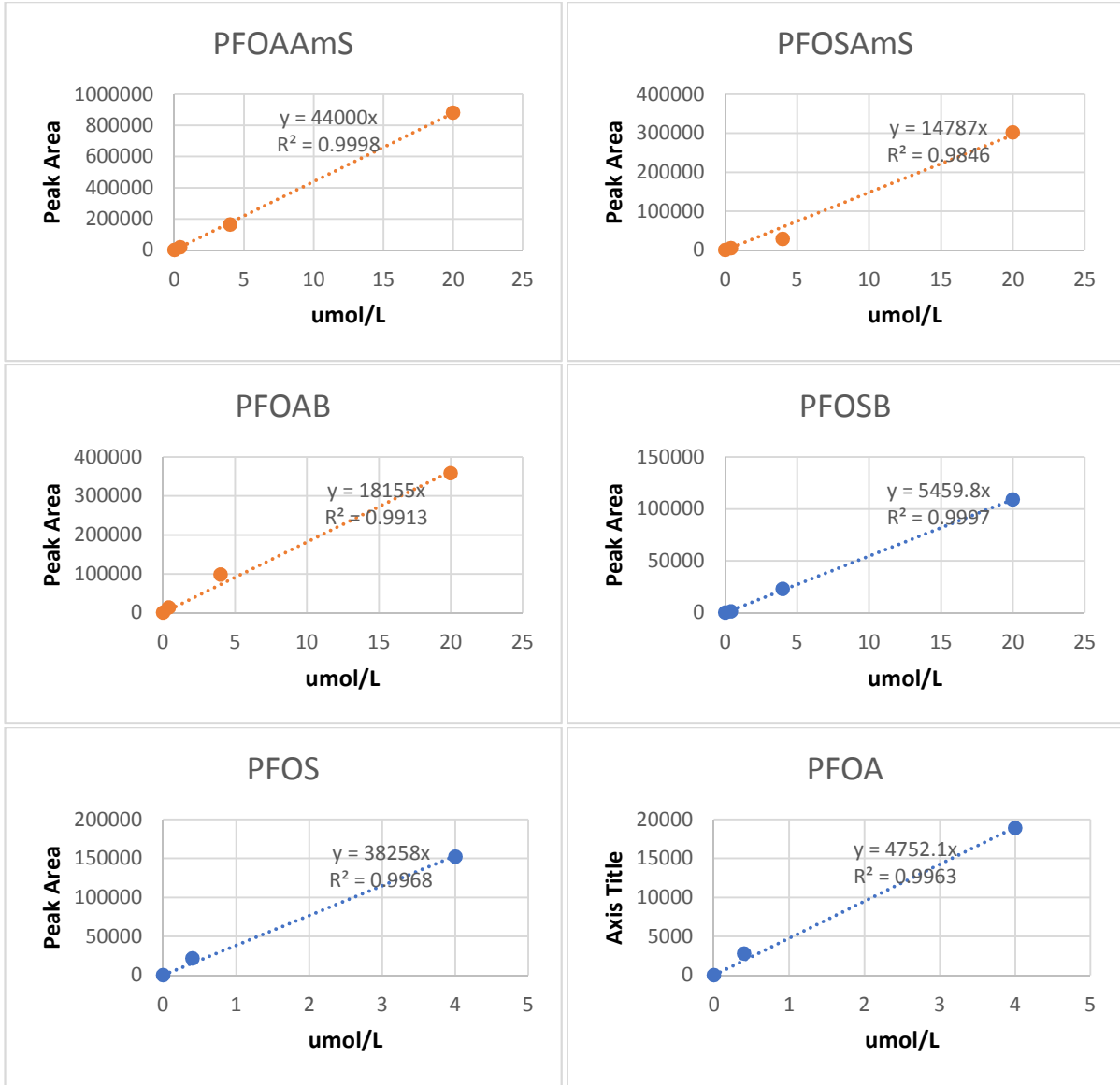
Figure 36: Calibration standard curves.

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