THE REMOVAL OF POLY- AND PERFLUOROALKYL SUBSTANCES BY NORTH AMERICAN WATER TREATMENT PRACTICES

by

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ABSTRACT

Poly- and perfluoroalkyl substances (PFASs) are a group of environmentally persistent man-made chemicals that are being detected in water sources all over the world including surface waters, ground waters, tap waters, bottled water, and municipal wastewater influents and effluents. These chemicals are used as surfactants in a wide variety of commercial and industrial products, creating multiple pathways of exposure to human beings. Numerous studies, both epidemiological and laboratory-based animal studies, have been done to determine the toxicological effects of PFASs and have found correlations between these chemicals and an assortment of adverse effects. One of the most concerning pathways is exposure via contaminated tap waters resulting from the inability of conventional water and wastewater treatment systems to remove these chemicals.

There were two main objectives for this project. The first was to measure the occurrence levels in raw water sources for 20 drinking water treatment utilities across the U.S., and evaluate the efficacy of various treatment processes in their removal of an extensive suite of PFASs including perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), and polyfluoroalkyl chemicals (i.e., PFCA and PFSA precursors). Detected concentrations of the stable end product perfluoroalkyl acids (PFCAs and PFSAs) for all samples collected were in the ng/L range for all utilities in this study with the exception of one, which had levels in the low μg/L range. While the precursor chemicals FOSA, N-MeFOSAA, and N-EtFOSAA were detected in the low ng/L range in some surface waters and treated wastewater effluents, none of the precursor chemicals examined in this study were measured above reporting levels in ground water. More importantly, conventional water treatment techniques such as ferric or alum coagulation, granular/micro-/ultra- filtration, aeration, oxidation (i.e.

permanganate), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) were mostly ineffective in removing PFASs from drinking water. In many cases, the concentration of PFCAs and PFSAs were actually slightly higher following oxidative treatments, suggesting some potential formation of these chemicals from yet unidentified precursors. Advanced treatment technologies, such as anion exchange and granular activated carbon, demonstrated removal of PFASs under some operational conditions. In contrast, reverse osmosis consistently demonstrated significant removal of PFASs from contaminated raw water sources at full-scale drinking water treatment plants.

The second objective was to evaluate two forms of advanced treatments at the bench scale including GAC and nanofiltration (NF). Virgin NF270 flat sheet membranes were tested at pressures ranging from 25 to 125 psi and using spiked deionized (DI) water and spiked artificial ground water (AGW). The effects of membrane fouling by humic acid in AGW was also tested under constant permeate flux conditions. The NF270 membranes, both virgin and fouled, demonstrated >93% removal for all perfluoroalkyl acids under all conditions tested. GAC efficacy was tested using rapid small scale columns packed with Calgon Filtrasorb®300 (F300) carbon and DI water with and without dissolved organic matter (DOM). DOM effects were also evaluated with F600 and Siemens AquaCarb®1240C with spiked and filtered natural river water. The F300 GAC had <20% breakthrough of all chemicals for the entirety of the spiked DI water experiment (125,000 bed volumes (BVs)). A dramatic effect was observed on the carbons when DOM was present, with >20% breakthrough of all PFAAs by 10,000 BVs.

PFASs are being detected in finished tap waters throughout the U.S., making it one pathway to human exposure because conventional water treatment practices are not effective in removing the chemicals. More advanced treatment techniques, such as AIX and GAC, have the ability to remove these chemicals with varying degrees

of success depending on the life of the media and the specific chemicals. Membrane processes, such as NF and RO, have proven to be the most effective methods of treatment. Further research needs to be performed on these less employed techniques as well as the toxicological effects of these chemicals to determine if the cost of upgrading utilities is worth the risk of exposure.

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LIST OF ABBREVIATIONS

Advanced Oxidation Process . . . . . AOP

Anion Exchange . . . . . AIX

Artificial Ground Water . . . . . AGW

Bed Volume . . . . . BV

Dissolved Air Flotation . . . . . DAF

Dissolved Organic Matter . . . . . DOM

Empty Bed Contact Time . . . . . EBCT

Granular Activated Carbon . . . . . GAC

Health Risk Limit . . . . . HRL

Ion Exchange IX

Method Detection Limit . . . . . MDL

Method Reporting Limit . . . . . MRL

Microfiltration . . . . . MF

Minnesota Department of Health . . . . . MDH

Nanofiltration . . . . . NF

New Jersey Department of Environmental Protection . . . . . NJDEP

Perfluoroalkyl Acid . . . . . PFAA

Perfluorocarboxylic Acid . . . . . PFCA

Perfluorosulfonic Acid . . . . . PFSA

Poly- and Perfluoroalkyl Substance . . . . . PFAS

Provisional Health Advisory . . . . . PHA

Rapid Small Scale Column Test . . . . . RSSCT

Reverse Osmosis . . . . . RO

River Bank Filtration . . . . . RBF

Soil Aquifer Treatment . . . . . SAT

Southern Nevada Water Authority . . . . . SNWA

Ultrafiltration . . . . . UF

Ultraviolet . . . . . UV

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CHAPTER 1

INTRODUCTION

Poly- and perfluoroalkyl substances (PFASs) have been receiving an increasing amount of attention in recent years because of numerous studies on their occurrence and fate in the environment as well as their potential toxicity to human beings. These compounds have been detected in waters across the globe, including remote regions in the arctic. Conventional water treatments have limited effects at removing the chemicals, resulting in one pathway to human exposure, and therefore advanced treatment methods must be tested and implemented to protect the population.

The primary goal of this project was to evaluate a variety of treatment practices, both conventional and advanced, in their ability to remove PFASs from water. Most treatments were evaulated on the full-scale. In the case of nanofiltration (NF), bench-scale experiments were necessary because a utility using NF was not available. Based on previous bench-scale studies, conventional treatments were not expected to have an affect on PFASs, but granular activated carbon (GAC), ion exchange (IX), and high pressure membrane treatments such as reverse osmosis (RO) and NF were expected to be effective at removing the chemicals.

The next chapter of this thesis is a literature review that provides an overview of the production and occurrence of PFASs in the environment, focusing mainly on contaminated waters, as well as the potential toxicological hazards associated with these compounds in humans and animal species. It also examines the fate of these chemicals in conventional and advanced water treatment systems.

Chapter 3 contains the results of a full scale study organized by the author in collaboration with the Southern Nevada Water Authority, New Jersey Department of Environmental Protection, Minnesota Department of Health, as well as water treat-

ment utilities across the U.S. The purpose of the study was to evaluate the occurrence of an extensive suite of 23 PFASs, and their fate during various water treatment processes including conventional treatment techniques such as coagulation followed by sedimentation or dissolved air flotation and/or filtration (i.e., granular, ultrafiltration, microfiltration), aeration and oxidation/disinfection (chlorine, chlorine dioxide, ozone, chloramination, potassium permanganate), as well as less frequently employed treatment techniques such as river bank filtration, GAC, IX, and RO. This chapter has been submitted for publication.

Bench-scale work on the removal of PFASs by GAC and NF was also performed, and is detailed in Chapter 4. Rapid small scale column tests were used to evaluate three carbons, including two bituminous coal and one coconut shell carbon, and the effects of competition when dissolved organic matter is present in the water. For the NF experiments, flat sheet NF270 membranes were employed to measure the rejection rates at various pressures and for different membrane conditions, e.g. virgin and fouled membranes. This chapter is also being prepared for submission for publication.

This thesis is concluded with a summary of the main findings from all of the work performed throughout the projects, and the effects these results might have in the water treatment industry. It also includes possible topics for future consideration.

CHAPTER 2

A LITERATURE REVIEW

Poly- and perfluoroalkyl substances (PFASs) are an environmentally persistent group of chemicals that are being found in various types of water sources all over the world, including tap waters. These chemicals have been used in a wide variety of industrial and consumer products including, but not limited to, firefighting foams, paper and cardboard coating materials employed in food packaging, ScotchGard™, and Teflon™. Drinking water is one route of exposure that may have led to increased concentrations in the serum of humans in most developed countries (USHHS 2009), but some of these compounds, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have also been detected in the blood of animals in remote regions of the world. For example, polar bears and harbor seals in the arctic have had both compounds detected in their blood (Houde 2006).

PFOA and PFOS are the two most commonly studied PFASs, and belong to the perfluoroalkyl acids (PFAAs) family. PFAAs are stable chemicals made of a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain. PFAA compounds are man-made chemicals that are stable in both water and soil (USHHS 2009). Conventional water treatment systems have been observed to be ineffective at removing PFAAs (Quiñones 2009). The widespread detection of these chemicals and their persistence in the environment has led the U.S. Environmental Protection Agency (EPA) to establish Provisionary Health Advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 μg/L, respectively, and PFOS and PFOA have been added to the EPA's Contaminant Candidate List 3 (CCL3) published in October 2009 (USEPA 2009). Six of the perfluorinated compounds have also been added to the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR

3). The UCMR 3 contains minimum reporting level (MRL) values for 28 currently unregulated compounds and two viruses. The six PFAAs and their MRLs are PFOS (0.04 μg/L), PFOA (0.02 μg/L), perfluorononanoic acid (PFNA) (0.02 μg/L), perfluorohexane sulfonic acid (PFHxS) (0.03 μg/L), perfluoroheptanoic acid (PFHpA) (0.01 μg/L), and perfluorobutane sulfonic acid (PFBS) (0.09 μg/L) (USEPA 2011).

The inability of conventional water and wastewater treatment systems (Sinclair 2006; Post 2009; Quiñones 2009) to remove PFASs combined with their persistence in the environment and widespread detection has created a concern for the possible toxicological effects they might have on humans. Studies on animals have shown possible hepatotoxicity, reproductive and developmental toxicity, immunotoxicity, hormonal effects, and carcinogenicity from exposure to these chemicals (Lau 2007), and recent epidemiological studies (Grandjean 2012; C8 2012) have observed adverse health effects in humans.

2.1 Fate of PFASs in the Environment

This section describes the manufacturing processes behind PFASs. It also details their application in commercial and industrial products. Finally, it concludes with potential pathways for environmental contamination.

2.1.1 Production

PFASs are mainly produced via two major commercial processes: electrochemical fluorination (ECF) and telomerisation (Martin 2004). In ECF, an organic compound is dissolved or dispersed in anhydrous hydrogen fluoride (aHF). The organic compound used will determine the final product and its purity. For example, 1-octanesulfonyl fluoride ($C_8H_{17}SO_2F$) is used to produce PFOS and 1-heptanecarbonyl fluoride will produce PFOA (Lau 2007). Once these organic compounds are in the aHF, an electric current is passed through them and all of the hydrogen atoms of the organic compound are replaced by fluorine. During ECF, fragmentation of the

alkyl chains can occur, resulting in branching and various impurities in the final product. Perfluorooctanesulfonyl fluoride (POSF) is one product that is formed, and it can be further reacted with methyl or ethyl amine to yield N-ethyl and N-methyl perfluorooctane sulfonamide (N-EtFOSA and N-MeFOSA). These products can be reacted with ethylene carbonate to form N-ethyl (or N-methyl) perfluorooctanesulfonamidoethanol, N-EtFOSE (or N-MeFOSE). These two compounds are the building blocks for 3M's products (Hekster 2002).

The other process, telomerisation, involves the reaction of iodopentafluoroethane with n units of tetrafluoroethene (TFE) (Hekster 2002). This is a two stage process. In the first stage, the perfluoroalkyl iodides are synthesized, and in the second stage the iodide is substituted by a functional group. Two important commercial products are produced directly from this method: perfluorocarboxylic acid (using oleum as the reactant) and perfluoroalkanesulfonyl chloride (using SO_2/Zn and Cl_2). Other products are produced indirectly by ethylenation followed by substitution of the iodide by a functional group of choice. The indirect products are the most important intermediates for perfluorinated surfactant production (Hekster 2002). All undesired products are removed by distillation, and the final products are linear perfluoro-n-alkyl compounds that are more pure than the ones produced by ECF. Telomerisation is a more expensive process because of the starting materials, but results in a more uniform product, and the process is used by Atofina, DuPont, Clariant, Daikan, and Asahi Glass (Hekster 2002).

2.1.2 Commercial Products

The properties of PFASs, most notably their ability to repel water and oil, have made them very appealing to various industries. Fluorinated surfactants are applied to carpets to form a protective, soil repellent coating. Two common product names for this application are ScotchGard™ (3M) and Zonyl™ (DuPont). Fluorinated chemicals are also used to produce water and grease proof paper used in food packaging (Lau

2007). The textile industry applies them for water, oil, soil, and stain repellence (Renner 2001). The leather industry waterproofs leather with them. PFASs also help contribute to the performance of aqueous film forming foams (AFFFs) used for fighting fires. Another application for them is that they are employed to create specialty surfactants for industrial application (Deng 2010).

2.1.3 Pathways into the Environment

According to Prevedouros (2006), chemical releases (both in air and industrial waste) from fluoropolymer manufacturing are responsible for more than 60% of the total emissions of perfluorocarboxylates. Other sources include landfill leaching from discarded products and packaging, wear from the textile and carpet industry, use of AFFFs and disposal of expired AFFFs, and emissions from reapplication to carpets or textiles (Hekster 2002). These sources can emit PFAAs and their precursors into the air, water, and soil.

There is not much information on what occurs after PFASs are released into the environment and how they manage to end up in water sources besides direct discharge. One potentially significant source is urban runoff. Muller (2011) looked at different inputs of PFAAs into a nonindustrial river catchment in Switzerland and found that runoff was a significant source. Also, Houtz (2012) peformed a study looking at PFASs in urban water runoff in San Fransico and detected both end product and precursor chemicals in the ng/L range. The U.S. Health Department (2009) stated that PFAAs do not break down or biodegrade in water or soil, and they are only expected to remain airborne for a few days to weeks before transporting back to water or soil. Adsorption to soil, sediments and sludge is expected to be limited based on the physicochemical properties of PFOA and PFOS, and they are most likely going to accumulate and travel in water sources (Higgins 2006; Prevedouros 2006; Lau 2007).

A question raised is how have PFASs been measured in blood serum of animals in remote areas in the arctic (Houde 2006) if they only travel via water? The answer

proposed is that the precursors are volatile and have the ability to travel in the air for long distances and degrade into PFAAs. A study done by Martin (2002) measured the concentrations of precursors in air and detected six fluorinated chemicals. Three of these, N-EtFOSE, N-MeFOSE, and n-EtFOSA, have the ability to degrade into PFOS. The other three were telomers whose degradation products are unknown as they have yet to be fully investigated (Prevedouros 2006). One potential suspected pathway of the volatilization of these precursors into the atmosphere is via marine aerosol from breaking waves and rough sea conditions as measurements have shown that these fluorinated compounds accumulate on upper sea levels (Prevedouros 2006).

2.2 Toxicology

The toxicological effects of some PFAAs have been studied extensively on a variety of animals including rats, mice, rabbits, hamsters, and monkeys. A few studies have also been done on humans involving inadvertently exposed workers. The effects between species have varied significantly, and for some species there has been variation between genders. This has created complications in determining whether or not PFAAs are toxic to humans.

2.2.1 Hepatotoxicity

Several short term animal studies have shown that PFOS and PFOA are capable of inducing peroxisome proliferation on the activated receptor alpha (Ikeda 1985; Ikeda 1987; Pastoor 1987; Sohlenius 1992; Sohlenius 1993; Berthiaume 2002). Peroxisome proliferator-activated receptor alpha (PPAR-α) agonism has been linked to tumor induction, especially in the liver, by several nongenotoxic carcinogens in rodents (Lau 2007). Vanden Huevel et al. (2006) demonstrated that mouse, rat and human PPAR-α are activated by PFOS and PFOA. Although PFOS was demonstrated to activate PPAR-α, other studies (Thomford 2002a; Thomford 2002b; Seacat 2003) have concluded that there was no evidence of peroxisome proliferation, which is mea-

sured by an increase in acyl-CoA oxidase activity. Seacat et al. (2003) did find a significant increase in relative liver weight in the high-dose male (1.51 mg/kg/day) and the high-dose female (1.77 mg/kg/day) rats exposed to PFOS. They also found increased absolute liver weight, decreased serum cholesterol, and increased serum alanine aminotransferase (ALT) activity in the high-dose males. Thomford (2002a) did not see gross or microscopic morphological alterations in the livers of Cynomolgus monkeys dosed with up to 2 mg/kg/day for 4 weeks. In a 183 day test of Cynomolgus monkeys dosed at 0, 0.03, 0.15, or 0.75 mg/kg/day PFOS, Seacat et al. (2002) found significant increases in relative liver weights in both males and females, but again not enough of a peroxisome proliferation increase to be considered significant.

The data on PFOA reveals more of a link between exposure and peroxisome proliferation, at least in rodents. Klaunig (2003) found that there is strong evidence to support PFOA induced liver toxicity and adenomas via PPAR-α-agonistic mode in rats. However, Yang et al. (2001 and 2002) compared the effects of exposure from PFOA on PPAR-α-null mice to wild ones. In the study of the wild mice, there was an increase in absolute liver weight as well as a significant increase in peroxisome proliferation, but they found that PFOA induced hepatomegaly to the same extent in the PPAR-α-null mice. This suggests that the effects were not PPAR-α-dependent for mice. Although there is evidence of the capability of PFOA to produce liver tumor in rats via peroxisome proliferation, it is possible that this bears little relevance to humans. A number of PPAR-α-agonistic drugs are toxic to rats, but have been used in human treatment for years without resulting in an increase in peroxisome proliferation (Ashby 1994).

Studies have also been done on some of the other PFASs from the PFAA family, including perfluorobutyric acid (PFBA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA), PFHxS, and perfluorobutane sulfonic acid (PFBS). PFBA, PFHxS, PFBuS, and PFDA, like PFOS and PFOA, were found to increase liver

weight in rats at certain doses (Harris 1989; 3M 2001; Hoberman 2003; van Otterdijk 2007a). Male Sprague-Dawley rats were dosed with 10 mg/kg/day PFDoA by Shi et al. (2007), and they found an increase in total serum cholesterol. One test group was dosed with 5 mg/kg/day PFDoA, and absolute liver weight was significantly reduced relative to the control group. Shi et al. (2007) concluded that this may have been due to a marked reduction in body weight.

2.2.2 Reproductive and Developmental Toxicity

There is strong evidence of reproductive and developmental toxicity in animals from PFOA and PFOS exposure. Studies have concluded that reduced fetal weight and increased neonatal mortality are two major symptoms of exposure during pregnancy in mice and rats (Lau 2007; Olsen 2009). Grasty (2003) dosed rats for 4 days during various stages of pregnancy with 25 mg/kg/day PFOS and discovered that there was an increase in neonatal deaths for later exposure periods during gestation. Other studies on the developmental effects of PFOS were performed by Lau et al. (2003) and Case et al. (2001). Lau et al. (2003) dosed pregnant rats on gestation days (GD) 2-21, and saw 95% of the pups died within the first day in the groups whose parent was dosed with 5 or 10 mg/kg/day. In the study by Case et al. (2001), pregnant rats were dosed with up to 3.75 mg/kg/day during GD 6-20. This resulted in a reduction of fetal body weight of 10% for the ones whose parent was dosed with 2.5 mg/kg/day PFOS and 24% reduction for the ones dosed with 3.75 mg/kg/day.

Neonatal mortality and birth weight reductions in mice were also seen as a result of PFOA exposure during a study conducted by Wolf et al. (2007). These mice were given 20 mg/kg/day PFOA for 2 days late in gestation (GD 15-17). Other mice in the study were given lower doses (5 mg/kg/day) during various GDs. Birth weight reductions, growth deficits, and developmental delays occurred in the mice exposed from GD 7-17 or GD 10-17, but not in those treated from GD 13-17 or GD 15-17. Fenton (2007) studied mice that had body weight deficits from exposure to PFOA

and found that by 6.5 weeks of age they were gaining weight faster than the controls. By 18 months of age, obesity and organ specific abnormalities were apparent.

Although there is evidence of PFOA interfering with fetal growth and neonatal mortality, there is little evidence of it interfering with other aspects of reproduction. Butenhoff et al. (2004) performed a two generation reproduction study with both male and female rats dosed with up to 30 mg/kg/day of PFOA and found no effects on estrous cycling, sperm number and quality, mating and fertility, or the histopathology of reproductive organs in the parents or F1 generations. Several studies also found no alterations in the sex organs of rats and monkeys that were dosed with PFOA for 4-26 weeks (Griffith 1980; Thomford 2001; Butenhoff 2002).

2.2.3 Immunotoxicity

Data on the immunotoxicity of PFASs is mostly limited to PFOA. Yang et al. (2000, 2001, 2002a, 2002b) have studied the immunological effects of PFOA exposure on mice. Their results indicated that it can lead to decreased body weight, elevation of liver weight, and decreases in the thymus and spleen weight. Once exposure ceased, spleen and thymus weights returned to normal within 5 to 10 days. Another conclusion reached by Yang et al. (2000), and later confirmed by DeWitt et al. (2007) was that PFOA exposure can lead to the suppression of inflammatory responses and can cause lymphoid organ atrophy and decreased de novo antibody production in certain strains of mice. It has also been shown to cause a dose dependent decrease in adipose tissue that recovers in approximately 2-5 days (Xie 2002; Xie 2003).

Only a few studies have been done on the immunotoxicity of some of the other PFAAs. Studies done on rats exposed to PFOS, PFBA, and PFHxS, and Cynomolgus monkeys exposed to PFOS did not reveal significant morphological alterations in the spleen, thymus, or mesenteric lymph nodes (Seacat 2002; Thomford 2002a; Thomford 2002b; Hoberman 2003; Seacat 2003; 3M 2007; van Otterdijk 2007a; van Otterdijk 2007b). Further studies are warranted on these chemicals as well as PFOA to verify

if immunotoxicity is occurring.

2.2.4 Hormonal Effects

Research has presented that PFAAs can have an effect on thyroid hormones as well as sex steroid hormone biosynthesis. A single dose of PFDA in rats reduced the thyroid hormones, thyroxine (T4) and triiodothyronine (T3), which are primarily responsible for regulating metabolism, and also lowered body temperature and depressed their heart rate (Langley 1985; Gutshall 1988). Gutshall (1989) found that it also reduces the responsiveness of the hypothalamic-pituitary-thyroid (HPT) axis and displaces circulating hormones from their plasma protein binding sites. PFOS is also thought to reduce T4 and T3 hormones by displacement (Lau 2003; Seacat 2003; Lau 2007).

Changes in sex steroid biosynthesis have been linked to PFAAs. PFOA given to adult male rats for 14 days resulted in a decrease in serum and testicular testosterone and an increase in serum estradiol levels (Bookstaff 1990; Cook 1992; Biegel 1995; Liu 1996). These effects could be serious, as hormonal alteration of this kind have been linked to the induction of Leydig cell adenomas seen in rats chronically exposed to PFOA (Biegel 2001).

2.2.5 Carcinogenicity

The carcinogenicity of PFOA has been studied to some extent. PFOA was looked at in two separate 2 year studies in Sprague Dawley rats. Riker (1987) dosed male and female rats with 0, 30, and 300 ppm/day PFOA and saw an increase in testicular Leydig cell tumors in the highest dosed rats. Biegel et al. (2001) found increased incidence of benign hepatocellular, testicular Leydig-cell, and pancreatic acinar-cell tumors in a group of male rats dosed at 300 ppm/day when compared to an ad libitum control and a pair-fed control group. Despite these findings, only one pancreatic carcinoma occurred in the Biegel et al. (2001) study.

PFOS has also been shown to be linked to an increase in liver hepatocellular adenomas in male and female rats. Thomford (2002b) dosed male and female rats with 0, 0.03, 0.1, 0.4, or 1.5 mg/kg/day PFOS for two years. There was an additional group, the recovery group, which was dosed with 1.5 mg/kg/day for one year and then kept on a control diet during the second year. Although there was a significant positive trend in hepatocellular adenomas in the rats dosed for two years, none was seen in the recovery group. The high dose recovery group did, however, show a significant increase in thyroid follicular cell adenomas relative to the controls, but the high dose group fed PFOS for two years did not. These rat studies found significant trends in different types of benign tumors after exposure to PFOS and PFOA, but only one or two of the rats developed carcinomas. Therefore more studies should be done to look at the potential for these adenomas to develop into malignant tumors.

2.2.6 Human Studies

There is plenty of occurrence data on human exposure to PFOA and PFOS throughout the world, but until recently, studies done on the toxicity of PFAAs have been limited to a few epidemiologic studies on occupational cohorts in the U.S. as well as a study in Denmark. These studies were also limited to PFOA and PFOS.

The two most recent studies (C8 2012; Grandjean 2012) did find statistically significant correlations between PFOA and PFOS and adverse health effects. Grandjean et al. (2012) looked at serum antibody concentrations against tetanus and diphtheria toxoids at ages 5 and 7 years from a total of 656 singleton births who were recruited during 1999-2001. The study concluded that elevated exposures to PFAAs were associated with reduced humoral immune response to routine childhood immunizations. In 2012, the C8 Science Panel investigated the relationship between certain types of cancer and exposure to PFOA, and concluded there is a probable link between PFOA and testicular and liver cancer.

Emmett et al. (2006) looked at human exposure to PFOA and found no evidence of adverse liver function. For reproductive and developmental problems, Joensen et al. (2009) found that in subjects exposed to both PFOA and PFOS there was a decrease in sperm number and quality. A study done by Stein (2009) looked at the relationship between PFOA and miscarriage and preeclampsia (pregnancy induced hypertension) in a group of women exposed to elevated levels of PFOA in the Mid-Ohio Valley and found no association between PFOA and miscarriage and a weak association between PFOA and preeclampsia. Steenland et al. (2010) examined seven studies that investigated the correlation of birth weight to PFOA exposure. Two of them found clear evidence of a relationship, but the other five did not find a significant association, which makes it difficult to determine any real conclusions. Lopez-Espinosa et al. (2011) recently performed an epidemiologic study on 3,706 boys and 2,931 girls between the ages of 8 and 18 years old who were exposed to PFOA and PFOS through contaminated water in the Mid-Ohio Valley and discovered a positive correlation between chemical exposure and a delay in pubertal maturation.

Immunotoxicity in humans was considered by Emmett et al. (2006) and Costa et al. (2009). Emmett et al. (2006) found no correlation between serum PFOA levels and lymphocytes, neutrophils, eosinophils, or basophils. Costa (2009) measured serum levels of IgG, IgM, and IgA (antibody molecules) in 34 male workers involved in the production of PFOA and saw 13% of the workers had elevated levels of IgA. However, because levels of these antibodies vary so much in the population and it was such a small study, more evidence is needed to reach a proper conclusion.

Three studies (Olsen 1998; Sakr 2007; Costa 2009) investigated the correlation between PFOA exposure and levels of estradiol and testosterone: Olsen and Costa found no significant association between PFOA and either sex hormone, but Sakr did with both. These conflicting conclusions warrant further testing.

In addition to the C8 (2012) study, there are a few other studies on the carcinogenicity of PFOA and PFOS. A study done in Denmark on PFOA by Eriksen et al. (2009) looked at 55,053 Danish adults between 55 and 65 years old, and followed them between when they signed up for the study (1993-1997) and 2006. They divided them up into quartiles based on their serum PFOA levels. 713, 332, 128, and 67 cases of prostate, bladder, pancreatic, and liver cancers, respectively, were found. There was only a slightly positive association with prostate and pancreatic cancer. In a U.S. occupational study by Lundin et al. (2009), there was some positive trend for prostate cancer based on job category (non-exposed, probably exposed, and definitely exposed). PFOS exposure was investigated by Alexander et al. (2003) who found that bladder cancer mortality was elevated among male workers who worked in high PFOS exposure jobs for more than one year. They did not find any statistically significant effect on mortality for most other types of cancer. Table 2.1 summarizes the toxicological data found on humans, and Table A.1 in Appendix A contains a summary of the toxicological studies on animals.

The U.S. epidemiologic studies were focused on high exposure groups living in areas where PFASs are produced. Drinking water contamination is thought to be one of the main exposure routes to humans. Other possibilities could be inhalation of the compounds or their precursors due to release from manufacturing companies or household product wear. Another form of exposure via the ingestion of contaminated foods that have been wrapped in PFAS containing packages. With relatively long half-lives and multiple exposure routes, it is not surprising that some PFASs are found in the blood serum of most U.S. citizens (USHHS 2009).

2.3 Occurrence of PFASs

PFASs and their precursors have been found in all types of waters throughout the world including surface, ground, tap, bottled, wastewater influents and effluents, industrial waste influents and effluents, rivers, lakes, and tributaries in the U.S.,

Table 2.1: Summary of the toxicological effects of PFOA and PFOS on humans

Toxicity	Effects	PFOA	PFOS	References
Hepatotoxicity	Adverse liver function	no	n/a	Emmett 2006
Reproductive/ Developmental Toxicity	Decreased sperm number and quality	yes	yes	Joensen 2009
	Miscarriage and preeclampsia	no	n/a	Stein 2009
	Late puberty in adolescents	yes	n/a	Lopez-Espinosa 2011
Immunotoxicity	Lymphocytes, neutrophils, eosinophils, or basophils	no	n/a	Emmett 2006
	Reduced humoral immune response to routine childhood immunizations in children aged 5 and 7 years	yes	yes	Grandjean 2012
	Slight increase in IgA levels, but not IgG or IgM antibodies	yes	n/a	Costa 2009
Hormonal Effects	Association with estradiol and testosterone levels	no	n/a	Olsen 1998; Costa 2009
	Association with estradiol and testosterone levels	yes	n/a	Sakr 2007
Carcinogenicity	Slightly positive association with prostate and pancreatic cancer	yes	n/a	Erikson 2009
	Association with bladder or liver cancer	no	n/a	Erikson 2009
	Association with testicular and kidney cancer	yes	n/a	C8 2012
	Some positive trend with prostate cancer	yes	n/a	Lundin 2009
	Elevated bladder cancer mortality	n/a	yes	Alexander 2003

Germany, Canada, South Korea, and Spain (Boulanger 2004; Sinclair 2006; Skutlarek 2006; Nakayama 2007; Ericson 2008; Furdui 2008; Plumlee 2008; D'eon 2009; Post 2009; Guo 2010). Detections have ranged from below detection limits to μg/L in some cases. Skutlarek (2006) found levels of up to 3.04 μg/L perfluorohexanoic acid (PFHxA), 33.9 μg/L PFOA, 1.45 μg/L PFBS, and 5.9 μg/L PFOS in the Moehne River in Germany. These concentrations were much higher than detection levels in most of the other studies which were generally in the low ng/L range. Table A.2 in Appendix A displays the occurrence data found in the literature.

2.3.1 United States

In the U.S., a number of PFAAs have been detected in surface waters including lakes, rivers, and tributaries in the ng/L range or lower (Boulanger 2004; Nakayama 2007; Furdui 2008; Plumlee 2008). They have also been detected in ground waters in the ng/L range or lower (Plumlee 2008; Post 2009). Sinclair et al. (2006) measured levels of several PFASs and two fluorotelomer precursors in effluents from wastewater treatment plants in New Jersey and detected concentration in the low ng/L range for all of the compounds tested except for PFOA which had median concentrations ranging from 67 ng/L to 697 ng/L. More details on the occurrence levels in these studies are provided in Table A.2 and in Chapter 3.

2.4 Water Treatment

Few studies have been done on the effectiveness of various treatment methods for the removal of PFAS compounds. Quiñones et al. (2009) looked at full-scale conventional treatment methods. Bench scale experiments with granular activate carbon (GAC) and ion exchange (IX) were performed by Lampert et al. (2007). There have been several studies on removal using membranes (Tang 2006; Steinle-Darling 2008; Quiñones 2009). Limited data are available on soil aquifer treatment (SAT), and coagulation/flocculation, filtration, and disinfection have yet to be studied

as standalone operations. Quiñones et al. (2009), Post et al. (2009), and Takagi et al. (2008) also looked at removal using various treatment trains in full-scale water treatment utilities.

2.4.1 Conventional Treatment Methods

Quiñones et al. (2009) compared the influent and effluent at several different drinking water treatment facilities. Three utilities used a treatment train consisting of conventional treatment processes. Processes used varied by utility, but consisted of coagulation/flocculation, filtration, deep bed filtration (DBF), chloramination, medium pressure ultraviolet, chlorination, and ozonation. Despite which treatment train was used, there was little to no attenuation of PFHxA, PFNA, PFDA, PFUdA, PFDoA, PFHxS, PFOA or PFOS. The result of this initial study suggests that conventional treatment methods are not effective in removing PFASs, and helps explain why coagulation/flocculation, filtration, and disinfection have not been studied as standalone operations.

2.4.2 GAC

Lampert et al. (2007) did a study on various doses of GAC for the removal of PFOA and PFOS. They saw >90% removal for both compounds when a dose of 0.1047 g or greater and one week of contact time was used during a batch study. When 0.0587 g GAC and one week of contact time was used, the results were about 50% removal of PFOA and 82% removal of PFOS. More PFASs and other types of activated carbon, powdered activated carbon for example, need to be studied in order to further understand the effectiveness behind this treatment method. If multiple PFASs are present in the feed solution, then perhaps competition will occur and only the largest PFASs will be attenuated.

2.4.3 IX

Lampert et al. (2007) also looked at different absorbents for the removal of PFOA and PFOS using IX, specifically with anion exchange (AIX) resins. Using the A-714 absorbent and 25 hours of contact time, their studied showed a >99% removal of both compounds. The lowest removal (˜33%) was found using the A-244 absorbent with 25 hours of contact time. This study looked at six different resin types, and all with the same contact time. Further studies are warranted to look at other resins as well as variable contact times. Regeneration also needs to be investigated as it will greatly affect the cost of implementing an ion exchange system intended for PFAS removal.

2.4.4 Membrane Processes

Steinle-Darling et al. (2008) investigated using nanofiltration (NF) with TFC-PA membranes: DK, DL, NF270, NF200 for the removal of perfluoropentanoic acid (PFPeA), PFOA and PFOS and saw ˜70%, >95%, and >95% removal of each, respectively. They also used TFC-PA membranes: DK, NF90, NF270 and witnessed a >90% decrease in the amount of PFOS. Tang et al. (2006) observed >99% removal of PFOS during RO using TFC-PA membranes: ESPA3, LC3, BW30, SG. Although RO and NF have been shown to be effective at removing PFOA and PFOS, several questions arise that need to be addressed. Are NF membrane pores small enough to exclude some of the smaller PFASs? How effective are the membranes at removing PFASs once they start to foul? Does the presence of PFASs cause the membrane to foul more rapidly? And, what is the best way to dispose of the concentrate?

2.4.5 Chemical Oxidation

The effects of indirect photolysis on PFAS precursor 8:2 FTOH was studied by Gauthier et al. (2005). Evidence from their study suggests that 8:2 FTOH undergoes indirect photolysis with the hydroxyl radical as the main degradation agent.

The photodegradation of 8:2 FTOH produced 8:2 FTAL, 8:2 FTCA, 8:2 FTUCA, PFOA and PFNA. In an effort to understand the pathways of photolysis, the photodegradation of 8:2 FTUCA was examined, and it produced considerable quantities of PFOA. In a separate study done by Plumlee et al. (2009), the effects of hydroxyl radical induced photolysis were tested on N-EtFOSE, N-EtFOSAA, N-EtFOSA, and FOSAA. The results of this study indicate that the four compounds do degrade and their final products are PFOA and FOSA, which did not undergo additional degradation. The photodegradation of these PFAS precursors may be an explanation for the detection of PFOA in water sources in remote regions since the precursors might be more volatile than the end-product PFASs.

2.4.6 SAT

Only two studies have been done on the effectiveness of SAT systems. One is an unpublished work from Colorado School of Mines (2010) that used river bank filtration (RBF) on drinking water and resulted in little attenuation of PFOA and PFOS with a 10 day subsurface travel time. Snyder et al. (2010) studied using SAT with a 2 year subsurface travel time on drinking water and observed a 28% decrease in PFOA and an increase in the concentration of PFOS.

2.4.7 Treatment Trains

Quiñones et al. (2009) saw the best removal of PFHxA, PFOA, PFNA, PFHxS, and PFOS using a treatment train consisting of microfiltration (MF)/RO, ultraviolet (UV) (medium pressure), followed by SAT. This treatment train caused concentrations to drop from the low ng/L range to below detection levels. Their success in removing these substances was most likely due to use of RO. Takagi (2008) looked at the effectiveness of rapid sand filtration followed by GAC and then chlorination on PFOA and PFOS and measured a drop from 92 ng/L to 4.1 ng/L and 4.5 ng/L to $<$0.1 ng/L, respectively. Based on the previously mentioned studies, GAC was most

likely responsible for the majority of removal. In 2010, Snyder et al. detected >90% removal of PFOA and >95% removal of PFOS using ESPA2 membranes with 85% recovery and 70 MGD flow using a treatment consisting of MF/RO/UV-advanced oxidation process (AOP)/direct injection (DI). Again, their success was likely due to membrane filtration using RO.

2.5 Conclusion

End-product PFASs and their chemical precursors are being detected in waters all over the world. There is some uncertainty about their toxicity in human beings, but a few epidemiologic studies that have been done show enough correlation to recognize these as potentially hazardous chemicals. Studies have revealed that these compounds are capable of causing a wide variety of problems in animals. Some of these symptoms appear to be reversible (effects on the spleen and thymus), while others are irreversible and potentially lethal (effects on reproduction and development). PFASs are extremely persistent in the environment and have relatively long half-lives in human beings. Therefore further studies must be done to reveal the real potential threats these chemicals have on humans.

Conventional methods of wastewater treatment are ineffective at removing PFASs. This means that wastewater treatment plants' effluent can contain varying quantities of these chemicals and their precursors when the effluent is released into the environment. Drinking water treatment plants downstream will then have contaminated influents, and since conventional methods of water treatment have also been shown to be ineffective, humans will be exposed via contaminated tap water. The concentration of these compounds in the drinking water will vary depending on the source of contamination—whether it is industrial or wastewater effluents. The limited bench-scale studies that have been done on advanced treatment methods have shown promising results for the removal of these chemicals, especially GAC, IX, and NF/RO membrane filtration. These methods as well as other advanced treatment

methods need to be explored further to verify their effectiveness at removing PFASs from contaminated water sources.

CHAPTER 3

TREATMENT OF POLY- AND PERFLUOROALKYL SUBSTANCES IN FULL-SCALE DRINKING WATER SYSTEMS

The near ubiquitous presence of poly- and perfluoroalkyl substances (PFASs) in humans and wildlife throughout the world has raised concerns about potential human exposure to these persistent and bioaccumulative chemicals. One potential pathway for human exposure may be the consumption of contaminated drinking water. This study measured concentrations of PFASs in raw water sources and evaluated various full-scale treatment techniques for the attenuation of PFASs in 20 drinking water treatment utilities throughout the U.S. A liquid-chromatography tandem mass-spectrometry method was used to enable measurement of a suite of 23 PFASs, including perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and various polyfluoroalkyl compounds (i.e., potential PFCA and PFSA precursors). While the precursor chemicals FOSA, N-MeFOSAA, and N-EtFOSAA were detected in the low ng/L range in some surface waters and treated wastewater effluents, none of the precursor chemicals examined in this study were measured above reporting levels in ground water. More importantly, conventional water treatment techniques such as ferric or aluminum sulfate coagulation, granular/micro-/ultra- filtration, aeration, oxidation (i.e. permanganate), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) were mostly ineffective in removing PFASs from drinking water. In many cases, the concentration of PFCAs and PFSAs were actually slightly higher following oxidative treatments, suggesting some potential formation of these chemicals from yet unidentified precursors. Advanced treatment technologies, such as anion exchange (AIX) and granular activated carbon (GAC), demonstrated removal of PFASs under some operational conditions. In contrast, reverse osmosis (RO) con-

sistently demonstrated significant removal of PFASs from contaminated raw water sources at full-scale drinking water treatment plants.

3.1 Introduction

Poly- and perfluoroalkyl substances (PFASs) are a group of chemicals that have been used directly in or as part of the manufacturing of a wide variety of industrial and consumer products including, but not limited to, firefighting foams, paper and cardboard coating materials employed in food packaging, ScotchGard™, and Teflon™. One of the most frequently utilized classes of PFASs are the perfluoroalkyl acids (PFAAs), which are stable chemicals made of a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain. These chemicals, which include carboxylic acids such as perfluorooctanoic acid (PFOA) and sulfonic acids such as perfluorooctane sulfonic acid (PFOS), are manufactured mainly by two major commercial processes: electrochemical fluorination and telomerisation (Martin 2004). During these processes, precursor chemicals are created and utilized as building blocks for the end product PFAAs. These PFAAs are stable in both water and soil, and persistent in the environment (USHHS 2009).

In the U.S., a number of PFAAs have been detected in surface waters including lakes, rivers, and tributaries in the ng/L range or lower (Nakayama 2007; Furdui 2008; Plumlee 2008), and they have been detected in ground waters in the ng/L range or lower (Plumlee 2008; Post 2009). Several PFAAs were also detected in effluents from wastewater treatment plants in New Jersey, with concentrations in the low ng/L range for all of the chemicals tested, except for PFOA, which had median concentrations for each utility ranging from 67 ng/L to 697 ng/L (Sinclair 2006). The persistence of PFAAs in the environment and widespread detection has created a concern for the possible exposure to animals and humans. Some of these chemicals, such as PFOA and PFOS, have been detected in the blood of animals in remote regions of the world, e.g., polar bears and harbor seals in the arctic (Houde 2006). Animal

studies have shown possible hepatotoxicity, reproductive and developmental toxicity, immunotoxicity, hormonal effects, and carcinogenicity (Lau 2007).

As far as human health is concerned, some of these chemicals have also been detected in finished/tap waters in the low ng/L range (Post 2009; Quiñones 2009). Drinking water exposure is one pathway that has likely led to increased concentrations in the serum of humans in most developed countries (USHHS 2009). A few epidemiological studies on humans have shown some adverse health impacts from exposure, including a recent report from the C8 Science Panel that linked PFOA to testicular and kidney cancer (C8 2012) and another study that found an association between PFOA and PFOS exposure and a reduced humoral immune response to routine childhood immunizations in children aged 5 and 7 years (Grandjean 2012). The potential toxicity, widespread detection, and potential presence in drinking water has led the U.S. Environmental Protection Agency (EPA) to establish Provisionary Health Advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 µg/L, respectively. In addition, PFOS and PFOA have been added to the EPA's Contaminant Candidate List 3 (USEPA 2009). These two chemicals as well as perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorobutane sulfonic acid (PFBS), and perfluorohexane sulfonic acid (PFHxS) were also added to the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR 3) (USEPA 2011). Since some PFAAs have been shown to have a potential to harm humans, it is imperative that treatment options are examined for their ability to remove these chemicals from contaminated drinking waters.

Previous studies assessed the occurrence of PFAAs in raw and finished waters of conventional drinking water treatment trains consisting of coagulation/flocculation, filtration, ozonation, chlorination, and chloramination (Post 2009; Quiñones 2009). These preliminary studies suggested these treatment systems were ineffective towards PFAA attenuation, but confirmation of these results is necessary at other full-scale

systems and for a wider spectrum of PFASs. To date, some less commonly employed processes, such as AIX, GAC, nanofiltration (NF), and RO have been evaluated at the bench scale and showed promise in removal of some of these chemicals (Tang 2006; Lampert 2007; Steinle-Darling 2008; Deng 2010). However, validation of performance of these processes at the full-scale is needed.

The objective of this study was to evaluate the ability of a wide spectrum of full-scale treatment techniques to remove PFASs from contaminated drinking water. The novelty of this study lies in the detailed examination of a wider range of full-scale treatment techniques, including conventional processes and advanced technologies, such as GAC, AIX, RO, advanced oxidation process (AOP), ultrafiltration (UF), dissolved air flotation (DAF), and river bank filtration (RBF). In addition, the removal of a wider range of PFASs, including all six PFASs on the UCMR 3 List, was evaluated. This study also brings new information on the occurrence levels and distribution of an expanded list of PFASs not previously examined in raw and treated waters throughout the US. To this end, a large suite of 23 PFASs (Table 3.1) was analyzed in raw and finished drinking water and at various steps along the treatment train. To enable this, samples were collected from multiple sampling events for 20 drinking water utilities throughout the U.S.

3.2 Materials and Methods

This section discusses site selection, sample extraction and sample analysis.

3.2.1 Site Selection

The majority of the utilities chosen for this study were selected because they were either known or expected to contain elevated levels of PFASs in their source water. As a result, occurrence data presented herein are not meant to be representative of the national occurrence of PFASs in North American drinking water source waters. The specific treatment processes employed by each utility (Table 3.2) was another

Table 3.1: Suite of Measured PFASs in this Study

PFAS Classes	Chemical Name	Abbreviation	M.W. (g/mol)	Molecular Formula	Relevant Regulatory Levels
PFCAs	Perfluorobutyric acid	PFBA	214	$C_4HF_7O_2$	7.0 µg/L[b]
	Perfluoropentanoic acid	PFPeA	264	$C_5HF_9O_2$	
	Perfluorohexanoic acid	PFHxA	314	$C_6HF_{11}O_2$	
	Perfluoroheptanoic acid	PFHpA	364	$C_7HF_{13}O_2$	
	Perfluorooctanoic acid	PFOA	414	$C_8HF_{15}O_2$	0.4 µg/L[a], 0.3 µg/L[b], 0.04 µg/L[c]
	Perfluorononanoic acid	PFNA	464	$C_9HF_{17}O_2$	
	Perfluorodecanoic acid	PFDA	514	$C_{10}HF_{19}O_2$	
	Perfluoroundecanoic acid	PFUnA	564	$C_{11}HF_{21}O_2$	
	Perfluorododecanoic acid	PFDoA	614	$C1_2HF_{23}O_2$	
PFSAs	Perfluorobutane sulfonic acid	PFBS	300	$C_4HF_9SO_3$	7.0 µg/L[b]
	Perfluorohexane sulfonic acid	PFHxS	400	$C_6HF_{13}SO_3$	
	Perfluorooctane sulfonic acid	PFOS	500	$C_8HF_{17}SO_3$	0.2 µg/L[a], 0.3 µg/L[b]
	Perfluorodecane sulfonic acid	PFDS	600	$C_{10}HF_{21}SO_3$	
Potential PFAS Precursors	Perfluorooctane sulfonamide	FOSA	499	$C_8H_2F_{17}NO_2S$	
	N-methyl perfluorooctane sulfonamidoacetic acid	N-MeFOSAA	571	$C_{11}H_6F_{17}NO_4S$	
	N-ethyl perfluorooctane sulfonamidoacetic acid	N-EtFOSAA	585	$C_{12}H_8F_{17}NO_4S$	
	4:2-fluorotelomer unsaturated carboxylic acid	4:2 FTUCA	258	$C_6H_2F_8O_2$	
	6:2-fluorotelomer unsaturated carboxylic acid	6:2 FTUCA	358	$C_8H_2F_{12}O_2$	
	8:2-fluorotelomer unsaturated carboxylic acid	8:2 FTUCA	458	$C_{10}H_2F_{16}O_2$	
	10:2-fluorotelomer unsaturated carboxylic acid	10:2 FTUCA	558	$C_{12}H_2F_{20}O_2$	
	4:2-fluorotelomer sulfonate	4:2 FtS	328	$C_6H_5F_9O_3S$	
	6:2-fluorotelomer sulfonate	6:2 FtS	428	$C_8H_5F_{13}O_3S$	
	8:2-fluorotelomer sulfonate	8:2 FtS	528	$C_{10}H_5F_{17}O_3S$	

[a]EPA PHA values, [b]MN Dept. of Health: Health Risk Limits (HRLs), [c]NJ Dept. of Environmental Protection: health-based drinking water guidance level; PFCA: perfluorocarboxylic acid; PFSA: perfluorosulfonic acid

criterion for the site selection process, which includes conventional treatment techniques such as coagulation followed by sedimentation or DAF and/or filtration (i.e., granular, ultrafiltration, microfiltration), aeration and oxidation/disinfection (chlorine, chlorine dioxide, ozone, chloramination, potassium permanganate), as well as less commonly employed treatment techniques such as RBF, GAC, AIX, and RO. Synoptic grab samples were taken before and after each treatment process, with almost all treatment processes evaluated on at least two separate occasions. Table 3.2 contains the sampling dates associated with each sampling event. Additional details on the treatment trains employed at each utility can be found in Appendix B. Raw water was sampled at all sites, and individual treatment steps and finished waters were evaluated at Utilities 4, 5, 7, 8, 11-20.

3.2.2 Chemicals and Reagents

With the exception of the analysis of water samples from Utility 20, analytical standards and isotopically labeled standards for all PFASs measured in this study (Table 3.1) were procured from Wellington Laboratories (Guelph, Ontario, Canada). This analytical suite of 23 chemicals included perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), and polyfluoroalkyl chemicals (i.e., PFCA and PFSA precursors). Whenever possible, matched isotope standards were used for quantitation of each PFAS. As discussed below, samples from Utility 20 were analyzed separately using an alternative protocol, as detailed in Appendix B: unless otherwise noted, all analytical details below pertain to all samples except for those for Utility 20. Working stock PFAS solutions and calibration standards were prepared in methanol and appropriate dilutions were made for automated solid phase extraction (ASPE) spiking solutions. All solutions and standards were stored at -20 °C. Trace analysis grade methanol and methyl tert-butyl ether (MTBE) were obtained from Burdick and Jackson (Muskegon, MI, USA). Ascorbic acid was purchased from Mallinckrod Chemicals (Phillipsburg, NJ, USA) and concentrated sulfuric acid was obtained from

Table 3.2: Utilities and Treatment Trains Evaluated in This Study

Utility ID	State	Source Water	Treatment Train	Raw Water Sampling Dates	Treatment Train Sampling Dates
1	WI	SW		8/9/2011	
2	OK	SW		8/23/2011	
3	AK	SW		8/22/2011	
4	CA	TWW	MF/RO/UV-AOP/DI/Cl_2	8/8/2011	12/6/2011 2/22/2012
5	AL	SW	MIEX/COAG/FLOC/ SED/MF/Cl_2	8/15/2011	12/13/2011 3/20/2012
6	CO	SW		4/9/2012	
7	CO	SW	RBF/ARR/SOFT/ SCC/UV-AOP/G- FIL/GAC	9/13/2011	5/1/2012 6/19/2012 8/21/2012
8	OH	SW	SED/COAG/FLOC/ SED/G-FIL/GAC/Cl_2	8/9/2011	12/12/2011 2/22/2012
9	NV	SW		9/19/2011	
10	CA	TWW	MF/UF/RO/UV-AOP	10/4/2011	1/09/2012 3/6/2012
11	NJ	SW/GW Mix	AER/COAG/FLOC/ SED/G-FIL/ClO_2		12/6/2011 3/14/2012
12	NJ	SW	O_3/DAF/Cl_2/CLM		3/21/2012 5/23/2012
13	NJ	GW	UV/Cl_2		3/21/2012 5/23/2012
14	NJ	GW	AIX/APT/Cl_2		5/30/2012 9/19/2012
15	NJ	GW	NaClO/MnO_4/G-FIL		12/13/2011
16	NJ	GW	ClO_2/Cl_2		11/29/2011
17	NJ	SW	MnO_4/O3/Cl_2		12/14/2011 4/3/2012
18	NJ	SW	APT/GAC/Cl_2		11/22/2011 4/3/2012
19	NJ	GW	Cl_2		11/29/2011
20	MN	GW	GAC/Cl_2		10/26/2006 to 06/20/2011

O_3: Ozone, COAG: Coagulation, FLOC: Flocculation, SED: Sedimentation, G-FIL: Granular Filtration, Cl_2: Hypocholorous/Hypocholorite, CLM: Chloramination, ClO_2: Chlorine Dioxide, GAC: Granular Activated Carbon Filtration, PAC: Powdered Activated Carbon, UV: UV Photolysis, AIX: Anion Exchange, DI: Disinfection, MIEX: Magnetic Ion Exchange, RBF: River Bank Filtration, SOFT: Softening, MF: Microfiltration, ARR: Aquifer Recharge and Recovery, SCC: Solids Contact Clarifier, AER: Aeration, APT: Aeration Packed Tower, MnO_4: Permanganate, UF: Ultrafiltration, SW: Surface Water, GW: Ground Water, TWW: Treated Wastewater Effluent

EM Scientific (Merck KGaA, Darmstadt, Germany). Reagent grade water was prepared with a Milli-Q Gradient water purification system (Millipore, Billerica, MA, USA).

3.2.3 Sample Collection and Preservation

All samples were collected in 1 L pre-cleaned wide mouth amber high-density polyethylene bottles (Rochester, NY, USA). A solution of ascorbic acid (0.05%) was added to all bottles prior to sampling for chlorine quenching. After sampling, bottles were kept on ice during transportation and stored at 4°C until extraction. Samples were extracted within 14 days of collection and, when necessary, samples were filtered prior to extraction with pre-ashed 90 mm glass fiber filters. Preliminary studies indicated no impact from filtration on the measured concentrations of target analytes.

3.2.4 Automated Solid Phase Extraction

ASPE was performed using Dionex AutoTrace 280 workstation (Thermo Scientific, Sunnyvale, CA, USA). Samples (1 L) were acidified to <pH 2 with concentrated sulfuric acid, then spiked with isotopically labeled standards prior to extraction. Samples were processed in batches of six. Pre-packed 200 mg, 6 cc HLB cartridges (Waters Corporation, Milford, MA, USA) were sequentially conditioned with 5 mL MTBE, 5 mL methanol, and 5 mL reagent water with flow rate of 15 mL/min. Samples were loaded at a rate of 15 mL/min. Cartridges were rinsed with 5 mL reagent grade water and dried for 30 min with nitrogen gas. Target analytes were eluted with 10 mL MeOH into 15 mL conical vials (Dionex) with a flow rate of 5 mL/min. Extracts were concentrated to a final volume of 500 µL or 1 mL with nitrogen gas.

3.2.5 Sample Analysis

Analysis of ASPE extracts was conducted via liquid-chromatography tandem mass-spectrometry (LCMSMS) using a previously reported method (Quiñones 2009),

adapted and expanded to include all analytes of interest. Briefly, an Agilent (Palo Alto, CA) G1312A binary pump and an HTC-PAL auto sampler (CTC Analytics, Zwingen, Switzerland) were used. Analytes were separated using a 150 × 4.6 mm Synergi Max-RP C12 column with a 4 µmpore size (Phenomenex, Torrance, CA) and a binary gradient consisting of 5.0mM ammonium acetate (v/v) in water (A) and 100% methanol (B) at a flow rate of 800 µL/min. An injection volume of 10 µL was used for all analyses. Contaminants from the aqueous channel were removed using a 4.0×10mm Hypercarb (Thermo Fisher Scientific, Waltham, MA) drop-in guard cartridge attached in-line before the LC purge valve. Remaining contaminants were separated from analyte peaks by installing a 75×4.6mm Synergy Max-RPC12 column with a 4 µm pore size (Phenomenex, Torrance, CA) in-line upstream from the injector valve. Tandem mass spectrometry was performed using an API 4000 triple-quadrupole mass spectrometer (Applied Biosystems, Foster City, CA). Using ESI negative ionization, optimal compound-dependent parameters were determined for additional analytes and source-dependent parameters optimized. The concentration of each analyte was determined by isotope dilution, surrogate standard or external calibration. Method reporting limits (MRLs) were based on method detection limits (MDL) calculated from seven replicate measurements of deionized water samples fortified with analytes and extracted as previously described. As an added cautionary measure, MRLs for each analyte were set conservatively at least five times the MDL, and higher as needed in consideration of known and unanticipated background sources. Compound-dependent analytical and quantitation parameters are detailed in Table B.1.

3.2.6 Quality Assurance and Quality Control

A minimum of seven calibration standards were used to construct a calibration curve for each analyte, with at least one calibration standard analyzed at or below the method MRL. Correlation coefficients were required to be at least 0.990 but typically

exceeded 0.995 using linear regression. A field blank was collected for each sampling event, extracted and analyzed. A laboratory reagent blank was also included in each extract batch. Acceptance criteria for data batch required any observable compound peaks in blanks to remain <1/3 MRL or else results be flagged and compound MRL adjusted for all samples in batch. Laboratory fortified reagent blanks, laboratory fortified matrix spikes, and a sample duplicate were incorporated into each extract batch to monitor analytical performance. Acceptance limits for recovery were set at 70-130% and at 30% relative percent difference for duplicates. Signal counts for internal and surrogate standard peaks were required to remain above 10% when compared to average peak counts in calibrators. Samples not meeting these criteria were reanalyzed and diluted for matrix reduction as needed. Samples where efforts did not produce acceptable QC criteria required be flagged as such. Table B.2 displays the average analytical error for duplicate analysis of each compound and recovery summaries for reagent water and matrix spikes for the project.

Detectable concentrations of 6:2 fluorotelomer sulfonate (FTS; Table 3.1) were observed in limited sample sets and on investigation, were attributed to LC cap inserts subject to repeated injection punctures. Results for this compound where excluded for batches where blanks did not meet QC criteria. Silicone-only inserts replaced PTFE-lined inserts for the remainder of this project.

3.2.7 Utility 20 Sample Analysis

Data evaluated for Utility 20 was collected using an alternate method. For this utility, only seven PFASs were measured: PFBA, PFPeA, PFHxA, PFOA, PFBS, PFHxS, and PFOS. These compounds had a reporting limit of 0.05 μg/L. A description of this method can be found in Appendix B.

3.3 Results and Discussion

This section examines the results from the sampling campaigns performed in this study.

3.3.1 Raw and Finished Water Occurrence Data

Though the primary objective of this study was to evaluate the removal of PFASs during full-scale drinking water treatment, meeting such an objective requires some understanding of PFAS occurrence in raw and finished waters. End-product PFAAs were frequently detected in both the raw and finished waters of many of the utilities sampled in this study. Chemicals that were detected in low ng/L concentrations, but had not previously been measured in surface waters, ground waters, or treated wastewater effluents in the literature reviewed included PFBA, PFPeA, PFHpA, N-MeFOSAA, and 6:2 FtS. PFBS was detected as well, but had previously only been measured in surface waters (Nakayama 2007). The three most commonly detected PFASs in the raw water samples (n = 39) were PFOS (84%), PFHxA (79%), and PFHxS (79%). Other chemicals that were frequently detected in the raw water samples included PFPeA (74%), PFHpA (74%), PFOA (74%), PFNA (66%), and PFBS (74%). Interestingly, PFHxA and PFPeA were frequently detected, but they are not included in the U.S. EPA UCMR3 Monitoring list. Among the PFCAs, PFBA and PFDA were only present in 34% of the samples, whereas longer chain PFCAs, PFUnA and PFDoA, were only detected in 13% and 11% of samples, respectively. Polyfluoroalkyl chemicals were also detected in some samples: 6:2 FtS, N-MeFOSAA, N-EtFOSAA, and FOSA were detected in 38%, 29%, 24% and 16% of samples, respectively. Several chemicals, such as PFDS, the FTUCAs, 4:2 FtS, and 8:2 FtS were not detected above MRLs in any of the samples taken. PFAS detection frequency in the finished waters was similar to the raw waters, except for PFDoA which was not detected in any finished water samples.

Table B.8 in Appendix B displays the range of concentrations found in the raw and finished water sources from the sampling campaign in this study as well as the ranges of North American values in the literature. Ranges include all of the concentrations of the raw and finished samples measured in this study and are grouped by the Utility's raw water source, i.e. surface waters, ground waters, blend of surface and groundwater, or utilities whose "raw water source" is 100% treated wastewater effluent. In addition, Table B.3, Table B.4, Table B.5, Table B.6, andTable B.7 in Appendix B contain the concentrations of all samples analyzed in this study. Data from Utility 20 was intentionally left out of the ranges presented in Table B.8 as its raw water source is highly contaminated by an industrial source, and is thus considered an outlier for this data set. The ranges measured in this study were mostly consistent with the literature, where literature data are available. The highest concentrations measured were in the raw water source of Utility 10 at 370 and 220 ng/L of PFPeA and PFOA, respectively. Utility 10, as well as Utilities 4 and 7, generally had the higher concentrations of most PFASs, which corresponds to all of these being highly wastewater-impacted sources (Utilities 4 and 10 are 100% impacted). None of the polyfluoroalkyl chemicals were detected in ground waters, but FOSA, N-MeFOSAA, and N-EtFOSAA were in both surface waters of Utilities 5, 7, and 17 (up to 1.7, 0.9, and 2.0 ng/L, respectively) and treated wastewater effluents of Utilities 4 and 10 (up to 0.42, 1.1, and 0.43 ng/L, respectively).

All raw and finished samples collected in this study, except for Utility 20, were in the low ng/L range for all PFASs analyzed. Aside from Utility 10, concentrations in the raw waters (of all PFASs) were less than 100 ng/L, and the highest detection in the finished waters was 62 ng/L of PFHxA. For three PFAAs, levels in some cases were higher than the MRLs for the U.S. EPA UCMR3, which are 10 ng/L for PFHpA, 20 ng/L for PFOA, and 40 ng/L for PFOS. Four utilities (Utility 5, 14, 16 and 19), were above the 10 ng/L level for PFHpA with values of 14, 13, 11, and 34 ng/L,

respectively, in at least one of their finished water samples. Six utilities were above the 20 ng/L level for PFOA: Utility 5 (two samples: 32 and 50 ng/L), Utility 11 (33 ng/L), Utility 14 (21 ng/L), Utility 15 (38 ng/L), Utility 18 (two samples: 24 and 27 ng/L), and Utility 19 (57 ng/L). Only Utility 5 was above the 40 ng/L level for PFOS in one of the two finished water samples taken (measured at 61 ng/L). However, none of the finished water samples exceeded the minimum reporting levels of 20, 90, and 30 ng/L for PFNA, PFBS, and PFHxS, respectively, on the UCMR3 list. Of the six chemicals that some utilities will be required to monitor on the U.S. EPA UCMR3 list, the results here suggest that PFHpA, PFOA, and PFOS, could be the most frequently detected. PFOA, PFOS, PFBA, and PFBS were measured at levels below U.S. EPA and state regulatory guidance levels, with the exception to one utility. Utility 19 in New Jersey was over (at 57 ng/L) its state guidance level of 40 ng/L for PFOA. Collectively, these data suggest that if the most stringent public health guidelines for these four chemicals are applied, the observed levels will be below the guidance levels for the majority of the utilities examined in this study.

3.3.2 Full Scale Treatment Efficacy

Figure 3.1 displays the removal efficacy of PFOA and PFOS of the various types of treatments measured at the utilities. Similar plots for all PFASs can be found in Appendix B (Figure B.1 to Figure B.11). Each treatment type had its influent and effluent sampled twice, except for Utilities 7, 11, and 15 which were sampled once, and the average and standard error of the two sampling campaigns are displayed. Although the removal percentages are believed to be a good representation of the treatment processes efficacy in most cases, the detected concentrations were sometimes less than double the MRL, and these data (as marked with an asterisk on the figures) were not regarded with the same credence.

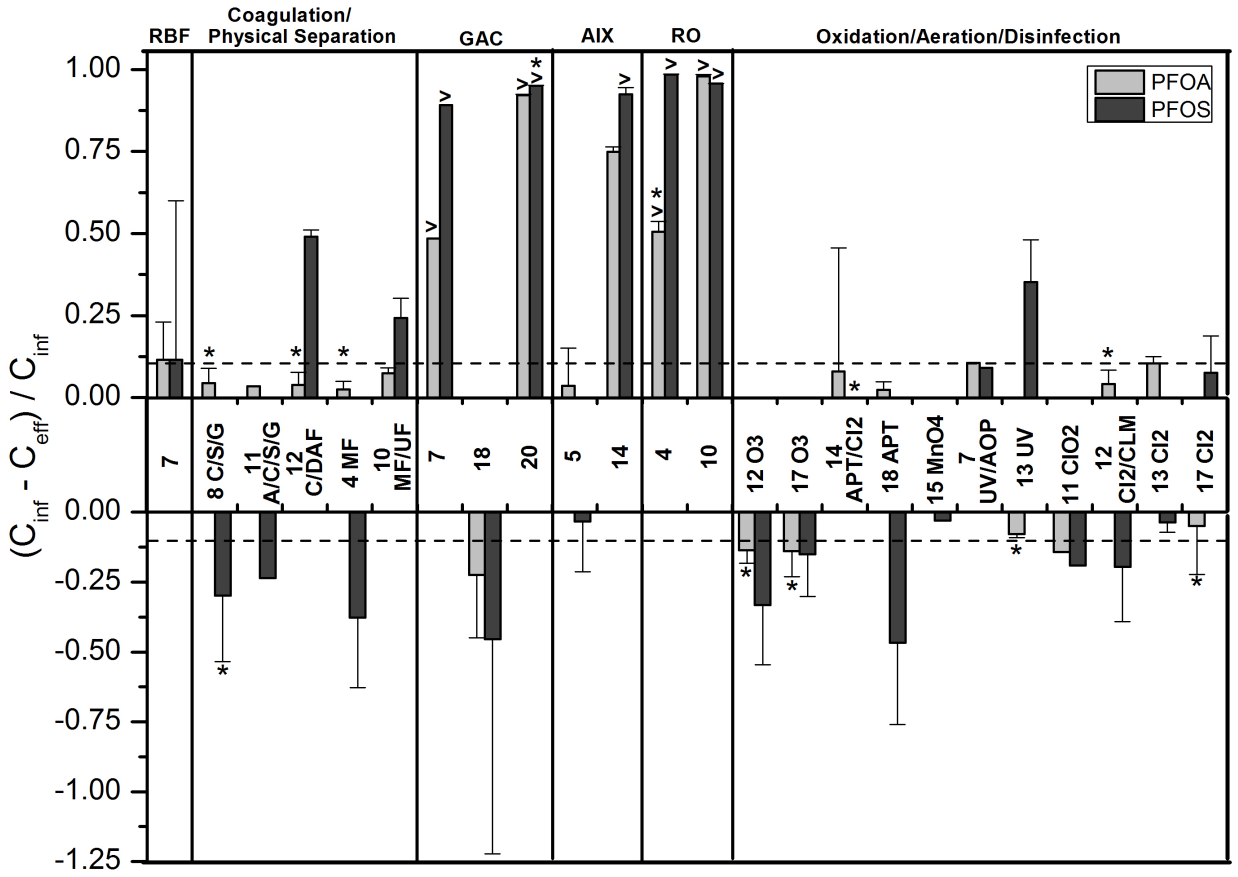


Figure 3.1: Figure 1: PFOA and PFOS Removal by Treatment: An asterisk "*" above each bar denotes an influent concentration that was less than three times the MRL. A greater than symbol denotes samples where the concentration was below the MRL in the effluent, but the MRL was used as a conservative estimate for the percent removal. The dashed lines at +/- 10% represent the range of error based on the average analytical variability multiplied by a conservative safety factor (˜3x) for the possible error associated with collecting grab samples before and after treatments. Cinf: influent concentration. Ceff: effluent concentration, A: Aeration, C: Coagulation, S: Sedimentation, G: Granular Filtration

3.3.3 Coagulation/Physical Separation

The efficacy of PFAS removal from coagulation followed by sedimentation or DAF and/or filtration was evaluated. Added coagulants included aluminum sulfate and polymer (Utility 8), aluminum sulfate (Utility 11), and polyaluminum chloride (PACl) (Utility 12). Coagulation followed by sedimentation did not lead to PFAS removal, but where sedimentation was replaced by DAF (such as at Utility 12), a 49% removal of PFOS was observed (Figure 3.1). Similarly, PFNA was also removed, albeit to a lesser extent (29%) by DAF. However, the detected shorter-chain PFCAs and PFSAs were not well removed by DAF. It is possible that the longer-chain PFAAs may have a higher affinity for the air/water interface resulting from the DAF air bubbles and are subsequently skimmed off with the surface scum. Improved removal of these longer-chain PFAAs by DAF should be studied further. Other physical separation technologies such as granular filtration with sand (Utility 8) and an anthracite/sand combination (Utility 12) had little effect on PFAS removal. An increase in PFOS concentration was observed after the coagulation/sedimentation/granular filtration processes at Utilities 8 and 11, but the average level was within 3 times of the MRL and associated error for Utility 8 and data from only one campaign was reported for Utility 11, therefore the error across multiple campaigns is unknown for Utility 11.

With respect to membrane filtration, the MF system at Utility 4 was not effective. The system uses polypropylene membranes with 0.2 micron rated pore size. Utility 10 splits their flow and runs the water in parallel through an MF system with a Microza MF Model UNA 620 A membrane having a nominal pore size of 0.1 micron, and a UF system with a nominal pore size of 0.02 micron. UF is presumed responsible for the partial removal (24%) of PFOS (MW = 500 g/mol) as shown in Figure 3.1, as the difference in pore size between it and the ineffective MF system at Utility 4 is much greater than the two MF systems compared to one another. PFDoA (MW = 614 g/mol) and FOSA (MW = 499 g/mol) also exhibited partial removals (44%

and 42%, respectively) during the MF/UF process at Utility 10, revealing UF may be partially effective towards larger PFAS compounds. However, PFUnA (MW = 564 g/mol), N-MeFOSAA (MW = 571 g/mol) and N-EtFOSAA (MW = 585 g/mol) were also detected in this water and were not removed. It is unknown why some large MW compounds were partially removed and others were not. Although only partial removal occurred from the UF process, there is a potential here for the use of tighter UF membranes for physical separation of larger-chain PFASs.

3.3.4 Oxidation/Aeration/Disinfection

Oxidation and disinfection processes were evaluated at Utilities 7, 11-15, 17, and 18 and included ozonation, aeration packed towers, potassium permanganate, ultraviolet (UV) treatment, AOP (UV/H_2O_2), chlorination (Cl_2) with and without chloramination, and chlorine dioxide. All of these processes proved mostly ineffective at all of the utilities (Figure 3.1). In fact, in many cases, the concentration of PFCAs and PFSAs were consistently slightly higher following oxidative treatments. However, these data are generally within the range of error associated with duplicate sampling events and/or analytical/grab sampling variability (i.e., $\pm$ 10%) or the data is within 3 times the MRL.

These data are not surprising, as PFASs are generally resistant to oxidation. AOPs, which utilize the hydroxyl radical, such as alkaline ozonation, peroxone, Fenton's reagent, and UV/hydrogen peroxide have been shown ineffective towards PFOA and PFOS (Hori 2004; Moriwaki 2005; Schroder 2005). However, other oxidation/reduction technologies, such as photocatalytic oxidation, photochemical oxidation, photochemical reduction, persulfate radical, thermally-induced reduction, and sonochemical pyrolysis, have been shown to be effective at degrading some PFAAs in water (Lazerte 1953; Hori 2005; Moriwaki 2005; Yamamoto 2007). However, most of these technologies are not employed in current drinking water treatment practices.

One exception in this group was the UV system (80 mJ/cm^2) at Utility 13, which interestingly resulted in partial removal of PFHxS (34%) and PFOS (35%) (Figure 3.1). UV photolysis has been demonstrated to be effective at degrading PFOS and PFOA (Hori 2004; Chen 2006; Chen 2007; Yamamoto 2007). However, the UV system at Utility 13 did not show removal of the PFCAs or the smaller chain sulfonate, PFBS. In addition, the UV-AOP process at Utility 7 operated at a dose of 500 mJ/cm^2 was not effective. Given these mixed results, one can expect minimal removal, if any, of PFASs in contaminated drinking water as a result of current UV treatment practices.

3.3.5 RBF

RBF was tested twice at Utility 7, with a travel time of approximately 10 days. Although minimal removal was observed for PFOA and PFOS, removal of the other chemicals was variable. For example, some chemicals showed removal, such as PFHxA (20%), PFDA (19%), and N-MeFOSAA (68%), while other chemicals actually increased in concentration, such as PFBA (-103% removal), PFHpA (-31%), PFBS (-63%), and FOSA (-20%). This variation is due to possible variability in influent concentrations (i.e., a wastewater effluent impacted river) and the fact that the raw and finished samples were not collected synoptically for 10 day travel time. One example of this variation is PFOS, which had the largest difference in concentration between samples of the raw water with levels at 7.3 ng/L during the first sampling on 05/01/12 and 35 ng/L during the second sampling on 06/19/12.

3.3.6 AIX Treatment

Two AIX treatments were examined at the full-scale in this study, though neither was intentionally used for PFAS removal. Utility 14 added Purolite FerrlX A33e media to a softener vessel which is the first treatment process in the train (Table 3.2). The iron infused AIX resin is designed for arsenic removal, and is only changed out once

performance decreases in this aspect. The system was installed in December 2011, but only used as needed for arsenic removal; therefore the resin for the two sample events was at most 5 and 9 months old. Interestingly, the resin was successful in removing some of the PFASs. In particular, PFHpA was partially removed (46%), as were PFOA (75%), and PFBS (81%). PFNA, which was only detected in one of the two raw water samples, exhibited >67% removal, whereas PFHxS and PFOS exhibited >97%, and >92% removals, respectively. Examining the removal efficiencies of both campaigns in Table 3.3, there appears to be a chain length effect for this particular ion exchange treatment, with the smaller chain PFCAs (< 314 g/mol), i.e., PFBA and PFHxA, exhibiting little to no removal, and the larger chain ones (>364 g/mol), i.e., PFHpA and PFOA, showing partial to significant removal. Similarly, in batch tests, an AIX resin (Siemens A-714) demonstrated >99% removal of PFOS and PFOA (Lampert 2007), while other bench-scale studies (Deng 2010; Senevirathna 2010) showed AIX resins capable of removing PFOS. It is possible that certain AIX resins can target PFAS sorption by ion exchange and/or hydrophobic interactions.

A magnetic anion exchange (MAIX) treatment process was also examined at Utility 5, where it is employed upfront in the treatment train (Table 3.2) to target total organic carbon. Unlike Utility 14 and previous bench-scale work, MAIX showed little to no removal of any of the chemicals at Utility 5. This may have been due to the operational method employed for this treatment process. The MAIX system at Utility 5 uses an up-flow fluidized-bed reactor with continuous regeneration (approximately 13 regenerations in a 24 hour period). Continual regeneration, as opposed to a complete resin replacement, or insufficient capacity and/or kinetics may be causes of its ineffectiveness at the full-scale, as previous studies have shown that conventional methods of AIX regeneration are ineffective for PFBS and PFOS (Carter 2010) and significant kinetic limitations can occur (Lampert 2007; Deng 2010).

The results from Utility 14's AIX column operation and past bench-scale studies indicate AIX is a promising technology for the removal of PFASs, despite what was observed at Utility 5. In order for AIX to be employed at the full-scale for PFAS removal, further AIX research is needed to identify which AIX resins are most suitable for PFAS removal, the selectivities of resins for different PFASs, and the most suitable regeneration techniques. In addition, a better understanding of sorption kinetics and competition with other anions and natural organic matter is necessary.

3.3.7 GAC Treatment

Four full-scale GAC systems were examined: details of these GAC systems at Utilities 7, 8, 18, and 20 can be found in the SI. PFAS levels at Utility 8 were too close to the MRLs, and as a result GAC performance for this system was not analyzed. Utility 20 is of particular interest, as it specifically employs GAC for PFAS removal. The system utilizes Calgon F600 coal-based media, and is set up with two contactors, a lead and a lag, that run in series with a flow between 1.4 to 1.5 m^3/min, and an empty bed contact time (EBCT) of about 13 minutes in each contactor. For this system, the removal efficacy reported in Table 3.3 was based on the average removal over the course of one year for the lag basin (4/25/2007 – 4/22/2008). During this period the lag effluent concentrations fell below the detection limits for all chemicals with the exception of PFBA.

Figure 3.2 displays the breakthrough of five different PFASs in the lead GAC bed over a five year period. Three important dates during the operation of this system, noted on the horizontal axis in Figure 3.2, are 09/22/2008, 10/05/2009, and 10/11/2010. During the first two dates, the flow was redirected so that the lag vessel became the lead, and the original lead vessel had its carbon replaced with virgin carbon. On 10/11/2010, all of the carbon in the system (both lead and lag vessels) was replaced with virgin carbon. These dates are reflected by the sharp decline in effluent concentrations for PFHxA, PFOA, and PFOS in the lead vessel. PFBA only

Table 3.3: Percent Removal for Most Effective Treatment Technologies

Site	#4	#4	#10	#10	#14	#14	#7	#20
Treatment	RO	RO	RO	RO	AIX	AIX	GAC	GAC
Sample Date	12/6/2011	2/22/2012	1/9/2012	3/6/2012	5/30/2012	9/19/2012	8/21/2012	4/25/2007 – 4/22/2008
PFBA	> 90%	> 82%	N/A	> 95%	-9%	0%	33%	-17%
PFPeA	> 79%	> 82%	> 99%	> 98%	0%	0%	74%	> 22%
PFHxA	> 97%	> 98%	> 99%	> 99%	14%	-14%	91%	> 68%
PFHpA	> 81%	> 86%	> 98%	> 95%	54%	38%	> 89%	N/A
PFOA	> 54%	> 47%	> 98%	> 98%	76%	73%	> 48%	> 92%
PFNA	> 87%	> 87%	> 98%	> 95%	N/A	> 67%	> 37%	N/A
PFDA	> 76%	> 67%	> 99%	> 99%	N/A	N/A	N/A	N/A
PFUnA	N/A	N/A	> 77%	> 71%	N/A	N/A	N/A	N/A
PFDoA	N/A	N/A	> 87%	> 84%	N/A	N/A	N/A	N/A
PFBS	> 93%	> 98%	> 96%	> 94%	83%	80%	> 96%	N/A
PFHxS	> 95%	> 94%	> 96%	> 90%	> 97%	> 98%	> 96%	> 41%
PFOS	> 98%	> 99%	> 96%	> 96%	> 90%	> 94%	> 89%	> 95%
PFDS	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
FOSA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N-MeFOSAA	> 43%	> 36%	> 84%	> 79%	N/A	N/A	N/A	N/A
N-EtFOSAA	N/A	N/A	> 55%	> 58%	N/A	N/A	N/A	N/A

exhibited a sharp decline when all of the carbon in the system was replaced. On 12/27/2007, PFHxA had a sharp decline back to zero break-through, but this point is believed to be an outlier as the GAC was not altered in anyway on this date. PFHxS was detected in the influent over the timespan, but all lead effluent samples were below the detection limits. Other than PFHxS, PFOS was the slowest to break through and PFBA was the fastest. The chemicals PFHxA and PFOA appear to exhibit similar initial breakthrough times in the lead GAC, but the smaller chain PFHxA reaches full breakthrough at a much faster rate. These findings are in general agreement with several batch test studies of the removal of PFASs using coal-based GAC showed that GAC was capable of attenuating PFOA, PFBS, and PFOS (Lampert 2007; Carter 2010; Senevirathna 2010).

As can be seen in Figure 3.2, PFBA exhibited breakthrough after about 2 months of operation, and was above 1.0 for its C/C_0 value from July 2007 to October 2010 (when all of the carbon was replaced). This is believed to be due to competitive effects with other sorbing species (perhaps longer chain PFASs and/or organic matter) leading to desorption and release of sorbed PFBA over time. The average influent concentrations were 1.45 $\pm$ 0.18 µg/L, so it is unlikely that the C/C_0 >1 was caused by influent variability. This chemical could be characterized as the limiting factor for GAC treatment in the removal of PFASs when present in the raw water source.

Utility 18 uses Calgon F300, but unlike Utility 20, the system is not specifically designed for PFAS removal. For the first sampling event, little change in the concentrations were observed for most of these chemicals. Interestingly, for the second sampling campaign the concentrations were higher for some of the PFAAs (i.e., PFOA (45%), PFDA (34%), and PFOS (122%)), in its effluent than the influent. The GAC for this system had not been reactivated or replaced with virgin carbon in over six years. Thus, these results suggest the GAC had been spent and the second sampling campaign may indicate leaching of chemicals. This finding is important in that it

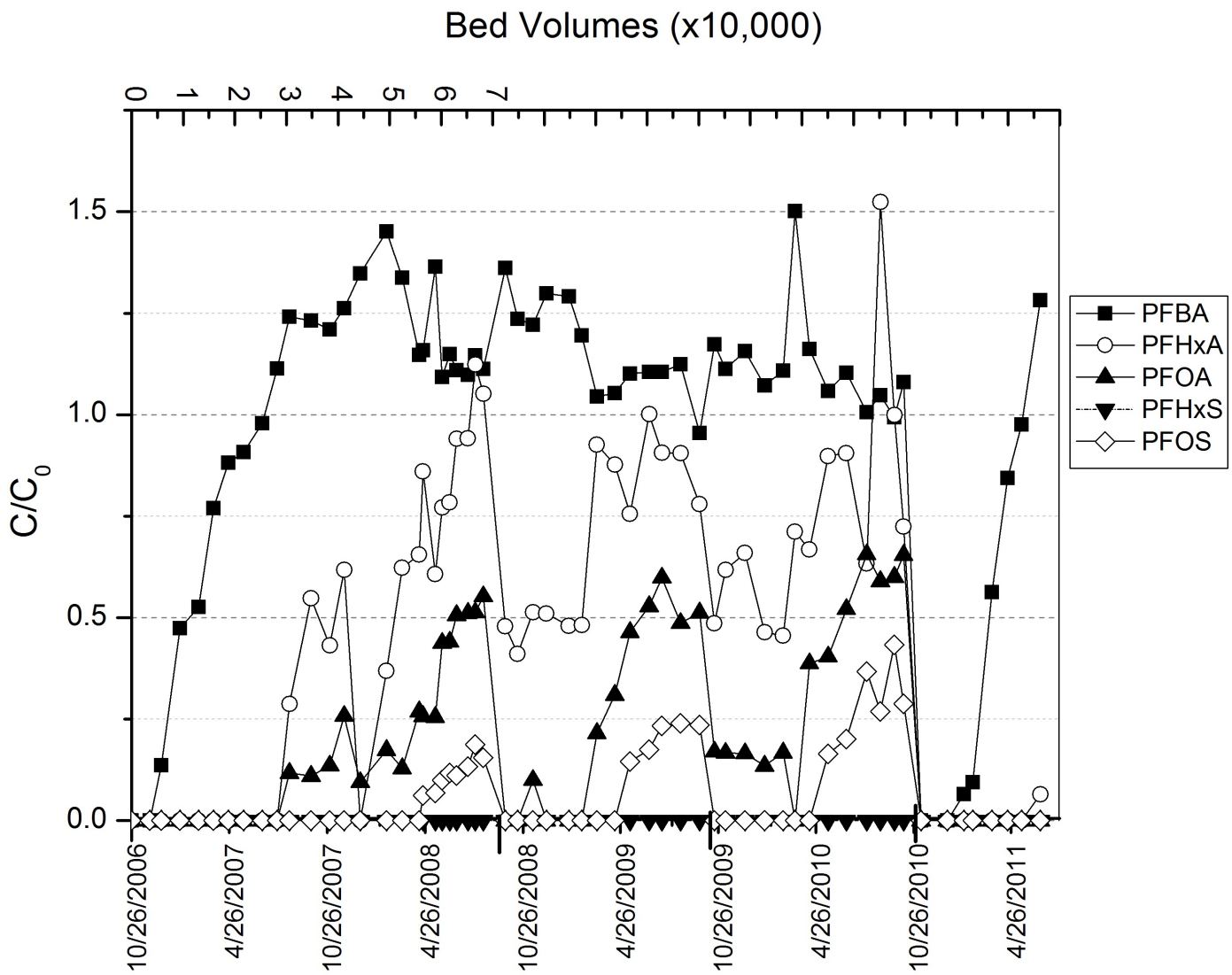


Figure 3.2: Breakthrough of PFAAs in Utility 20 GAC System. Every 3 months corresponds to approximately 10,000 BVs. BV axis stops at 70,000 BVs because the system was first altered on 8/13/2008 (or ˜69,000 BVs).

highlights the importance of carbon replacement and/or regeneration for ensuring removal of PFASs by GAC.

Utility 7 also employs GAC treatment with six parallel GAC contact chambers containing 80 m^2 of Norit GAC300, an empty bed contact time of 10.4 min, and an average flow of about 114 m^3/d. This GAC system was specifically designed to target the removal of trace (ng/L) organic contaminants. The removal percentages for this site are displayed in Table 3.3. The larger chain PFCAs, PFHpA, PFOA, and PFNA, as well as the PFSAs, PFBS, PFHxS, and PFOS were all attenuated to below MRLs. Three shorter chain chemicals PFCAs, PFBA, PFPeA, and PFHxA had partial removal at 33%, 74%, and 91%, respectively, which corresponds to the increased affinity of longer-chain PFCAs for organic carbon as observed in previous studies (Higgins 2006).

The overall results indicate for the longer chain PFASs, GAC systems were effective at Utilities 7 and 20. Both full scale systems appear to have chain length dependent breakthrough, and also the sulfonic acids being removed for a longer period of time than the carboxylic acids. Utility 20 operated its lead vessels for approximately 10 months before initial breakthrough of PFHxA or PFOA, and for 18 months before PFOS started to breakthrough. However, if the shorter-chain PFBA is targeted for removal, an alternative treatment strategy would need to be employed.

3.3.8 RO Treatment

Two California potable reuse sites employing RO were examined in this study (Utilities 4 and 10). Utility 4 uses polyamide Hydranautics ESPA2 membranes in a three stage array with a 12 gfd flux rate and 85% recovery, and Utility 10 uses Toray and Hydraunautics RO membranes with an RO flux rate of 11.6 - 11.9 gfd and 80% recovery. All PFASs were below the MRLs in the collected samples immediately following the RO systems, making this the most effective form of treatment evaluated in this study. Results in a bench-scale study (Tang 2006) of RO membranes showed

similar rejection of PFOS (> 99%).

Effective rejection of PFASs by RO is especially important for the shortest chain PFAS in this study, PFBA, which proved to be recalcitrant through all other treatment techniques evaluated at the full-scale. Despite RO's effectiveness, however, RO would likely be the most costly method for removal. Looser (and less costly) membrane systems, such as NF, or tight NF, could prove to be just as capable of rejecting PFASs as compared to RO in full-scale plants since NF has been deemed potentially effective (> 95%) in bench-scale experiments using NF270 membranes (Steinle-Darling 2008), though PFBA was not included in these bench-scale evaluations and PFPeA demonstrated only 72% removal.

3.4 Conclusion

This study examined the removal of a large suite of PFASs across different drinking water treatment systems throughout the US. Certain end product PFAAs that had not previously been measured in the literature were detected at levels in the low ng/L ranges in surface water, groundwater and treated wastewater sources, however most of the precursor chemicals examined in the study were below MRLs for all samples taken. The EPA and states like New Jersey and Minnesota have taken steps towards regulating some of the PFCAs and PFSAs. Although almost all of the finished water samples taken from this study were in compliance with these regulatory levels, a few utilities were near these limits.

The inability of the full-scale common conventional treatments, such as coagulation followed by physical separation processes, and chemical oxidation, aeration and disinfection, to remove PFASs will become an issue for some utilities if low ng/L regulatory levels are promulgated for these chemicals. In this event, those utilities with significant PFAS levels in their raw water sources will need to examine additional mitigation strategies, such as alternative treatment technologies. Several PFAS were observed to be removed by RO, GAC, and AIX at the full-scale. However, GAC and

AIX were less effective at removing the shorter chain PFASs, whereas RO treatment was effective at even the smallest PFAS studied, PFBA. Given the difficulty in removing PFASs from drinking water, a multiple barrier treatment approach should be considered to provide both robustness and reliability in drinking water treatment systems in which PFAS removal is desired.

CHAPTER 4

NANOFILTRATION AND GRANULAR ACTIVATED CARBON TREATMENT OF PERFLUOROALKYL ACIDS

Perfluoroalkyl acids (PFAAs) are being detected in various water sources all around the world. These chemicals are of concern because of their persistence in the environment and their potential toxicological effects on humans exposed to PFAAs through a variety of possible exposure routes, including contaminated drinking water. This bench-scale study evaluated the efficacy of two forms of advanced treatment, nanofiltration (NF) and granular activated carbon (GAC) adsorption, in their ability to remove PFAAs from water. A liquid-chromatography tandem mass-spectrometry method was used to measure a suite of PFAAs, including six perfluorocarboxylic acids and three perfluorosulfonic acids. Virgin NF270 flat sheet membranes were tested at pressures ranging from 25 to 125 psi using spiked deionized (DI) water and spiked artificial ground water (AGW). The effects of membrane fouling by humic acid in AGW was also tested under constant permeate flux conditions. The NF270 membranes, both virgin and fouled, demonstrated >93% removal for all PFAAs under all conditions tested. During the experiments with virgin membranes, only PFBS and PFHxS were detected in the permeate waters at concentrations ranging from 12-41 ng/L and 30-40 ng/L, respectively. GAC efficacy was tested using rapid small-scale columns packed with Calgon Filtrasorb®300 (F300) carbon and DI water with and without natural dissolved organic matter (DOM). DOM effects were also evaluated with F600 and Siemens AquaCarb®1240C with spiked and filtered natural river water. The F300 GAC had <20% breakthrough of all chemicals for the entirety of the spiked DI water experiment (125,000 bed volumes (BVs)). A dramatic effect was observed on the carbons when DOM was present with >20% breakthrough of all

PFAAs by 10,000 BVs. Full breakthrough (100%) of all PFAAs occurred with 1240C carbon, and all but four chemicals, PFHxA, PFNA, PFDA, and PFOS achieved full breakthrough for the F600 and F300 carbons.

4.1 Introduction

Poly- and perfluoroalkyl substances (PFASs) are a growing concern in the world because of their persistence in natural environments. A subset of these substances is the PFAA family. The basic structure of a PFAA is a carbon backbone surrounded by fluorine atoms and an acid group located at the end of the carbon chain. They are frequently added to a variety of industrial and consumer products for their water and oil- repelling abilities. Common items containing PFASs include ScotchGard™ and Teflon™, and they are also used in food packaging products (Lau 2007). The chemicals are also found as an ingredient in aqueous firefighting foams (AFFF), and utilized in specialized industries including semiconductor and metal plating (Deng 2010).

The two most commonly studied PFAAs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). These two chemicals have proven to be recalcitrant both in the environment and in conventional water and wastewater treatment utilities (Sinclair 2006; Quiñones 2009). The full scale study in Chapter 3 looked at the removal efficacy of a suite of 23 PFASs by a variety of conventional and advanced treatments. Conventional treatments, including coagulation followed by sedimentation and/or filtration (i.e., granular, ultrafiltration, microfiltration), aeration and oxidation/disinfection (chlorine, chlorine dioxide, chloramination, potassium permanganate), were found to be mostly ineffective. A few advanced processes, such as GAC and reverse osmosis (RO), showed promise in their abilities to attenuate these compounds. GAC exhibited chain length dependency effects with the smaller chain PFCAs, e.g. perfluorobutanoic acid (PFBA), breaking through the fastest. RO, the most costly advanced treatment process examined, proved most effective, rejecting

all detected PFAAs, even PFBA, to below their method reporting limits (MRLs). Unfortunately, NF, a less costly membrane treatment process, was not evaluated at the full-scale in that study.

Bench-scale work on removal efficiency of PFASs using advanced treatments is limited. One NF study (Steinle-Darling 2008) measured the rejection capacities of four NF membranes (NF270, NF200, DK, and DL) on a suite of 15 PFASs. The flat sheet membranes were tested originally as virgin membranes, and then fouled with an alginate solution to observe the effect of a fouled layer. Average rejections were 99.3% by clean membranes, and 95.3% by fouled membranes for the sulfonates, and for perfluorooctane sulfonamide (FOSA) it decreased from about 93% to 43% as a result of fouling. Unfortunately, the effect of fouling was not calculable for the PFCAs due to large errors in the data, as these chemicals could be beneficial into interpreting the processes causing decreased rejection. While removal was generally good (93% or higher), the trans-membrane pressure was not increased to maintain a constant flux across the membrane's surface for the fouled membranes. Maintaining a constant permeate flux is important for comparing the rejection capacity of a fouled and an unfouled membrane because it has been shown (Bellona 2010) that cake enhanced concentration polarization can cause a decrease in flux and an increase in solute transport across the membrane surface. By not maintaining a constant permeate flux, the lower volume of water could artificially inflate the concentration in the permeate.

To date, multiple batch test studies on PFAA removal have been done on GAC and they have been limited to mostly PFOS and PFOA (Qiang 2009; Deng 2010; Senevirathna 2010), with the exception of one study that also looked at perfluorobutane sulfonic acid (PFBS) (Carter 2010). These studies revealed that GAC can be effective at removing PFAAs under certain conditions, but its efficacy is reduced when ions, such as SO_4^{2-} and Cr(VI), are introduced as a result of competition (Deng 2010).

Batch and column tests with a suite of PFAAs present have yet to be performed using GAC, so the kinetic and competitive effects are unknown. Studies on the effects of other potentially limiting factors for GAC performance with these chemicals, such as the presence of DOM, have yet to be explored as well. Rapid small scale column tests (RSSCTs) are the most commonly used tool for GAC evaluation, though issues arise when attempting to scale treatment performance these tests are not representative of full scale systems with trace organics when DOM is present (Corwin 2010).

The objective of this study was to evaluate two advanced treatment techniques, GAC and NF, for the removal of a suite of PFAAs of varying sizes, including both PFCAs and perfluorosulfonic acids (PFSAs), from water. NF experiments were conducted to evaluate the rejection behavior of unfouled and fouled NF270 membranes. For GAC, RSSCTs were performed to: 1) compare 3 carbons of varying composition, two bituminous coal and one coconut shell carbon, in their removal efficacy; and 2) assess the effect of DOM on GAC removal efficiency using a natural water source spiked with PFAAs.

4.2 Materials and Methods

This section describes the materials used and the set up for each experiment. It also describes how the samples were prepared and analyzed.

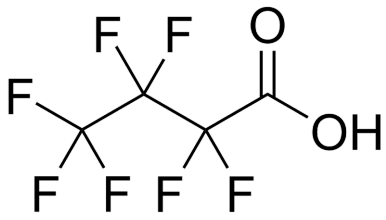
4.2.1 Materials

The NF270 (Dow/FilmTec, Minneapolis, MN), a polyamide thin-film composite flat-sheet membrane, was used for all NF experiments. Three different types of GAC, whose properties are listed in Table 4.1, were evaluated for the RSSCT experiments, including Filtrasorb®300 (F300) and F600 (Calgon Carbon Corporation, Pittsburg, PA) and AquaCarb® 1240C (Siemens Water Technologies, Munich, Germany). Raw PFAS materials for the spiking solution were obtained from Sigma Aldrich, and included perfluorobutyric acid (PFBA) (214 g/mol), perfluoropentanoic

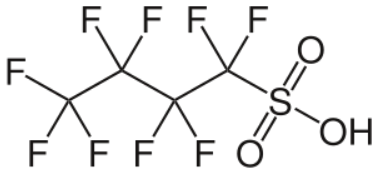
acid (PFPeA) (264 g/mol), perfluorohexanoic acid (PFHxA) (314 g/mol), PFOA (414 g/mol), perfluorononanoic acid (PFNA) (464 g/mol), perfluorodecanoic acid (PFDA) (514 g/mol), PFBS (300 g/mol), perfluorohexane sulfonic acid (PFHxS) (400 g/mol), and PFOS (500 g/mol). Figure 4.1 displays the chemical structures of PFBA and PFBS.

Table 4.1: Properties of the Three Activated Carbons Evaluated

Name	F300	F600	1240C
Manufacturer	Calgon	Calgon	Siemens
Carbon Type	Bituminous Coal	Bituminous Coal	Coconut Shell
Mesh Size, U.S. Sieve	12x40	12x40	12x40
Iodine No., mg I2/g	900	850	1100
Abrasion No., Wt. %	78	80	85
Apparent Density, g/cc	0.48	0.62 - 0.65	0.46 - 0.52



(a) PFBA



(b) PFBS

Figure 4.1: Chemical Structures of PFBA and PFBS

4.2.2 Membrane Experiments

The set-up for the membrane experiments was the same system previously described (Bellona 2010), with a few modifications. The two major modifications were a larger feed volume (200 L barrel) which enabled the system to be operated in flow

through mode (as opposed to recycling the permeate and concentrate back into the feed tank which was done in Steinle-Darling (2008)), and the two SEPA cells were run in succession with the concentrate from the first as the feed to the second to provide experimental duplication. Three experiments were performed. The first was with spiked DI water and virgin membranes. This was followed by an experiment with new membranes and spiked AGW, whose recipe is described in a previous study (Sepulvado pending publication). These membranes were then fouled with a solution containing Aldrich Humic Acid (AHA) with DOM levels at 2.5 mg/L (method described below), and the third experiment with the spiked AGW matrix was performed again with a fouled layer present.

For all three experiments, feeds were spiked with approximately 1 µg/L of each PFAS and feed flow was kept constant at 1 L/min with a temperature of approximately 18̊ C, and a pH of 6.7. For the two virgin membrane experiments, the apparatus was operated for 2.5 hours starting at 25 psi, and the pressure was increased in increments of 25 psi every 30 minutes with samples of feed, concentrate, and permeates for PFASs taken at 15 and 30 minutes. A prior study (Steinle-Darling 2008) observed that PFASs reach steady-state rejection with the NF270 after a few minutes, suggesting a 30 min experimental duration for each pressure was sufficient. Samples of feed, concentrate and permeates were also taken every 30 minutes for salts, metals, and TOC analysis. Permeate flow was measured using a differential flowmeter (Cole Parmer, Model #32908-43), and verified with a graduated cylinder and stopwatch. For the second AGW experiment with the fouled membrane, 30 min intervals were used again, but pressures were increased to match permeate flux conditions in the first AGW experiment.

The same two flat sheet membranes were used for both AGW experiments. In order to foul the membranes with an organic fouling layer, a 200 L solution was created based on previous research (Tang 2007) with 1 mMol Ca^{2+}, 10 mMol total

ionic strength, and AHA added to raise the TOC level to approximately 2.5 mg/L. During the fouling process, the system was run with the permeate and concentrate being recycled back into the feed tank. Prior to the addition of AHA, the system was run for 24 hours to equilibrate the membranes with the background electrolytes with pressure held constant at 125 psi and permeate flow monitored for stabilization. Once permeate flow stabilized, AHA was added to the feed, and a constant permeate flow of 20 mL/min was maintained by increasing pressure until the flux declined by 35%, which occurred after 200 min of operation. **??** displays the normalized specific permeate flux decline during the fouling stage. Samples were taken for salts, metals and TOC analysis before and after the addition of AHA, as well as in the final minutes. For the fouling solution, pH was approximately 6.5 and temperature was 18̊ C.

4.2.3 GAC Experiments

Two RSSCT experiments were performed for this study. The first had triplicate columns loaded with F300 carbon, and the second had a total of six columns with duplicate columns containing each of the F300, F600 and 1240C carbons. All columns used were glass columns and prepared the same way: the carbon was ground up until the diameter was approximately 0.21 mm (60x80 mesh size, US sieves), and then decanted with DI water for uniformity. The diameter of the column was 0.7 cm, over 33x the diameter of the particles to prevent channeling effects. Once the carbon was wet, it remained as a slurry solution for the remainder of the experiments. To degas the carbon, the carbon slurry was boiled for 5 minutes in DI water, then poured into a 50 mL falcon tube and placed on a shaker table for 24 hours. Next, a dropper was used to transfer carbon by hand to a depth of 1 cm in the column, which also contained a layer of glass beads and glass wool. More glass wool was then inserted into the column to hold the carbon in place. A three-way stopcock was placed on both sides of the column with a sample line running from it for both the influent and effluent. All columns were run in up flow mode at a rate of 1.0 mL/min using a low

speed Ismatec® HPLC pump yielding an empty bed contact time (EBCT) of 0.38 minutes.

For the triplicate F300 columns, the feed solution was DI water nominally spiked with 1 µg/L of each PFAA. The feed for the second experiment was water collected from Clear Creek (Golden, CO) that was filtered through a 1 micron filter, and then nominally spiked with about 1 µg/L of each PFAA. Column effluent samples were collected every 3 to 4 days, and influent samples were taken once per week. A summary of parameters can be found in Table C.2 in Appendix C.

4.2.4 Sample Preparation and Analysis

All samples were collected in 20 mL plastic scintillation vials. Aqueous samples were prepared and analyzed by isotope dilution using direct injection with LC/MS/MS, a method detailed in Sepulvado (pending publication). Limits of quantification (LOQs) were 20 ng/L for all of the PFCAs, and 10 ng/L for all of the PFAAs.

TOC samples were analyzed using a Sievers model 5310C total organic carbon analyzer. The method used was Method 5310 C (persulfate oxidation/UV irradiation) from "Standard Methods for the Examination of Water and Wastewater". Salts were measured using a Dionex ICS-90 ion chromatography system using EPA method 300.1 (Hautman 1997). Metals were analyzed using a Perkin-Elmer Optima 3000.

4.2.5 Quality Assurance and Quality Control

For the LC/MS/MS runs, a double blank was placed in between sets of six samples. For all batches analyzed in this study, at least three blanks containing only the stable isotope surrogate standards were analyzed throughout the batch to enable evaluation of possible sample carryover. For the GAC column experiments, triplicates were run for the initial experiment, followed by duplicates for each carbon type for the latter experiments. In the NF experiment, the system was operated in flow through mode and the feed solution was well-mixed, so all influent samples were considered

replicates. The analytical variation for these replicates is displayed in Table C.1 in Appendix C. Samples of the permeates and influent were analyzed for salts, metals, and TOC to ensure that the integrity of the membranes stayed intact throughout the experiment, and the result can be found in Table C.3 in Appendix C.

Prior to the GAC experiments, the system were operated with no media present to test for PFAA contamination by running DI water through the system and sampling all ports. A similar process was performed for the membrane apparatus. All samples analyzed had concentrations below the LOQs for all chemicals. Sorption tests were also performed on each system using a spiked DI water with no GAC present for the RSSCTs and no membrane present for the NF experiment. The materials used in the experiments were selected in order to reduce PFAA sorption, which was validated by matching influent and effluent concentrations during the sorption tests.

4.3 Results and Discussion

This section analyzes and interprets the results from the samples taken during the NF and GAC experiments.

4.3.1 Membrane Experiments

Precautionary samples of salts, metals and TOC were taken to test the integrity of the membrane throughout the experiment. TOC data were limited to the samples of the fouling solution with AHA in it because levels of TOC in the AGW feeds were measured to be about 0.5 mg/L, which is also the analytical variability (+/- 0.5 mg/L) of the method used. Approximately 82% rejection was observed by the two membranes for TOC during the fouling process. According to the manufacturer's website, the NF270 is expected to have rejection rates for sodium chloride and magnesium sulfate of 50% and >98%, respectively. As can be seen in Table S3 in the SI, the rejection for sulfate surpassed the manufacturer's specifications for all samples at >99%. Calcium and sodium were rejected well above 50% throughout the dura-

tion of the experiment, with the exception of four samples. For the lowest flow rate, 4.5 ml/min, with the two fouled membrane, a higher concentration of calcium was observed in the permeates than in the feed. Also for the next flow rate, 9 ml/min, a lower rejection rate was observed for calcium for the two fouled membranes (64% and 36%) compared to the other pressures and the virgin membranes which were all >80%. There are two potential reasons that this occurred. The first is that residual calcium was in the permeate tubing from the fouling solution, which had a concentration of 34 mg/L versus the 0.2 mg/L in the AGW feed, and contaminated these four samples. The second possibility is that some of the calcium was in the fouling layer on the membrane surface and was pushed through into the permeates. This phenomenon was only observed with calcium, and none of the other metals or salts, which may be explained by calcium having the largest difference in concentration between the fouling solution and the AGW feed solution. Since this only occurred with calcium, and at the low flow rates but not the high ones, the integrity of the membranes was believed to have stayed intact for the duration of the experiments.

Table 4.2 shows the average percent rejection (n = 4) of the two membranes for each PFAA in the three experiments at different flux conditions. Permeate concentrations for PFOS and all of the PFCAs were below their LOQs. PFBS and PFHxS, however, were detected in the permeate above their LOQs (10 ng/L and 20 ng/L, respectively), in the virgin membrane experiments. In fact, for the spiked DI water, PFBS and PFHxS were detected at all pressures with the exception at 25 psi for PFHxS, and with concentration ranges of 12-41 ng/L and 30-40 ng/L, respectively. The detection of the two smaller molecular weight PFSAs, but not PFOS, suggests that the size of the chemical is affecting rejection rates. For the AGW virgin-membrane experiment, PFBS was detected at the higher pressures (75, 100, and 125 psi) at concentrations of 13-20 ng/L. Although these two chemicals were detected in the permeates, rejection rates for all PFASs were > 93%. Excluding

PFBA, the shortest chain PFCA which had a lower feed concentration (350 ng/L) than the other chemicals, rejection rates were all > 95%. Interestingly, the shortest chain PFCA in the Steinle-Darling et al. (2008) study was PFPeA, and it only had a rejection of 72% with the virgin membrane using spiked DI water. This study had a shorter chain PFCA, PFBA, which had a higher rejection rate at > 93%, and PFPeA had > 97% rejection.

The permeates from the AGW experiment with the fouled membrane did not have any PFAA concentrations above their LOQs. Therefore it was observed that the fouling layer on the NF270 did not have a negative effect on PFAA rejection. In fact, the two chemicals that were detected in the permeate of the virgin membranes, PFBS and PFHxS, were not detected in the permeates of the fouled membranes, suggesting that the fouling layer increased rejection capacity. An increase in rejection has been shown for some organic chemicals resulting from changes in the membrane surface characteristics from a fouling layer such as contact angle (an index of hydrophobicity), zeta-potential, functionality, and surface morphology (Xu 2006). The cause of increased rejection in this experiment is believed to be a result of the fouling layer causing a decrease in pore size preventing the smaller chain PFSAs from crossing the membrane surface. . Results from these experiments contradict the findings in Steinle-Darling et al. (2008). One possible cause of this contradiction is believed to be a result of increasing the trans-membrane pressure to maintain a constant permeate flux for comparison. The effects of an organic fouling layer have been shown (Bellona 2010) to increase the transport of certain trace organics through cake enhance concentration polarization. This process also causes a decrease in permeate flux leading to a lower volume of water. Therefore, it is possible that PFAA concentrations would have been the same in the permeate for the virgin and fouled membranes in the Steinle-Darling et al. (2008) experiment, but levels were slightly elevated in the permeate of the fouled membranes because of the lower volume of water from the permeate flux

Table 4.2: NF270 PFAA Rejection Results. Rejection measurements arising from permeate samples with PFASs measured above the LOQ are in bold and italicized. *PWP: Pure Water Permeability

Membrane/ Water	Pressure (psi)	Permeate Flow (ml/min)	PWP*	PFBA	PFPeA	PFHxA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
LOQ (ng/L)				20	20	20	20	20	20	10	10	10
AGW Virgin	25	4.5	100%	> 94%	> 97%	> 95%	> 97%	> 98%	> 97%	> 99%	> 99%	> 99%
	50	9	100%	> 94%	> 97%	> 95%	> 97%	> 97%	> 97%	> 99%	> 99%	> 99%
	75	13.5	100%	> 94%	> 97%	> 95%	> 97%	> 98%	> 97%	***99%***	> 99%	> 99%
	100	16	100%	> 95%	> 97%	> 95%	> 97%	> 98%	> 97%	***98%***	> 99%	> 99%
	125	20.5	100%	> 94%	> 97%	> 95%	> 97%	> 98%	> 97%	***98%***	> 99%	> 99%
AGW Fouled	40	4.5	63%	> 95%	> 97%	> 95%	> 97%	> 98%	> 97%	> 99%	> 99%	> 99%
	70	9	71%	> 94%	> 97%	> 95%	> 97%	> 97%	> 97%	> 99%	> 99%	> 99%
	96	13.5	78%	> 94%	> 97%	> 95%	> 97%	> 97%	> 96%	> 99%	> 99%	> 99%
	110	16	91%	> 94%	> 97%	> 95%	> 97%	> 98%	> 97%	> 99%	> 99%	> 99%
	140	20.5	89%	> 94%	> 97%	> 95%	> 97%	> 98%	> 97%	> 99%	> 99%	> 99%
DI Virgin	25	5.5	100%	> 93%	> 97%	> 95%	> 97%	> 98%	> 97%	***97%***	> 97%	> 99%
	50	7.5	100%	> 93%	> 97%	> 95%	> 97%	> 98%	> 98%	***98%***	***98%***	> 99%
	75	12	100%	> 93%	> 97%	> 95%	> 95%	> 97%	> 97%	***96%***	***97%***	> 99%
	100	16	100%	> 94%	> 97%	> 95%	> 97%	> 98%	> 98%	***96%***	***96%***	> 99%
	125	19	100%	> 93%	> 97%	> 95%	> 97%	> 97%	> 98%	***95%***	***96%***	> 99%

decline. However, there were two other major differences between the experiments: 1) the system for this experiment was run in flow through mode, whereas the permeate and concentrate were recycled in the other; and 2) both studies had different water qualities for their feed, where this study used a spiked AGW, and the other used a spiked DI water. PFAA interactions with the membrane surface could be changed by all three of these differences, but the effects on rejection of PFAAs as a result of changing the ionic strength of the feed were tested and found to be minimal (Steinle-Darling 2008), therefore water quality differences are less likely to be a cause for the contradiction.

In regards to flow-through mode, scouring on the membrane surface was observed in the experiment described here. The foul layer, which originally had the membrane functioning at about 65% of its pure water permeability, was apparently scoured off over time by the cross-flow velocity, and at the final two fluxes the membrane was functioning at about 90% (Table 2). A comparison of the PFAA concentrations in the concentrate and influent revealed that all PFAAs were within the error associated with analytical variability, suggesting that the chemicals were not significantly adsorbing to the membrane surface (fouled or unfouled) at any of the flux conditions. These data suggest minimal interactions between the PFAAs and the fouling layer on the membrane surface on the order of hours. This result agrees with the Steinle-Darling et al. (2008) study, which found that only FOSA, an uncharged PFAA precursor chemical that was not present in this study, was the only chemical that had significant interactions with the membrane surface; therefore, it is not likely that the difference between flow-through and recycle mode caused the contradiction in results between the two studies. Table C.4 in Appendix C provides the details for this analysis.

The NF270 membrane had high rejection of all PFAAs in the suite examined for this study, including the shorter chain PFCAs. These bench scale results are promising as NF is a less costly process than RO, which was the only treatment

type that was found to effectively remove PFBA during a full scale study (Chapter 3). Further experiments are warranted using either the NF270 or even a looser NF membrane at the pilot scale and/or full scale.

4.3.2 GAC Experiments

Breakthrough curves for the average of the three F300 columns from the RSSCT experiment with spiked DI water are displayed in Figure 4.2. Initial breakthrough occurred at approximately 30,000 bed volumes (BVs), or 8 days of operation, for all of the chemicals except for PFNA, PFDA, and PFHxS which started at 45,000 BVs, and PFOS whose effluent values never measured more than 2% (at 98,000 BVs) of influent concentration. For the 125,000 BVs (˜33 days) for which this experiment was conducted, only the two smallest PFAAs, PFBA and PFPeA, had > 10% breakthrough (at approximately 72,000 and 83,000 BVs, respectively). Other PFAAs that reached > 5% breakthrough, in order of breakthrough, included PFOA (˜56,000 BVs), PFHxA (˜72,000 BVs), PFBS (˜83,000BVs), and PFHxS (˜83,000 BVs). The two largest chain PFCAs, PFNA and PFDA, as well as the largest chain PFSA, PFOS, never reached > 5% breakthrough. The two smallest chain PFCAs had the greatest breakthrough, and the two largest PFCAs had the smallest breakthrough. This chain length dependent pattern was expected to be observed based on full scale data (Appleman submitted). GAC was expected to be effective, at least with PFBS, PFOS, and PFOA based on previous batch tests (Lampert 2007; Qiang 2009; Carter 2010; Senevirathna 2010), but had not been previously evaluated using bench-scale using column tests. Overall, the F300 exhibited excellent removal of these chemicals for most of the duration of this experiment.

Breakthrough results of all PFAAs from the next set of columns, using filtered Clear Creek water with a DOC of 1.7 mg/L, can be found in Figure C.2, Figure C.3, and Figure C.4 in Appendix C. All PFASs had a breakthrough of > 20% within the first 3 days (˜11,000 BVs) of operation for all three carbons—levels that had not

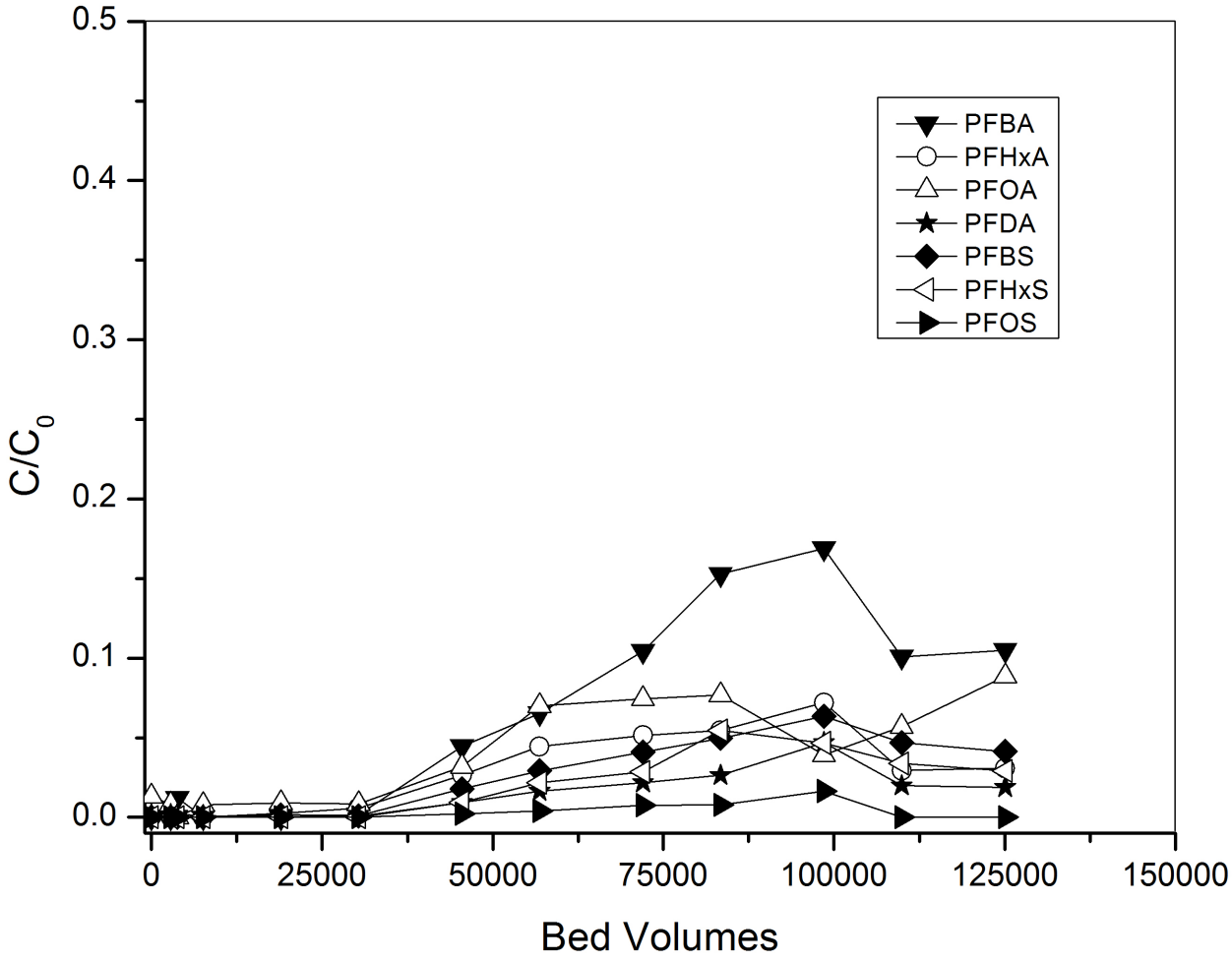


Figure 4.2: Average PFAA Breakthrough for Three F300 Columns with Spiked DI Water. PFPeA and PFNA have been removed for aesthetics.

been reached for any chemicals within the 125,000 BVs of the DOM-free experiments. PFBA and PFPeA, the two shortest chain PFCAs, were the fastest to breakthrough for all three carbons, exceeding full (100%) breakthrough by 11,000 BVs. When the effluent concentration exceeds the influent, it is believed to be due to competitive effects with other sorbing species (perhaps longer chain PFAAs and/or organic matter) leading to desorption and release of sorbed PFBA and PFPeA over time. For the F600 and 1240C carbons, PFOA also achieved full breakthrough within 11,000 BVs, and for the F300 carbon it took about 26,000 BVs. The rapid breakthrough makes it clear that the presence of DOM has a large effect on carbon performance in the removal of PFAAs. This effect is likely attributed to the organic matter occupying pore space or sorption sites in the GAC rendering it unable to sorb other compounds. Although other studies have not been performed on the competitive effects of DOM with PFAAs, similar results have been seen in batch and pilot column studies with other organic compounds, i.e. pesticides and pharmaceuticals, where both powdered activated carbon (PAC) (Matsui 2003; Dickenson 2010) and GAC (Matsui 2002) removal efficacy was significantly reduced as a result of competition for adsorption sites with DOM.

Figure 4.3 was created in an effort to compare the performance of the three types of carbon. These compare the breakthrough of PFBA, PFHxA, PFOA, and PFOS. Figure C.5, Figure C.6, Figure C.7, Figure C.8, and Figure C.9 in Appendix C display comparisons of the other PFAAs.As a result of the initial breakthrough of all PFAAs for the three carbons occurring by the second sampling (about 11,000 BVs), the extent of breakthrough has to be addressed in order to compare carbon performance. PFBA and PFPeA reached full breakthrough by 11,000 BVs for all three carbons. By this time, PFOA had also achieved full breakthrough for the 1240C and the F600, but only reached 59% breakthrough for the F300. The most notable differences in performance between the three carbons were observed for the larger chemicals PFNA,

PFDA, and PFOS. These three chemicals had breakthroughs of 75%, 78%, and 69%, respectively, with the 1240C and similar breakthroughs of 63%, 83%, and 64% with the F600. The F300 carbon clearly outperformed these with breakthroughs of 32%, 31%, and 26% for PFNA, PFDA, and PFOS, respectively. The difference between the F600 and the 1240C is more apparent when looking at breakthrough over the entire duration of the experiment where all PFAAs reached full breakthrough for the 1240C, but PFHxA, PFNA, PFDA, and PFOS never achieved full breakthrough for the F600. For carbon comparison, these results make it apparent that with DOM present, the F300 was the most effective of the three, followed by the F600, then the 1240C. One possible explanation is that the coconut-based carbons, like 1240C, have a more microporous structure, than coal-based carbons, like F300 and F600 (MWH 2005). It is possible that the tighter structure resulted in a kinetic limitation, causing this carbon to be less effective than the other two. The slightly better performance in the F300 versus the F600 is also likely due to its physical structure. The F300 has a higher Iodine No. of 900 mg I2/g than F600 (850 mg I2/g), which indicates F300 has a higher microporosity and Brunauer-Emmett-Teller (BET) surface area and more favorable for the sorption of the PFAAs (Sontheimer 1988).

4.4 Conclusion

This study looked at the efficacy of NF and GAC for the removal of PFAAs using bench-scale experiments. The NF270 membrane was observed to reject almost all of these chemicals to below LOQs at various pressures and with two different water matrices. When a fouled layer was present on the membrane, it still maintained the same high and sometimes better rejection rates as it had with virgin membranes. These findings are promising in that NF treatment could be an effective method for a variety of PFAA molecular weights and pilot- and full-scale systems.

GAC was assessed using RSSCTs in an attempt to observe the kinetic effects of a flow through system and compare different types of carbon. The effect of the

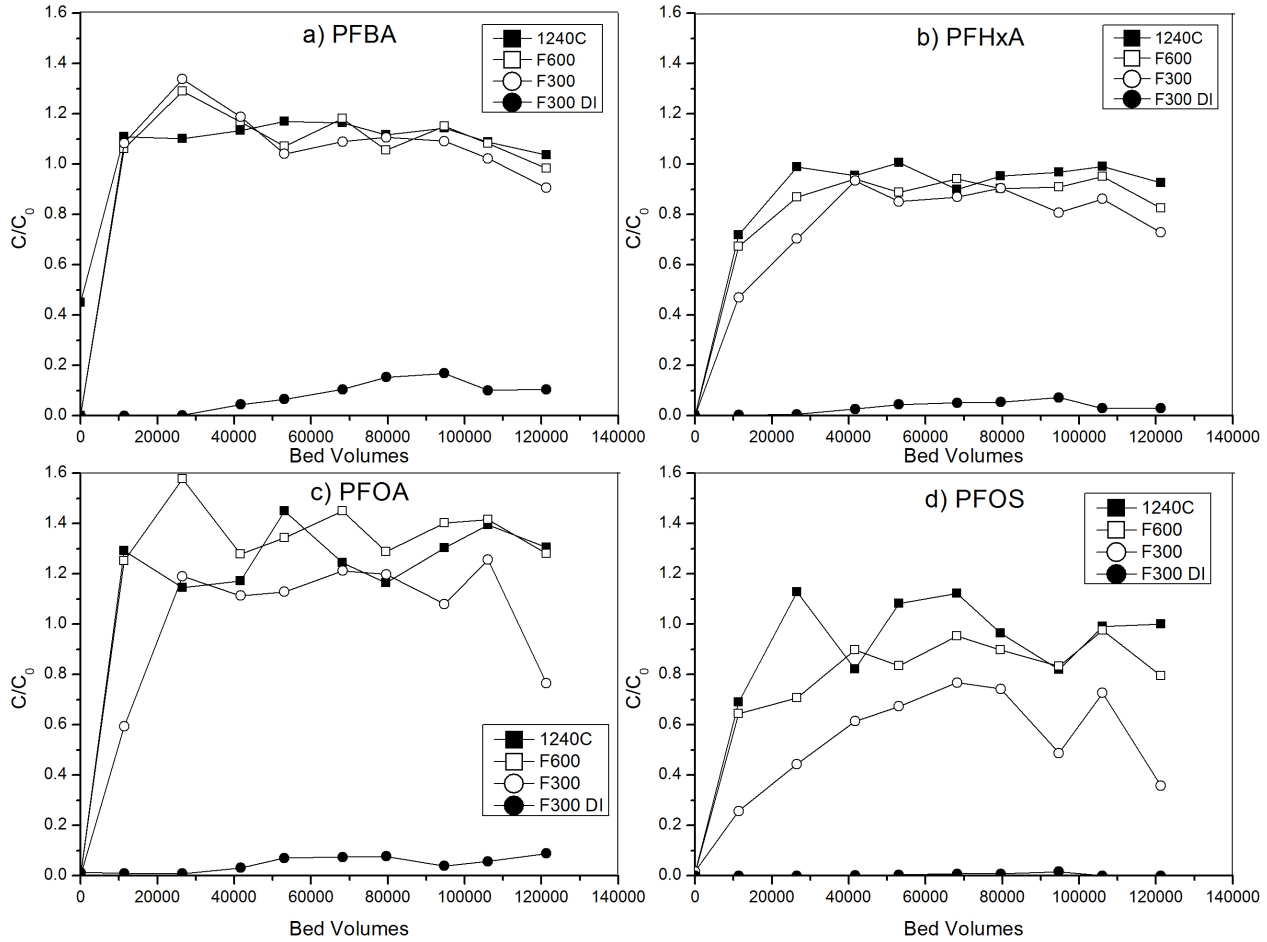


Figure 4.3: Carbon Breakthrough Comparison of Four PFAAs. Comparison of breakthrough times for PFBA, PFHxA, PFOA and PFOS with three different carbons (1240C, F300, and F600) and two different water matrices (spiked River water and spiked DI water).

presence of DOM was also evaluated, where results indicate that GAC is more effective at removing PFAAs in low DOC DI water than when DOC is present at 1.7 mg/L. Of the three carbons, the F300 performed the best, but it still had issues with the shorter chain PFCAs, PFBA and PFPeA. Future studies should be performed looking at other types of carbons to determine if there is a carbon that is capable of targeting these smaller chemicals and scaling RSSCTs for PFAAs removal at full-scale should be explored.

CHAPTER 5
CONCLUSION

PFASs are a persistent, prevalent, and very likely toxic group of chemicals that are finding their way into people's drinking water across the U.S. Two recent epidemiological studies (C8 2012; Grandjean 2012) found correlations suggesting that PFOA is a carcinogen, and that PFOA and PFOS both have adverse immunological effects. These results are in addition to animal studies that found numerous other adverse health effects including hepatotoxicity and possible reproductive and developmental toxicities. Thus, human exposure is a big concern. The EPA, and some states, such as New Jersey and Minnesota, are beginning to implement regulatory levels on a few of these chemicals in drinking waters.

This project found that full-scale common conventional treatments, such as coagulation followed by physical separation processes, and chemical oxidation and disinfection, did not remove these chemicals very effectively, if at all. RBF treatment appears to be ineffective as well. In addition, possible production was observed by some of the oxidation treatments. Several PFASs were observed to be removed by RO, GAC, and AIX at the full-scale. However, GAC and AIX were less effective at removing the shorter chain PFASs, whereas RO treatment was effective at even the smallest PFAS studied, PFBA.

The bench-scale study performed with RSSCTs observed that in the presence of DOM, GAC's efficacy to remove these chemicals is exhausted at a much faster rate. Therefore, a pretreatment step would be required to remove the DOM before utilizing a GAC filter. NF was deemed effective at rejecting these chemicals with both virgin membranes and membranes with an organic fouled layer. This process needs to be studied further at the pilot scale (and ideally the full scale) as it is a less expensive

process than RO, and might be equally effective at rejecting PFASs.

There is likely going to be a push for lower regulatory levels for these chemicals as more conclusive evidence of their toxicity is discovered and released to the public. The inability of common conventional treatments to remove PFASs will become an issue for some utilities if low ng/L regulatory levels are promulgated for these chemicals. In this event, those utilities with significant PFAS levels in their raw water sources will need to examine additional mitigation strategies, such as alternative treatment technologies. Utilities that have shorter chain PFASs, e.g. PFBA and PFPeA, in their raw water source will likely find a need to implement NF or RO treatments. In an absence of the shorter chain chemicals, less costly treatments, such as AIX and/or GAC, may be adequate. Multiple barrier approaches might help to extend the life of the treatment steps and also protect against unnecessary exposure via contaminated tap water. Manufacturers are continuing to produce these chemicals for use in various industries, and because of their recalcitrant properties, human exposure is inevitable. Therefore, it is imperative that they are better understood in terms of their toxicity, and that steps are taken to limit exposure whenever possible.

5.1 Recommendations For Future Work

This project looked at a wide variety of treatments at the full-scale, and a couple of treatments at the bench scale to shed light on their potential to remove PFASs from raw water sources to protect humans from one potential route of exposure. The health effects of exposure to these chemicals needs to be studied further to help establish discreet regulatory levels. These levels will likely dictate the selection of treatment processes for utilities with these chemicals in their raw water source. Throughout the project, questions and observations arose that have the potential for future research topics:

- The selection of raw water sources was biased for this project because utilities chosen were suspected or known to have PFASs in their raw water. This potentially resulted in abnormally high detection frequencies of these chemicals. Collecting raw water samples from more sites selected randomly throughout the U.S. would provide a better idea of occurrence levels.

- Sampling for the full-scale treatment study was performed using synoptic grab samples which were useful to gauge an estimate of the efficacy of certain treatments. Composite sampling could prove useful to provide more insight into certain treatments, especially those where possible formation of PFASs was observed. It could also be performed to verify the results from this project.

- At most, sampling was performed two times for each treatment process, except for Utility 20. This was considered sufficient because results from each sampling were consistent. The performance of certain treatment processes, such as GAC, IX, and RO, are time dependent. Therefore, it would be useful to sample these treatments periodically over the course of months or years to see how the age of the media affects the potential to remove PFASs.

- NF was tested using flat sheet membranes on the bench scale under very specific conditions, making it difficult to assume the same results would occur in a full-scale treatment system. This treatment should be investigated further at pilot- and full-scale.

- The RSSCT GAC experiments were used to compare carbons and observe the effects of DOM on the removal of PFASs. There is a potential to design RSSCTs using GAC for the removal of trace organics that makes it possible to scale the results. This option could be explored and its accuracy tested using RSSCTs with the carbon and raw water from Utility 20.

- Further AIX research is needed to identify which AIX resins are most suitable for PFAS removal, the selectivities of resins for different PFASs, and the most suitable regeneration techniques. In addition, a better understanding of sorption kinetics and competition with other anions and natural organic matter is necessary.

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APPENDIX A - SUPPLEMENTAL INFORMATION FOR CHAPTER 2

Table A.1: Summary of the toxicological effects of PFOA and PFOS on animals

Toxicity	Effects	PFOA	PFOS	References
Hepatotoxicity	PPAR-α proliferation	yes	yes	Berthiaume 2002; Ikeda 1985, 1987; Pastoor 1987; Sohlenius 1992, 1993
	PPAR-α proliferation	n/a	no	Thomford, 2002a, 2002b; Seacat 2003
	PPAR-α activation	yes	yes	Vanden Hueval 2006
	Increased relative liver weight	n/a	yes	Seacat 2002, 2003
	Increased absolute liver weight, decreased serum cholesterol, increased ALT activity	n/a	yes	Seacat 2003
	Gross/microscopic morphological alterations in liver	n/a	no	Thomford 2002a
	Liver toxicity and adenomas	yes	n/a	Klaunig 2003
	Increased absolute liver weight, increased PPAR-α proliferation	yes	n/a	Yang 2001, 2002
Reproductive/ Developmental Toxicity	Reduced fetal weight, increased neonatal mortality	yes	yes	Lau 2007; Olsen 2009
	Increased neonatal deaths	n/a	yes	Gratsy 2003
	Death of newborns within first day	n/a	yes	Lau 2003
	Reduced fetal weight	n/a	yes	Case 2001
	Neonatal mortality, reduced birth weight, growth deficits, developmental delays	yes	n/a	Wolf 2007
	Birth weight deficits, obesity by 18 months of age and organ specific abnormalities	yes	n/a	Fenton 2007
	Estrous cycling, sperm number and quality, mating and fertility, histopathology of reproductive organs	no	n/a	Butenhoff 2004

Table A.1: Continued.

Toxicity	Effects	PFOA	PFOS	References
	Alterations in sex organs	no	n/a	Butenhoff 2002; Thomford 2001; Griffith 1980
Immunotoxicity	Decreased body weight, elevation of liver weight, decreased thymus and spleen weight	yes	n/a	Yang 2000, 2001, 2002a, 2002b
	Suppression of inflammatory responses, lymphoid organ atrophy, decreased de novo antibody production	yes	n/a	Yang 2000; DeWitt 2008
	Dose dependent decrease in adipose tissue	yes	n/a	Xie 2002, 2003
	Morphological alterations in the spleen, thymus, or mesenteric lymph nodes	n/a	no	Hoberman 2003; Seacat 2002, 2003; Thomford 2002a, 2002b; 3M 2007a; van Otterdiijk 2007a, 2007b
	Reduced T4 and T3 hormones	n/a	yes	Lau 2003, 2007; Seacat 2003
	Decreased serum and testicular testosterone, increased serum estradiol levels	yes	n/a	Biegel 1995; Bookstaff 1990; Cook 1992; Liu 1996
Carcinogenicity	Increased testicular Leydig cell tumors	yes	n/a	Riker 1987
	Increased incidence of benign hepatocellular, testicular Leydig-cell, and pancreatic acinar-cell tumors	yes	n/a	Biegel 2001
	Increased liver hepatocellular adenomas, increased thyroid follicular cell adenomas	n/a	yes	Thomford 2002b

Table A.2: Occurrence Data on PFASs from Literature

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFBA									None found
PFPeA									None found
PFHxA	WW influent	Korea	15	15		nd - 13.4	80%		Guo 2010
PFHxA	WW effluent	Korea	15	15		1.1 - 14.8	100%		Guo 2010
PFHxA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFHxA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFHxA	Industrial inf.	Korea	3	3		nd - 13.3	67%		Guo 2010
PFHxA	Industrial eff.	Korea	3	3		1.6 - 16.1	100%		Guo 2010
PFHxA	Tap	Spain	1	1	4	<.87		<.87	Ericson 2008
PFHxA	River	Spain	1	1	4	<.87		<.87	Ericson 2008
PFHxA	Bottled	Spain	1	1	4	<.87		<.87	Ericson 2008
PFHxA	River	Rhine River, Germany	1	38		nd - 77	32%	nd	Skutlarek 2006
PFHxA	Surface	Ruhr area, Germany		22		nd - 1248	68%	5.5	Skutlarek 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFHxA	River	Moehne River, Germany	1	12		nd - 3040	67%	255	Skutlarek 2006
PFHxA	Drinking	Ruhr area, Germany		21		nd - 56	67%	5	Skutlarek 2006
PFHxA	Drinking	Outside Ruhr, Germany		16		nd - 9	6%	nd	Skutlarek 2006
PFHxA	River	US	1	80	100	<1 - 23	54%	5.14	Nakayama 2007
PFHpA	lake	US/Canada	5	19		nd - 2.1	26%		Furdui 2008
PFHpA	tributary	US/Canada	3			nd - 13.4	67%		Furdui 2008
PFHpA	WW effluent	Canada	6	6		1.9 - 7.1	100%		Furdui 2008
PFHpA	WW influent	Canada	1	1		1.9	100%		Furdui 2008
PFHpA	WW influent	Korea	15	15		nd - 11.8	73%		Guo 2010
PFHpA	WW effluent	Korea	15	15		nd - 16.1	67%		Guo 2010
PFHpA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFHpA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFHpA	Industrial inf.	Korea	3	3		nd - 6.3	67%		Guo 2010

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFHpA	Industrial eff.	Korea	3	3		1.2 - 4.9	100%		Guo 2010
PFHpA	Tap	Spain	1	1	4	<.61 - 3.02		0.64	Ericson 2008
PFHpA	River	Spain	1	1	4	<.61 - 3.38		0.72	Ericson 2008
PFHpA	Bottled	Spain	1	1	4	<.61		<.61	Ericson 2008
PFHpA	River	Rhine River, Germany	1	38		nd - 11	11%	nd	Skutlarek 2006
PFHpA	Surface	Ruhr area, Germany		22		nd - 148	14%	nd	Skutlarek 2006
PFHpA	River	Moehne River, Germany	1	12		nd - 989	67%	98	Skutlarek 2006
PFHpA	Drinking	Ruhr area, Germany		21		nd - 23	10%	nd	Skutlarek 2006
PFHpA	Drinking	Outside Ruhr, Germany		16		nd	0%	nd	Skutlarek 2006
PFHpA	River	US	1	80	100	<1 - 329	67%	14.8	Nakayama 2007
PFOA	surface	Canada	1	14	3	<2.1 - 19			D'eon 2009
PFOA	lake	US/Canada	5	19		.1 - 6.7	100%		Furdui 2008
PFOA	tributary	US/Canada	3			4.1 - 38.1	100%		Furdui 2008
PFOA	WW effluent	Canada	6	6		9.4 - 54.7	100%		Furdui 2008

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOA	WW influent	Canada	1	1		6.5	100%		Furdui 2008
PFOA	WW influent	Korea	15	15		2.3 - 37.4	100%		Guo 2010
PFOA	WW effluent	Korea	15	15		3.4 - 49.2	100%		Guo 2010
PFOA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFOA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFOA	Industrial inf.	Korea	3	3		4.3 - 615	100%		Guo 2010
PFOA	Industrial eff.	Korea	3	3		6.4 - 591	100%		Guo 2010
PFOA	Tap	Spain	1	1	4	.32 - 6.28		1.03	Ericson 2008
PFOA	River	Spain	1	1	4	<.22 - 24.9		1.65	Ericson 2008
PFOA	Bottled	Spain	1	1	4	<.16 - .67		0.36	Ericson 2008
PFOA	GW, unconfined, raw	NJ, USA	12	12		nd - 33	67%	7.5	Post 2009
PFOA	GW, unconfined, finished	NJ, USA	2	2		5.0 - 6.0	100%	5.5	Post 2009

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOA	GW, semi-confined, raw	NJ, USA	1	1		25 - 27		26	Post 2009
PFOA	GW, confined, raw	NJ, USA	1	1		nd	0%	nd	Post 2009
PFOA	GW, confined, finished	NJ, USA	1	1		nd	0%	nd	Post 2009
PFOA	SW, raw	NJ, USA	8	8		nq - 35	88%	12.5	Post 2009
PFOA	SW, finished	NJ, USA	4	4		nq - 39	50%	<27	Post 2009
PFOA	GW, unconfined	NJ, USA	7	7	32	18 - 140	100%	69	Post 2009
PFOA	SW	NJ, USA	1	1	1	40.0	100%	40	Post 2009
PFOA	River	Rhine River, Germany	1	38		nd - 48	66%	2	Skutlarek 2006
PFOA	Surface	Ruhr area, Germany		22		nd - 3640	77%	54	Skutlarek 2006
PFOA	River	Moehne River, Germany	1	12		nd - 33900	75%	3750	Skutlarek 2006
PFOA	Drinking	Ruhr area, Germany		21		nd - 519	71%	43	Skutlarek 2006
PFOA	Drinking	Outside Ruhr, Germany		16		nd - 4	19%	nd	Skutlarek 2006
PFOA	lake	US	2	16		15 - 70	100%	39.5	Boulanger 2004

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOA	River	US	1	80	100	<1 - 287	92%	12.6	Nakayama 2007
PFOA	Surface	CA, USA	2	7		nd - 36			Plumlee 2008
PFOA	Ground	CA, USA	7	7		nd - 28			Plumlee 2008
PFOA	Wastewater eff.	NY, USA	1	1	12	142 - 398		239	Sinclair 2006
PFOA	Wastewater eff.	NY, USA	1	1	12	66 - 202		135	Sinclair 2006
PFOA	Wastewater eff.	NY, USA	1	1	3	435 - 851		663	Sinclair 2006
PFOA	Wastewater eff.	NY, USA	1	1	6	361 - 1050		697	Sinclair 2006
PFOA	Wastewater eff.	NY, USA	1	1	8	132 - 196		165	Sinclair 2006
PFOA	Wastewater eff.	NY, USA	1	1	4	58 - 78		67	Sinclair 2006
PFNA	surface	Canada	1	14	3	<.125 - 3			D'eon 2009
PFNA	lake	US/Canada	5	19		nd - 2	78%		Furdui 2008
PFNA	tributary	US/Canada	3			1.6 - 4.1	100%		Furdui 2008
PFNA	WW effluent	Canada	6	6		3 - 5.4	100%		Furdui 2008
PFNA	WW influent	Canada	1	1		4.2	100%		Furdui 2008

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFNA	WW influent	Korea	15	15		nd - 19.4	73%		Guo 2010
PFNA	WW effluent	Korea	15	15		nd - 15.8	67%		Guo 2010
PFNA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFNA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFNA	Industrial inf.	Korea	3	3		<.7 - 1.4	100%		Guo 2010
PFNA	Industrial eff.	Korea	3	3		.7 - 1.3	100%		Guo 2010
PFNA	Tap	Spain	1	1	4	.22 - .52		0.42	Ericson 2008
PFNA	River	Spain	1	1	4	.36 - .64		0.43	Ericson 2008
PFNA	Bottled	Spain	1	1	4	.13 - .42		0.31	Ericson 2008
PFNA	River	US	1	80	100	<1 - 194	90%	5.7	Nakayama 2007
PFNA	Wastewater eff.	NY, USA	1	1	12	35 - 376		107	Sinclair 2006
PFNA	Wastewater eff.	NY, USA	1	1	12	4.0 - 11		6	Sinclair 2006
PFNA	Wastewater eff.	NY, USA	1	1	3	<10		<10	Sinclair 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFNA	Wastewater eff.	NY, USA	1	1	6	<10		<10	Sinclair 2006
PFNA	Wastewater eff.	NY, USA	1	1	8	<10		<10	Sinclair 2006
PFNA	Wastewater eff.	NY, USA	1	1	4	<10		<10	Sinclair 2006
PFDA	surface	Canada	1	14	3	<.125 - 2.8			D'eon 2009
PFDA	lake	US/Canada	5	19		nd - 2.4	43%		Furdui 2008
PFDA	tributary	US/Canada	3			.8 - 2	100%		Furdui 2008
PFDA	WW effluent	Canada	6	6		1.2 - 4.9	100%		Furdui 2008
PFDA	WW influent	Canada	1	1		1.6	100%		Furdui 2008
PFDA	WW influent	Korea	15	15		nd - 5.1	60%		Guo 2010
PFDA	WW effluent	Korea	15	15		nd - 4.2	87%		Guo 2010
PFDA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFDA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFDA	Industrial inf.	Korea	3	3		nd - 2.7	67%		Guo 2010
PFDA	Industrial eff.	Korea	3	3		<.5 - .6	100%		Guo 2010

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFDA	Tap	Spain	1	1	4	<.82		<.82	Ericson 2008
PFDA	River	Spain	1	1	4	<.82		<.82	Ericson 2008
PFDA	Bottled	Spain	1	1	4	<.82		<.82	Ericson 2008
PFDA	River	US	1	80	100	<1 - 120	85%	13.2	Nakayama 2007
PFDA	Surface	CA, USA	2	7		6.0 - 19			Plumlee 2008
PFDA	Ground	CA, USA	7	7		nd - 19			Plumlee 2008
PFDA	Wastewater eff.	NY, USA	1	1	12	18 - 47		34	Sinclair 2006
PFDA	Wastewater eff.	NY, USA	1	1	12	<2.5 - 3		3	Sinclair 2006
PFDA	Wastewater eff.	NY, USA	1	1	3	<2.5		<2.5	Sinclair 2006
PFDA	Wastewater eff.	NY, USA	1	1	6	6.0 - 13		10	Sinclair 2006
PFDA	Wastewater eff.	NY, USA	1	1	8	<2.5		<2.5	Sinclair 2006
PFDA	Wastewater eff.	NY, USA	1	1	4	<2.5		<2.5	Sinclair 2006
PFUnA	surface	Canada	1	14	3	nd - 1.1			D'eon 2009
PFUnA	lake	US/Canada	5	19		nd - 1.4	48%		Furdui 2008

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFUnA	tributary	US/Canada	3			.5 - 1.1	100%		Furdui 2008
PFUnA	WW effluent	Canada	6	6		nd - 1.5	67%		Furdui 2008
PFUnA	WW influent	Canada	1	1		5.7	100%		Furdui 2008
PFUnA	WW influent	Korea	15	15		nd - .8	7%		Guo 2010
PFUnA	WW effluent	Korea	15	15		nd - .6	20%		Guo 2010
PFUnA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFUnA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFUnA	Industrial inf.	Korea	3	3		nd - <.5	33%		Guo 2010
PFUnA	Industrial eff.	Korea	3	3		nd - <.5	33%		Guo 2010
PFUnA	Tap	Spain	1	1	4	<.43		<.43	Ericson 2008
PFUnA	River	Spain	1	1	4	<.43		<.43	Ericson 2008
PFUnA	Bottled	Spain	1	1	4	<.43		<.43	Ericson 2008
PFUnA	River	US	1	80	100	<1 - 52.1	82%	5.67	Nakayama 2007

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFUnA	Wastewater eff.	NY, USA	1	1	12	5.0 - 10		8	Sinclair 2006
PFUnA	Wastewater eff.	NY, USA	1	1	12	<2.5		<2.5	Sinclair 2006
PFUnA	Wastewater eff.	NY, USA	1	1	3	4.0 - 6		5	Sinclair 2006
PFUnA	Wastewater eff.	NY, USA	1	1	6	<2.5		<2.5	Sinclair 2006
PFUnA	Wastewater eff.	NY, USA	1	1	8	<2.5		<2.5	Sinclair 2006
PFUnA	Wastewater eff.	NY, USA	1	1	4	<2.5		<2.5	Sinclair 2006
PFDoA	lake	US/Canada	5	19		nd - 2.6	57%		Furdui 2008
PFDoA	tributary	US/Canada	3			.2 - .8	100%		Furdui 2008
PFDoA	WW effluent	Canada	6	6		nd - 4.2	67%		Furdui 2008
PFDoA	WW influent	Canada	1	1		8.1	100%		Furdui 2008
PFDoA	WW influent	Korea	15	15		nd	0%		Guo 2010
PFDoA	WW effluent	Korea	15	15		nd	0%		Guo 2010
PFDoA	Livestock inf.	Korea	3	3		nd	0%		Guo 2010

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFDoA	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFDoA	Industrial inf.	Korea	3	3		nd	0%		Guo 2010
PFDoA	Industrial eff.	Korea	3	3		nd	0%		Guo 2010
PFDoA	Tap	Spain	1	1	4	<.34		<.34	Ericson 2008
PFDoA	River	Spain	1	1	4	<.34		<.34	Ericson 2008
PFDoA	Bottled	Spain	1	1	4	<.34		<.34	Ericson 2008
PFDoA	River	US	1	80	100	<1 - 4.46	47%	1.95	Nakayama 2007
PFtriDA									None found
PFTDA	Tap	Spain	1	1	4	<.90		<.90	Ericson 2008
PFTDA	River	Spain	1	1	4	<.90		<.90	Ericson 2008
PFTDA	Bottled	Spain	1	1	4	<.90		<.90	Ericson 2008
PFBS	Tap	Spain	1	1	4	<.27		<.27	Ericson 2008
PFBS	River	Spain	1	1	4	<.27		<.27	Ericson 2008

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFBS	Bottled	Spain	1	1	4	<.27		<.27	Ericson 2008
PFBS	River	Rhine River, Germany	1	38		nd - 46	74%	6.5	Skutlarek 2006
PFBS	Surface	Ruhr area, Germany		22		nd - 71	82%	9	Skutlarek 2006
PFBS	River	Moehne River, Germany	1	12		nd - 1450	67%	353.5	Skutlarek 2006
PFBS	Drinking	Ruhr area, Germany		21		nd - 18	71%	8	Skutlarek 2006
PFBS	Drinking	Outside Ruhr, Germany		16		nd - 20	19%	nd	Skutlarek 2006
PFBS	River	US	1	80	100	<1 - 9.41	62%	2.46	Nakayama 2007
PFHxS	lake	US/Canada	5	19		nd - 1.8	52%		Furdui 2008
PFHxS	tributary	US/Canada	3			nd - 15.4	33%		Furdui 2008
PFHxS	WW effluent	Canada	6	6		3 - 9.4	100%		Furdui 2008
PFHxS	WW influent	Canada	1	1		10.7	100%		Furdui 2008
PFHxS	WW influent	Korea	15	15		nd - 10	60%		Guo 2010
PFHxS	WW effluent	Korea	15	15		nd - 10.5	93%		Guo 2010

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFHxS	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFHxS	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFHxS	Industrial inf.	Korea	3	3		nd - 30.2	33%		Guo 2010
PFHxS	Industrial eff.	Korea	3	3		nd - 14.5	33%		Guo 2010
PFHxS	Tap	Spain	1	1	4	<.18 - .28		0.23	Ericson 2008
PFHxS	River	Spain	1	1	4	<.18 - .78		0.42	Ericson 2008
PFHxS	Bottled	Spain	1	1	4	<.18		<.18	Ericson 2008
PFHxS	River	US	1	80	100	<1 - 35.1	99%	5.66	Nakayama 2007
PFHxS	Surface	CA, USA	2	7		2.3 - 12			Plumlee 2008
PFHxS	Ground	CA, USA	7	7		3.8 - 17			Plumlee 2008
PFHxS	Wastewater eff.	NY, USA	1	1	12	5.0 - 39		13	Sinclair 2006
PFHxS	Wastewater eff.	NY, USA	1	1	12	<2.5 - 8		5	Sinclair 2006
PFHxS	Wastewater eff.	NY, USA	1	1	3	2.0 - 3		2	Sinclair 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFHxS	Wastewater eff.	NY, USA	1	1	6	2.0 - 4		3	Sinclair 2006
PFHxS	Wastewater eff.	NY, USA	1	1	8	3.0 - 8		6	Sinclair 2006
PFHxS	Wastewater eff.	NY, USA	1	1	4	6.0 - 12		7	Sinclair 2006
PFHpS	WW influent	Korea	15	15		nd - 8.2	60%		Guo 2010
PFHpS	WW effluent	Korea	15	15		nd - .8	20%		Guo 2010
PFHpS	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFHpS	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFHpS	Industrial inf.	Korea	3	3		nd - 2.6	33%		Guo 2010
PFHpS	Industrial eff.	Korea	3	3		nd - 1.5	33%		Guo 2010
PFHpS	Surface	CA, USA	2	7		nd - 12			Plumlee 2008
PFHpS	Ground	CA, USA	7	7		nd - 8.1			Plumlee 2008
PFOS	surface	Canada	1	14	3	.56 - 80			D'eon 2009
PFOS	WW effluent	Canada	7	7		27 - 191			D'eon 2009
PFOS	lake	US/Canada	5	19		.1 - 37.6	100%		Furdui 2008

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOS	tributary	US/Canada	3			2.6 - 22.9	100%		Furdui 2008
PFOS	WW effluent	Canada	6	6		8.6 - 208.5	100%		Furdui 2008
PFOS	WW influent	Canada	1	1		20.0	100%		Furdui 2008
PFOS	WW influent	Korea	15	15		nd - 40	93%		Guo 2010
PFOS	WW effluent	Korea	15	15		.9 - 8.9	100%		Guo 2010
PFOS	Livestock inf.	Korea	3	3		nd	0%		Guo 2010
PFOS	Livestock eff.	Korea	3	3		nd	0%		Guo 2010
PFOS	Industrial inf.	Korea	3	3		nd - 68.1	67%		Guo 2010
PFOS	Industrial eff.	Korea	3	3		nd - 5.7	33%		Guo 2010
PFOS	Tap	Spain	1	1	4	.39 - .87		0.59	Ericson 2008
PFOS	River	Spain	1	1	4	<.24 - 5.88		2.03	Ericson 2008
PFOS	Bottled	Spain	1	1	4	<.24		<.24	Ericson 2008
PFOS	River	Rhine River, Germany	1	38		nd - 26	89%	5.5	Skutlarek 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOS	Surface	Ruhr area, Germany		22		nd - 193	59%	5	Skutlarek 2006
PFOS	River	Moehne River, Germany	1	12		nd - 5900	67%	223	Skutlarek 2006
PFOS	Drinking	Ruhr area, Germany		21		nd - 22	52%	3	Skutlarek 2006
PFOS	Drinking	Outside Ruhr, Germany		16		nd - 6	13%	nd	Skutlarek 2006
PFOS	lake	US	2	16		11 - 121	100%	36.5	Boulanger 2004
PFOS	River	US	1	80	100	<1 - 132	100%	28.9	Nakayama 2007
PFOS	Surface	CA, USA	2	7		4.8 - 56			Plumlee 2008
PFOS	Ground	CA, USA	7	7		19 - 192			Plumlee 2008
PFOS	Wastewater eff.	NY, USA	1	1	12	9.0 - 68		31	Sinclair 2006
PFOS	Wastewater eff.	NY, USA	1	1	12	4.0 - 10		6	Sinclair 2006
PFOS	Wastewater eff.	NY, USA	1	1	3	3.0 - 5		4	Sinclair 2006
PFOS	Wastewater eff.	NY, USA	1	1	6	7.0 - 11		9	Sinclair 2006
PFOS	Wastewater eff.	NY, USA	1	1	8	4.0 - 7		5	Sinclair 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
PFOS	Wastewater eff.	NY, USA	1	1	4	8.0 - 10		9	Sinclair 2006
PFDS	Tap	Spain	1	1	4	<1.0		<1.0	Ericson 2008
PFDS	River	Spain	1	1	4	<1.0		<1.0	Ericson 2008
PFDS	Bottled	Spain	1	1	4	<1.0		<1.0	Ericson 2008
PFDS	Surface	CA, USA	2	7		3.4 - 44			Plumlee 2008
PFDS	Ground	CA, USA	7	7		nd - 15			Plumlee 2008
FOSA	Tap	Spain	1	1	4	<.19		<.19	Ericson 2008
FOSA	River	Spain	1	1	4	<.19 - .20		<.19	Ericson 2008
FOSA	Bottled	Spain	1	1	4	<.19		<.19	Ericson 2008
FOSA	lake	US	2	16		nd - 2.3	88%	0.95	Boulanger 2004
FOSA	Surface	CA, USA	2	7		nd - 3.5			Plumlee 2008
FOSA	Ground	CA, USA	7	7		nd - 4.3			Plumlee 2008
N- Et-FOSAA	lake	US	2	16		nd - 11	94%	7.25	Boulanger 2004

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
N- Et-FOSAA	Surface	CA, USA	2	7		nd - 31			Plumlee 2008
N- Et-FOSAA	Ground	CA, USA	7	7		nd - 26			Plumlee 2008
N-MeFOSAA									None found
4:2 FtS									None found
6:2 FtS									None found
8:2 FtS									None found
4:2 FTCA									None found
4:2 FTUCA									None found
6:2 FTCA									None found
6:2 FTUCA									None found
8:2 FTCA	Wastewater eff.	NY, USA	1	1	12	<2.5 - 7		3	Sinclair 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
8:2 FTCA	Wastewater eff.	NY, USA	1	1	12	<2.5 - 6		2	Sinclair 2006
8:2 FTCA	Wastewater eff.	NY, USA	1	1	3	<2.5		<2.5	Sinclair 2006
8:2 FTCA	Wastewater eff.	NY, USA	1	1	6	<2.5		<2.5	Sinclair 2006
8:2 FTCA	Wastewater eff.	NY, USA	1	1	8	<2.5		<2.5	Sinclair 2006
8:2 FTCA	Wastewater eff.	NY, USA	1	1	4	<2.5		<2.5	Sinclair 2006
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	12	<2.5 - 29		4	Sinclair 2006
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	12	<2.5 - 6		2	Sinclair 2006
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	3	<2.5		<2.5	Sinclair 2006
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	6	<2.5		<2.5	Sinclair 2006
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	8	<2.5		<2.5	Sinclair 2006

Table A.2: Continued.

PFAS	Water Source	Location	# of waters	# of sites	# of samples	Conc. Range (ng/L)	Detection Frequency (%)	Median (ng/L)	References
8:2 FTUCA	Wastewater eff.	NY, USA	1	1	4	<2.5		<2.5	Sinclair 2006
10:2 FTCA									None found
10:2 FTUCA									None found

APPENDIX B - SUPPLEMENTAL INFORMATION FOR CHAPTER 3

B.1 Utility Descriptions

This section describes the Utilities that were sampled during the full-scale treatment study.

B.1.1 Utility 4

The microfiltration (MF) system at Utility 4 uses polypropylene membranes with 0.2 micron rated pore size. It has a 20.4 gfd flux rate at 90% recovery and is backwashed every 22 minutes with full cleaning every 21 days. The permeate flow is 86 mgd. The manufacturer is Siemens/Memcor, and the model is CS (submerged MF system, vacuum driven). The reverse osmosis (RO) system uses polyamide hydranautics ESPA2 membranes in a 3 stage array with 12 gfd flux rate and 85% recovery. It has a 70 mgd permeate flow from fifteen 5 mgd trains. The UV system is a Trojan UVPhox system with low pressure, high output lamps. There are nine 8.75 mgd trains which total up to a 70 mgd flow rate.

B.1.2 Utility 5

Utility 5 utilizes a MIEX system, and treats 3 MGD a day with about 13 regenerations performed throughout a 24 hr period. Also at midnight 4.4 gallons of Virgin Resin are added to the contactor. which is 18 ft x18.2 ft and 15.5ft deep.

B.1.3 Utility 7

The treatment train at Utility 7 begins with river bank filtration (RBF) into a utility about 34 miles north of the main treatment plant. The source water travels through sediments for approximately 10 days before it reaches the next stage in treatment, which is aquifer recharge and recovery (ARR). ARR gives the water another approximately 30 days travel time. After ARR, the water is pumped south

to the main treatment facility where it goes through caustic softening, followed by a solids contact clarifier. Next, it undergoes UV treatment. The UV system is TrojanUVPhox, and consists of 12 trains with a design dose >500 MJ/cm^2. This step is followed by dual media filters with 780 ft^2 of Norit 816 carbon capable of running between 3 and 8 MGD. Six GAC contact chambers follow containing 858 ft^2 of Norit GAC300 each with an empty bed contact time of 10.4 min. The average flow through this treatment process is about 5 MGD.

B.1.4 Utility 8

The system at Utility 8 starts with primary sedimentation (alum and polymer are added for coagulation) and flocculation. From the sedimentation basins, the water travels to the sand filters. There are 47 sand filters. All filters are set at a flow rate of 6 MGD which corresponds to a filtration rate of 3.0 gpm/ft^2. Their GAC system consists of 12 contactors, and each contains approximately 600,000 pounds of carbon at a depth of 11-11.5 ft. The goal is to have an empty bed contact time (EBCT) of at least 15 minutes, but the flow through the contactors varies from 10 MGD to 18 MGD depending on the season and time of day. The in-service contactors are backwashed about once a week. The current carbon is Calgon F400, but the carbon has varied in the past. On-site reactivation of the carbon is performed from April to October. Carbon loss from the reactivation is about 7% per year. This is made-up in each contactor with virgin carbon.

B.1.5 Utility 10

After the tertiary sampling point sodium hypochlorite and ammonium hydroxide are added to create an average of 3 mg/l chloramines. The flow then splits between a Toray UF and a Pall MF operated in parallel. The MF and UF are both operated at 29-30 gfd and 93-95% recovery. The MF/UF product water is combined in a common break tank and then fed to two parallel RO trains. King Lee Technologies

Y2K antiscalant is added before the Toray and Hydraunautics RO membranes. RO flux rate is 11.6 to 11.9 gfd and recovery is 80%. RO permeate water is combined and hydrogen peroxide is added to a concentration of 3 μg/L. A Trojan UVPhox reactor employing 254 nanometer wavelength light and 12.6kW of electricity is used on the final 700 gpm flow.

B.1.6 Utility 11

Water from shallow wells and deep wells as well as water from a local river and reservoir undergo aeration before being blended together. Two rapid mix stations follow, with 9.20 mg/L hydrated lime and 0.50 mg/L ClO2 added to the first station, and 25.8 mg/L hydrated lime slurry, 20.0 mg/L CO_2, and aluminum sulfate are added to the second. The water then undergoes flocculation, followed by sedimentation. The next step is anthracite/sand filtration, and 2.6 mg/L hydrated lime slurry, 0.95 mg/L Cl_2 gas, and anionic polyacrylamide (an anionic polymer) are injected into the water. After filtration, the water travels to the clearwell where 1.75 mg/L Cl_2 gas is added.

B.1.7 Utility 12

Utility 12 operates with an average flow about 110 mgd from a reservoir supply that has a 200 mgd capacity. The plant utilizes pH adjustment with sulfuric acid (when required), pre-ozonation, coagulation with PACl, powdered activated carbon (when needed for taste and odor control), high rate dissolved air flotation (DAF) for pre-filter solids removal, chlorination for CT, dual media filters, pH adjustment with caustic (corrosion control), and secondary disinfection with chloramines. The ozone system includes ozone generation using LOX and ozone dissolution using submerged diffusers with a contact time of about 10 minutes.

B.1.8 Utility 13

Utility 13 draws water from a well with an approximate capacity of 3 mgd. Their UV system, Aquaray H2O by Ozonia, has 2 reactors each capable of treating 3 mgd with a dosage of 80 mJ/cm^2 and the UV transmittance is 95%.

B.1.9 Utility 14

Utility 14 is run at 350 gpm. Purolite FerrlX A33emedia is added to the softener vessel for arsenic removal. It is a highly porous anion resin impregnated with iron oxide. After the purolite filter, CP-718 (a Coyne chemical product) is added. It is a polyphosphate added to control scaling and sequester iron. It then goes through an aeration tower for VOC removal, and then into the clearwell where sodium hypochlorite is added. About 2 gallons of CP718 and 5-7 gallons of hypochlorite are added daily.

B.1.10 Utility 15

At Utility 15, sodium hypochlorite 0.8%, and permanganate are added before the greensand filters and lime and klenphos after the filters, in that order. The well pumps 500gpm.

B.1.11 Utility 17

The process train at Utility 17 consists of intake screens, KMnO4 (when in use), coag/floc/clar, ozonation, sand filtration (with some pre-chlorination), then chlorination followed by pH adjustment. During the two sample dates for this study, $KMnO_4$ was not being used. Their flow was between 50-55 MGD. The ozone system consists of WEDECO Effizon Technology Ozone Generators. Post-chlorine dosing was about 2.27-2.33 μg/L.

B.1.12 Utility 18

The #1 basin at Utility 18 holds 750,000 gallons and the #2 holds 500,000 gallons. At a rate of 5.0mgd, the detention time is around 5.8 hours±. The system starts with an aeration packed tower, followed by GAC, then hypochlorite. Their 8 GAC towers hold 20,000 lbs of Calgon F300 each. The GAC is replaced with virgin GAC approximately every 5 years, but samples for this study were taken with carbon that has been utilized for about 6 years.

B.1.13 Utility 20

The MN water treatment plant utilizes Calgon F600 media in their GAC system. Two basins that are 12 ft in diameter containing approximately 8.9 ft of GAC are set up to run in succession with a flow between 380 to 400 gpm. This set up gives each basin an empty bed contact time (EBCT) of about 13 minutes. Concentrations of PFBA, PFPeA, PFHxA, PFOA, PFBS, PFHxS, and PFOS have been monitored for nearly five years on the influent and the lead basin effluent, and for 16 months on the lag basin.

B.2 Utility 20's PFAS Method

Samples are collected in 250 mL high density polyethylene bottles while wearing nitrile gloves. Bottles are labeled and samples are placed in a cooler with an ice pack (except in winter, so they don't freeze). No preservative is added. When ready for preparation, the bottle is warmed up to room temp, shaken, and an aliquot is removed and placed into a plastic autosampler vial. It is then spiked with internal standards procured from Wellington Laboratories (Guelph, Ontario, Canada) and Matrix spike solution (a matrix spike is performed for every single unknown water sample). The spikes are in acetonitrile (ACN).

An Agilent (Palo Alto, CA) 1100 HPLC pump was used for all analyses. Analytes were separated using a Betasil C8 50 x 2.1 mm column with 3 um pore size. A binary

gradient consisting of 0.1% formic acid (v/v) in water (A) and 0.1% formic acid and ACN (B) was used. The gradient was as follows: 30% B held for 0.25 min with a flow of 0.4 mL/min, then increased to 45% B over the next 3.5 min with the same flow, and then ramped to 90% B within 1 min with a change in flow from 0.4 to 0.6 mL/min after 0.75 min. Over the next 1.5 min, flow remained the same and % B was reduced to 30%, and the final parameters were 30% B and 0.4 mL/min flow.

An injection volume of 10 µL was used for all analyses. An Upchurch PEEK 0.5 µm prefilter and a betasil C8 30 x 3 mm, 5 µm precolumn were used. Tandem mass spectrometry was performed using a Quattro Micro MS/MS from Waters using ESI negative ionization. For most of the data, the reporting limit (RL) was 0.3 µg/L for all analytes. After 4/4/2011 RLs changed to 0.05 µg/L, which is about 10x the current method detection limits.

Table B.1: Compound Dependent Analytical and Quantitation Parameters

Abbreviation	Retention Time (min)	[a]MRMTransition	Quantitation	[b]CR (ug/L)	[c]MRL (ng/L)
PFBA	6.3	213 > 169	Isotope Dilution ([$^{13}C_4$] PFBA)		
	0.50-125	5			
PFPeA	7.1	263 > 219	Isotope Dilution ([$^{13}C_5$] PFPeA)	0.50-125	2
PFHxA	8.2	313 > 269	Isotope Dilution ([$^{13}C_2$] PFHxA)	0.10-25	0.5
PFHpA	9.4	363 > 319	Isotope Dilution ([$^{13}C_4$] PFHpA)	0.10-25	0.5
PFOA	10.2	413 > 369	Isotope Dilution ([$^{13}C_4$] PFOA)	0.50-125	5
PFNA	10.8	463 > 419	Isotope Dilution ([$^{13}C_5$] PFNA)	0.10-25	0.5
PFDA	11.4	513 > 469	Isotope Dilution ([$^{13}C_2$] PFDA)	0.10-25	0.5
PFUnA	12.2	563 > 519	Isotope Dilution ([$^{13}C_2$] PFUnA)	0.10-25	0.5
PFDoA	13.3	613 > 569	Isotope Dilution ([^{13}C] PFDoA)	0.10-25	0.25
PFBS	7.1	299 > 99	Surrogate Standard ([$^{18}O_2$] PFHxS)	0.10-25	0.25
PFHxS	9.4	399 > 80	Isotope Dilution ([$^{18}O_2$] PFHxS)	0.10-25	0.25
PFOS	10.7	499 > 80	Isotope Dilution ([$^{13}C_4$] PFOS)	0.10-25	0.25
PFDS	12	599 > 99	Surrogate Standard ([$^{13}C_4$] PFOS)	0.10-25	0.10
FOSA	13	498 > 78	Isotope Dilution ([$^{13}C_8$] FOSA)	0.10-25	0.25
N-MeFOSAA	11.8	570 > 419	Isotope Dilution (d3-N-MeFOSAA)	0.10-25	0.25
N-EtFOSAA	12.2	584 > 419	Isotope Dilution (d3-N-EtFOSAA)	0.10-25	0.25
4:2 FTUCA	7.3	257 > 193	Surrogate Standard ([$^{13}C_2$] 6:2FTUCA)	0.10-25	2
6:2 FTUCA	9.8	357 > 293	Isotope Dilution ([$^{13}C_2$] 6:2FTUCA)	0.10-25	2
8:2 FTUCA	11	457 > 393	Isotope Dilution ([$^{13}C_2$] 8:2FTUCA)	0.10-25	2
10:2 FTUCA	12.7	557 > 493	Isotope Dilution ([$^{13}C_2$] 10:2FTUCA)	0.10-25	2
4:2 FtS	8.1	327 > 81	External Calibration	0.10-25	0.5
6:2 FtS	10.2	427 > 81	External Calibration	0.10-25	0.5
8:2 FtS	11.4	527 > 81	External Calibration	0.10-25	0.5

[a]Multiple Reaction Monitoring; [b]Concentration Range; [c]Minimum Reporting Limit

Table B.2: Analytical Variability and Spike Recovery Data

PFAS	Variability of Replicate Samples		Project Spike Recoveries in Reagent Water (n=28)			Project Matrix Spike Recoveries (n=20)		
	Avg diff (n=28)	Max	[a]SC (ng/L)	[b]MR (%)	RSD (%)	SC (ng/L)	MR (%)	RSD (%)
PFBA	2%	23%	20	102	9.4	20	109	11.1
PFPeA	4%	16%	20	98	12.9	20	100	14.3
PFHxA	7%	17%	10	99	9.0	10	107	9.7
PFHpA	5%	18%	10	97	12.8	10	103	19.4
PFOA	7%	20%	20	98	12.1	20	99	19.9
PFNA	4%	22%	10	97	9.8	10	100	12.7
PFDA	3%	21%	10	94	12.3	10	99	11.4
PFUnA	1%	4%	10	91	12.4	10	90	13.9
PFDoA	1%	10%	10	100	8.5	10	103	9.1
PFBS	4%	20%	10	102	9.5	10	107	20.3
PFHxS	4%	21%	10	91	8.2	10	84	15.0
PFOS	6%	24%	10	97	7.0	10	97	15.0
PFDS	1%	40%	10	84	14.1	10	105	19.2
FOSA	2%	15%	10	96	9.1	10	89	7.0
N-MeFOSAA	4%	29%	10	97	12.8	10	94	15.3
N- Et-FOSAA	3%	20%	10	97	15.0	10	97	13.9
4:2 FTUCA	0%	5%	10	98	14.7	10	85	15.1
6:2 FTUCA	0%	5%	10	95	11.8	10	107	11.9
8:2 FTUCA	0%	5%	10	96	13.7	10	100	11.2
10:2 FTUCA	0%	5%	10	93	11.7	10	94	9.3
4:2 FtS	0%	4%	10	96	21.6	10	107	23.6
6:2 FtS	5%	39%	10	101	22.6	10	97	19.3
8:2 FtS	1%	18%	10	70	27.8	10	64	36.7

[a]Spike Concentration; [b]Mean Recovery

Table B.3: PFCA Sample Data in ng/L

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
1	WI	Surface	1	Raw_1	< 5.0	< 2.0	0.7	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
1	WI	Surface	1	Raw_2	< 5.0	< 2.0	< 0.5	1.3	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
2	OK	Surface	1	Raw_1	< 5.0	< 2.0	< 0.5	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
2	OK	Surface	1	Raw_2	9.1	< 2.0	< 0.5	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
3	AK	Surface	1	Raw_1	< 5.0	< 2.0	< 0.5	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
3	AK	Surface	1	Raw_2	< 5.0	< 2.0	< 0.5	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
4	CA	WW eff	1	Raw	< 5.0	12.0	10.0	3.6	9.3	5.0	3.5	< 0.5	< 0.5
4	CA	WW eff	2_1	Raw	< 50	9.4	13	2.6	11	3.6	1.6	0.53	0.26
4	CA	WW eff	2_1	pre RO	< 50	9.6	19	2.7	11	3.8	2.1	0.61	< 0.27
4	CA	WW eff	2_1	post RO	< 5.1	< 2.0	< 0.51	< 0.51	< 5.1	< 0.51	< 0.51	< 0.51	< 0.25
4	CA	WW eff	2_1	post UV	< 5.2	< 2.1	< 0.52	< 0.52	< 5.2	< 0.52	< 0.52	< 0.52	< 0.26
4	CA	WW eff	2_1	Finished	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
4	CA	WW eff	2_2	Raw	29	11	18	3.4	10	3.9	1.5	< 0.50	< 0.25
4	CA	WW eff	2_2	pre RO	28	11	22	3.5	9.5	3.9	1.5	< 0.50	< 0.25
4	CA	WW eff	2_2	post RO	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
4	CA	WW eff	2_2	post UV	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25

Table B.3: Continued.

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
4	CA	WW eff	2_2	Finished	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
5	AL	Surface	1	Raw	31.0	3.1	6.5	4.1	18.0	0.7	< 0.5	< 0.5	< 0.5
5	AL	Surface	2_1	Raw	40	6.5	15	8.8	33	< 0.53	< 0.53	< 0.53	< 0.26
5	AL	Surface	2_1	post MIEX	29	5.9	15	7.3	28	0.55	< 0.50	< 0.50	< 0.25
5	AL	Surface	2_1	Finished	37	6.5	16	9.3	32	0.7	< 0.50	< 0.50	< 0.25
5	AL	Surface	2_2	Raw	17	4.4	38	12	50	0.73	< 0.50	< 0.50	< 0.25
5	AL	Surface	2_2	post MIEX	17	5.2	44	15	54	0.79	< 0.50	< 0.50	< 0.25
5	AL	Surface	2_2	Finished	19	4.9	47	14	50	0.76	< 0.50	< 0.50	< 0.25
7	CO	Surface	1	Raw	< 5.0	14.0	14.0	4.8	16.0	5.7	2.5	< 0.5	< 0.5
7	CO	Surface	2_1	Raw	6.5	8.8	18	3.7	13	4.8	1.6	< 0.50	< 0.25
7	CO	Surface	2_1	Post RBF	9.5	9.8	16	5.9	10	5.1	1.3	< 0.50	< 0.25
7	CO	Surface	2_1	Raw water	16	19	18	7.7	24	2.2	< 0.50	< 0.50	< 0.25
7	CO	Surface	2_1	Before UV/AOP	14	18	17	6.6	19	1.8	< 0.50	< 0.50	< 0.25
7	CO	Surface	2_1	After UV/AOP	14	19	17	6.2	17	1.8	< 0.50	< 0.50	< 0.25
7	CO	Surface	2_1	Before GAC	15	17	11	4.5	9.7	0.79	< 0.50	< 0.50	< 0.25
7	CO	Surface	2_1	After GAC	10	4.4	0.97	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
7	CO	Surface	2_2	Raw	< 5.0	12	21	5.8	16	5.0	2.1	< 0.50	< 0.25
7	CO	Surface	2_2	Post RBF	13	14	15	5.9	16	4.7	1.7	< 0.50	< 0.25
8	OH	Surface	1	Raw	12.0	2.3	2.2	1.3	8.9	1.5	< 0.5	< 0.5	< 0.5
8	OH	Surface	2_1	Raw	< 5.0	< 2.0	0.75	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_1	pre GAC	< 5.0	< 2.0	0.93	0.54	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_1	post GAC	< 5.0	< 2.0	0.76	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25

Table B.3: Continued.

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
8	OH	Surface	2_1	Finished	< 5.0	< 2.0	0.91	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_2	Raw	< 5.0	< 2.0	0.69	< 0.50	5.6	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_2	pre GAC	< 5.0	< 2.0	0.57	< 0.50	5.1	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_2	post GAC	< 5.0	< 2.0	0.57	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
8	OH	Surface	2_2	Finished	< 5.0	< 2.0	0.52	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
9	NV	Surface	1	Raw_1	< 5.0	< 2.0	0.6	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
9	NV	Surface	1	Raw_2	< 5.0	< 2.0	< 0.5	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5	< 0.5
10	CA	WW eff	1	Raw	25.0	370.0	90.0	18.0	210.0	7.6	82.0	0.9	2.7
10	CA	WW eff	2_1	Raw	< 2.5	130	88	13	170	8.9	50	0.94	2.5
10	CA	WW eff	2_1	Post MF/UF	< 2.5	120	96	13	160	13	54	1.1	1.0
10	CA	WW eff	2_1	Post RO	< 2.5	< 1.0	< 0.25	< 0.25	< 2.5	< 0.25	< 0.25	< 0.25	< 0.13
10	CA	WW eff	2_1	Post AOP	< 2.5	< 1.0	< 0.25	< 0.25	< 2.5	< 0.25	< 0.25	< 0.25	< 0.13
10	CA	WW eff	2_2	Raw	< 100	110	82	11	220	11	76	1.4	2.2
10	CA	WW eff	2_2	Post MF/UF	< 100	98	85	11	200	10	68	1.7	1.6
10	CA	WW eff	2_2	Post RO	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
10	CA	WW eff	2_2	Post AOP	< 5.0	< 2.0	< 0.50	< 0.50	< 5.0	< 0.50	< 0.50	< 0.50	< 0.25
11	NJ	Blend	2_1	Raw	< 5.3	3.6	3.6	2.8	43	1.5	< 0.53	< 0.53	< 0.26
11	NJ	Blend	2_1	pre-Cl dioxide	< 5.5	< 2.2	2.9	1.8	17	0.96	< 0.55	< 0.55	< 0.28

Table B.3: Continued.

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
11	NJ	Blend	2_1	post-Cl dioxide	< 5.1	< 2.0	2.6	2	17	0.84	< 0.51	< 0.51	< 0.25
11	NJ	Blend	2_1	Finished	< 5.1	< 2.0	2.9	1.6	17	0.83	< 0.51	< 0.51	< 0.26
11	NJ	Blend	2_2	Raw	< 5.0	2.0	3.1	2.5	29	1.3	< 0.50	< 0.50	< 0.25
11	NJ	Blend	2_2	pre-Cl dioxide	< 5.0	2.1	3.1	2.5	28	1.4	< 0.50	< 0.50	< 0.25
11	NJ	Blend	2_2	post-Cl dioxide	< 5.0	2.0	3.2	2.5	32	1.5	< 0.50	< 0.50	< 0.25
11	NJ	Blend	2_2	Finished	< 5.0	2.3	3.7	2.9	33	1.6	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_1	Raw	< 5.0	2.8	3.6	3.1	11	2.0	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_1	post O3	< 5.0	3.4	3.6	3.1	13	2.3	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_1	post DAF	< 5.0	3.5	3.8	3.2	12	2.0	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_1	Finished	< 5.0	3.4	3.8	2.9	11	2.0	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_2	Raw	< 5.0	3.8	4.2	3.8	11	2.0	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_2	post O3	6.3	4.0	4.5	3.5	12	2.7	0.61	< 0.50	< 0.25
12	NJ	Surface	2_2	post DAF	< 5.0	3.8	4.4	3.7	12	1.5	< 0.50	< 0.50	< 0.25
12	NJ	Surface	2_2	Finished	< 5.0	3.9	4.5	3.9	12	1.8	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_1	Raw	< 5.0	9.9	8.2	3.9	11	1.2	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_1	post UV	< 5.0	9.5	8.2	4.1	12	1.8	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_1	Finished	< 5.0	9.9	8	4.1	11	1.6	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_2	Raw	5.1	10	7.3	4.5	15	2.4	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_2	post UV	< 5.0	9.5	7.3	4.4	16	1.8	< 0.50	< 0.50	< 0.25
13	NJ	Ground	2_2	Finished	5.5	9.2	7.7	4.3	14	2.0	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_1	Raw	11	12	14	15	68	< 0.50	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_1	post purolite	12	12	12	6.9	16	< 0.50	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_1	Finished	15	12	12	6.8	19	< 0.50	< 0.50	< 0.50	< 0.25

Table B.3: Continued.

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
14	NJ	Ground	2_2	Raw	12	14	14	16	120	1.5	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_2	btwn APT & IX	12	14	16	10	32	< 0.50	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_2	post IX	12	15	16	13	21	< 0.50	< 0.50	< 0.50	< 0.25
14	NJ	Ground	2_2	Finished									
15	NJ	Ground	2_1	Raw	14	12	19	8.2	38	47	1.1	< 0.50	< 0.25
15	NJ	Ground	2_1	Finished	14	12	20	7.6	38	55	1.2	< 0.50	< 0.25
16	NJ	Ground	2_1	Raw	12	13	26	12	18	1.2	< 0.50	< 0.50	< 0.25
16	NJ	Ground	2_1	Finished	10	14	26	11	17	1.3	< 0.50	< 0.50	< 0.25
17	NJ	Surface	2_1	Raw	< 5.0	2.3	2.3	1.4	9.5	0.98	< 0.50	< 0.50	< 0.25
17	NJ	Surface	2_1	pre O3	< 5.0	2	2.2	1.5	8.6	1.1	0.52	< 0.50	< 0.25
17	NJ	Surface	2_1	post O3	< 5.0	2.5	2.4	1.4	9.0	0.96	< 0.50	< 0.50	< 0.25
17	NJ	Surface	2_1	Finished	< 5.0	2.5	2.3	1.6	11	1.1	0.55	< 0.50	< 0.25
17	NJ	Surface	2_2	Raw	< 5.0	4.9	6.3	3	13	2.1	1.2	< 0.50	< 0.25
17	NJ	Surface	2_2	pre O3	< 5.0	5.1	6.2	2.8	13	1.9	1.3	< 0.50	< 0.25
17	NJ	Surface	2_2	post O3	< 5.0	5.1	8	3.9	16	3.1	2.8	0.8	< 0.25
17	NJ	Surface	2_2	Finished	< 5.0	5.2	6.6	2.8	14	2.6	1.4	< 0.50	< 0.25
18	NJ	Surface	2_1	Raw	< 5.0	4.9	8.5	5.1	22	1.3	< 0.50	< 0.50	< 0.25
18	NJ	Surface	2_1	btwn APT & GAC	< 5.2	5.5	7.3	5.1	22	1.8	0.59	< 0.52	< 0.26
18	NJ	Surface	2_1	post GAC	< 5.0	4.8	6.1	4.4	22	1.7	0.54	< 0.50	< 0.25
18	NJ	Surface	2_1	Finished	< 5.0	6.6	6.4	5.8	24	1.9	0.65	0.51	< 0.25
18	NJ	Surface	2_2	Raw	< 5.0	6.6	6.5	6.1	21	2.4	0.73	< 0.50	< 0.25
18	NJ	Surface	2_2	btwn APT & GAC	< 5.0	6.9	6.8	5.7	20	2.4	0.97	< 0.50	< 0.25
18	NJ	Surface	2_2	post GAC	6.3	6.4	8.7	6.3	29	2.7	1.3	< 0.50	< 0.25
18	NJ	Surface	2_2	Finished	5.6	8.3	8.1	5.8	27	3.1	1.3	< 0.50	< 0.25

Table B.3: Continued.

ID	State	Source Water	#	Description	PFBA	PFPnA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
19	NJ	Ground	2_1	Raw	27	44	67	33	49	5.6	1.5	0.63	< 0.25
19	NJ	Ground	2_1	Finished	28	43	62	34	57	5.8	1.6	0.64	< 0.25

Table B.4: PFSA Sample Data in ng/L

ID	State	Source Water	#	Description	PFBS	PFHxS	PFOS	PFDS
1	WI	Surface	1	Raw_1	< 0.3	< 0.3	0.6	< 0.1
1	WI	Surface	1	Raw_2	< 0.3	0.4	0.5	< 0.1
2	OK	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 0.1
2	OK	Surface	1	Raw_2	< 0.3	< 0.3	0.4	< 0.1
3	AK	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 0.1
3	AK	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 0.1
4	CA	WW eff	1	Raw	4.1	10.0	17.0	< 0.1
4	CA	WW eff	2_1	Raw	3.6	5.2	8.6	< 0.10
4	CA	WW eff	2_1	pre RO	3.7	5.3	14	< 0.11
4	CA	WW eff	2_1	post RO	< 0.25	< 0.25	< 0.25	< 0.10
4	CA	WW eff	2_1	post UV	< 0.26	< 0.26	< 0.26	< 0.10
4	CA	WW eff	2_1	Finished	< 0.25	< 0.25	< 0.25	< 0.10
4	CA	WW eff	2_2	Raw	8.6	4.7	16	< 0.10
4	CA	WW eff	2_2	pre RO	10	4.3	18	< 0.10
4	CA	WW eff	2_2	post RO	< 0.25	< 0.25	< 0.25	< 0.10
4	CA	WW eff	2_2	post UV	< 0.25	< 0.25	< 0.25	< 0.10
4	CA	WW eff	2_2	Finished	< 0.25	< 0.25	< 0.25	< 0.10
5	AL	Surface	1	Raw	< 0.3	4.7	21.0	< 0.1
5	AL	Surface	2_1	Raw	15	8.2	27	< 0.11
5	AL	Surface	2_1	post MIEX	14	6.9	23	< 0.10
5	AL	Surface	2_1	Finished	15	8.2	22	< 0.10
5	AL	Surface	2_2	Raw	47	8.8	47	< 0.10
5	AL	Surface	2_2	post MIEX	29	12	57	< 0.10
5	AL	Surface	2_2	Finished	37	10	61	< 0.10
7	CO	Surface	1	Raw	4.9	11.0	12.0	< 0.1
7	CO	Surface	2_1	Raw	4.8	7.4	7.3	< 2.0

Table B.4: Continued.

ID	State	Source Water	#	Description	PFBS	PFHxS	PFOS	PFDS
7	CO	Surface	2_1	Post RBF	8.8	9	10	< 0.10
7	CO	Surface	2_1	Raw water	12	18	9.5	< 0.10
7	CO	Surface	2_1	Before UV/AOP	9.5	15	11	< 0.10
7	CO	Surface	2_1	After UV/AOP	9.4	15	10	< 0.10
7	CO	Surface	2_1	Before GAC	6.4	5.8	2.3	< 0.10
7	CO	Surface	2_1	After GAC	< 0.25	< 0.25	< 0.25	< 0.10
7	CO	Surface	2_2	Raw	7.7	13	35	< 0.10
7	CO	Surface	2_2	Post RBF	11	14	14	0.15
8	OH	Surface	1	Raw	2.5	0.8	1.6	< 0.1
8	OH	Surface	2_1	Raw	0.87	0.43	0.49	< 0.10
8	OH	Surface	2_1	pre GAC	0.7	0.49	0.52	< 0.10
8	OH	Surface	2_1	post GAC	0.41	< 0.25	< 0.25	< 0.10
8	OH	Surface	2_1	Finished	0.44	< 0.25	< 0.25	< 0.10
8	OH	Surface	2_2	Raw	1.0	0.30	0.43	< 0.10
8	OH	Surface	2_2	pre GAC	0.84	0.30	0.66	< 0.10
8	OH	Surface	2_2	post GAC	0.41	< 0.25	< 0.25	< 0.10
8	OH	Surface	2_2	Finished	0.44	< 0.25	< 0.25	< 0.10
9	NV	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 0.1
9	NV	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 0.1
10	CA	WW eff	1	Raw	1.7	3.7	4.6	< 0.1
10	CA	WW eff	2_1	Raw	2.9	3.2	4.3	< 0.050
10	CA	WW eff	2_1	Post MF/UF	2.9	3.2	3	< 0.050
10	CA	WW eff	2_1	Post RO	< 0.13	< 0.13	< 0.13	< 0.050
10	CA	WW eff	2_1	Post AOP	< 0.13	< 0.13	< 0.13	< 0.050
10	CA	WW eff	2_2	Raw	4.1	2.7	7.1	< 0.10
10	CA	WW eff	2_2	Post MF/UF	4.1	2.6	5.8	< 0.10
10	CA	WW eff	2_2	Post RO	< 0.25	< 0.25	< 0.25	< 0.10
10	CA	WW eff	2_2	Post AOP	< 0.25	< 0.25	< 0.25	< 0.10

Table B.4: Continued.

ID	State	Source Water	#	Description	PFBS	PFHxS	PFOS	PFDS
11	NJ	Blend	2_1	Raw	1.2	2.0	1.8	< 0.11
11	NJ	Blend	2_1	pre-Cl dioxide	0.95	1.2	1.5	< 0.11
11	NJ	Blend	2_1	post-Cl dioxide	0.86	1.3	1.4	< 0.10
11	NJ	Blend	2_1	Finished	0.87	1.1	1.4	< 0.10
11	NJ	Blend	2_2	Raw	2.0	1.1	1.7	< 0.10
11	NJ	Blend	2_2	pre-Cl dioxide	2.2	1.2	2.1	< 0.10
11	NJ	Blend	2_2	post-Cl dioxide	2.1	1.1	2.5	< 0.10
11	NJ	Blend	2_2	Finished	2.5	1.1	2.6	< 0.10
12	NJ	Surface	2_1	Raw	2.6	2.1	2.2	< 0.10
12	NJ	Surface	2_1	post O3	2.8	2.2	3.4	< 0.10
12	NJ	Surface	2_1	post DAF	2.6	2.2	1.8	< 0.10
12	NJ	Surface	2_1	Finished	2.7	2.0	1.8	< 0.10
12	NJ	Surface	2_2	Raw	2.1	2.8	4.2	< 0.10
12	NJ	Surface	2_2	post O3	2.2	2.8	4.7	< 0.10
12	NJ	Surface	2_2	post DAF	2.2	2.7	2.3	< 0.10
12	NJ	Surface	2_2	Finished	2.4	2.7	3.2	< 0.10
13	NJ	Ground	2_1	Raw	2.9	6.8	18	< 0.10
13	NJ	Ground	2_1	post UV	3.0	4.6	14	< 0.10
13	NJ	Ground	2_1	Finished	3.1	4.6	14	< 0.10
13	NJ	Ground	2_2	Raw	3.7	7.6	27	< 0.10
13	NJ	Ground	2_2	post UV	3.4	4.9	14	< 0.10
13	NJ	Ground	2_2	Finished	3.3	5.1	15	< 0.10
14	NJ	Ground	2_1	Raw	3.3	8.6	2.6	< 0.10
14	NJ	Ground	2_1	post purolite	0.57	< 0.25	< 0.25	< 0.10
14	NJ	Ground	2_1	Finished	0.58	0.32	< 0.25	< 0.10
14	NJ	Ground	2_2	Raw	3.5	11	4.5	< 0.10
14	NJ	Ground	2_2	post IX	0.71	< 0.25	< 0.25	< 0.10
14	NJ	Ground	2_2	Finished	0.5	< 0.25	< 0.25	< 0.10
15	NJ	Ground	2_1	Raw	0.5	1.7	3.3	< 0.10
15	NJ	Ground	2_1	Finished	0.48	1.6	3.4	< 0.10
16	NJ	Ground	2_1	Raw	0.43	0.48	0.48	< 0.10
16	NJ	Ground	2_1	Finished	0.43	0.44	0.51	< 0.10
17	NJ	Surface	2_1	Raw	0.76	1.8	1.8	< 0.10
17	NJ	Surface	2_1	pre O3	0.82	1.9	2.6	< 0.10
17	NJ	Surface	2_1	post O3	0.96	1.9	2.6	< 0.10

Table B.4: Continued.

ID	State	Source Water	#	Description	PFBS	PFHxS	PFOS	PFDS
17	NJ	Surface	2_1	Finished	0.94	1.9	2.7	< 0.10
17	NJ	Surface	2_2	Raw	3	3.2	5.5	< 0.10
17	NJ	Surface	2_2	pre O3	3.1	3	5.3	< 0.10
17	NJ	Surface	2_2	post O3	4	3.6	6.9	< 0.10
17	NJ	Surface	2_2	Finished	3.6	3.3	5.6	< 0.10
18	NJ	Surface	2_1	Raw	2.1	5.9	2.9	< 0.10
18	NJ	Surface	2_1	btwn APT & GAC	2.1	5.8	5.1	< 0.10
18	NJ	Surface	2_1	post GAC	2	5.5	3.5	< 0.10
18	NJ	Surface	2_1	Finished	1.9	5.6	4.7	< 0.10
18	NJ	Surface	2_2	Raw	3.6	3.9	4.6	< 0.10
18	NJ	Surface	2_2	btwn APT & GAC	3.6	3.6	5.4	< 0.10
18	NJ	Surface	2_2	post GAC	3.4	4	12	< 0.10
18	NJ	Surface	2_2	Finished	3.4	4.2	9.4	< 0.10
19	NJ	Ground	2_1	Raw	1.4	2.2	2.1	< 0.10
19	NJ	Ground	2_1	Finished	1.5	2.1	2.2	< 0.10

Table B.5: Precursor Sample Data in ng/L

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
1	WI	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
1	WI	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
2	OK	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
2	OK	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
3	AK	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
3	AK	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
4	CA	WW eff	1	Raw	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	1.4	< 0.5
4	CA	WW eff	2_1	Raw	< 0.26	0.38	0.32	< 2.1	< 2.1	< 2.1	< 2.1	< 0.52		< 0.52
4	CA	WW eff	2_1	pre RO	< 0.27	0.44	0.33	< 2.1	< 2.1	< 2.1	< 2.1	< 0.53		< 0.53
4	CA	WW eff	2_1	post RO	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.51		< 0.51
4	CA	WW eff	2_1	post UV	< 0.26	< 0.26	< 0.26	< 2.1	< 2.1	< 2.1	< 2.1	< 0.52		< 0.52
4	CA	WW eff	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
4	CA	WW eff	2_2	Raw	< 0.25	0.67	0.32	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	1.0	< 0.50
4	CA	WW eff	2_2	pre RO	< 0.25	0.39	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.99	< 0.50
4	CA	WW eff	2_2	post RO	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
4	CA	WW eff	2_2	post UV	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
4	CA	WW eff	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
5	AL	Surface	1	Raw	1.5	0.8	2.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
5	AL	Surface	2_1	Raw	0.85	0.5	0.79	< 2.1	< 2.1	< 2.1	< 2.1	< 0.53		< 0.53
5	AL	Surface	2_1	post MIEX	1.9	1.0	2.4	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
5	AL	Surface	2_1	Finished	0.76	0.81	1.5	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
5	AL	Surface	2_2	Raw	1.4	0.84	2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
5	AL	Surface	2_2	post MIEX	1.5	0.87	2.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
5	AL	Surface	2_2	Finished	1.7	0.9	2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
7	CO	Surface	1	Raw	< 0.3	0.7	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	3.7	< 0.5
7	CO	Surface	2_1	Raw	< 0.25	0.64	0.32	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	1.8	< 0.50
7	CO	Surface	2_1	Post RBF	< 0.25	0.25	0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
7	CO	Surface	2_1	Raw water	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.54	< 0.50
7	CO	Surface	2_1	Before UV/AOP	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
7	CO	Surface	2_1	After UV/AOP	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
7	CO	Surface	2_1	Before GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 40	< 0.50	< 0.50	< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
7	CO	Surface	2_1	After GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
7	CO	Surface	2_2	Raw	0.25	1.2	0.60	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	3.5	< 0.50
7	CO	Surface	2_2	Post RBF	0.35	0.31	0.58	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	2.6	< 0.50
8	OH	Surface	1	Raw	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
8	OH	Surface	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
8	OH	Surface	2_1	pre GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
8	OH	Surface	2_1	post GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
8	OH	Surface	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
8	OH	Surface	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
8	OH	Surface	2_2	pre GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
8	OH	Surface	2_2	post GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
8	OH	Surface	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
9	NV	Surface	1	Raw_1	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
9	NV	Surface	1	Raw_2	< 0.3	< 0.3	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	< 0.5	< 0.5
10	CA	WW eff	1	Raw	< 0.3	0.6	< 0.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.5	1.8	< 0.5

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
10	CA	WW eff	2_1	Raw	0.27	0.74	< 0.13	< 1.0	< 1.0	< 1.0	< 1.0	< 0.25	< 0.25	< 0.25
10	CA	WW eff	2_1	Post MF/UF	0.15	0.83	0.29	< 1.0	< 1.0	< 1.0	< 1.0	< 0.25	< 0.25	< 0.25
10	CA	WW eff	2_1	Post RO	< 0.13	< 0.13	< 0.13	< 1.0	< 1.0	< 1.0	< 1.0	< 0.25	< 0.25	< 0.25
10	CA	WW eff	2_1	Post AOP	< 0.13	< 0.13	< 0.13	< 1.0	< 1.0	< 1.0	< 1.0	< 0.25	< 0.25	< 0.25
10	CA	WW eff	2_2	Raw	0.42	1.1	0.43	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
10	CA	WW eff	2_2	Post MF/UF	< 0.25	1.2	0.6	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
10	CA	WW eff	2_2	Post RO	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
10	CA	WW eff	2_2	Post AOP	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
11	NJ	Blend	2_1	Raw	< 0.26	< 0.26	< 0.26	< 2.1	< 2.1	< 2.1	< 2.1	< 0.53		< 0.53
11	NJ	Blend	2_1	pre-Cl dioxide	< 0.28	< 0.28	< 0.28	< 2.2	< 2.2	< 2.2	< 2.2	< 0.55		< 0.55
11	NJ	Blend	2_1	post-Cl dioxide	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.51		< 0.51
11	NJ	Blend	2_1	Finished	< 0.26	< 0.26	< 0.26	< 2.0	< 2.0	< 2.0	< 2.0	< 0.51		< 0.51
11	NJ	Blend	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
11	NJ	Blend	2_2	pre-Cl dioxide	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
11	NJ	Blend	2_2	post-Cl dioxide	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
11	NJ	Blend	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_1	post O3	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_1	post DAF	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_2	post O3	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.61	< 0.50
12	NJ	Surface	2_2	post DAF	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
12	NJ	Surface	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.59	< 0.50
13	NJ	Ground	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
13	NJ	Ground	2_1	post UV	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
13	NJ	Ground	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
13	NJ	Ground	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	1.2	< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
13	NJ	Ground	2_2	post UV	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.58	< 0.50
13	NJ	Ground	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.61	< 0.50
14	NJ	Ground	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
14	NJ	Ground	2_1	post purolite	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
14	NJ	Ground	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
14	NJ	Ground	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
14	NJ	Ground	2_2	post IX	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
14	NJ	Ground	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
15	NJ	Ground	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
15	NJ	Ground	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
16	NJ	Ground	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
16	NJ	Ground	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
17	NJ	Surface	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
17	NJ	Surface	2_1	pre O3	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
17	NJ	Surface	2_1	post O3	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
17	NJ	Surface	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
17	NJ	Surface	2_2	Raw	< 0.25	< 0.25	0.98	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.66	< 0.50
17	NJ	Surface	2_2	pre O3	< 0.25	< 0.25	0.85	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.8	< 0.50
17	NJ	Surface	2_2	post O3	< 0.25	< 0.25	1.3	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	1.5	0.56
17	NJ	Surface	2_2	Finished	< 0.25	< 0.25	0.72	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	1.6	< 0.50
18	NJ	Surface	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
18	NJ	Surface	2_1	btwn APT & GAC	< 0.26	< 0.26	< 0.26	< 2.1	< 2.1	< 2.1	< 2.1	< 0.52	< 0.52	< 0.52
18	NJ	Surface	2_1	post GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	< 0.50	< 0.50
18	NJ	Surface	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	2.2	< 0.50
18	NJ	Surface	2_2	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.97	< 0.50
18	NJ	Surface	2_2	btwn APT & GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.63	< 0.50
18	NJ	Surface	2_2	post GAC	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.6	< 0.50
18	NJ	Surface	2_2	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50	0.62	< 0.50

Table B.5: Continued.

ID	State	Source Water	#	Description	FOSA	[b]N-MF	[c]N-EF	*4:2	*6:2	*8:2	*10:2	[a]4:2	[a]6:2	[a]8:2
19	NJ	Ground	2_1	Raw	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.50		< 0.50
19	NJ	Ground	2_1	Finished	< 0.25	< 0.25	< 0.25	< 2.0	< 2.0	< 2.0	< 2.0	< 0.51		< 0.51

[a]FtS, [b]N-MeFOSAA, [c]N-EtFOSAA, *FTUCA

Table B.6: PFAS Data from Utility 20's Lead GAC Vessels

Date	PFBA (μg/L)		PFPeA (μg/L)		PFHxA (μg/L)		PFOA (μg/L)		PFBS (μg/L)		PFHxS (μg/L)		PFOS (μg/L)	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
10/26/06	1.83	< 0.05	< 0.05	< 0.05	0.12	< 0.05	0.72	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	1.02	< 0.05
11/29/06	1.74	< 0.05	< 0.05	< 0.05	0.25	< 0.05	0.66	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	1.10	< 0.05
12/20/06	1.78	0.24	< 0.05	< 0.05	0.38	< 0.05	0.62	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	1.03	< 0.05
1/24/07	1.87	0.88	< 0.05	< 0.05	0.25	< 0.05	0.76	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	1.08	< 0.05
2/28/07	1.78	0.94	< 0.05	< 0.05	0.31	< 0.05	0.58	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.53	< 0.05
3/28/07	1.92	1.48	< 0.05	< 0.05	0.23	< 0.05	0.70	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	1.17	< 0.05
4/25/07	1.78	1.57	< 0.05	< 0.05	0.18	< 0.05	0.65	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.97	< 0.05
5/23/07	1.81	1.64	< 0.05	< 0.05	0.16	< 0.05	0.83	< 0.05	< 0.05	< 0.05	0.21	< 0.05	1.04	< 0.05
6/27/07	1.77	1.73	< 0.05	< 0.05	0.14	< 0.05	0.83	< 0.05	< 0.05	< 0.05	0.08	< 0.05	1.20	< 0.05
7/25/07	1.60	1.78	0.07	< 0.05	0.13	< 0.05	0.72	< 0.05	< 0.05	< 0.05	0.07	< 0.05	1.24	< 0.05
8/17/07	1.58	1.96	0.08	< 0.05	0.19	0.06	0.69	0.08	0.05	< 0.05	0.09	< 0.05	1.38	< 0.05
9/26/07	1.51	1.87	0.08	0.07	0.16	0.09	0.63	0.07	< 0.05	< 0.05	0.09	< 0.05	1.09	< 0.05
10/31/07	1.50	1.82	0.05	< 0.05	0.15	0.06	0.59	0.08	< 0.05	< 0.05	0.08	< 0.05	0.98	< 0.05
11/27/07	1.49	1.89	0.08	0.06	0.15	0.09	0.58	0.15	< 0.05	< 0.05	0.08	< 0.05	0.97	< 0.05
12/27/07	1.37	1.85	0.07	< 0.05	0.18	< 0.05	0.58	0.06	< 0.05	< 0.05	0.09	< 0.05	0.92	< 0.05
2/14/08	1.49	2.16	< 0.05	< 0.05	0.17	0.06	0.52	0.09	< 0.05	< 0.05	0.08	< 0.05	0.87	< 0.05
3/14/08	1.49	2.00	0.06	0.06	0.16	0.10	0.59	0.08	< 0.05	< 0.05	0.07	< 0.05	0.88	< 0.05
4/15/08	1.40	1.61	0.05	0.06	0.13	0.08	0.60	0.16	< 0.05	< 0.05	0.08	< 0.05	0.86	< 0.05
4/22/08	1.41	1.64	0.05	< 0.05	0.17	0.15	0.63	0.16	< 0.05	< 0.05	0.08	< 0.05	0.91	0.06
5/15/08	1.23	1.68	0.06	0.07	0.14	0.09	0.57	0.15	< 0.05	< 0.05	0.07	< 0.05	0.91	0.06
5/28/08	1.44	1.58	0.07	0.06	0.14	0.11	0.60	0.26	< 0.05	< 0.05	0.08	< 0.05	0.86	0.09
6/11/08	1.43	1.65	< 0.05	0.05	0.16	0.13	0.52	0.23	< 0.05	< 0.05	0.07	< 0.05	0.73	0.09
6/24/08	1.36	1.51	0.06	0.07	0.14	0.13	0.46	0.23	< 0.05	< 0.05	0.08	< 0.05	0.76	0.08
7/15/08	1.36	1.50	< 0.05	0.07	0.15	0.14	0.55	0.28	< 0.05	< 0.05	0.07	< 0.05	0.81	0.11

Table B.6: Continued.

Date	PFBA (μg/L)		PFPeA (μg/L)		PFHxA (μg/L)		PFOA (μg/L)		PFBS (μg/L)		PFHxS (μg/L)		PFOS (μg/L)	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
7/29/08	1.37	1.57	0.06	0.07	0.14	0.16	0.50	0.26	< 0.05	< 0.05	0.07	< 0.05	0.82	0.15
8/13/08	1.33	1.48	0.06	0.07	0.14	0.15	0.45	0.25	< 0.05	< 0.05	0.08	< 0.05	0.71	0.11
9/23/08	1.27	1.74	0.05	0.06	0.16	0.08	0.52	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.70	< 0.05
10/16/08	1.31	1.62	< 0.05	< 0.05	0.16	0.07	0.57	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.75	< 0.05
11/14/08	1.39	1.70	0.05	0.06	0.16	0.08	0.53	0.05	< 0.05	< 0.05	0.07	< 0.05	0.66	< 0.05
12/9/08	1.36	1.77	0.06	0.05	0.14	0.07	0.55	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.77	< 0.05
1/20/09	1.41	1.83	0.06	0.06	0.15	0.07	0.57	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.71	< 0.05
2/13/09	1.45	1.74	0.06	0.06	0.17	0.08	0.56	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.76	< 0.05
3/13/09	1.50	1.57	0.06	0.06	0.13	0.12	0.55	0.12	< 0.05	< 0.05	0.06	< 0.05	0.88	< 0.05
4/16/09	1.46	1.54	0.06	0.07	0.13	0.11	0.50	0.16	< 0.05	< 0.05	0.07	< 0.05	0.76	< 0.05
5/14/09	1.41	1.55	< 0.05	< 0.05	0.15	0.11	0.49	0.23	< 0.05	< 0.05	0.06	< 0.05	0.75	0.11
6/19/09	1.43	1.58	0.07	0.07	0.14	0.14	0.54	0.29	< 0.05	< 0.05	0.07	< 0.05	0.75	0.13
7/13/09	1.40	1.55	< 0.05	0.05	0.12	0.11	0.45	0.27	< 0.05	< 0.05	0.06	< 0.05	0.67	0.16
8/17/09	1.37	1.54	< 0.05	0.06	0.14	0.12	0.54	0.26	< 0.05	< 0.05	0.06	< 0.05	0.70	0.17
9/21/09	1.57	1.50	0.12	0.06	0.16	0.12	0.55	0.28	< 0.05	< 0.05	0.06	< 0.05	0.75	0.18
10/19/09	1.35	1.59	0.07	0.05	0.13	0.07	0.45	0.08	< 0.05	< 0.05	0.06	< 0.05	0.78	< 0.05
11/9/09	1.37	1.53	0.05	0.05	0.11	0.07	0.53	0.09	< 0.05	< 0.05	0.05	< 0.05	0.73	< 0.05
12/15/09	1.34	1.55	< 0.05	< 0.05	0.11	0.08	0.45	0.07	< 0.05	< 0.05	0.07	< 0.05	0.75	< 0.05
1/21/10	1.35	1.45	0.08	< 0.05	0.15	0.07	0.40	0.05	< 0.05	< 0.05	0.05	< 0.05	0.50	< 0.05
2/24/10	1.33	1.47	0.06	0.06	0.18	0.08	0.41	0.07	< 0.05	< 0.05	0.06	< 0.05	0.48	< 0.05
3/18/10	1.06	1.60	< 0.05	0.06	0.10	0.07	0.32	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.55	< 0.05
4/14/10	1.28	1.49	< 0.05	< 0.05	0.14	0.10	0.50	0.19	< 0.05	< 0.05	0.06	< 0.05	0.76	< 0.05
5/19/10	1.28	1.35	0.06	0.07	0.12	0.11	0.52	0.21	< 0.05	< 0.05	0.07	< 0.05	0.75	0.12
6/22/10	1.30	1.44	0.05	0.07	0.11	0.10	0.47	0.25	< 0.05	< 0.05	0.06	< 0.05	0.70	0.14
7/30/10	1.29	1.30	0.06	< 0.05	0.18	0.12	0.41	0.27	< 0.05	< 0.05	0.07	< 0.05	0.53	0.20
8/25/10	1.22	1.28	< 0.05	< 0.05	0.09	0.14	0.48	0.28	< 0.05	< 0.05	0.06	< 0.05	0.80	0.22

Table B.6: Continued.

Date	PFBA (μg/L)		PFPeA (μg/L)		PFHxA (μg/L)		PFOA (μg/L)		PFBS (μg/L)		PFHxS (μg/L)		PFOS (μg/L)	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
9/20/10	1.34	1.33	0.06	0.06	0.13	0.13	0.44	0.27	< 0.05	< 0.05	0.07	< 0.05	0.58	0.25
10/7/10	1.20	1.30	0.06	0.06	0.16	0.12	0.47	0.31	< 0.05	< 0.05	0.06	< 0.05	0.71	0.20
11/9/10	1.14	< 0.05	< 0.05	< 0.05	0.11	< 0.05	0.38	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.73	< 0.05
12/28/10	1.15	< 0.05	< 0.05	< 0.05	0.10	< 0.05	0.41	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.59	< 0.05
1/28/11	1.19	0.08	< 0.05	< 0.05	0.13	< 0.05	0.39	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.68	< 0.05
2/14/11	1.31	0.12	0.06	< 0.05	0.13	< 0.05	0.45	< 0.05	< 0.05	< 0.05	0.06	< 0.05	0.79	< 0.05
3/21/11	1.55	0.87	0.06	< 0.05	0.16	< 0.05	0.51	< 0.05	0.03	< 0.05	0.07	< 0.05	0.82	< 0.05
4/20/11	1.32	1.11	0.05	< 0.05	0.12	< 0.05	0.51	< 0.05	0.03	< 0.05	0.07	< 0.05	0.67	< 0.05
5/16/11	1.34	1.30	0.06	< 0.05	0.13	< 0.05	0.46	< 0.05	0.03	< 0.05	0.05	< 0.05	0.75	< 0.05
6/20/11	1.30	1.67	0.05	0.02	0.12	0.01	0.45	< 0.05	0.02	< 0.05	0.07	< 0.05	0.66	< 0.05

Table B.7: PFAS Data from Utility 20's Lag GAC Vessels

Date	PFBA (μg/L)		PFPeA (μg/L)		PFHxA (μg/L)		PFOA (μg/L)		PFBS (μg/L)		PFHxS (μg/L)		PFOS (μg/L)	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
4/25/07	1.78	0.54	< 0.05	< 0.05	0.18	< 0.05	0.65	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.97	< 0.05
5/23/07	1.81	0.97	< 0.05	< 0.05	0.16	< 0.05	0.83	< 0.05	< 0.05	< 0.05	0.21	< 0.05	1.04	< 0.05
6/27/07	1.77	1.27	< 0.05	< 0.05	0.14	< 0.05	0.83	< 0.05	< 0.05	< 0.05	0.08	< 0.05	1.20	< 0.05
7/25/07	1.60	1.38	0.07	< 0.05	0.13	< 0.05	0.72	< 0.05	< 0.05	< 0.05	0.07	< 0.05	1.24	< 0.05
8/17/07	1.58	1.69	0.08	< 0.05	0.19	< 0.05	0.69	< 0.05	0.05	< 0.05	0.09	< 0.05	1.38	< 0.05
9/26/07	1.51	1.96	0.08	< 0.05	0.16	< 0.05	0.63	< 0.05	< 0.05	< 0.05	0.09	< 0.05	1.09	< 0.05
10/31/07	1.50	1.95	0.05	< 0.05	0.15	< 0.05	0.59	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.98	< 0.05
11/27/07	1.49	2.06	0.08	< 0.05	0.15	< 0.05	0.58	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.97	< 0.05
12/27/07	1.37	2.18	0.07	< 0.05	0.18	< 0.05	0.58	< 0.05	< 0.05	< 0.05	0.09	< 0.05	0.92	< 0.05
2/14/08	1.49	2.48	< 0.05	< 0.05	0.17	< 0.05	0.52	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.87	< 0.05
3/14/08	1.49	2.48	0.06	< 0.05	0.16	< 0.05	0.59	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.88	< 0.05
4/15/08	1.40	1.98	0.05	< 0.05	0.13	< 0.05	0.60	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.86	< 0.05
4/22/08	1.41	1.96	0.05	< 0.05	0.17	< 0.05	0.63	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.91	< 0.05
5/15/08	1.23	1.74	0.06	0.05	0.14	< 0.05	0.57	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.91	< 0.05
5/28/08	1.44	1.84	0.07	0.05	0.14	< 0.05	0.60	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.86	< 0.05
6/11/08	1.43	1.85	< 0.05	< 0.05	0.16	0.05	0.52	< 0.05	< 0.05	< 0.05	0.07	< 0.05	0.73	< 0.05
6/24/08	1.36	1.70	0.06	0.06	0.14	0.06	0.46	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.76	< 0.05
7/15/08	1.36	1.66	< 0.05	0.06	0.15	0.06	0.55	0.06	< 0.05	< 0.05	0.07	< 0.05	0.81	< 0.05
7/29/08	1.37	1.75	0.06	0.06	0.14	0.10	0.50	0.05	< 0.05	< 0.05	0.07	< 0.05	0.82	< 0.05
8/13/08	1.33	1.64	0.06	0.07	0.14	0.10	0.45	< 0.05	< 0.05	< 0.05	0.08	< 0.05	0.71	< 0.05

Table B.8: Occurrence Levels by Water Source

Raw Water Source	Ground Water (ng/L)			Surface Water (ng/L)			Surface/ground Water mix (ng/L)		Treated Wastewater Effluent (ng/L)	
PFAS	Raw (5[j])	Finished (5)	Lit.	Raw (11)	Finished (6)	Lit.	Raw (1)	Finished (1)	Raw (2)	Lit.
PFBA	< 5.0 - 28	< 5.0 - 27		< 5.0 - 40	< 5.0 - 5.6		< 5.0	< 5.0	< 5.0 - 29	
PFPeA	9.9 - 44	9.2 - 43		< 2.0 - 14	< 2.0 - 8.3		2.0 - 3.6	< 2.0 - 2.3	9.4 - 370	
PFHxA	7.3 - 67	7.7 - 62	1.0[g], 1.2[g]*	< 0.50 - 38	0.52 - 8.1	< 1.0 - 29[g], < 1.0 - 23[g]*	3.1 - 3.6	2.9 - 3.7	10.0 - 90	7.9 - 14[g]
PFHpA	3.9 - 33	4.1 - 34		< 0.50 - 12	< 0.50 - 5.8		2.5 - 2.8	1.6 - 2.9	2.6 - 18	
PFOA	11.0 - 68	11.0 - 57	nd - 140[d,f,g], nd - 11[d,g]*	< 5.0 - 50	< 5.0 - 27	nd - 287[a,b,c,d,e,g], nd - 39[e,g]*	29 - 43	17 - 33	9.3 - 220	15 - 1,050[g,h]
PFNA	< 0.50 - 47	< 0.50 - 55	< 1.0[g], 1.1[g]*	< 0.50 - 5.7	< 0.50 - 3.1	nd - 194[b,c,g], < 1.0 - 9.7[g]*	1.3 - 1.5	0.83 - 1.6	3.6 - 11	5.1 - 5.5[g]
PFDA	< 0.50 - 1.5	< 0.50 - 1.6	nd - 19[d,g], < 1.0[g]*	< 0.50 - 2.5	< 0.50 - 1.4	nd - 120[b,c,d,g], < 1.0 - 3.3[g]*	< 0.50	< 0.50	1.5 - 82	1.6 - 47[g,h]
PFUnA	< 0.50 - 0.63	< 0.50 - 0.64	< 1.0[g], <1.0[g]*	< 0.50	< 0.50 - 0.51	nd - 52.1[b,c,g], < 1.0[g]*	< 0.50	< 0.50	< 0.50 - 1.4	< 1.0 - 10[g,h]

Table B.8: Continued.

Raw Water Source	Ground Water (ng/L)			Surface Water (ng/L)			Surface/ground Water mix (ng/L)		Treated Wastewater Effluent (ng/L)	
PFAS	Raw (5[j])	Finished (5)	Lit.	Raw (11)	Finished (6)	Lit.	Raw (1)	Finished (1)	Raw (2)	Lit.
PFDoA	< 0.25	< 0.25	< 1.0[g], <1.0[g]*	< 0.25	< 0.25	nd - 4.46[b,c,g], < 1.0[g]*	< 0.25	< 0.25	< 0.25 - 2.7	< 1.0[g]
PFBS	0.43 - 3.7	0.43 - 3.3		< 0.25 - 47	0.44 - 3.6	< 1 - 9.41[c]	1.2 - 2	0.87 - 2.5	1.7 - 8.6	
PFHxS	0.48 - 8.6	0.32 - 5.1	1.8 - 17[d,g], 2.2[g]*	< 0.25 - 13	< 0.25 - 5.6	nd - 35.1[b,c,d,g], < 1.0 - 12[g]*	1.1 - 2	1.1	2.7 - 10	< 2.5 - 12[g,h]
PFOS	0.48 - 27	< 0.25 - 15	10 - 192[d,g], 9.4[g]*	< 0.25 - 47	< 0.25 - 9.4	< 1.0 - 132[a,c,d,g], < 1.0 - 22[g]*	1.7 - 1.8	1.4 - 2.6	4.3 - 17	3.0 - 68[g,h]
PFDS	< 0.10	< 0.10	nd - 15[d]	< 0.10	< 0.10	3.4 - 44[d]	< 0.10	< 0.10	< 0.10	
FOSA	< 0.25	< 0.25	nd - 4.3[d]	< 0.25 - 1.5	< 0.25 - 1.7	nd - 3.5[a,d]	< 0.25	< 0.25	< 0.25 - 0.42	
N-MeFOSAA	< 0.25	< 0.25		< 0.25 - 1.2	< 0.25 - 0.9		< 0.25	< 0.25	< 0.25 - 1.1	
N-EtFOSAA	< 0.25	< 0.25	nd - 26[d]	< 0.25 - 2.3	< 0.25 - 2.0	nd - 31[a,d]	< 0.25	< 0.25	< 0.25 - 0.43	
4:2 FTUCA	< 2.0	< 2.0		< 2.0	< 2.0		< 2.0	< 2.0	< 2.0	
6:2 FTUCA	< 2.0	< 2.0		< 2.0	< 2.0		< 2.0	< 2.0	< 2.0	

Table B.8: Continued.

Raw Water Source	Ground Water (ng/L)			Surface Water (ng/L)			Surface/ground Water mix (ng/L)		Treated Wastewater Effluent (ng/L)	
PFAS	Raw (5[j])	Finished (5)	Lit.	Raw (11)	Finished (6)	Lit.	Raw (1)	Finished (1)	Raw (2)	Lit.
8:2 FTUCA	< 2.0	< 2.0		< 2.0	< 2.0		< 2.0	< 2.0	< 2.0	< 2.5 - 29[h]
10:2 FTUCA	< 2.0	< 2.0		< 2.0	< 2.0		< 2.0	< 2.0	< 2.0	
4:2 FtS	< 0.50	< 0.50		< 0.50	< 0.50		< 0.50	< 0.50	< 0.50	
6:2 FtS	< 0.50 - 1.2	< 0.50 - 0.61		< 0.50 - 3.7	< 0.50 - 2.2		< 0.50	< 0.50	< 0.50 - 1.8	
8:2 FtS	< 0.50	< 0.50		< 0.50	< 0.50		< 0.50	< 0.50	< 0.50	

[a]Boulanger et al., 2004; [b]Furdui et al., 2008; [c]Nakayama et al., 2007; [d]Plumlee et al., 2008; [e]Post et al., 2009, 2006 study; [f]Post et al. 2009, 2008 study; [g]Quinones, 2009; [h]Sinclair and Kannan, 2006; *finished water; [j]n-value in this study

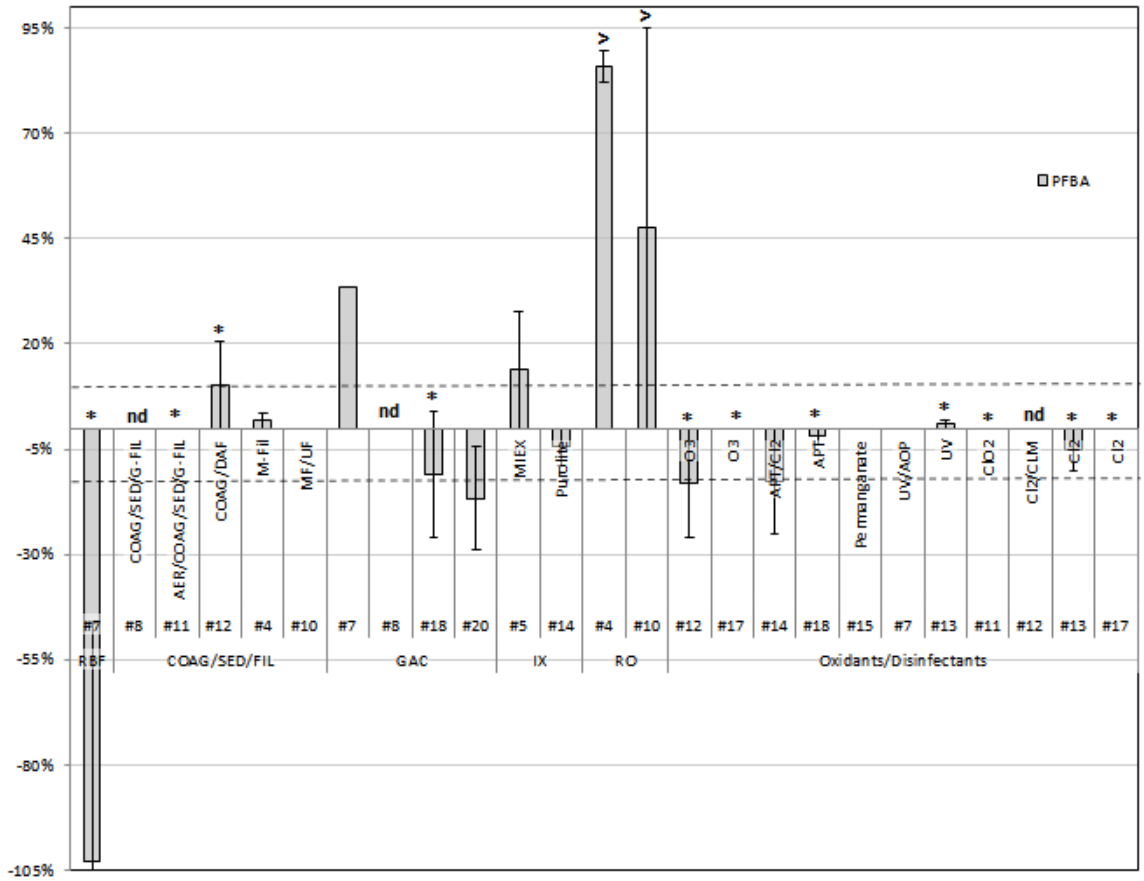

Figure B.1: Removal of PFBA by Treatment Process

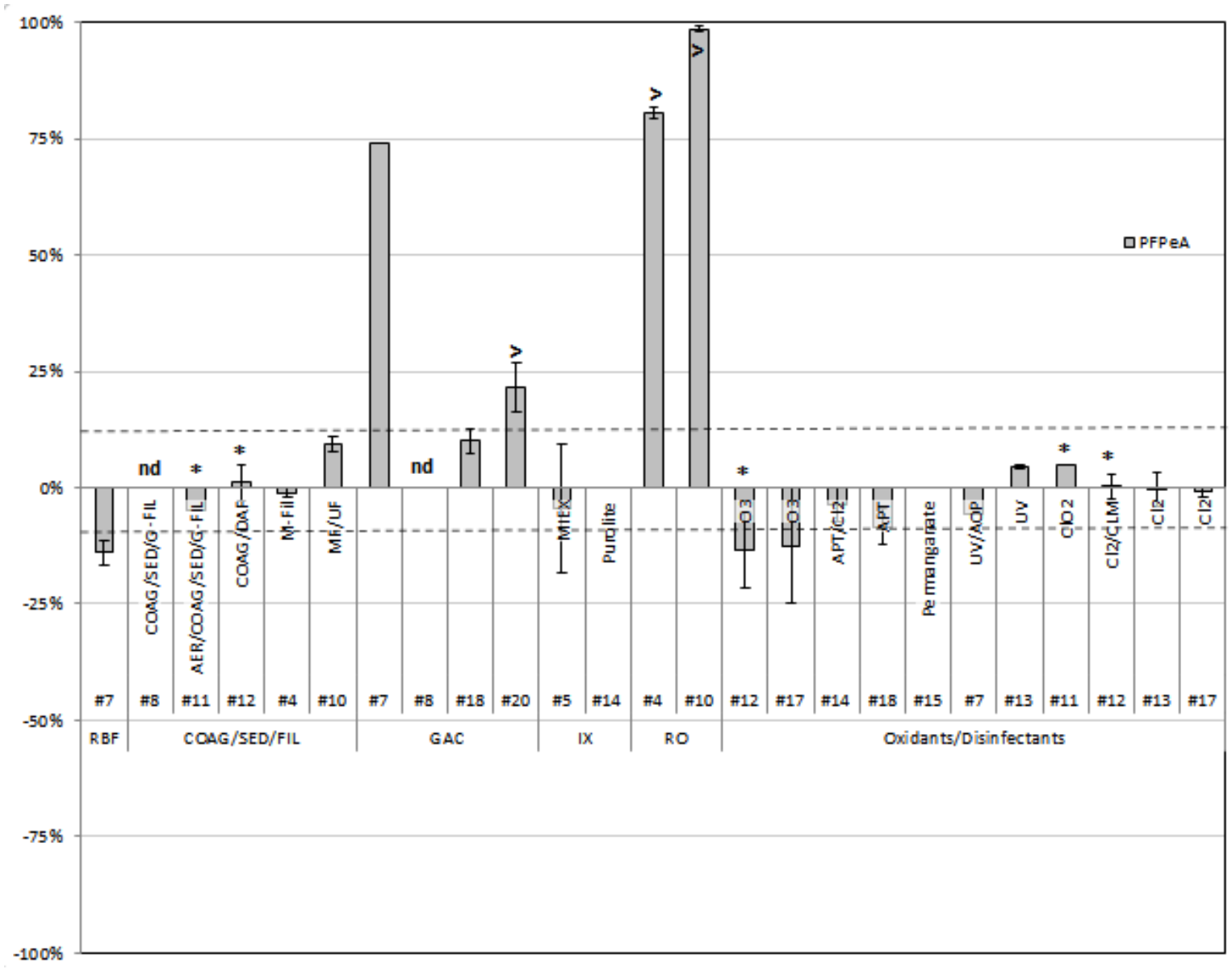

Figure B.2: Removal of PFPeA by Treatment Process

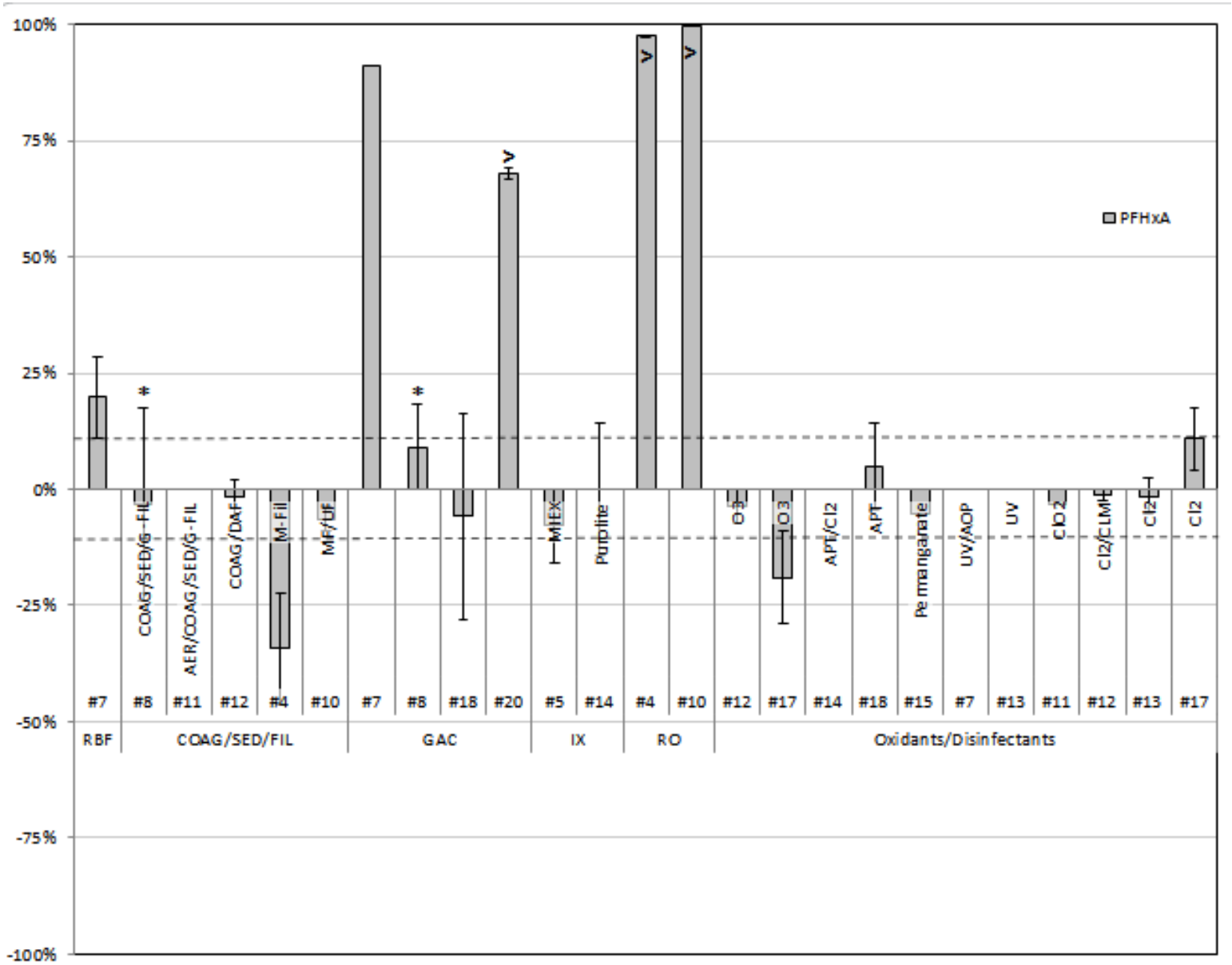

Figure B.3: Removal of PFHxA by Treatment Process

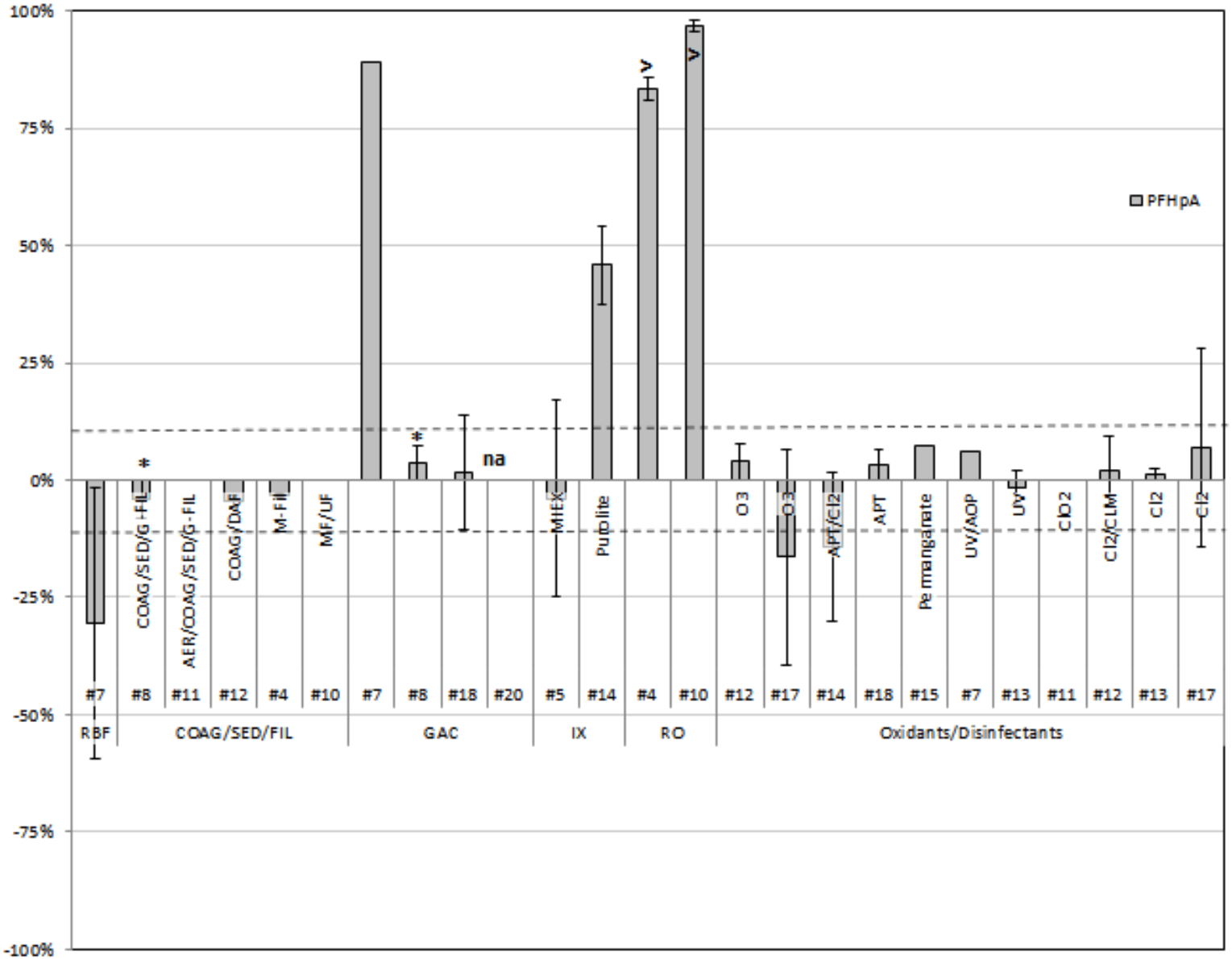

Figure B.4: Removal of PFHpA by Treatment Process

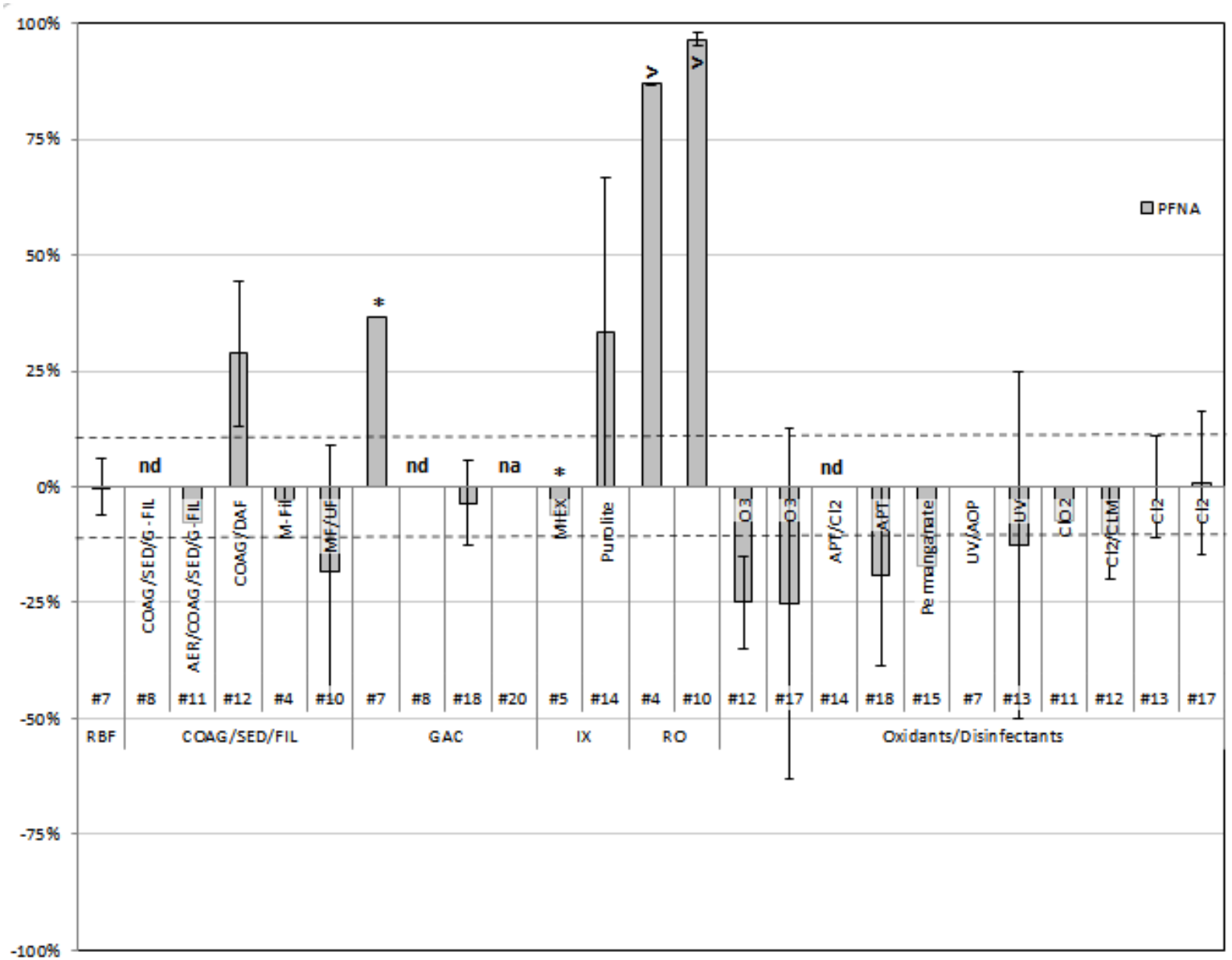

Figure B.5: Removal of PFNA by Treatment Process

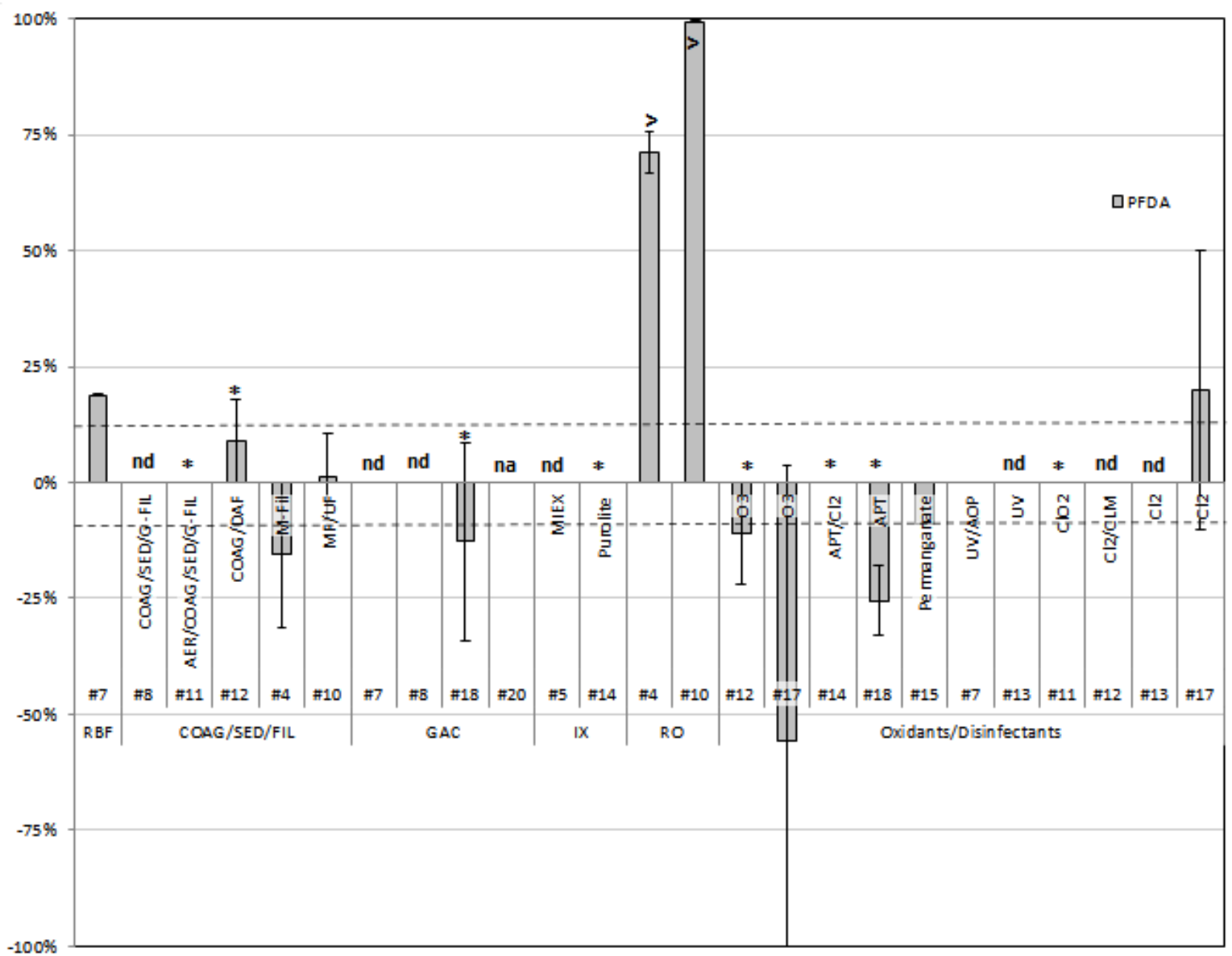

Figure B.6: Removal of PFDA by Treatment Process

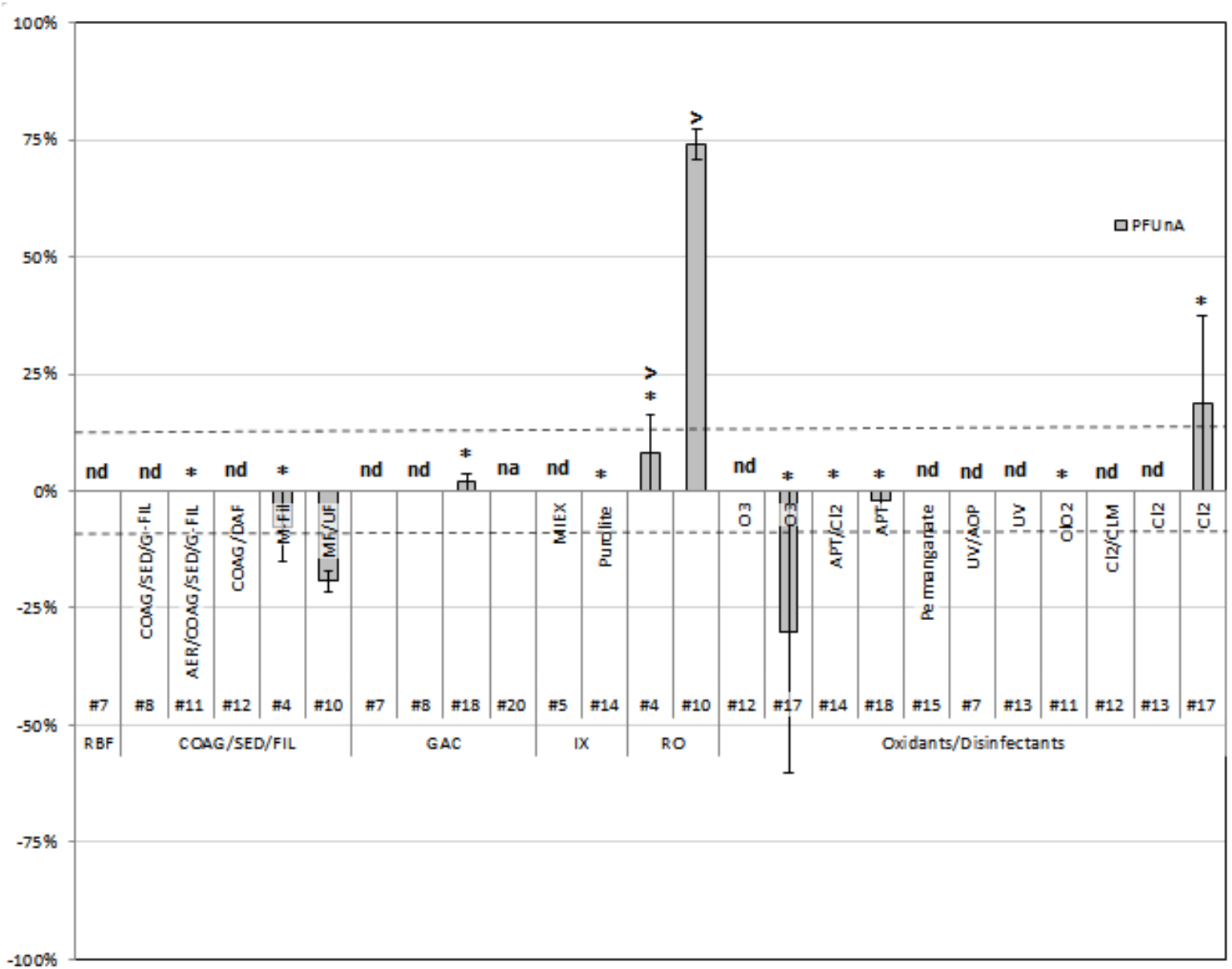

Figure B.7: Removal of PFUnA by Treatment Process

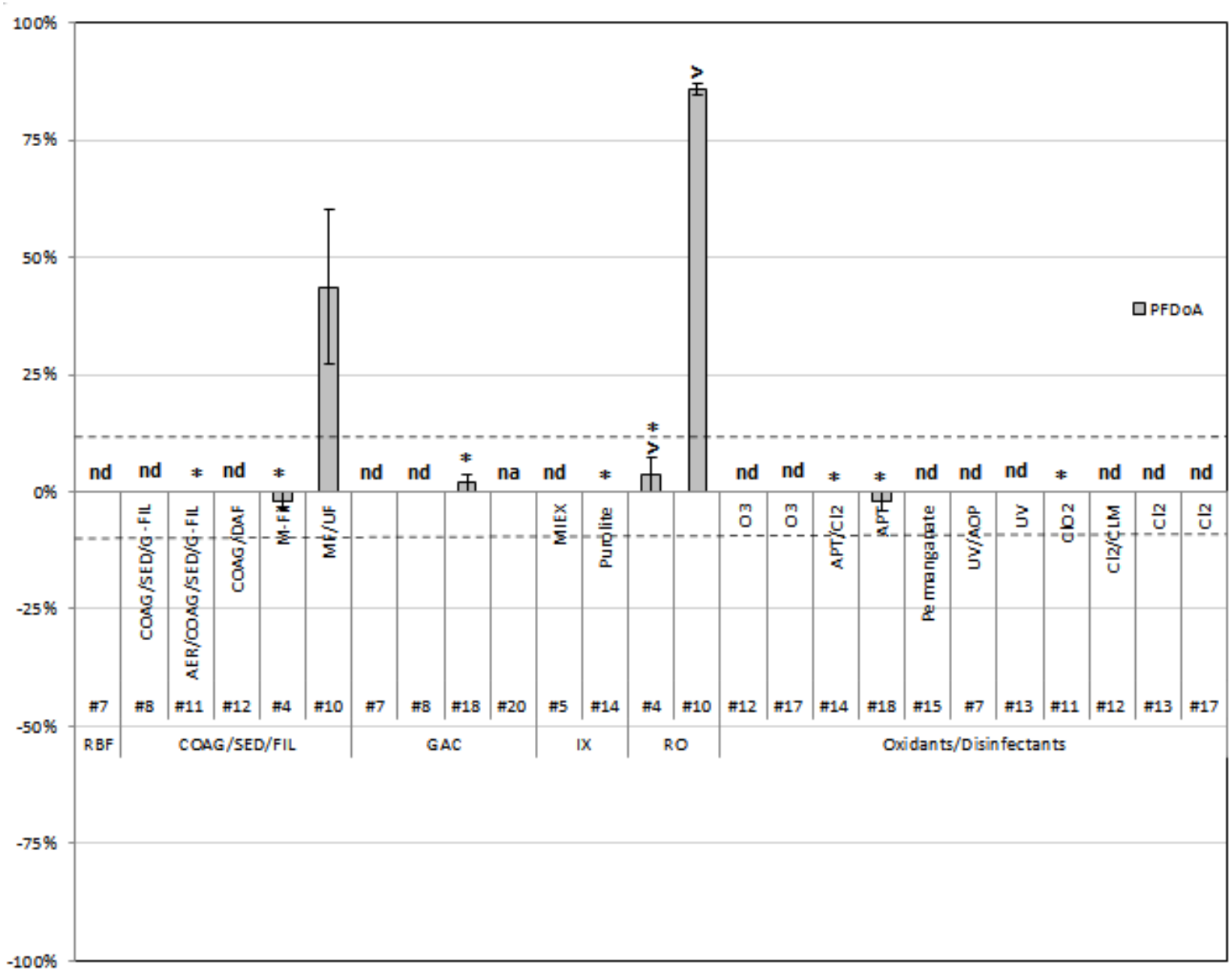

Figure B.8: Removal of PFDoA by Treatment Process

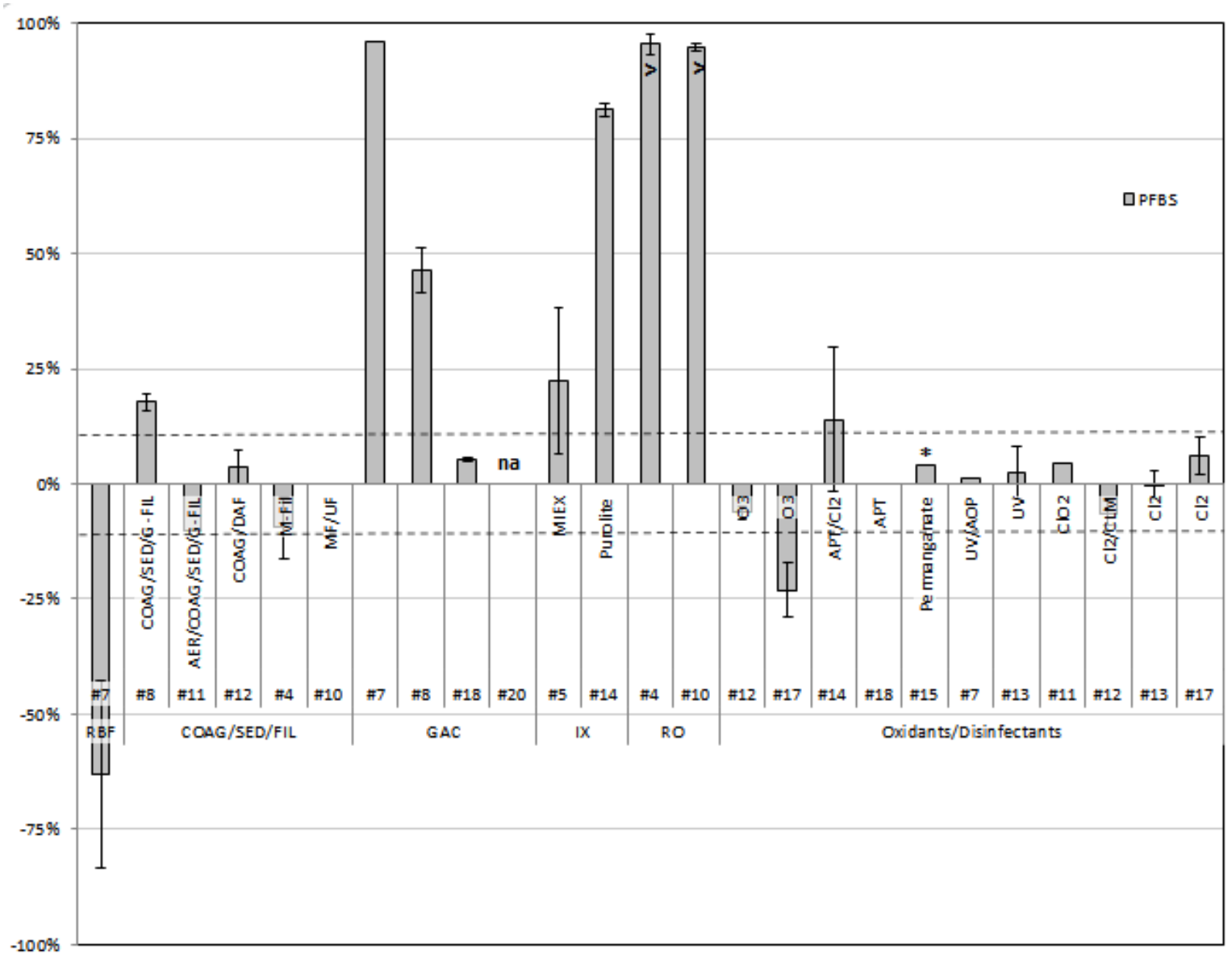

Figure B.9: Removal of PFBS by Treatment Process

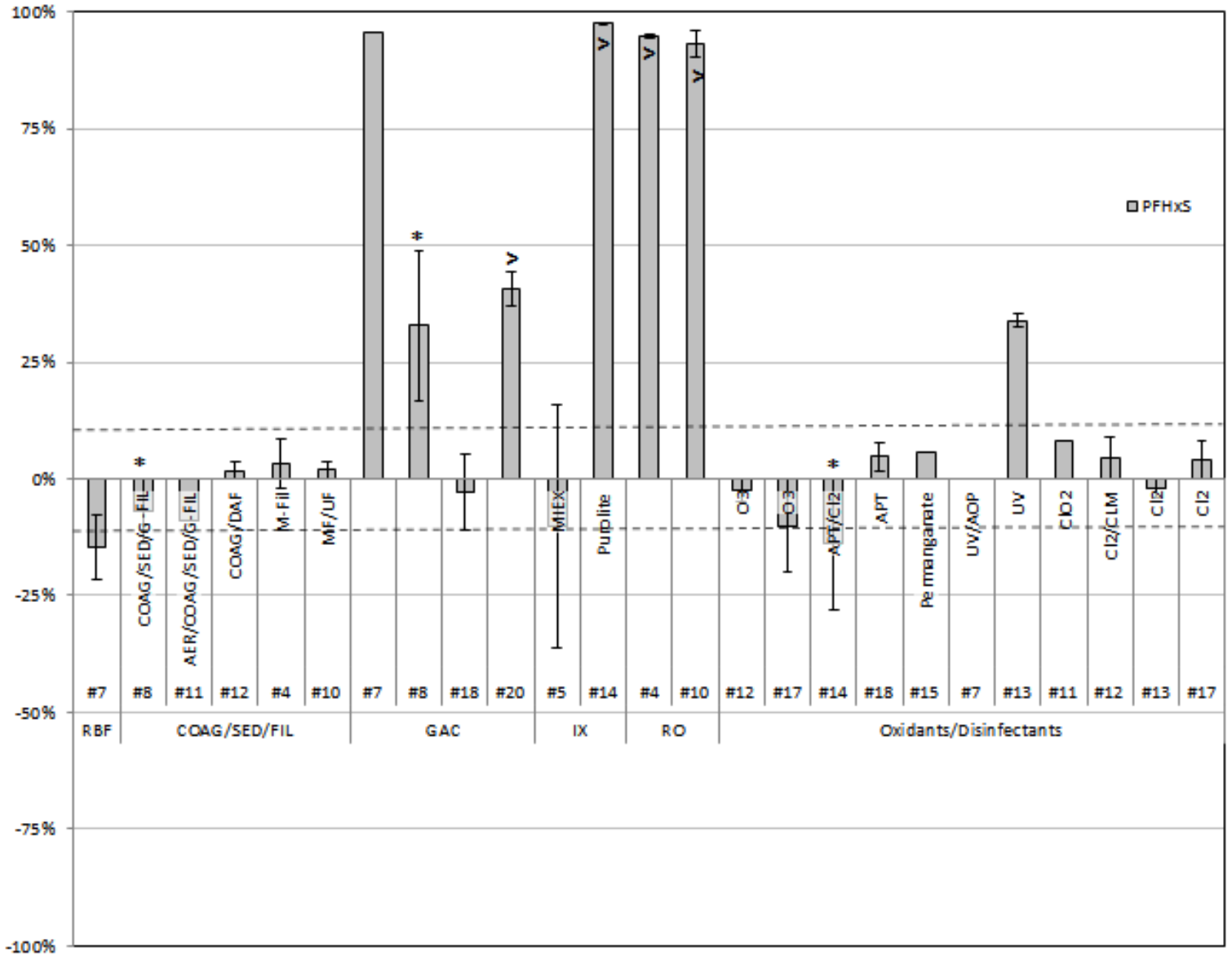

Figure B.10: Removal of PFHxS by Treatment Process

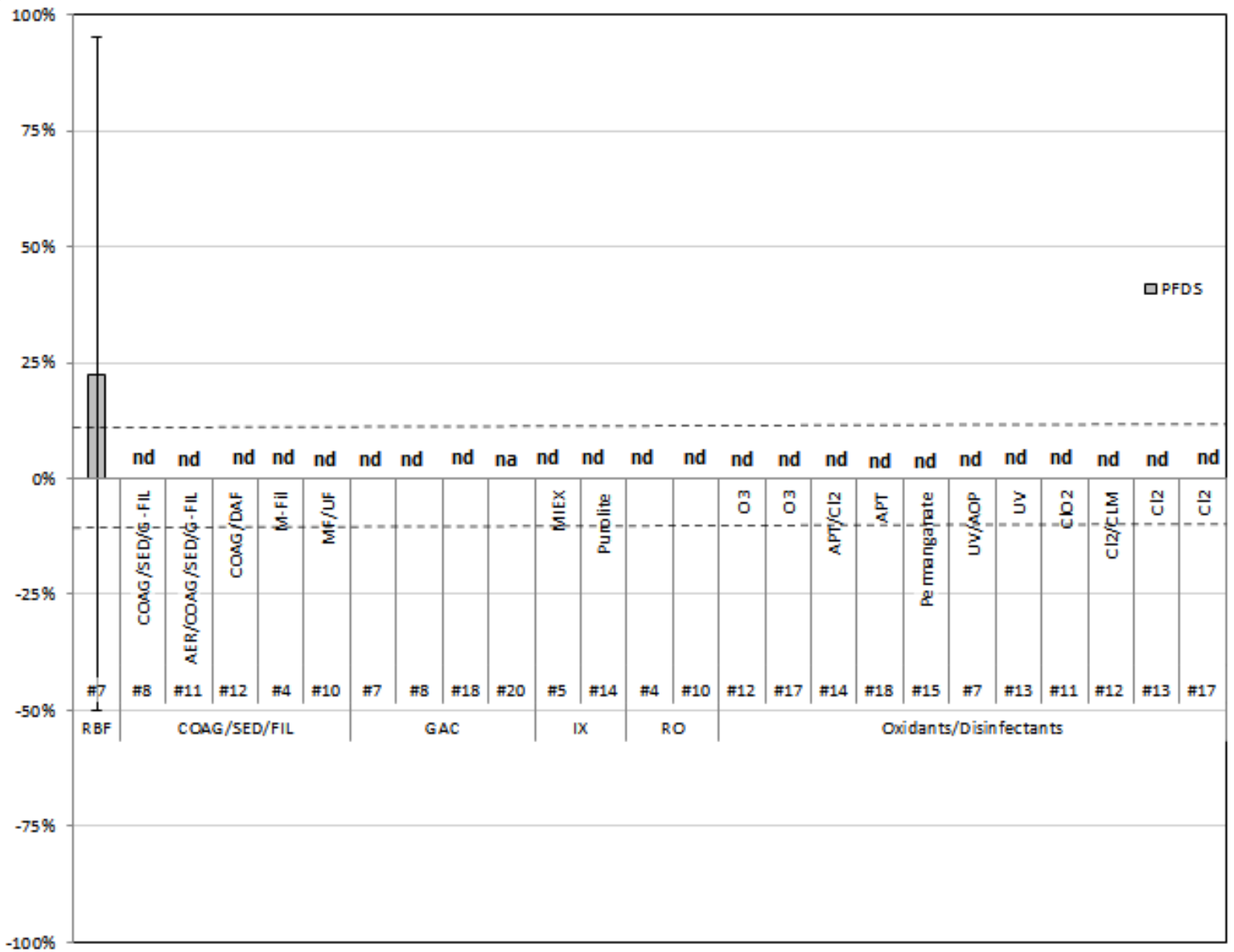

Figure B.11: Removal of PFDS by Treatment Process

APPENDIX C - SUPPLEMENTAL INFORMATION FOR CHAPTER 4

Table C.1: Relative Percent Difference of Replicate Samples from Membrane Experiments

PFAS	Average (n=30)	Max
PFBA	7%	17%
PFPeA	6%	21%
PFHxA	4%	14%
PFOA	5%	15%
PFNA	6%	16%
PFDA	8%	30%
PFBS	8%	22%
PFHxS	5%	16%
PFOS	8%	23%

Table C.2: Summary of Column Experiments

Water Source	Spiked DI	Filtered (1 µm) and spiked Clear Creek Water		
PFAA Concentrations	1 ug/L	1 ug/L		
# of Columns	3	2	2	2
Carbon	F300	F300	F600	AquaCarb 1240C
Carbon Material	Coal	Coal	Coal	Coconut
Carbon Size	60x80	60x80	60x80	60x80
Column Width (cm)	0.7	0.7	0.7	0.7
Column Height (cm)	10	10	10	10
Carbon Depth (cm)	1	1	1	1
Flow Rate (mL/min)	1	1	1	1
Duration (days)	43	32	52	38

Table C.3: Metals, Salts and Organic Carbon Rejection Percentages

		Membrane 1					Membrane 2				
	Flow (ml/min)	Calcium	Sodium	Chloride	Sulfate	TOC	Calcium	Sodium	Chloride	Sulfate	TOC
Virgin	4.5	89%	89%	83%	> 99%	14%	93%	88%	80%	> 99%	-11%
	9	95%	95%	90%	> 99%	23%	94%	95%	89%	> 99%	0%
	13.5	> 98%	94%	92%	99%	0%	95%	95%	92%	> 99%	-12%
	16	95%	96%	92%	> 99%	1%	95%	96%	93%	> 99%	-6%
	20.5	> 98%	95%	93%	99%	0%	94%	96%	93%	> 99%	2%
Fouling Process	18 (no AHA)	88%	65%	67%	nd	-10%	86%	61%	65%	nd	-30%
	20 (AHA)	82%	58%	63%	nd	82%	84%	60%	64%	nd	80%
	20 (AHA)	85%	61%	64%	nd	82%	82%	57%	64%	nd	82%
Fouled	4.5	-61%	87%	75%	> 99%	-3%	Err	86%	73%	> 99%	-3%
	9	64%	93%	88%	> 99%	7%	36%	93%	89%	> 99%	12%
	13.5	94%	94%	91%	99%	22%	93%	95%	92%	> 99%	26%
	16	> 98%	95%	92%	99%	3%	94%	96%	93%	> 99%	10%
	20.5	> 98%	95%	92%	99%	6%	92%	96%	93%	> 99%	4%

Table C.4: Percent Difference of Concentrate and Influent for NF270

Water		Volume (L)	PFBA	PFPeA	PFHxA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
AGW1	Concentrate	148.095	51,559	103,630	63,736	101,619	126,338	112,845	136,979	143,488	131,640
	Influent	150	50,889	105,259	63,852	103,333	124,704	106,926	149,444	152,852	138,111
	Difference in mass		670	(1,629)	(116)	(1,715)	1,634	5,919	(12,466)	(9,364)	(6,471)
	% difference by mass		1%	2%	0%	2%	1%	5%	9%	6%	5%
	% change by mass		1%	-2%	0%	-2%	1%	6%	-8%	-6%	-5%
AGW2	Concentrate	148.095	47,025	100,449	62,602	100,046	119,317	109,444	133,322	141,294	128,605
	Influent	150	51,926	101,333	61,333	97,667	120,852	98,741	137,815	142,481	121,667
	Difference in mass		(4,901)	(885)	1,269	2,380	(1,535)	10,703	(4,493)	(1,188)	6,938
	% difference by mass		10%	1%	2%	2%	1%	10%	3%	1%	6%
	% change by mass		-9%	-1%	2%	2%	-1%	11%	-3%	-1%	6%
DI	Concentrate	148.2	48,119	102,167	62,537	99,568	125,586	125,183	138,979	149,042	128,879
	Influent	150	45,481	98,741	61,333	97,852	122,148	118,593	134,259	142,296	129,963
	Difference in mass		2,638	3,426	1,203	1,717	3,438	6,591	4,719	6,745	(1,084)
	% difference by mass		6%	3%	2%	2%	3%	5%	3%	5%	1%
	% change by mass		6%	3%	2%	2%	3%	6%	4%	5%	-1%

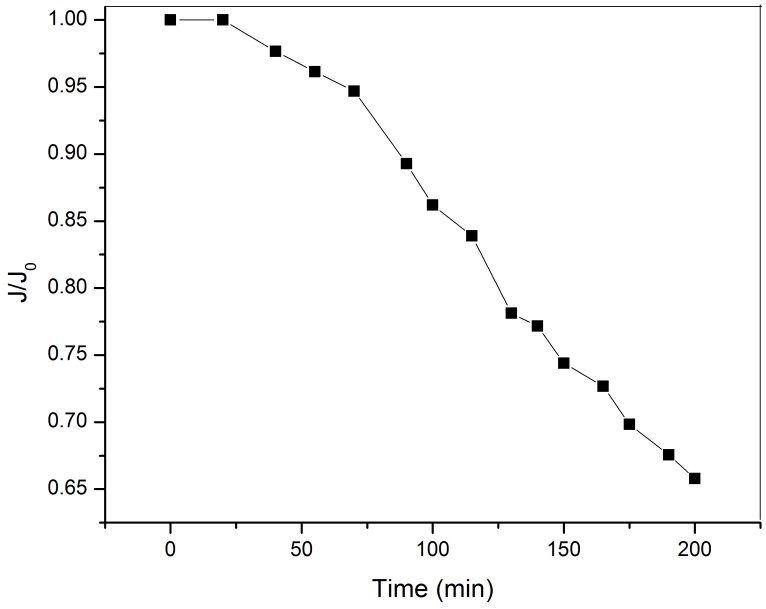

Figure C.1: Membrane Fouling Process. Normalized specific flux change where J_0 is the specific permeate flux at time 0 (i.e. constant flux normalized to net driving pressure, J/J_0).

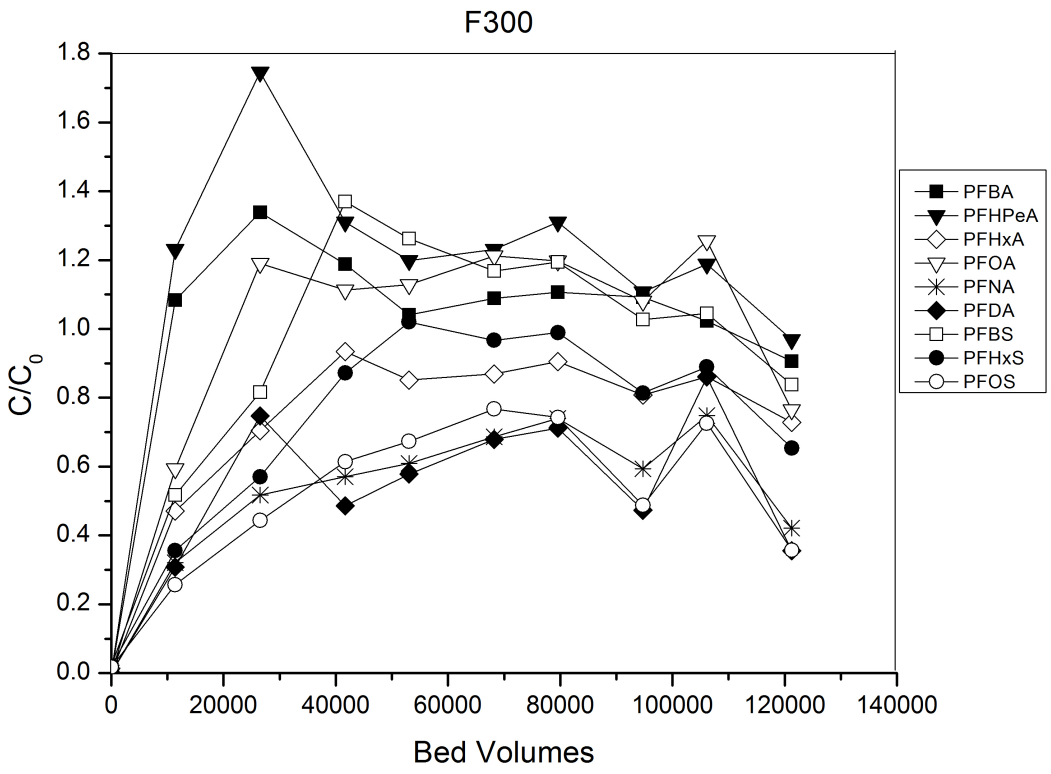

Figure C.2: Breakthrough Graphs for F300 for all PFAAs

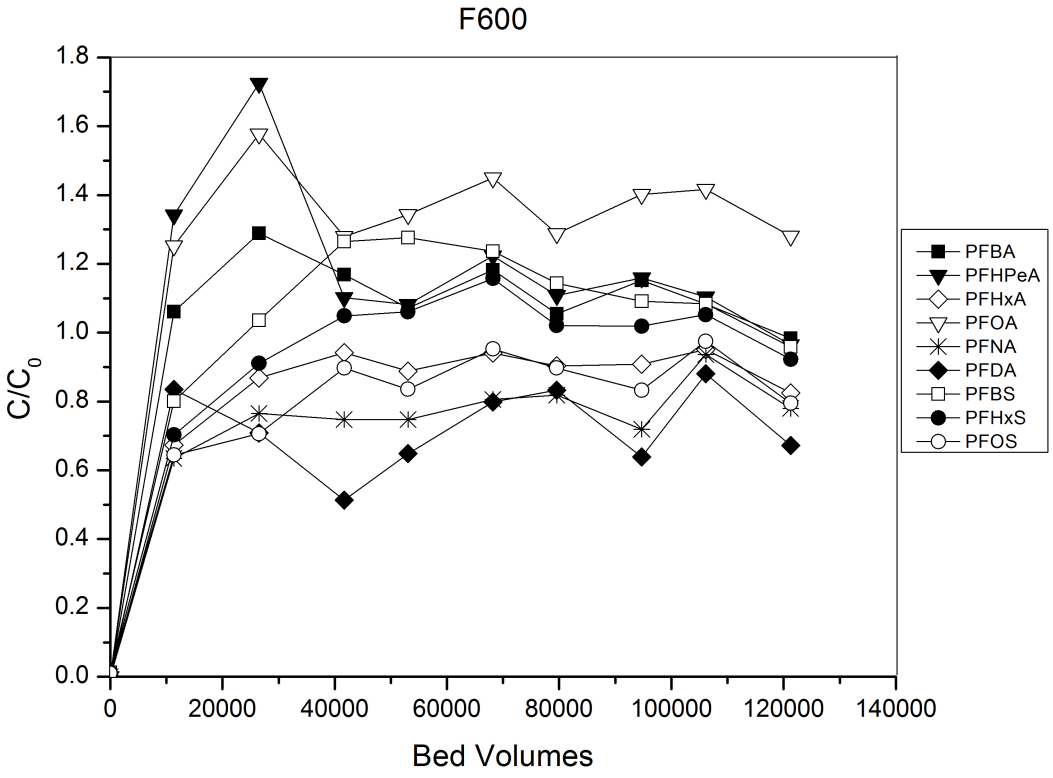

Figure C.3: Breakthrough Graph for F600 for all PFAAs.

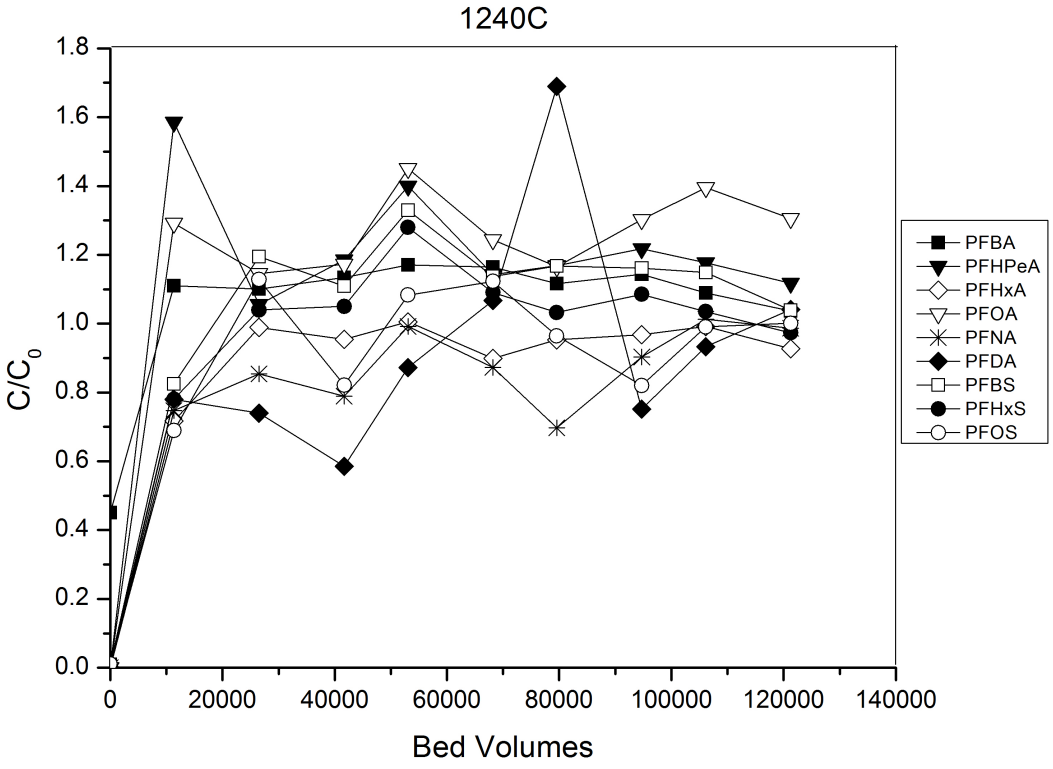

Figure C.4: Breakthrough Graph 1240C for all PFAAs.

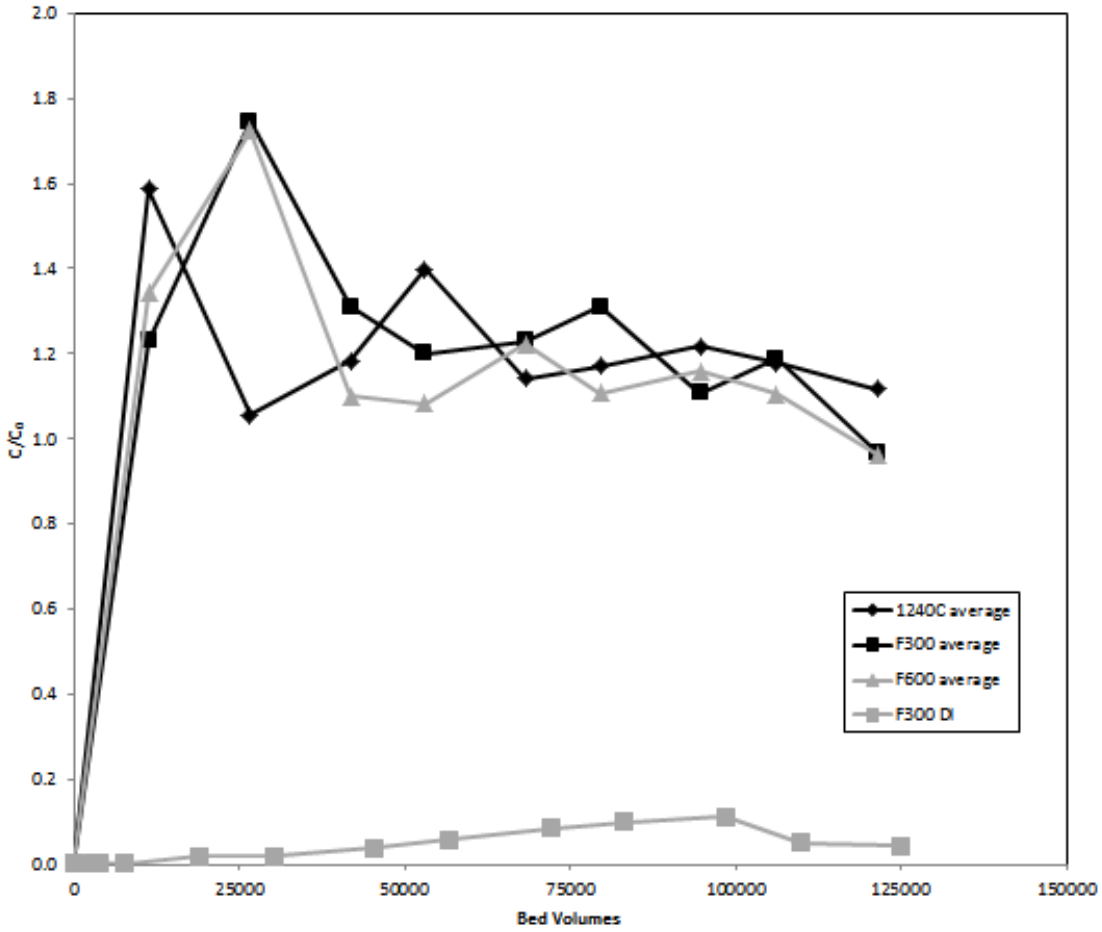

Figure C.5: Breakthrough Comparison Graph of PFPeA

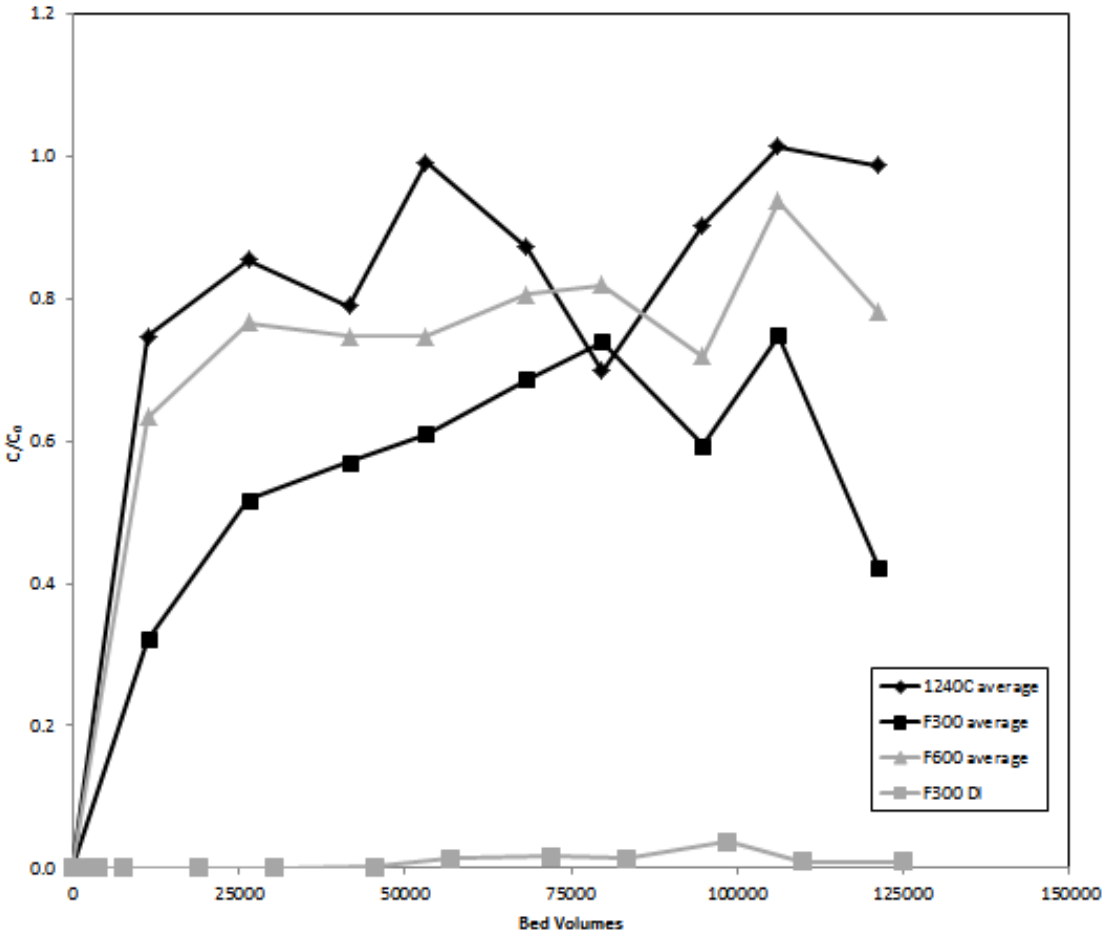

Figure C.6: Breakthrough Comparison Graph of PFNA

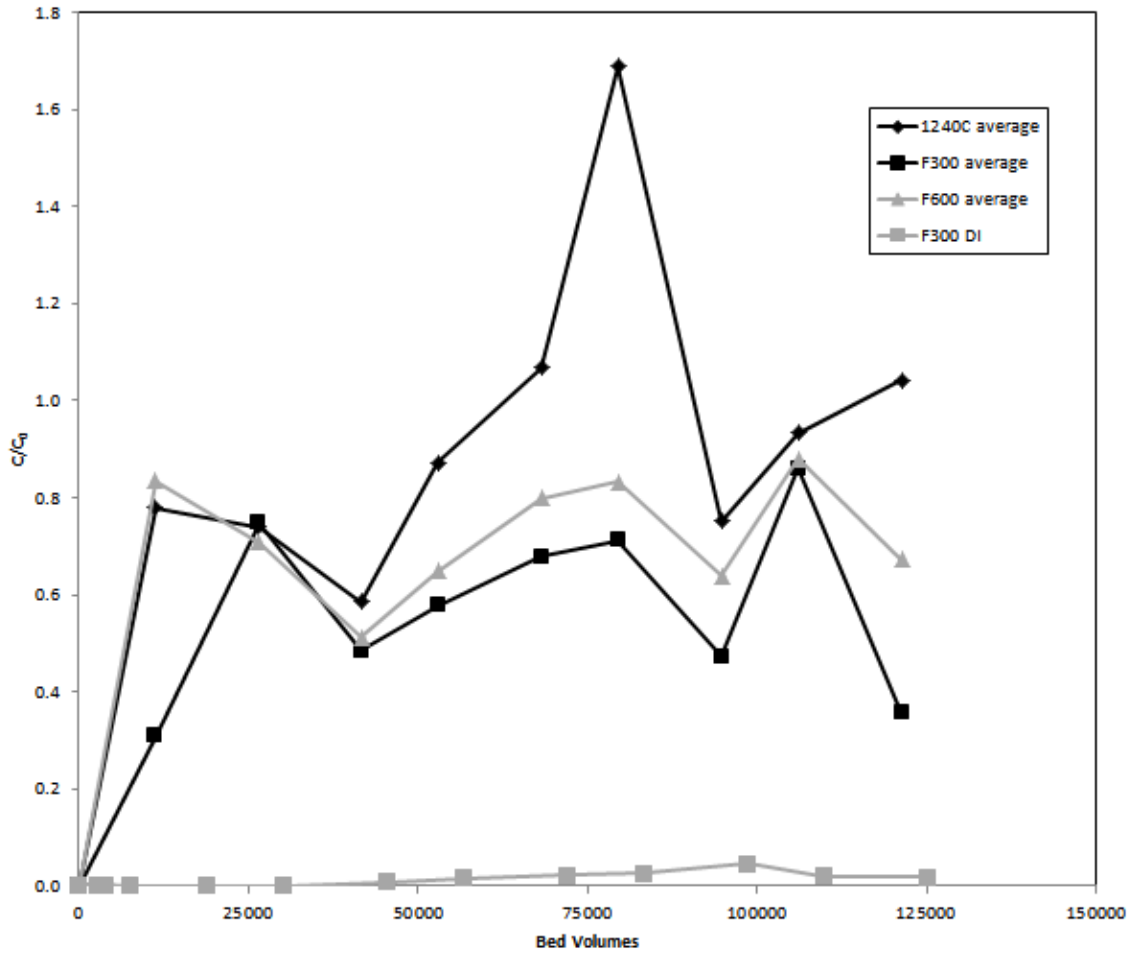

Figure C.7: Breakthrough Comparison Graph of PFDA

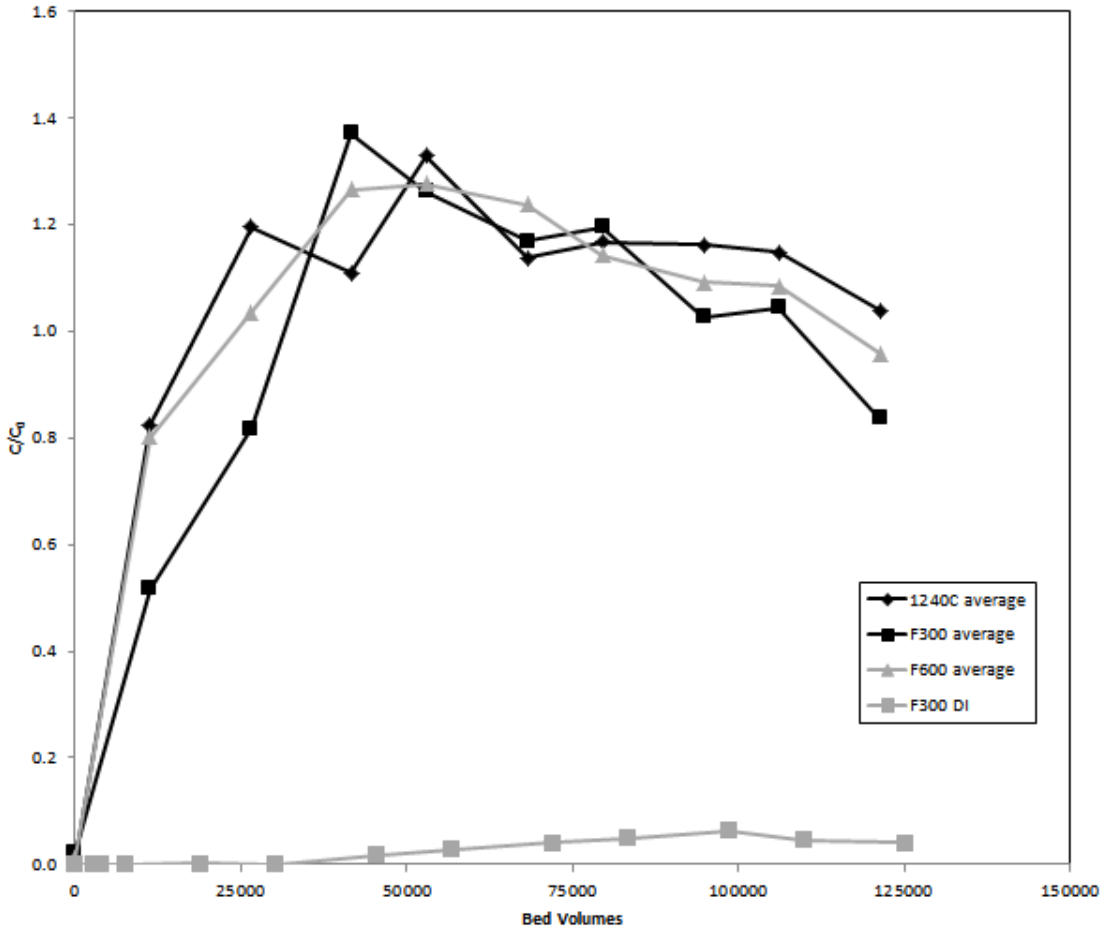

Figure C.8: Breakthrough Comparison Graph of PFBS

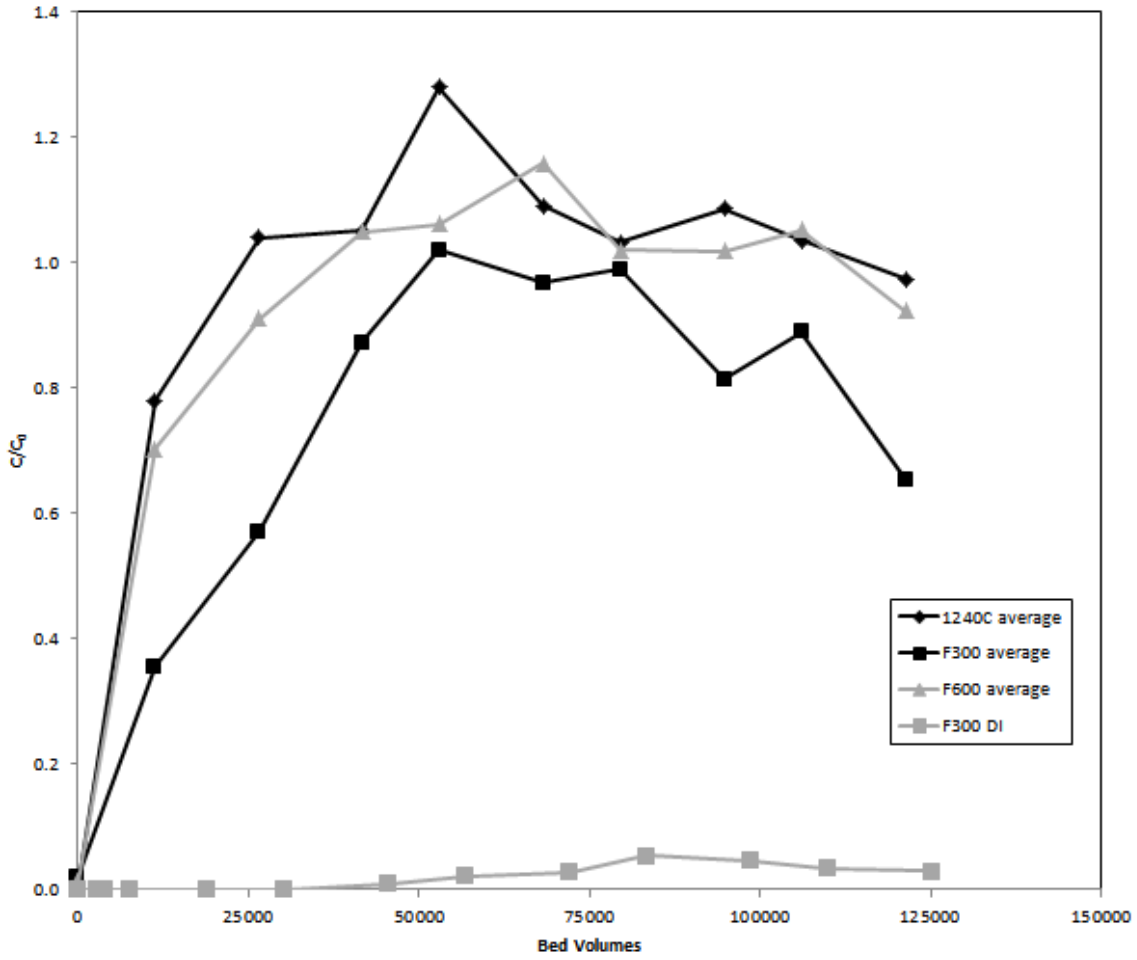

Figure C.9: Breakthrough Comparison Graph of PFHxS