WATER RESEARCH 51 (2014) 246–255

Available online at www.sciencedirect.com

ScienceDirect

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# Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems

Timothy D. Appleman [a], Christopher P. Higgins [a,*], Oscar Quiñones [b], Brett J. Vanderford [b], Chad Kolstad [c], Janie C. Zeigler-Holady [b], Eric R.V. Dickenson [a,b,**]

[a] Civil and Environmental Engineering Department, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA

[b] Applied Research and Development Center, Water Quality Research and Development Division, Southern Nevada Water Authority, Henderson, NV 89015, USA

[c] Minnesota Department of Health, St. Paul, MN 55155, USA

ARTICLE INFO

*Article history:*
Received 5 August 2013
Received in revised form
25 October 2013
Accepted 27 October 2013
Available online 7 November 2013

*Keywords:*
PFOA
PFOS
Occurrence
Treatment
Full-scale
Reverse osmosis
Granular actived carbon
Anion exchange

ABSTRACT

The near ubiquitous presence of poly- and perfluoroalkyl substances (PFASs) in humans has raised concerns about potential human health effects from these chemicals, some of which are both extremely persistent and bioaccumulative. Because some of these chemicals are highly water soluble, one major pathway for human exposure is the consumption of contaminated drinking water. This study measured concentrations of PFASs in 18 raw drinking water sources and 2 treated wastewater effluents and evaluated 15 full-scale treatment systems for the attenuation of PFASs in 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) and perfluorosulfonic acids (PFSAs). Despite the differences in reporting levels, the PFASs that were detected in >70% of the source water samples ($n$ = 39) included PFSAs, perfluorobutane sulfonic acid (74%), perfluorohexane sulfonic acid (79%), and perfluorooctane sulfonic acid (84%), and PFCAs, perfluoropentanoic acid (74%), perfluorohexanoic acid (79%), perfluoroheptanoic acid (74%), and perfluorooctanoic acid (74%). More importantly, water treatment techniques such as ferric or alum coagulation, granular/micro-/ultrafiltration, aeration, oxidation (i.e., permanganate, ultraviolet/hydrogen peroxide), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) were mostly ineffective in removing PFASs. However, anion exchange and granular activated carbon treatment preferably removed longer-chain PFASs and the PFSAs compared to the PFCAs, and reverse osmosis demonstrated significant removal for all the PFASs, including the smallest PFAS, perfluorobutanoic acid.



* *Corresponding author*. Tel.: +1 720 984 2116.
** *Corresponding author*. Tel.: +1 702 856 3668.
E-mail addresses: chiggins@mines.edu (C.P. Higgins), eric.dickenson@snwa.com (E.R.V. Dickenson).

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http://dx.doi.org/10.1016/j.watres.2013.10.067

## 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 class of PFASs are the perfluoroalkyl acids (PFAAs), which are stable chemicals made of a carbon backbone surrounded by fluorine atoms and a terminal acid group, such as carboxylic or sulfonic acid. These PFAAs are extremely resistant to degradation and thus stable in both water and soil and highly persistent in the environment (Buck et al., 2011; ATSDR, 2009).

Unlike most other persistent and bioaccumulative organic pollutants (e.g. dioxin, polychlorinated biphenyls), PFAAs are water soluble. A number of PFAAs have been detected in U.S. surface waters, including lakes, rivers, and tributaries, in the ng/L range or lower (Furdui et al., 2008; Mak et al., 2009; Nakayama et al., 2007; Plumlee et al., 2008; Post et al., 2012; ATSDR, 2009), and they have also been detected in ground waters at similar concentrations (Plumlee et al., 2008; Post et al., 2009). In one study (Sinclair and Kannan, 2006), several PFAAs were detected in effluents from wastewater treatment plants in New York, with concentrations in the low ng/L range for all of the chemicals tested, except for perfluorooctanoic acid (PFOA), which had median concentrations for each utility ranging from 67 ng/L to 697 ng/L. The high persistence of PFAAs in the environment and widespread detection has created a concern for the possible exposure to animals and humans. PFOA, perfluorononanoic acid (PFNA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS) are found in the serum of virtually all U.S. residents (Kato et al., 2011). Some of these chemicals, including PFOA and PFOS, have been detected in the blood of animals in remote regions of the world (Houde et al., 2006). Due to concerns about widespread occurrence and potential health effects, major U.S. manufacturers of PFOS and PFHxS stopped production in 2002 (Butenhoff et al., 2009), while the worldwide use of PFOA and longer chain PFCA homologues is currently being phased out by their major manufacturers (Lindstrom et al., 2011). Replacements for these phased-out compounds include less extensively studied shorter chain PFASs, such as PFHxA and other fluorinated compounds, which generally are more rapidly excreted in humans and animals than the longer chain-length compounds (DuPontTM, 2011; Gordon, 2011). However, these shorter-chain PFASs are still highly persistent in the environment (Ritter, 2010; Gordon, 2011).

As far as potential human exposure is concerned, some of these chemicals have also been detected in U.S. finished/tap waters in the low ng/L range (Post et al., 2009; Quiñones and Snyder, 2009), and higher levels (hundreds of ng/L to several μg/L) of some PFASs have been found in finished drinking water, particularly near sites of industrial use (Emmett et al., 2006; Rumsby et al., 2009; Skutlarek et al., 2006). Drinking water exposure is one pathway that may have contributed to increased concentrations in the serum of humans in most developed countries (Post et al., 2012; ATSDR, 2009) and serum levels of PFOA, PFOS, and PFHxS were increased in communities with contaminated drinking water (ATSDR, 2013; Hölzer et al., 2008; Post et al., 2009). Other potential routes of human exposure include ingestion from food, food packaging, treated carpets, upholstery, and clothing, house dust, protective sprays, and waxes sold as consumer products (Post et al., 2012).

Human epidemiological studies have found associations with numerous health endpoints resulting from exposure, including drinking water exposure (Post et al., 2012; Saikat et al., 2013). An independent panel of prominent environmental epidemiologists concluded that probable links exist between six adverse health conditions and PFOA exposure in a community with contaminated drinking water, including kidney cancer and testicular cancer (C8 2012, Vieira et al., 2013). A number of associations of PFAA exposure with health effects have been reported in the general population, including a study that found an association between PFOA and PFOS exposures and a reduced humoral immune response to routine childhood immunizations in children aged 5 and 7 years (Grandjean et al., 2012).

In 2009, the U.S. Environmental Protection Agency (EPA) established Provisionary Health Advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 μg/L, respectively, in response to an emergency situation in Decatur, Alabama, which were meant to protect from short term exposure (USEPA, 2013). In addition, PFOS and PFOA have been added to the EPA's Contaminant Candidate List 3 of chemicals under consideration for future drinking water regulation in the U.S. (USEPA, 2009). These two chemicals as well as perfluoroheptanoic acid (PFHpA), PFNA, perfluorobutane sulfonic acid (PFBS), and PFHxS were also added to the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR 3) which requires nationwide monitoring by public water suppliers to provide occurrence data needed for regulatory decision making (Post et al., 2012; USEPA, 2012). As some PFAAs have been shown to have a potential to harm humans, it is imperative that treatment options be examined for their ability to remove these chemicals from contaminated water sources.

Previous studies assessed the occurrence of PFAAs in raw and finished waters of full-scale conventional drinking water treatment trains (Post et al., 2009; Quiñones and Snyder, 2009), where the latter study examined treatment systems that consisted of coagulation/flocculation, filtration, ozonation, chlorination, and chloramination processes (Quiñones and Snyder, 2009). These studies suggested these treatment systems were ineffective towards PFAA removal, but confirmation of these results has not been shown at other types of full-scale systems or for a wider spectrum of PFASs. To date, some less commonly employed processes, such as anion exchange (AIX), granular activated carbon (GAC), nanofiltration (NF), and reverse osmosis (RO) have been evaluated at the bench scale and showed promise in the removal of some of these chemicals (Deng et al., 2010; Lampert et al., 2007; Steinle-Darling and Reinhard, 2008; Tang et al., 2006; Appleman et al., 2013). GAC and RO have also been evaluated at the full-scale in a few studies performed outside of the U.S. (Eschauzier et al., 2012; Flores et al., 2013; Takagi et al., 2011; Thompson et al., 2011), where GAC was somewhat ineffec-

tive for the shorter chain-length PFAAs, though RO was able to remove all PFAAs present in the feed water. The performance of AIX has yet to be validated at the full-scale, and demonstration of full-scale GAC and RO performance has been limited in the U.S.

The objective of this study was to evaluate the ability of a wide spectrum of full-scale treatment techniques to remove PFASs from contaminated raw water or potable reuse sources. The novelty of this study lies in the targeted examination of a wide range of U.S. 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 wide 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 (including some compounds that were not previously examined that have the potential to degrade into PFAAs) in raw and treated waters throughout the U.S., though water sources thought to be potentially impacted by PFASs were specifically targeted. To this end, a large suite of 23 PFASs [Table S1 in the Supplemental Information (SI)] was analyzed in raw water, finished drinking water, potable reuse product water, and at various steps along the treatment train. To enable this, samples were collected during multiple sampling events for 15 full-scale treatment systems throughout the U.S., including 2 potable reuse treatment systems.

## 2. Materials and methods

### 2.1. Site selection

The majority of the utilities chosen for this study (Table S2) were selected because they were either known from previous monitoring or expected based on their source waters to contain detectable PFASs (i.e., impacted by upstream wastewater effluent discharge). 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. PFASs concentrations were measured in 20 source waters located in the states of Wisconsin (1), Oklahoma (1), Alaska (1), California (2), Alabama (1), Colorado (2), Ohio (1), Nevada (1), Minnesota (1) and New Jersey (9). The source waters included 11 surface waters, 6 groundwaters, 1 surface water and groundwater blend and 2 treated wastewaters. The specific treatment processes employed by each utility was another criterion for the site selection process, which includes somewhat common 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, AOP, and RO. Synoptic grab samples were taken before and after each treatment process (except for RBF), with almost all treatment processes evaluated on at least two separate occasions. A 3% average error for duplicate samples was calculated and a 10% error associated with grab sampling was assumed, since composite samples were not collected. Additional details on sampling and the treatment trains employed at each utility can be found in the SI as well as sampling data associated with each sampling event. Source water was sampled at all sites, and individual treatment steps and finished or potable reuse product waters were evaluated at 15 treatment systems: Utilities 4, 5, 7, 8, and 10-20 (Table 1).

### 2.2. Sample extraction and analysis

**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 S1) were procured from Wellington Laboratories (Guelph, Ontario, Canada). This analytical suite of 23 chemicals included 9 perfluorocarboxylic acids (PFCAs), 4 perfluorosulfonic acids (PFSAs), perfluorooctane sulfonamide (FOSA), 2 perfluorosulfonamidoacetic acids, 4 fluorotelomer unsaturated carboxylic acids (FTUCAs), and 3 fluorotelomer sulfonic acids (FTSAs). The list of precursor chemicals in this study is not comprehensive, and was limited by the method applied. 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 the SI. 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 Mallinckrodt Chemicals (Phillipsburg, NJ,

**Table 1 – Treatment trains evaluated in this study.**

| Utility ID | Treatment train |
|---|---|
| 4 | MF/RO/UV-AOP/DI/$Cl_2$ |
| 5 | AIX/COAG/FLOC/SED/MF/$Cl_2$ |
| 7 | RBF/ARR/SOFT/SCC/UV-AOP/G-FIL (Biological)/GAC |
| 8 | SED/COAG/FLOC/SED/G-FIL/GAC/$Cl_2$ |
| 10 | MF/UF/RO/UV-AOP |
| 11 | AER/COAG/FLOC/SED/G-FIL/$ClO_2$ |
| 12 | $O_3$/DAF/$Cl_2$/CLM |
| 13 | UV/$Cl_2$ |
| 14 | AIX/APT/$Cl_2$ |
| 15 | $Cl_2$/$MnO_4$/G-FIL |
| 16 | $ClO_2$/$Cl_2$ |
| 17 | $MnO_4$/$O_3$/$Cl_2$ |
| 18 | APT/GAC/$Cl_2$ |
| 19 | $Cl_2$ |
| 20 | GAC/$Cl_2$ |

AER: Aeration, AIX: Anion Exchange, APT: Aeration Packed Tower, ARR: Aquifer Recharge and Recovery, CLM: Chloramination, $Cl_2$: Hypocholorous/Hypocholorite, $ClO_2$: Chlorine Dioxide, COAG: Coagulation, DAF: Dissolved Air Flotation, DI: Direct Injection, $O_3$: Ozone, FLOC: Flocculation, GAC: Granular Activated Carbon Filtration, G-FIL: Granular Filtration, GW: Ground Water, MF: Microfiltration, $MnO_4$: Permanganate, RBF: River Bank Filtration, RO: Reverse Osmosis, SCC: Solids Contact Clarifier, SED: Sedimentation, SOFT: Softening, UF: Ultrafiltration, UV: UV Photolysis, UV-AOP: UV Photolysis with Advanced Oxidation (Hydrogen Peroxide).

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

### 2.3. Sample analysis

Samples were prepared using ASPE, with ASPE extracts analyzed by liquid-chromatography tandem mass-spectrometry (LC-MS/MS) using a previously reported method (Quiñones and Snyder, 2009), adapted and expanded to include all analytes of interest. Details of the ASPE and LC-MS/MS methods as well as the extensive quality assurance and quality control measures [e.g., method reporting limits (MRLs)] are provided in the SI.

## 3. Results and discussion

### 3.1. Source and finished water occurrence data

Though the primary objective of this study was to evaluate the removal of PFASs during full-scale water treatment, meeting such an objective required some understanding of PFAS occurrence in source and finished waters. End-product PFAAs were frequently detected in both the source and finished waters of many of the utilities sampled in this study. The three most commonly detected PFASs in the source water samples ($n$ = 39) were PFOS (84%) (MRL = 0.25 ng/L), PFHxA (79%) (MRL = 0.5 ng/L), and PFHxS (79%) (MRL = 0.25 ng/L), though the MRLs of the PFASs did vary. Other chemicals that were frequently detected in the source water samples included perfluoropentanoic acid (PFPeA) (74%) (MRL = 2 ng/L), PFHpA (74%) (MRL = 0.5 ng/L), PFOA (74%) (MRL = 5 ng/L), PFNA (66%) (MRL = 0.5 ng/L), and PFBS (74%) (MRL = 0.25 ng/L). Interestingly, PFHxA and PFPeA were frequently detected, but they are not included in the UCMR 3. Also, the occurrence frequency of PFOA could be higher considering its MRL is 10–20 times higher. Among the PFCAs, perfluorobutanoic acid (PFBA) (MRL = 5 ng/L) and perfluorodecanoic acid (PFDA) (MRL = 0.25 ng/L) were only present in 34% of the samples, though the MRL for PFBA is 10–20 times higher, whereas longer chain PFCAs, perfluoroundecanoic acid (PFUnA) (MRL = 0.5 ng/L) and perfluorododecanoic acid (PFDoA) (MRL = 0.25 ng/L), were only detected in 13% and 11% of samples, respectively. 6:2 fluorotelomer sulfonic acid (6:2 FTSA) (MRL = 0.5 ng/L), *N*-methyl perfluorooctane sulfonamidoacetic acid (*N*-MeFOSAA) (MRL = 0.25 ng/L), *N*-ethyl perfluorooctane sulfonamidoacetic acid (*N*-EtFOSAA) (MRL = 0.25 ng/L), and FOSA (MRL = 0.25 ng/L) were also detected in 38%, 29%, 24% and 16% of samples, respectively. Several chemicals, such as perfluorodecane sulfonic acid (PFDS) (MRL = 0.1 ng/L), the FTUCAs (MRLs = 2 ng/L), 4:2 fluorotelomer sulfonic acid (4:2 FTSA) (MRL = 0.5 ng/L), and 8:2 fluorotelomer sulfonic acid (FTSA) (MRL = 0.5 ng/L) were not detected above MRLs in any of the samples. PFAS detection frequency in the finished waters from conventional treatment trains containing coagulation/flocculation, filtration (i.e., granular, ultrafiltration, microfiltration), and/or disinfection was similar to the source waters, except for PFDoA which was not detected in any finished water sample.

The range of concentrations found in the source and finished or potable reuse product waters from the sampling campaigns in this study as well as the ranges of North American values from a detailed, though not comprehensive, literature survey can be found in Table S5. Ranges include all of the concentrations of the source and finished or product 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 4 and 10 whose "raw water source" is 100% treated wastewater effluent). In addition, Tables S6 and S7 contain the concentrations of all samples analyzed in this study. Data from Utility 20 had higher levels than the other sites because its raw water source is highly contaminated by an industrial source. These data are not presented in Table S5, but are displayed in a different format because there are more data for this site. The concentration ranges measured in this study were similar for the chemicals that had previously been quantified in other studies in North America for sites that were believed not to be heavily contaminated by industrial sources. The highest concentrations measured were in the source water 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 higher concentrations of most PFASs, which corresponds with all of these being highly wastewater-impacted sources, where Utilities 4 and 10 are 100% impacted. *N*-MeFOSAA, *N*-EtFOSAA, FOSA, FTUCAs and FTSAs (except 6:2 FTSA) were not detected in ground waters, but FOSA, *N*-MeFOSAA, and *N*-EtFOSAA were in the surface waters of Utilities 5, 7, and 17 (up to 1.7, 0.9, and 2.0 ng/L, respectively) and the treated wastewater effluents of Utilities 4 and 10 (up to 0.42, 1.1, and 0.43 ng/L, respectively).

The detected PFASs in finished waters from drinking water treatment systems (except for Utility 20), were in the low ng/L range, where the highest detection was 62 ng/L of PFHxA at site 19. The MRLs in this study (Table S3) were much lower than the EPA method for UCMR 3, which are 10 ng/L for PFHpA, 20 ng/L for PFOA, and 40 ng/L for PFOS (USEPA, 2012). Three PFAAs were found in some samples to contain higher concentrations than the UCMR 3 MRLs. 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 MRLs of 20, 90, and 30 ng/L for PFNA, PFBS, and PFHpA, respectively, on the UCMR 3 list. Of the six chemicals that will be monitored under the UCMR 3, 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 guidance levels, with the exception of one utility. Utility 19 in New Jersey was over (at 57 ng/L) the state guidance level of 40 ng/L for PFOA. Collectively, these data suggest that if existing 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.

### 3.2. *Full scale treatment efficacy*

Fig. 1 displays the removal efficacy of the well-studied PFAAs, PFOA and PFOS, as a result of the various types of treatments employed by the utilities. Similar plots for all measured PFAAs can be found in the SI (Figures S1-1 to S1-11). 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.

#### 3.2.1. *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 PFAA removal, but where DAF was used instead of sedimentation (such as at Utility 12), a 49% removal of PFOS was observed (Fig. 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 impact on PFAA removal. An increase in PFOS concentration was observed after the coagulation/sedimentation/granular filtration processes at Utilities 8 and 11 However, the average level was within the error of duplicate sampling events for Utility 8, whereas for Utility 11, the data presented are only from one sampling campaign.

With respect to low pressure membrane filtration, the MF system at Utility 4 was not effective; in fact, a slight increase in PFOS concentration was observed at this utility, though it is within the error of duplicate sampling events. 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. This MF/UF system was also mostly ineffective, however partial reductions were observed, i.e., 24% of PFOS, 44% of PFDoA and 42% of FOSA. Given the large MF/UF pore sizes and the molecular weights of these compounds (499–614 g/mol), they should pass through these membranes with ease and it is unknown why partial reductions of these chemicals were observed.

#### 3.2.2. *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 (Fig. 1). In fact, in many cases, the concentration of PFCAs and PFSAs were consistently slightly higher following oxidative treatments.

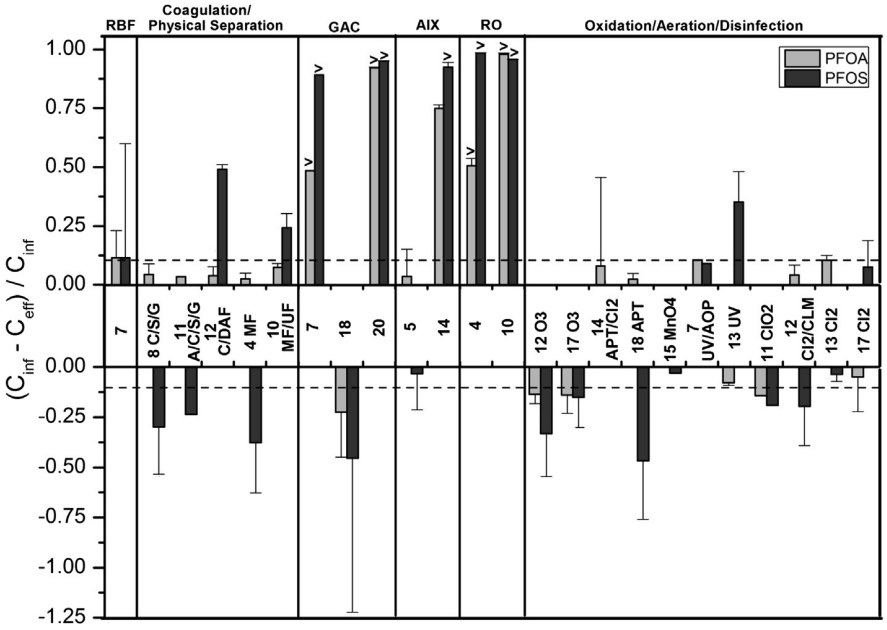


**Fig. 1 – PFOA and PFOS Removal by Treatment: A greater than symbol " > " denotes samples where the concentration was below the MRL in the effluent, but the MRL was used as a conservative estimate for the percent removal. The dashed lines at ±10% represent the range of error based on the average analytical variability multiplied by a conservative safety factor (~3×) for the possible error associated with collecting grab samples before and after treatments. $C_{inf}$: influent concentration. $C_{eff}$: effluent concentration, A: Aeration, C: Coagulation, S: Sedimentation, G: Granular Filtration.**

However, these data are generally within the range of error associated with sampling and analytical variability (i.e., ±10%).

The lack of removal of PFAAs via these full-scale processes is not surprising, as PFAAs 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 at the bench-scale (Hori et al., 2004; Moriwaki et al., 2005; Schroder and Meesters, 2005). 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 (Hori et al., 2005; Lazerte et al., 1953; Moriwaki et al., 2005; Yamamoto et al., 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%) (Fig. 1). UV photolysis has been demonstrated to be effective at degrading PFOS and PFOA (Chen et al., 2007; Chen, 2006; Hori et al., 2004; Yamamoto et al., 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/hydrogen peroxide process at Utility 7 operated at a high dose (>500 mJ/cm$^2$) for trace organic contaminant removal was not effective. Given these mixed results, one might expect minimal removal, if any, of PFAAs in contaminated drinking water as a result of current UV treatment practices.

#### 3.2.3. *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 possibly due to variability in influent concentrations from the wastewater effluent impacted river, combined with the fact that raw and post-RBF samples were not collected synoptically for the 10 day travel time. Another potential explanation is the transformation of precursor compounds into end products through the riverbank. One example of the influent variation is for 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 event and 35 ng/L during the second sampling event just six weeks later. Similar variation was observed in a study on infiltrated water from the infiltrated Rhine River water in the Netherlands (Eschauzier et al,. 2010).

#### 3.2.4. *AIX treatment*

Two AIX treatments were examined at the full-scale in this study, though they were not designed for PFAS removal. Utility 14 added Purolite FerrlX A33e media to a softener vessel which is the first treatment process in the train (Table 1). 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 is only used when the arsenic concentration is high enough that removal is necessary; therefore the resin for the two sampling events was at most 5 and 9 months old. Interestingly, the resin was successful in reducing some of the PFAS levels. 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. The PFSAs were preferably removed over the PFCAs. Examining the removal efficiencies of both campaigns in Table 2, 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 et al., 2007), while other bench-scale studies (Deng et al., 2010; Senevirathna et al., 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 treatment process was also examined at Utility 5, where it is employed upfront in the treatment train (Table 1) to target total organic carbon. Unlike Utility 14 and previous bench-scale work, this process 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 AIX system at Utility 5 uses an upflow fluidized-bed reactor with continuous regeneration (approximately 13 regenerations in a 24 h period). Continual regeneration, as opposed to a complete resin replacement, or insufficient capacity due to improper operation and/or kinetics may be causes of its ineffectiveness at the full-scale. Previous studies have shown that conventional methods of AIX regeneration are ineffective for PFBS and PFOS (Carter and Farrell, 2010) and significant kinetic limitations can occur (Deng et al., 2010; Lampert et al., 2007).

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 PFAS, suitable regeneration techniques, and required frequency for resin changes. In addition, a better understanding of sorption kinetics and competition with other anions and natural organic matter is necessary.

#### 3.2.5. *GAC treatment*

Four full-scale GAC systems were examined. Details for 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 from groundwater. 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 and 1.5 m$^3$/min, and an empty bed contact time (EBCT) of

**Table 2 – Percent removal for most effective PFAS 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 |

N/A – not available.

approximately 13 min in each contactor. For this system, the removal efficacy reported in Table 2 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.

Fig. 2 displays the breakthrough of five different PFASs in the lead GAC bed over a five year period at Utility 20. Similar initial breakthrough curves of PFBA, PFPeA, and PFHxA within the first two years were observed previously (Eschauzier et al., 2011). Every three months corresponds to approximately 10,000 bed volumes (BVs). The BV axis stops at 70,000 BVs because the system was first altered on 8/13/2008 (or ~69,000 BVs). Three important dates during the operation of this system, noted on the horizontal axis in Fig. 2, are 09/22/2008, 10/05/2009, and 10/11/2010. On 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 exhibited a sharp decline when all of the carbon in the system was replaced. On 12/27/2007, the effluent value of PFHxA had a sharp decline back to below its MRL, but this observation 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 bench-scale studies of the removal of PFASs using coal-based GAC that showed GAC was capable of removing PFOA, PFBS, and PFOS (Carter and Farrell, 2010; Lampert et al., 2007; Senevirathna et al., 2010; Appleman et al., 2013).

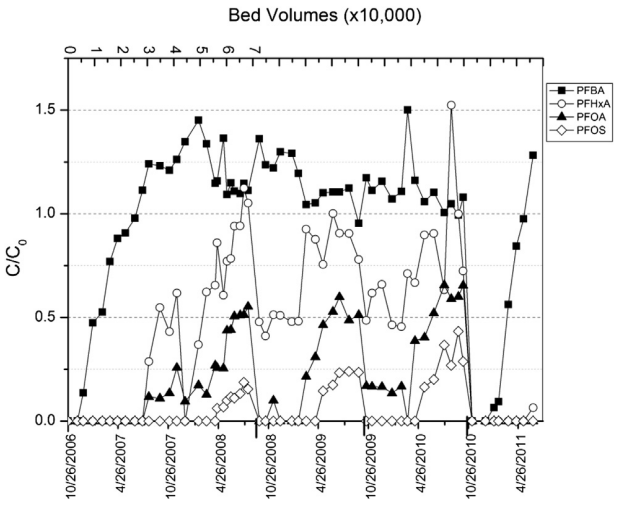


**Fig. 2 – Breakthrough of PFASs in Utility 20 GAC System. Every three months corresponds to approximately 10,000 BVs. BV axis stops at 70,000 BVs because the system was first altered on 8/13/2008 (or ~69,000 BVs).**

As can be seen in Fig. 2, PFBA exhibited breakthrough after about two 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). A similar result of increased effluent concentration was observed with PFBS in another study (Eschauzier et al., 2012). 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, a phenomena that was observed for PFBA (Gellrich and Knepper, 2011). The average influent concentrations were 1.45 ± 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 (coal-based) GAC to treat surface water, but unlike Utility 20, the system is not specifically designed for PFAS removal. For the first sampling event, little change in the concentrations was observed for most of these chemicals. Interestingly, for the second sampling campaign, the concentrations were higher for some of the PFASs [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 highlights the importance of carbon replacement and/or regeneration for ensuring removal of PFASs by GAC. This was also seen in the Takagi et al. (2011) study where fresh carbon was deemed effective for PFOA and PFOS removal, but the same carbon tested one year later was no longer effective at the removal of these chemicals.

Utility 7 also employs GAC treatment with six parallel GAC contact chambers containing 24.3 $m^3$ of Norit (coal-based) GAC300, an empty bed contact time of ~10 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 2. The longer chain PFCAs (PFHpA, PFOA, and PFNA), as well as the PFSAs (PFBS, PFHxS, and PFOS), were all removed to below MRLs. Three shorter chain 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 (Eschauzier et al., 2012; Appleman et al., 2013; Higgins and Luthy, 2006).

The overall results indicate for the longer chain PFASs, GAC systems were effective at Utilities 7 and 20. Utilities 7 and 20 appear to have chain length dependent PFAS 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. It is important to point out that the presence of dissolved organic matter either in groundwater or surface water can have an effect on the breakthrough behavior (Appleman et al., 2013). However, if the shorter-chain PFBA is targeted for removal, an alternative treatment strategy would need to be employed.

#### 3.2.6. *RO treatment*

Two U.S. California potable water reuse plants 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 Hydranautics RO membranes with an RO flux rate of 12 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 et al., 2006) of RO membranes showed similar rejection of PFOS (>99%), and also in a full-scale study in Australia (Thompson et al., 2011) where all PFAAs present in the feed (PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS) were below their limit of reporting values in the RO permeate.

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, RO would likely be the most costly method for removal. 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 and Reinhard, 2008; Appleman et al., 2013). Another important factor to consider with these membrane treatment systems is the disposal of the concentrate, which will contain the rejected PFASs, and add to the cost of operation of these systems.

## 4. Conclusion

A study on available treatment technologies for the treatment of PFAS was conducted at full-scale U.S. water treatment plants. This study demonstrates that full-scale conventional treatments in the U.S., such as coagulation followed by physical separation processes, and chemical oxidation, aeration and disinfection, were unable to remove PFASs. This will become an issue for some utilities if low ng/L regulatory levels are promulgated for these chemicals. In this event, utilities with significant PFAS levels in their raw water sources will need to examine additional mitigation strategies, such as alternative treatment technologies. The levels of several PFASs, such as PFOA and PFOS, were reduced by current day RO, GAC, and AIX practices at the full-scale. However, GAC and AIX were less effective at removing the shorter chain PFASs, whereas RO treatment was effective for even the smallest PFAS studied, PFBA.

## Acknowledgements

The authors thank the Water Research Foundation (WaterRF #4322), the New Jersey Department of Environmental Protection (NJDEP), the Colorado School of Mines Edna Bailey Sussman Foundation, and the Southern Nevada Water Authority (SNWA) Summer Hire program for financial support for this project. We thank Drs. Gloria Post and Judy Louis at NJDEP for their careful review of this manuscript. In addition, the authors thank Professor Jörg Drewes at the Colorado School of Mines for his advisement and guidance of the project, Carin Huset at the Minnesota Department of Health for the analytical measurement of PFCAs and PFSAs of samples from the Minnesota site, and Josephine Chu at SNWA for her help with PFAS sample preparation.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.10.067.

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