Legacy and emerging perfluoroalkyl substances in the Cape Fear River Watershed of North Carolina: Occurrence and fate during conventional and advanced water treatment processes

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ED_002096A_00003069-00001

Abstract

Long-chain perfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten traditionally studied PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) occurrence in the Cape Fear River (CFR) watershed, (2) fate in drinking water treatment processes, and (3) adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in the raw water of a drinking water treatment plant (DWTP), but concentrations of traditionally studied PFASs were high. The US Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctane sulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L (n=37). Six other PFECAs were detected with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. PFAS adsorbability on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased PFAS affinity for PAC, while replacement of additional CF_2 groups with ether oxygens did not lead to further affinity changes.

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Introduction

Perfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.[1] Until 2000, long-chain PFASs, such as perfluorocarboxylic acids (PFCAs) with 7 or more carbon atoms and perfluorosulfonic acids (PFSAs) with 6 or more carbon atoms, were predominantly used.[2] Accumulating evidence about ecotoxicological and human health effects[3, 4] associated with exposure to long-chain PFASs has led to increased regulatory attention. Recently the U.S. Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) concentrations in drinking water.[5, 6] Over the last decade, production of long-chain PFASs has declined in Europe and North America, and manufactures are moving towards short-chain PFASs and fluorinated alternatives.[7-10] Some fluorinated alternatives were recently identified,[8, 11] but the majority of the organofluorine loading to the aquatic environment remains unidentified.[12-14]

One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)). The ammonium salt of PFPrOPrA is a known PFOA alternative that has been produced since 2010 with the trade name "GenX".[15] According to the manufacturer, the ether oxygen enables "very rapid bioelimination"[15]; however, except for the PFPrOPrA data reported by the manufacturer,[16-18]

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little information is available on pharmacokinetic behavior, toxicity, or environmental fate and transport of PFECAs. To the knowledge of the authors, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,[19] and no published data are available on the fate of PFECAs during water treatment.

The strong C-F bond makes PFASs refractory to abiotic and biotic degradation,[20] and most water treatment processes are ineffective for legacy PFAS removal.[21-26] Processes capable of removing PFCAs and PFSAs include nanofiltration,[27] reverse osmosis[24], ion exchange,[27, 28] and activated carbon adsorption,[27, 28] with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were to (1) identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) evaluate PFAS adsorbability by powdered activated carbon (PAC).

Materials and Methods

Water samples: Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2 in SI). Samples were collected from the raw water tap at each DWTP daily as either 8-hour composite (DWTP A, 127 samples) or 24-hour composite (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250-mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until analysis (within 1 week of receiving). On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train (raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, disinfection by medium pressure UV lamps and free chlorine). Operational conditions of DWTP C on the sampling day are listed in Table S2 in SI. Samples were collected in 1-L HDPE bottles and stored at room temperature until analysis. On the same day, grab samples of CFR water were collected in six

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20-L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4°C until use in PAC adsorption experiments.

Adsorption experiments: PFAS adsorption by PAC was studied in batch reactors (amber glass bottles, 0.45 L CFR water). PFECA adsorption was studied at ambient concentrations (~1,000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs ~10-800% of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Background water matrix characteristics are summarized in Table S3 in SI. A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus OH, mean diameter: 12 μm, BET surface area: 1460 m^2/g)[29] proved effective for PFAS removal in a prior study[28] was used at doses of 30, 60 and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis.

PFAS analysis: Information about analytical standards and the liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for PFAS quantification is provided in SI.

Results and Discussion

PFAS occurrence in drinking water sources: Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1. In communities A and B, only legacy PFASs were detected (mean ∑PFAS: 355 ng/L in community A, 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3 in SI. In community A, PFCAs with 4-8 carbons, perfluorohexane sulfonic acid (PFHxS) and PFOS were detected at median concentrations > QLs. Mean and median concentrations were 44 and 29 ng/L, respectively, for PFOS, and 46 and 34 ng/L, respectively, for PFOA. During the 127-day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days, and the mean over the entire study period was 90 ng/L. Similar legacy PFAS concentrations were observed in the same area ten years ago,[30] suggesting that PFAS source(s) upstream of community A have long-term negative

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impacts on drinking water quality. Relating total PFAS concentration to average daily stream flow (Figure S4 in SI) illustrated a general trend of low PFAS concentrations at high flow and high concentrations at low flow, consistent with the hypothesis of upstream point source(s). In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were the most frequently detected, with mean concentrations of 12 and 19 ng/L, respectively. Mean and median PFOA and PFOS concentrations were <QL, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), legacy PFAS concentrations were low, and only mean (and median) concentrations of PFBA and PFPeA were >QLs. However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately eight times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S3 in SI).

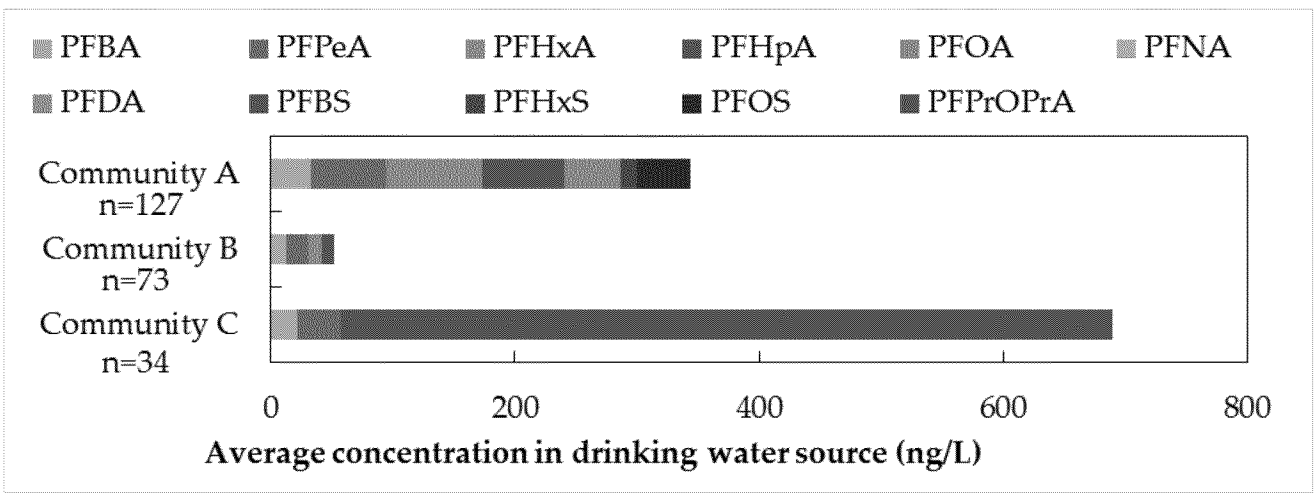

Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples

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with concentrations < QLs were considered as 0 when calculating averages, and average concentrations < QLs were not plotted.

PFAS fate in conventional and advanced water treatment processes: To investigate whether PFASs can be removed from the impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and several advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous reports.[21-25] The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA and PFMOAA may have increased after ozonation, possibly due to the oxidation of precursor compounds.[24] Disinfection with medium pressure UV lamps and free chlorine (located the between BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but only to a limited extent.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400-500 μg/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA and PFO3OA)[11] had peak areas 2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging PFASs suggests the necessity of incorporating them into routine monitoring.

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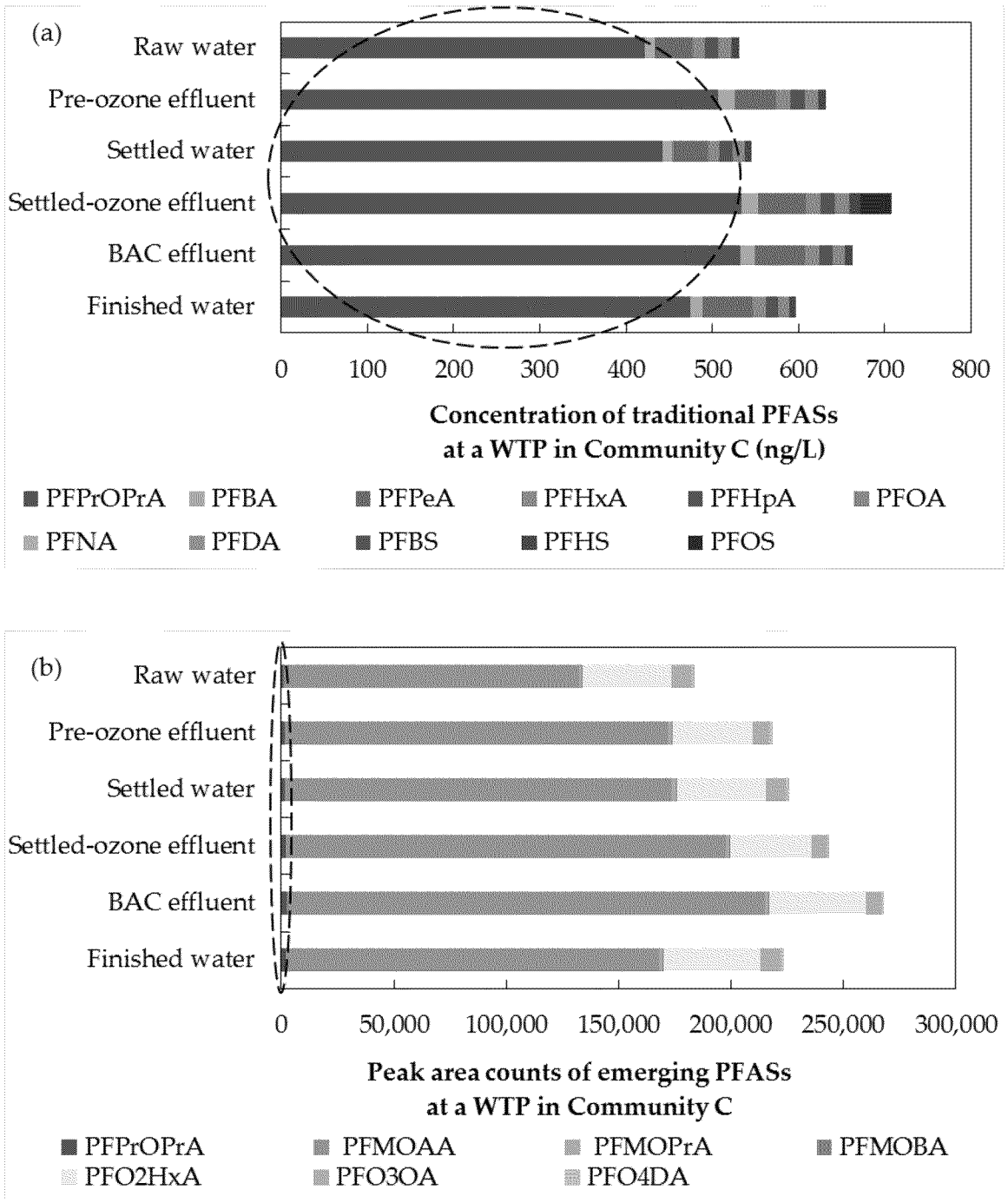

Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for emerging PFECAs, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted in dashed ovals for reference. Compounds with concentrations <QL were not plotted.

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PFAS adsorption by PAC: PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.[23, 24, 28] It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 hour, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with carbon chain length ≥7. At a PAC dose of 60 mg/L, >80% removal was achieved for PFCAs with carbon chain length ≥8 over the same time. At a PAC dose of 100 mg/L, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5 in SI. PFMOAA could not be quantified by the analytical method used in this test; however, based on the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) were poorly adsorbed by PAC (Figure 3), it is expected that PFMOAA adsorption is negligible at the tested conditions.

To compare the affinity of different PFASs for PAC, the PFAS removal percentages in solution were plotted as a function of PFAS chain length (the sum of carbon (including branched), ether oxygen, and sulfur atoms) (Figure 3(b)). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, which agrees with previous studies.[23, 24, 28] PFECAs exhibited lower adsorbabilities than PFCAs of the same chain length (e.g. PFMOBA<PFHxA), suggesting that the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA~PFO2HxA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have a higher affinity for PAC than mono-ether PFECAs (e.g., PFPeA>PFMOBA), but a lower affinity than multi-ether PFECAs (e.g., PFPeA<PFO3OA).

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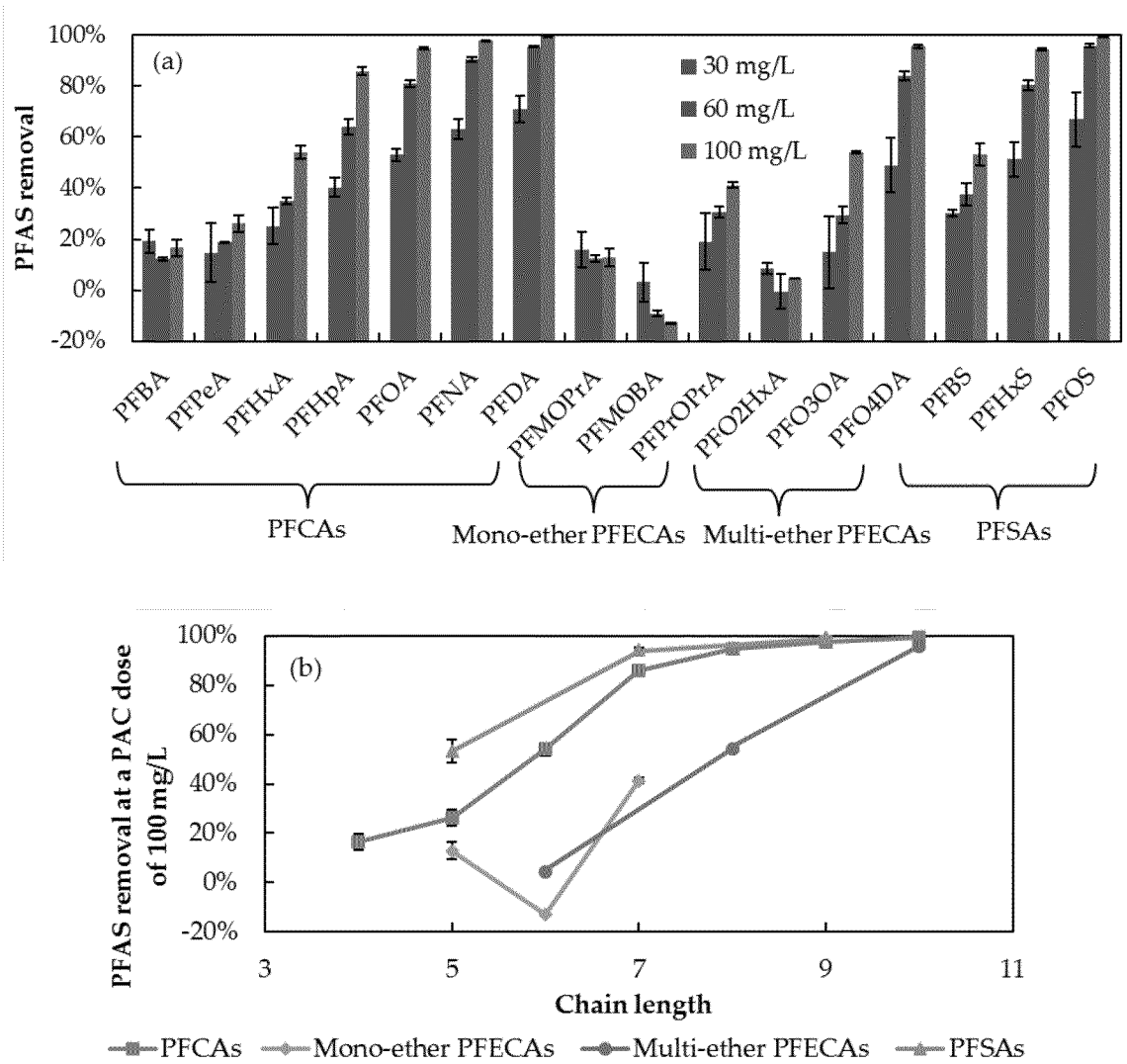

Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were spiked at ~1000 ng/L and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

In either framework, it is clear that the presence of ether groups in PFECAs changes their propensity to leave the aqueous phase and adsorb on PAC. It can thus be inferred that the incorporation of ether groups changes physiochemical properties, such as the octanol-water

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partition coefficient and aqueous solubility of PFECAs relative to PFCAs. Consequently, it is reasonable to expect that fate and transport of PFECAs in natural and engineered systems will differ from that of legacy PFCAs. For example, while PFPrOPrA ("GenX") may be less bioaccumulative than PFOA, which it is replacing, the adsorption data here suggest PFPrOPrA is less hydrophobic than PFOA. Thus, when released to the environment, PFPrOPrA has a higher tendency to remain in the aqueous phase and is more difficult to remove from drinking water sources by adsorptive means.

To the knowledge of the authors, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. This work documents concentrations of legacy PFASs over the course the CFR, and the emergence of PFECAs as an important class of fluorinated alternatives that dominated the PFAS signature downstream of a PFAS manufacturer. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with data reported from this DWTP in the third unregulated contaminant monitoring rule (UCMR3) conducted by USEPA[31]. However, the detection of potentially high levels of PFECAs, and the difficulty to effectively remove not only legacy PFASs but also PFECAs with many water treatment processes, suggest the need for broader discharge control and contaminant monitoring.

Acknowledgement

This research was supported by the National Science Foundation (Award # 1550222), the Water Research Foundation (Project 4344), and the North Carolina Urban Water Consortium. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

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