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Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

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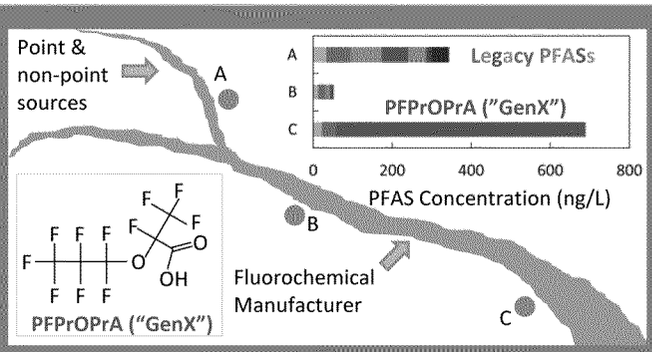
Supporting Information

Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic 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. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl 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 sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.[1] Until 2000, long-chain perfluoroalkyl sulfonic acids [$C_nF_{2n+1}SO_3H$; $n \geq 6$ (PFSAs)] and perfluoroalkyl carboxylic acids [$C_nF_{2n+1}COOH$; $n \geq 7$ (PFCAs)] were predominantly used.[2] Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs[3,4] has led to an increased level of 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 perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.[5,6] Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.[7−10] Some fluorinated alternatives were recently identified,[8,11] but others remain unknown[12−14] because they are either proprietary or manufacturing byproducts.

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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). The ammonium salt of PFPrOPrA is a known PFOA alternative[15] that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,[15] and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),[16−20] little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C−F bond makes PFASs refractory to abiotic and biotic degradation,[21] and most water treatment processes are ineffective for legacy PFAS removal.[22−27] Processes capable of removing PFCAs and PFSAs include nanofiltration,[28] reverse osmosis,[25] ion exchange,[28,29] and activated carbon adsorption,[28,29] with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on 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). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (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 they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. 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, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 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 (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 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. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm_v) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μm, BET surface area of 1460 m^2/g)[30] proven to be effective for PFAS removal in a prior study[29] 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 losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography−tandem mass spectrometry (LC−MS/MS) methods for PFAS quantification is provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence of PFASs 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.

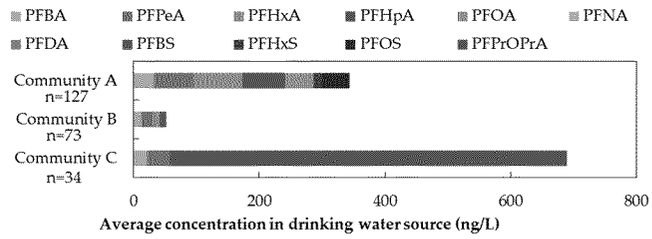

Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean ∑PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,[31] suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80−85% $C_nF_{2n+1}COOH$; n = 7−9) in 2006 to short-chain (76% $C_nF_{2n+1}COOH$; n = 5−6) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

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Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLs, 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), only mean concentrations of PFBA and PFPeA were above the QLs. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.[32] However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 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 S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and 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 studies.[22−26] 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 because of the oxidation of precursor compounds.[25] Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

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 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2−113 times greater than that of PFPrOPrA (Figure 2b).

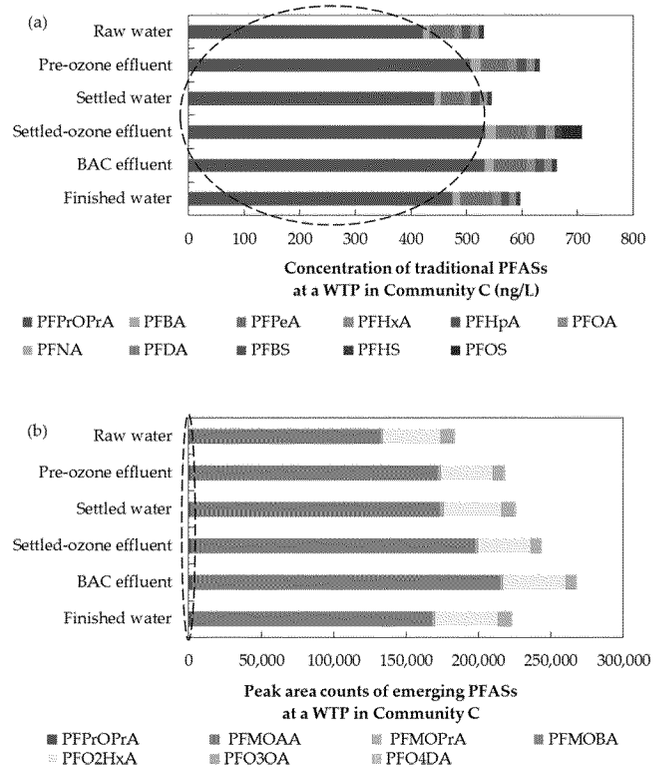

Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with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

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.[24,25,29] It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥7. At the same PAC dose, 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. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of 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) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

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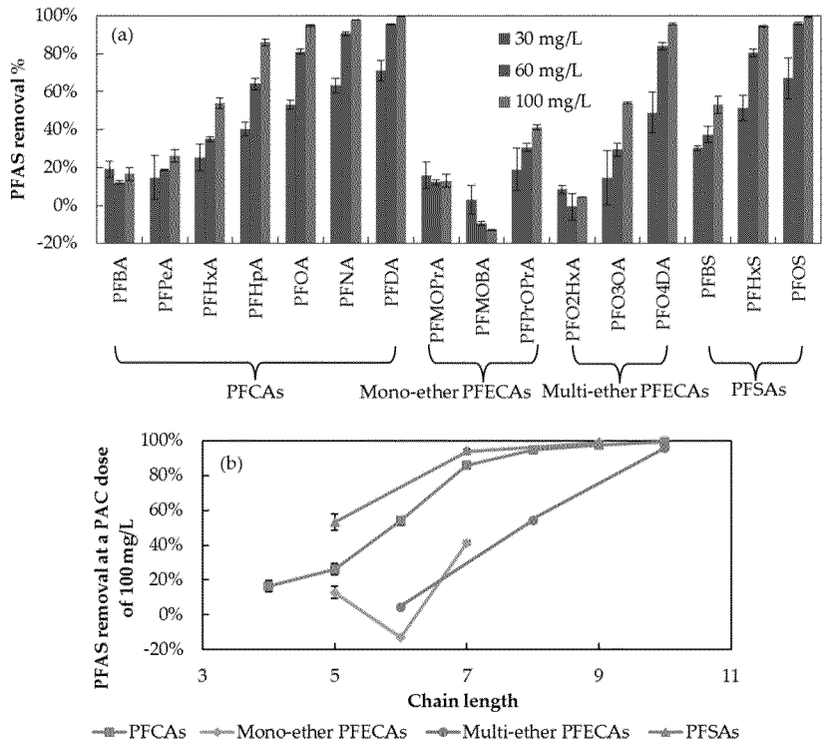

Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages,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

studies.[24,25,29] PFECAs exhibited adsorbabilities lower than those of 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, PFPrOPrA ~ PFO3OA). 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 an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

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Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

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