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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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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37 ## Introduction

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

53 One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was
54 recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing
55 facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-
56 methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-
57 2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA),
58 perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid
59 (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)). The ammonium salt of
60 PFPrOPrA is a known PFOA alternative that has been produced since 2010 with the trade name
61 "GenX".[15] According to the manufacturer, the ether oxygen enables "very rapid
62 bioelimination"[15]; however, except for the PFPrOPrA data reported by the manufacturer,[16-18]
63 little information is available on pharmacokinetic behavior, toxicity, or environmental fate and

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64 transport of PFECAs. To the knowledge of the authors, the only other published PFECA
65 occurrence data are for PFPrOPrA in Europe and China,[19] and no published data are available
66 on the fate of PFECAs during water treatment.

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

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

76 Materials and Methods

77 **Water samples**: Source water of three DWTPs treating surface water in the CFR watershed was
78 sampled between June 14 and December 2, 2013 (Figure S2 in SI). Samples were collected from
79 the raw water tap at each DWTP daily as either 8-hour composite (DWTP A, 127 samples) or 24-
80 hour composite (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250-mL
81 HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly
82 basis. All samples were stored at room temperature until analysis (within 1 week of receiving).
83 On August 18, 2014, grab samples were collected at DWTP C after each unit process in the
84 treatment train (raw water ozonation, coagulation/flocculation/sedimentation, settled water
85 ozonation, biological activated carbon (BAC) filtration, disinfection by medium pressure UV
86 lamps and free chlorine). Operational conditions of DWTP C on the sampling day are listed in
87 Table S2 in SI. Samples were collected in 1-L HDPE bottles and stored at room temperature
88 until analysis. On the same day, grab samples of CFR water were collected in six 20-L HDPE

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

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

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

103 Results and Discussion

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

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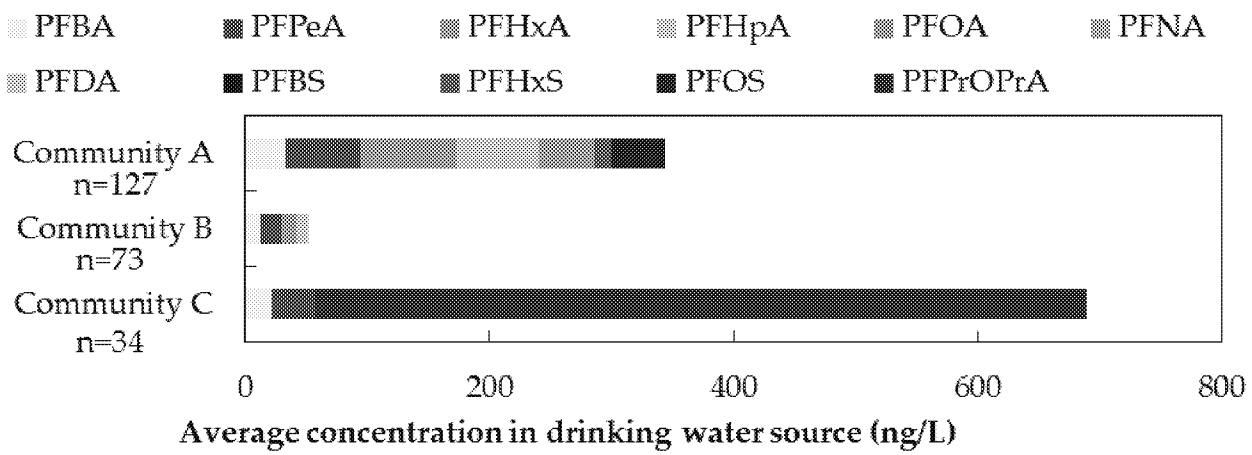
115 total PFAS concentration to average daily stream flow (Figure S4 in SI) illustrated a general
116 trend of low PFAS concentrations at high flow and high concentrations at low flow, consistent
117 with the hypothesis of upstream point source(s). In community B, perfluorobutanoic acid
118 (PFBA) and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

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



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

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

136

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

148 Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was
149 similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in
150 Figure 1; i.e., PFPrOPrA concentrations (400-500 μg/L) greatly exceeded legacy PFAS
151 concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA and PFO3OA)[11] had peak areas
152 2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging
153 PFASs suggests the necessity of incorporating them into routine monitoring.

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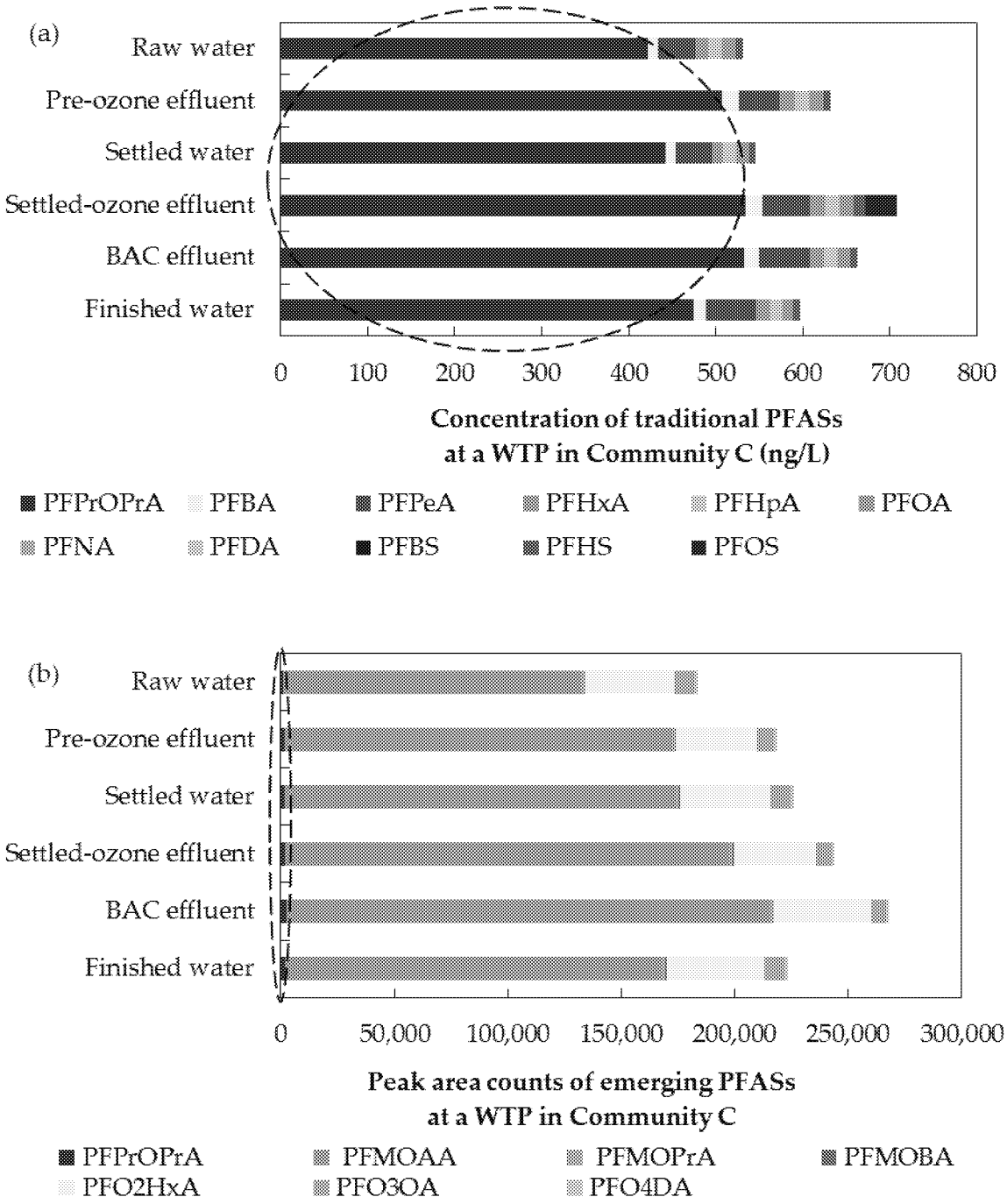

Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for emerging PFECAs, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted in dashed ovals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

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

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

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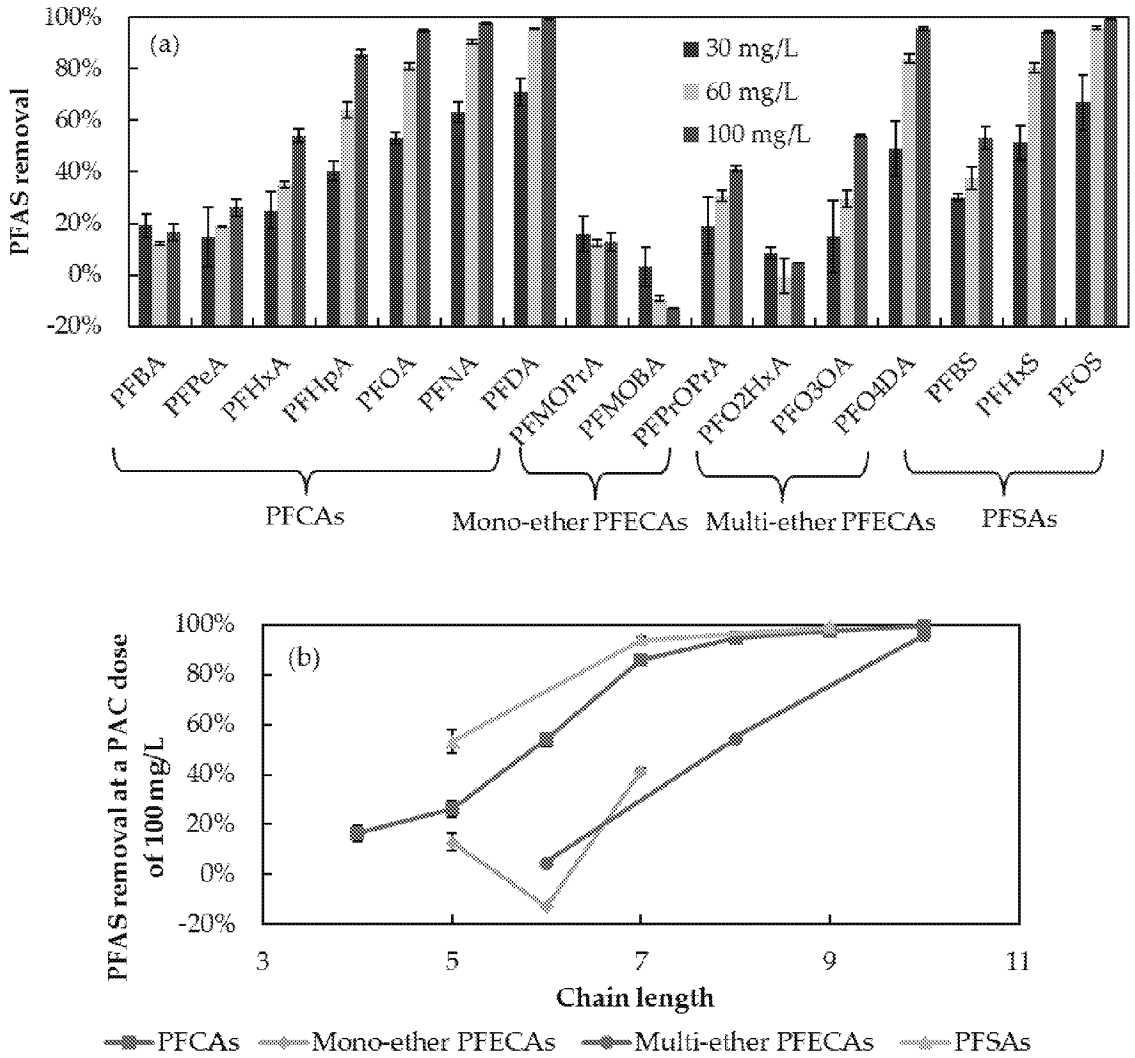

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190 **Figure 3.** PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a
191 function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were
192 spiked at ~1000 ng/L and the emerging PFASs were at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

195

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

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

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

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