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Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain

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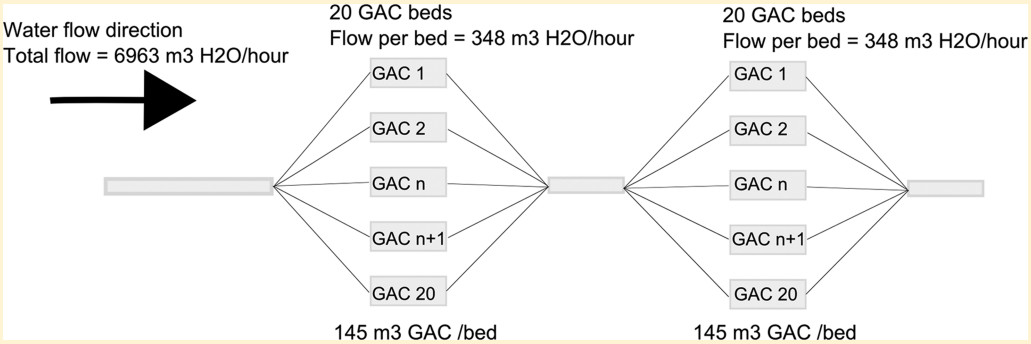
Supporting Information



ABSTRACT: The behavior of polyfluoralkyl acids (PFAAs) from intake (raw source water) to finished drinking water was assessed by taking samples from influent and effluent of the several treatment steps used in a drinking water production chain. These consisted of intake, coagulation, rapid sand filtration, dune passage, aeration, rapid sand filtration, ozonation, pellet softening, granular activated carbon (GAC) filtration, slow sand filtration, and finished drinking water. In the intake water taken from the Lek canal (a tributary of the river Rhine), the most abundant PFAA were PFBA (perfluorobutanoic acid), PFBS (perfluorobutane sulfonate), PFOS (perfluorooctane sulfonate), and PFOA (perfluorooctanoic acid). During treatment, longer chain PFAA such as PFNA (perfluorononanoic acid) and PFOS were readily removed by the GAC treatment step and their GAC effluent concentrations were reduced to levels below the limits of quantitation (LOQ) (0.23 and 0.24 ng/L for PFOS and PFNA, respectively). However, more hydrophilic shorter chain PFAA (especially PFBA and PFBS) were not removed by GAC and their concentrations remained constant through treatment. A decreasing removal capacity of the GAC was observed with increasing carbon loading and with decreasing carbon chain length of the PFAAs. This study shows that none of the treatment steps, including softening processes, are effective for PFAA removal, except for GAC filtration. GAC can effectively remove certain PFAA from the drinking water cycle.The enrichment of branched PFOS and PFOA isomers relative to non branched isomers during GAC filtration was observed during treatment. The finished water contained 26 and 19 ng/L of PFBA and PFBS. Other PFAAs were present in concentrations below 4.2 ng/L The concentrations of PFAA observed in finished waters are no reason for concern for human health as margins to existing guidelines are sufficiently large.

INTRODUCTION

PFAAs (perfluoroalkyl acids) are composed of a fully fluorinated alkyl chain of varying length in combination with a sulfonic, carboxylic, or phosphonic headgroup. This compound family is a subgroup of the larger family of polyfluoroalkyl substances (PFASs).[1,2] These compounds show high persistence in the environment and some are bioaccumulative and capable of inducing developmental toxicity.[3] Polarity and aqueous solubility of the PFAA increase with decreasing carbon chain length. Perfluoroalkyl substances have been detected in drinking water at concentrations typically in the low ng/L range,[4−6] with occasionally higher concentrations (lower μg/L level) in some contaminated areas.[7] These findings suggest that PFAAs are not or poorly removed during drinking water treatment. Since the exposure of humans to PFAAs occurs partly via drinking water,[8,9] information is needed about their presence in drinking water and their removal during treatment processes.

The relationship between PFAAs in source and drinking water was shown in several studies by sampling both the influent of the treatment and the produced finished drinking water. A positive correlation between both concentrations has been observed,[10,11] with levels detected in the raw water

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Table 1. Concentrations of PFAAs (Arithmetic Mean in ng/L with Range in Brackets) Encountered in Different Sampled Processes[a]

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
Rhine at Lobith (n = 12)[23]	34 (<1.0−120)	na	1.2 (<1.0−4.0)	1.2 (<1.0−2)	4.3 (2.0−9.0)	<1.0	<1.0	21 (3.0−70)	2.1 (<1.0−4.0)	15 (7.0−33)
intake Lek canal (n = 2)	33 (11−52)	1.7 (1.2−2.5)	2.8 (2.3−3.4)	1.4 (1.0−2.0)	4.4 (3.8−5.1)	0.6 (0.5−0.8)	0.6 (0.4−1.0)	35 (31−42)	2.0 (1.9−2.2)	8.2 (6.7−10)
effl. coagulation (n = 6)	21 (9.6−47)	2.0 (1.1−2.7)	3.2 (2.5−3.5)	1.6 (0.9−2.0)	4.4 (3.6−5.1)	0.7 (0.5−0.8)	0.7 (0.4−0.9)	30 (31−29)	2.0 (1.8−2.2)	8.6 (6.1−11)
effl. first rapid sand filtration (n = 6)	18 (<9.5−41)	1.6 (1.1−2.2)	3.3 (2.5−4.0)	1.9 (0.9−2.4)	4.6 (3.1−5.5)	0.7 (0.4−0.9)	0.6 (0.4−0.8)	27 (17−34)	2.0 (1.8−2.2)	7.8 (6.2−9.4)
after dune passage (n = 2)	32 (32−33)	2.2 (1.7−2.8)	4.0 (3.6−4.5)	2.5 (1.7−3.6)	9.2 (7.0−11)	1.0 (0.9−1.1)	0.3 (0.3−0.5)	16 (13−20)	3.0 (2.8−3.2)	12 (10−13)
effl. second rapid sand filtration (n = 2)	32 (32−34)	1.7 (1.2−2.4)	3.9 (3.6−4.4)	2.4 (1.7−3.6)	9.3 (8.5−11)	1.0 (0.7−1.4)	0.3 (0.2−0.3)	16 (14−19)	3.3 (3.1−3.5)	13 (9.8−15)
effl. ozonation (n = 2)	31 (29−34)	1.6 (1.5−1.8)	3.8 (3.4−4.3)	2.5 (2.1−3.2)	9.0 (7.3−9.8)	0.90 (0.6−1.1)	0.2 (0.2−0.3)	17 (16−17)	3.2 (3.0−3.4)	12 (9.0−16)
infl first GAC filtration (n = 5)	29 (25−34)	1.5 (1.3−1.6)	3.7 (2.5−4.5)	2.8 (1.5−3.6)	8.8 (6.1−12)	0.8 (0.6−1.3)	0.3 (0.2−0.9	15 (13−17)	3.0 (2.2−3.5)	11 (7.9−18)
effl. first GAC filtration (n = 5)	28 (27−30)	1.8 (1.6−2.4)	4.0 (3.3−4.7)	3.1 (2.3−3.7)	11 (8.9−13)	0.7 (0.4−1.3)	0.1	20 (18−25)	3.3 (3.0−3.6)	3.8 (2.6−6.2)
effl. second GAC filtration (n = 5)	30 (29−32)	2.9 (2.0−4.6)	4.4 (3.8−5.0)	2.7 (0.9−4.1)	5.3 (0.8−9.4)	<0.24	<0.09	20 (11−27)	0.54 (<0.65−0.9)	<0.23
finished drinking water (n = 5)	30 (27−33)	2.6 (2.0−3.5)	4.4 (3.8−5.3)	2.6 (1.4−3.8)	5.1 (3.6−6.7)	<0.24	<0.09	20 (17−24)	0.6 (0.5−0.8)	<0.23
tap water Amsterdam (n = 1)	na	2.7	5.2	1.9	5.7	<0.13	<0.09	19	1.3	0.4
LOQ[b]	9.5	0.8	0.8	0.8	0.8	0.2	0.1	0.2	0.6	0.2
blank conc.	1.5	<LOQ	<LOQ	<LOQ	0.25	<LOQ	<LOQ	<LOQ	0.05	<LOQ

[a]Average concentrations of samples collected in sampling campaigns one and two. For comparative purpose, concentrations of PFAAs in the river Rhine from another study are included. na = not analyzed. [b]See SI Table S2 for LOQ derivations.

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sometimes being identical to those in the produced drinking water.[12,13] The relationship between levels of PFAAs in source and drinking water depends on the number and types of treatment steps in between. The role of the individual treatment steps at the operational plant scale in the removal of PFAAs has not been assessed in peer reviewed literature, with the exception of efficacy of GAC for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).

It appears that the treatment technology most frequently applied for the removal of PFAA from contaminated water is granular activated carbon filtration (GAC).[14] However contradicting reports can be found on the efficacy of GAC treatment.[6] Fresh GAC is known to remove most perfluoroalkyl acid (PFAA) homologues with alkyl chains longer than those of PFOA or perfluorobutanoic acid (PFBS) from the water at the batch scale.[15,16] In practice, GAC either does not appear to be effective in removing PFAAs [12,17] or only during a limited period of time.[18] Almost invariably, these conclusions are based on the measurement of PFOA and PFOS only.

The use of membrane technology, such as reverse osmosis (RO) and nano filtration (NF), to remove PFAAs from water has been shown to be successful for PFAA with an alkyl chain longer than perfluoropentanoic acid (PFPeA) and perfluoropentane sulfonate (PFPS).[19−21] Despite these results, the implementation of membrane technology in drinking water treatment remains low due to operational costs and the problem of concentrate (or brine) disposal.

The present work aims at evaluating the efficacy of removing PFAAs from raw source water by the various treatment steps operating in a full scale drinking water production site. Apart from PFOA and PFOS, this study focuses on the behavior of other PFAA, in particular short-chained PFAAs for which little information exists other than that they are difficult to remove by common treatment techniques including GAC.[14] To this end, the concentrations of PFAAs were quantified directly prior to and immediately after each treatment step. This study is the first to investigate isomer-specific behavior during treatment.

We hypothesize that only the GAC treatment step will remove PFAAs. The removal rates will depend on the loading of the GAC filters, which imply that increasingly aged GAC filters will show a decreasing removal capacity regarding PFAAs.

MATERIALS AND METHOD

Water Treatment. The source of drinking water for the city of Amsterdam (Netherlands) is the Lek canal, which is fed by river Rhine water. After intake (70 million m^3/year), water is pretreated (coagulation and rapid sand filtration) at Nieuwegein and then transported by pipeline (±40 km) to the western part of The Netherlands (Leiduin) where the water is slowly filtered through dunes (see ref 22). After reabstraction, the water is further treated using rapid sand filtration, softening, ozonation, GAC filtration, and slow sand filtration to produce the finished drinking water.

In the process scheme of Leiduin, a two-stage carbon filtration is applied. Out of a total of 40 filters of 58 m^2 area*2.5 m depth, 20 filters are used as first stage filters and the other 20 are used as second stage filters (see SI, Figure S9). All filters are operated with an empty bed contact time (EBCT) of 20 min, resulting in a total EBCT of 40 min. Each newly installed filter is employed initially as a second stage filter and is switched to the first stage after 15 months of operation. After another 15 months, the carbon is reactivated and is put back into service as a second stage filter. Hence, the carbon is reactivated once every 2.5 years, which corresponds to a maximal total loading of 80 m^3 H_2O/kg GAC.

The carbon used is Norit ROW 0.8S (density 330−360 kg/m^3). During the carbon filtration process, the DOC content is reduced from 2 to 1 mg/L C at a pH of 8.1 (saturation index 0.25−0.45) and a water hardness of 1.5 mmol Ca per L.

Sampling Campaign. A total of 54 samples were collected in January and September 2010. During the first sampling round, one grab sample was taken at the following treatment steps: intake in Lek canal (source water), effluent of the coagulation step, effluent of the first rapid sand filtration, effluent of the dune passage, effluent of the second rapid sand filtration, influent of the first GAC filtration, effluent of the first GAC, effluent of the second GAC, and the finished drinking water.

In the second sampling round, the same sampling points were resampled approximately every two hours during a period of 10 h, with a total number of between 2 and 6 samples collected at each sampling point (see Table 1), thus reflecting the hourly variation in concentrations. From the total set of samples thus obtained (2−6 replicates from 10 points), for each sampling point a single sample was selected in such a way that it corresponded to sampling of the same parcel of water (taking into account the hydrological retention time, cf. Table S1). This allowed us to follow the fate of the PFAA throughout the entire purification plant.

In order to specifically evaluate GAC regeneration dependence, during the second sampling round additional samples from effluents of individual GAC filters with differing lifetimes (preloadings) were taken.

A detailed description of the drinking water production process from surface water from the Lek canal to finished water and sample locations is presented in the SI Figures S1 to S4).

All samples were collected in 1 L polypropylene (PP) containers which were prerinsed with methanol three times and then oven-dried at 70 °C. Before sampling, bottles were thoroughly rinsed three times with sampled water. Sampling points consisted of stainless steel taps with stainless steel tubing running continuously (never closed) for all but one sampling location (intake) where sample was taken directly from the surface water stream. Samples were transported to the laboratory and conserved at 4 °C until extraction; samples were extracted within two weeks after collection.

The chemicals used and the method of analysis are described in the SI. The amount of sample extracted was 250 mL, this proved to be an optimum in the work so far, but apparently not for the samples of the September sampling round.

Quality control. All samples were extracted in duplicate. The first set collected in January 2010 was also injected in duplicate. Because injection duplicates did not show large deviations (average: 10%; stdev: 9%), the samples collected in September 2010 were injected singularly. Concentrations reported in Table 1 are the average of both sampling campaigns unless explicitly stated otherwise. Quantification of all measurements was performed with a linear eleven point calibration line (with $r^2 > 0.99$ for all analytes). Samples were all quantified within the linear dynamic range (0.07 to 140 pg absolute injected) of the calibration line (see Figure S6 in SI). Analyte concentrations were corrected for total procedural recovery of the mass labeled internal standards (SI Table S4). LOQs are given in SI Table S2.

Anaytes were identified and quantified using the criteria reported in our previous study.[22] Blank samples of the PP sampling bottles were prepared in the laboratory by filling a bottle of 1 L with doubly distilled water to test for possible contamination occurring during each sampling round. The analysis of the blank samples followed the same procedure that was used for the other samples. Average concentrations in the field blanks (given in Table S2 of the SI) were constant, and comparable with previous sampling campaigns.[22] Procedural blanks were analyzed for each batch of samples. Injection of methanol in between approximately every 10 sample injections did not show contamination and flushed the system clean. LOQs were calculated according to the method described in footnote e of Table S2 of the SI.

Because at the time of analysis no isotope labeled standards of branched isomers of PFOA and PFOS were available, special attention had to be given to the identification of the branched isomers. Under the experimental conditions used, branched isomers elute prior to the peak of the non branched homologue. Branched isomers coeluted in a single peak in the case of PFOA and in two distinct peaks in the case of PFOS. Since the earliest eluting peak of branched PFOS never contributed more than 5% to the total peak response of all branched isomers (see Figure S8 of the SI), for the calculation of branched to non branched ratios only the second eluting peak was used.

The isomers were identified on the basis of retention time (with a ± 0.3 min window); the presence of transitions one and two (see SI); and by looking at the ratio of both transitions (tr1/tr2) which was significantly different for the branched and the non branched isomers: tr1/tr2 L-PFOA 1.3; stdev 0.1; tr1/tr2 B-PFOA 0.8; stdev 0.2; tr1/tr2 L-PFOS 1.6; stdev 0.5; and tr1/tr2 B-PFOS 4.1; stdev 0.6. The concentrations of branched PFOA and PFOS isomers were quantified assuming they have a response factor similar to that of the non branched isomers. Although this may lead to biased quantification of the branched isomers, the main purpose was to compare the relative levels of branched isomers between samples.

Statistics used. Statistical tests were performed using SPSS v.16.0 (www.spss.com) unless explicitly stated otherwise. Concentration increases and decreases for each analyte between different locations sampled were tested with a one-way ANOVA and a Games-Howell post hoc test (with $p < 0.5$) after testing for normality (with a Kolmogorov–Smirnov test) within the sampled location groups.

RESULTS AND DISCUSSION

The analysis of water samples in the different drinking water production steps showed the presence of PFAAs in all samples analyzed. First, we will discuss the overall set of data generated by the two sampling campaigns that are reported in Table 1.

In general, the finished drinking water contained short chained PFBA, PFPeA, PFHxA, PFOA, PFBS, and PFHxS; while longer chained PFAA such as PFNA and PFOS were well removed from the drinking water (Table 1). The concentrations of PFAA along the drinking water treatment show that most treatment processes do not remove perfluoroalkyl acids from the water. Concentrations of PFBA and PFBS ranged from <9.5 to 52 ng/L and from 11 to 42 ng/L respectively (see Table 1). The averages of the other analytes measured: PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, and PFOS ranged between <LOQ and 18 ng/L. Because the recoveries for PFBA were rather low, the concentrations should be taken as indicative. Comparatively low PFBA recoveries are not uncommon in these types of samples and have been reported before.[24]

Concentrations of PFAA in the intake water found in this study are similar to results reported by the RIWA in 2009[23] in the river Rhine at Lobith (Dutch-German Border) (see Table 1 and SI S8) and by Möller et al[24] for the river Rhine. The relatively high concentrations of PFBA and PFBS measured in the river Rhine and in the Lek canal have been attributed to an industrial point source upstream in the German part of the Lower Rhine.[25] The concentration levels and relative abundances of the various PFAA in water from the sampling location Lobith[23] were similar to those of water taken in the Lek canal (using MANOVA analysis with a Wilks's lambda post hoc test ($\alpha = 0.28$)); indicating that the concentration pattern found in the source water in the present study is similar to that of the river Rhine. Monitoring results published on a regular basis during the period 2007–2009 by the RIWA [23,26,27] on PFOA and PFOS in the Lek canal showed that their concentrations at this intake location do not fluctuate much over the years (e.g., PFOS in Figure S5 and Table S9 of the SI). Although the yearly averages of PFBA and PFBS concentrations in the river Rhine at Lobith are similar to the intake concentrations, they exhibit a much larger variability in concentration levels than those of PFOA and PFOS. This is reflected in the variability in PFBA and PFBS levels in the pretreatment steps (see Table 1).

Although a decrease is observed for PFBA in the coagulation step (see Table 1), this decrease appears to be non significant ($\alpha = 0.904$ and $\alpha = 0.412$, respectively, ANOVA) and can be attributed to the large variability in the influent concentrations and the analytical uncertainty.

Rapid and slow sand filtration treatment steps as well as dune filtration through sandy aquifers did not remove PFAA to any appreciable extent. This is in agreement with previous studies where riverbank filtration through sandy soils [28,29] and dune passage[22] did not remove PFAA.

PFAA concentrations in the finished drinking water were highest for PFBA and PFBS, with maxima of 33 and 24 ng/L max, respectively (Table 1). PFPeA, PFHpA, PFOA, and PFHxS were present at concentrations varying between 0.43 and 4.4 ng/L (Table 1). The concentrations of PFAA observed in the finished water in the present study are highly similar to those in tap water in the city of Amsterdam measured elsewhere.[30] This indicates that the concentrations in the finished drinking water and in tap water do not differ much. Tap water from other European countries has been shown to contain comparable concentrations of PFAAs.[31]

When comparing the concentrations of PFAA in finished drinking water and in the intake water, rather than using intake water data, data of effluents from the dune infiltration (see Table 1) were used. This was done because of the lag time involved between the influent of the dune area and the effluent of the dune area, which is between 30 and 135 days on average.[22] The decrease in the total concentration of PFAAs observed between the effluent dunes (77 ± 3.3 ng/L) and the finished water (60 ± 3.0 ng/L) is a result of the decreases of PFOA, PFNA, PFHxS, and PFOS. This is in contrast to results reported by Quinones et al.[12] who found that compound specific concentrations were similar in influent and effluent (even for PFOS) when GAC filtration was used. In the present study the shorter chain PFAAs, i.e., <C8, were found to

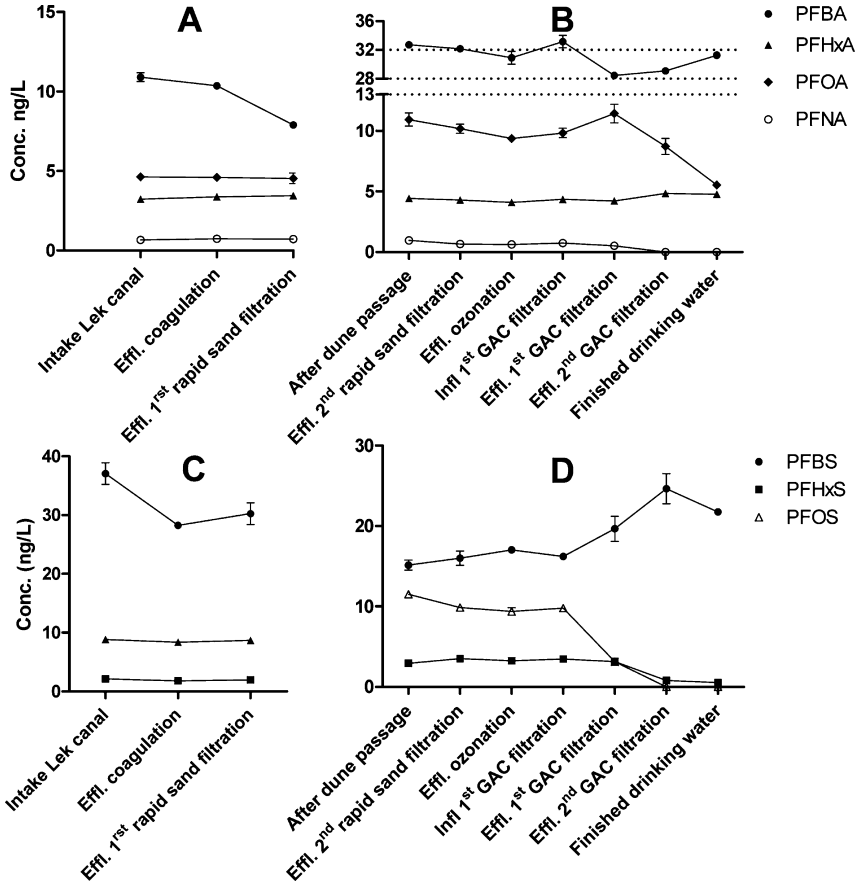

Figure 1. Concentrations of perfluoroalkyl acids (ng/L) (sampled in September 2010) during water pretreatment in Nieuwegein (A and C), and during water postdune infiltration treatment at Leiduin (B and D). Data shown are from the sampling series that accounts for the hydrological retention (see Methods section for further details). Error bars represent the standard deviation of the duplicate extraction of one sample.

dominate the total PFAA concentrations, in particular in the finished water.

The concentrations encountered in drinking water are in general in the low ng/L range. This is similar to results from other studies which reported concentrations in the same order of magnitude.[31]

Hydrological Retention Time. As mentioned in the Materials and Methods section one series of grab samples in the second sampling round took into account the hydrological retention time of a parcel of water flowing through the treatment plant. This allows better visibility of the processes occurring during the water treatment. Concentrations from this series of the second sampling round only are shown in Figure 1; the pretreatment (graphs A and C) and post-treatment (graphs B and D) are represented separately due to the lag time involved in the filtration (see Materials and Methods section water treatment and ref 22).

The concentrations of PFAAs shown in Figure 1 remain constant during the first three treatment steps (Figure 1A,C) except for PFBA and PFBS. We have no definitive explanation for this observation so far. If removal due to coagulation would have occurred, then a relationship between the alkyl chain length and removal efficiency would be expected;[32] this is however not the case as longer chained PFAAs levels remained constant throughout the pretreatment steps. Possibly, the low and variable recovery of PFBA could be a reason for the non explainable behavior.

In the post-treatment (Figure 1B,D), all analyte levels remain constant over the first four treatment steps. Ozonation clearly does not affect the concentrations of PFAAs. This is in agreement with batch experiments[33] and can be explained by the strength of the C−F bond in PFAAs.[34] The persistence of PFAAs toward ozonation is further supported by the use of perfluoroalkyl acids as enhancers in advanced oxidation processes (e.g., refs 34,35). The water softening step, by addition of caustic soda (NaOH), which is the treatment process that is applied between effluent ozonation and influent GAC, did not show any appreciable removal of PFAAs.

A significant decrease was observed for PFOS after the first GAC passage, indicating that little GAC capacity is needed for the removal of PFOS (only one filtering step is needed, see figure 1D). In the second GAC filter, a significant decrease of the concentration was found for PFOA, PFNA, PFHxS indicating that more capacity (GAC filtration step 1 and 2) is needed for the removal of these homologues. The concentration of PFOS also decreased further to below the LOQ in the second treatment step. From Figure 1D it can be seen that PFNA, PFDA (shown in Table 1), PFOS and PFHxS are completely removed during GAC treatment, while PFOA only decreases about 50% after the GAC filtration. The removal of long-chained PFAA has also been observed in other studies.[10,18,36]

The increase in PFBS concentration observed in Figure 1D is possibly due to the desorption of previously adsorbed PFBS which may be displaced by highly sorptive matrix components

that compete for active sorption sites. The same effect was also shown in soil columns experiments, where short chain PFAA were desorbed by additional input of a longer chain PFAA to the columns.[37,38] A difference in matrix effects as an explanation for different recoveries in GAC influents and GC effluents is quite unlikely, as the major matrix interferences in the water have already been removed prior to the GAC filtration and the microcontaminants that are present in influents (and mostly absent in the effluent due to the GAC adsorption) do not influence the recovery of PFAAs. Finally, we cannot rule out that variability is introduced as a result of using ^{13}C-PFHxS instead of ^{13}C-PFBS as internal standard.

GAC Performances. Since the GAC treatment steps did prove efficient in the removal of certain PFAA, additionally the effluents of six individual GAC filters were sampled to gain insight in the processes during filtration. To that end, two types of GAC filter categories were sampled: filters with relatively short lifetimes (497−580 days) and filters with long lifetimes (894−937 days), which correspond to moderately and highly loaded GAC filters, respectively. The sampling would potentially show: (i) if PFAA removal was determined by GAC preloading, then a relation between filter loading and removal efficiency would be expected; (ii) if a difference in adsorption capacity between the PFAA exists, different removal efficiencies are expected for the same filter loading such as seen in the paragraph above.

The results of the sampling of the different filters showed that for PFBA, PFPeA, PFHxA, PFOA, and PFBS the relative concentrations (C/C_0) observed after passage of the moderately loaded GAC filters are equal to those of the highly loaded GAC filters (Table S8 of the SI). This finding indicates that these PFAA are not well removed by the operating GAC filtration and that breakthrough of these compounds had already occurred (confirmed in table 1). On the opposite, PFDA is completely removed and concentrations after passage of both the moderately and the heavily loaded GAC filters are <LOQ. For PFOS (both the branched and nonbranched isomers) and PFHxS, the more highly loaded filters (older age) show a higher relative concentration (i.e., closer to one) than the moderately loaded filters. This is confirmed by the regression analysis of the data in Figure 2 which show a significant ($p < 0.05$) correlation ($r^2 = 0.68$; 0.86 and 0.90, respectively). This result indicates that there is a relation between filter loading and removal efficiency: younger filters do remove more PFAAs.

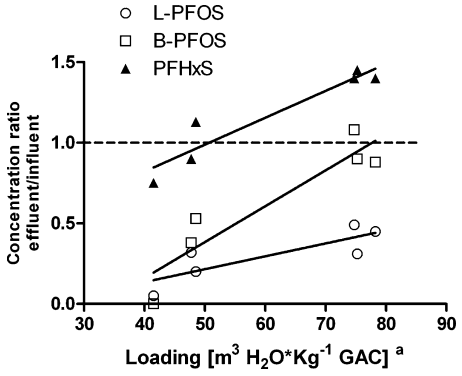

Figure 2. Relative concentrations (ratio of concentration in GAC filter effluent: concentration in GAC influent' of branched PFOS (B-PFOS), non branched PFOS (L-PFOS) and PFHxS against GAC loading. Samples ($n = 6$) taken in Sept 2010 of the individual GAC beds. Loads were calculated using the total water flow in the GAC filtration step divided by the total amount of beds multiplied with the age of the sampled GAC bed.

The relative concentration of PFHxS after passage of the highly loaded GAC bed amounted to a value higher than one (see Figure 2), suggesting desorption of possibly previously sorbed PFHxS. In column experiments competitive displacement of shorter chain PFAA has been observed and explained as being the result of competition with longer chain PFAA.[38]

The breakthrough of short-chain PFAA (PFBS and <C8 for the carboxylates) can be attributed to their lower adsorption capacity to GAC in combination with the running lifetime of the GAC. Lower sorption of shorter chain PFAA (i.e., ≤ C8) has been observed before in batch studies with sediments in ref 32. The results show that the adsorption coefficient decreases by 0.50 to 0.60 log units with each $-CF_2-$ group less in the molecule and by an additional 0.23 log units for the perfluorocarboxylates as compared to the perfluorosulfonates. As can be seen in Table 1 at the operational level we indeed observe that with decreasing chain length sorption decreases and that perfluorosulfonates do adsorb more strongly than perfluorocarboxylates with the same fluorocarbon chain length. One study[15] which determined the Freundlich isotherm constant of PFOA, PFBS, and PFOS to GAC at the batch scale, found K_F [(mg PFAA/g sorbent)(mg PFAA/l)$^{-n}$] values of 9.3 < 11.8 < 41 ± 15 for PFBS, PFOA, and PFOS, respectively. In another study, a similar relation between K_f and chain length was reported.[36] In the present study, we indeed see that the removal efficiency increases in the same order. Also, the monitoring of treatment plant effluents at a contaminated site in Oakdale, U.S. showed that order of breakthrough occurred from short to longer chain PFAA: PFBA, PFPeA, and PFHxA, respectively.[31] Finally, in a monitoring campaign near a contaminated site which investigated the behavior of PFAA after the installation of GAC filters,[6] it was found that PFHxA < PFBS < PFHxS < PFOS was the order of breakthrough (no other PFAA were reported). Although we do not differentiate in the order of breakthrough for the short chain PFAAs (i.e., PFBS and PFHxA), Figure 2 shows that PFHxS has a faster breakthrough than PFOS. In future research, it is recommended to start monitoring breakthrough of ionic acids such as PFAAs shortly after GAC beds have been newly installed.

Behavior of Isomers. The percentages of branched isomers relative to the total (sum branched and non branched) PFOA and PFOS concentrations were calculated for each of the treatment processes. As mentioned above, the percentages should be taken as indicative since the absolute quantification of isomers is based on response factors of the non-branched isomers. It was found that the behavior of branched PFOS and PFOA homologues in GAC filter beds is different from that of the non branched compounds. The percentage of branched PFOA remained constant throughout the process from dune passage to effluent first GAC filtration: 9% (stdev = 1%). In the effluent of the second GAC filter, however, the branched PFOA accounts for 21% (stdev = 3%) of the total PFOA concentration. A similar but more pronounced pattern is seen for PFOS. Between the dune passage and influent GAC the averaged branched PFOS contribution is 41% (stdev = 2%). After the first GAC treatment step, the contribution increases to 62% (stdev = 3%). After the second GAC treatment, both the non branched and the branched isomers drop to below the

LOQ. This is also confirmed by Figure 2 which shows that the slope of relative concentration vs loading relationship for the branched PFOS is 2.8 times higher than that of the non-branched PFOS, indicating that the non-branched PFOS is more adsorbable than the branched PFOS. We conclude that the non-branched homologues of both PFOA and PFOS absorb more strongly to the GAC than the branched isomers. Earlier studies on the adsorption behavior of isomers found a decreasing sorption capacity with increased degree of branching.[39] A possible explanation is the molecular volume of the different branched isomers being smaller leading to a smaller Gibbs free energy gain from adsorption than the non branched isomer.[40]

Environmental Relevance. . The present study shows that the removal of short chain PFAA such as PFBA and PFBS from drinking water is problematic. It is expected that PFBS and PFHxA will become more abundant in the future as they are as a compound or part of, slowly replacing PFOS and PFOA as a result of reductions in emissions and production volumes of the latter two PFAA due to implemented guidelines.[41−43] Although short chain compounds are less bioaccumulative and toxic than longer chain PFAA they are persistent in the environment and are considered undesirable in drinking water. The reported PFAA in this work are therefore relevant for precautionary reasons. It is expected that the adsorption capacity of GAC filters for polar compounds, such as PFBA (typically breakthrough of more than 10% prior to a load of 50 m^3 H_2O/kg GAC), decreases to virtually zero after one year standing time. This is also observed for polar compounds such as, e.g., clofibric acid which was shown to have a breakthrough at about 17 m^3/kg.[44] In order to reduce the concentrations of these compounds in drinking water, the option of reducing of the emissions from certain point sources (like the PFBA/PFBS point source on the lower Rhine[24]) would appear more efficient than to spend money for a more frequent exchange of GAC in a number of waterworks.

The preferential sorption of the non-branched isomer compared to the branched isomers is an interesting finding which indicates the presence of isomer specific mechanisms in the environment that could potentially have repercussions for existing risk models.

No definitive European guidelines for the concentrations of PFAAs in drinking water currently exist. The concentrations of PFOA and PFOS in finished water observed in the present study are far below German provisional health-based guideline values for safe lifelong exposure (determined by the German Drinking Water Commission),[45] at 0.3 μg/L for the sum of PFOA and PFOS. Recently published proposed provisional guideline values[14] for PFBA (7 μg/L) and PFBS (3 μg/L) are not exceeded by the concentrations of these compounds observed in finished water in the present study. This also holds for the Provisional Health Advisories from the U.S. Environmental Protection Agency of 0.4 and 0.2 μg/L for PFOA and PFOS, respectively, in drinking water.[46] These values are in agreement with the recommended health-based drinking water concentrations of 0.04 μg/L calculated by Post et al.[47] if one takes into account the correction factor for subchronic to chronic exposure.

Concentrations observed are no reason for concern for human health as the margins to the existing provisional health-guideline values for the different PFAAs remains sufficiently high and the risk quotients remain low.

■ ASSOCIATED CONTENT

Supporting Information

Contents: Description of the drinking water production process, measured concentration tables, recoveries, mass transitions applied, and standards/analyte combination. This material is available free of charge via the Internet at http://pubs.acs.org.

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