Evaluation of the Removal Efficiency of Per- and Polyfluoroalkyl Substances in Drinking Water

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Introduction

PFASs are of rising concern due to their persistence in the environment and their potential for bioaccumulation in humans and wildlife [1]. PFASs are used as dirt- and stain-repellent like in food packaging, textile and aqueous film forming foams (AFFFs) or in industrial processes like as surfactants and emulsifiers. PFASs can be released into the environment through point sources such as sewage treatment plants (STPs) but also due to firefighting exercises with PFAS-containing AFFFs or nonpoint sources such as surface runoff [1]. Thus, drinking water source areas like groundwater and surface water can be impacted by PFAS contamination and can be an exposure route for humans [2]. PFASs have half-lives of several years in the human body and high exposure to PFASs is possibly connected to adverse health effects such as the risk of high cholesterol and blood lipid levels, delayed puberty in girls, decreased fertility, increased Body Mass Index (BMI), bladder cancer, kidney cancer, prostate cancer, testicular cancer [3]. Thus, various countries have established guideline values for PFASs in drinking water, for example the National Food Agency in Sweden recommends that the concentration of the sum of 11 different PFASs (i.e. C_4-C_{10} perfluorocarboxylic acids (PFCAs), C_4, C_6, C_8 perfluorosulfonic acids (PFSAs) and 6:2 fluorotelomer sulfonic acid (6:2 FTSA)) should not exceed 90 ng L^{-1} in drinking water.

In Uppsala, Sweden, time-trend analysis of certain PFASs in blood serum indicated exponential increase over time, in contrast to cohorts from other cities, and drinking water was identified as the main exposure source [2]. The contamination most likely originated from a fire training facility in the north of Uppsala where PFAS-containing AFFFs were used and contaminated the nearby groundwater, which is used as raw water for drinking water production [4]. However, conventional treatment processes such as sand-filtration, coagulation, flocculation, sedimentation, oxidation, disinfection are ineffective for the removal of PFASs in drinking water treatment plants (DWTPs) [5, 6]. Treatment methods like granular activated carbon (GAC), ion exchange and reverse osmosis can effectively remove PFASs from water [5-7]. But, these treatment techniques showed low removal efficiency for shorter chained PFASs and decreasing removal efficiency over time due to saturation of the filter material such as GAC, and ion exchange [7]. Thus, more studies on efficient treatment methods for PFASs in drinking water are needed.

The aim of this study was to evaluate the treatment efficiency for PFASs in a full-scale DWTP in Uppsala, Sweden. The specific objectives include to i) assess the temporal trends of the incoming raw water for the DWTP originating from PFAS-contaminated groundwater, ii) investigate the removal efficiency of PFASs and total organic carbon (TOC) using GAC filters over time in the full-scale DWTP, and iii) evaluate the influence of the flow rate for the GAC filters in the full-scale DWTP.

Materials and methods

In total, 15 PFASs (i.e. C_4–C_{12} PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA), C_4, C_6, C_8, C_{10} PFSAs (PFBS, PFHxS, PFOS, PFDS), perfluorooctanesulfonamide (FOSA), and 6:2 FTSA) were assessed for investigating the temporal trends of the incoming raw water and in the GAC filters which were analysed by ALS Scandinavia, Sweden, according to DIN method 38407-42 (data are provided from Uppsala Vatten och Avfall AB). In addition, 27 PFASs (i.e. C_4–C_{14} C_{16}, C_{18} PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C_4, C_6, C_8, C_{10} PFSAs (PFBS, PFHxS, PFOS, PFDS), FOSA, methyl and ethyl FOSAs, methyl and ethyl perfluorooctane sulfonamidoethanols (FOSEs), perfluorooctanesulfonamidoacetic acid (FOSAA), methyl and ethyl FOSAAs, and 6:2 FTSA) were examined for the GAC flow rate experiments in the full-scale DWTP which were analysed as described previously [8].

The DWTP includes five treatment steps, i.e. aeration, softening, sand filtration, ten GAC filters and disinfection with chlorine. The used GAC types were Filtrasorb® 400 (Chemviron Carbon iodine number = 1050 mg g^{-1}, surface area = 1050 m^2 g^{-1}, effective size = 0.6–0.7 mm) and AquaSorb® 2000 (Jacobi, iodine number = 950 mg g^{-1}, surface area of 950 m^2 g^{-1}, effective size of 0.4–1.2 mm). PFAS concentrations were measured in the incoming raw water from two groundwater wells (well 1 and well 2). A fire training facility is located in the north of Uppsala which is probably a source for the groundwater contamination with PFASs due to the usage of PFAS-containing AFFFs. Well 1 is located near the city of Uppsala within the groundwater flow path, while well 2 is located further away from the likely PFAS contamination source in the south of the city of Uppsala. In addition, PFASs were analysed before and after the GAC filters in the full-scale DWTP over a period of more than one and a half years (from April 2015 to February 2017) and for the GAC flow rate experiment to investigate the removal efficiency of PFASs using different flow rates (i.e. flow rate of 15, 30 and 45 L s^{-1}) in the full-scale DWTP from November to December 2016. Finally, the concentrations of TOC and PFASs were analysed after relevant treatment steps. Linear regression parameters were calculated using one-way ANOVA (analysis of variance) with a significance level of $\alpha = 0.05$. Half times and doubling times were calculated using equation 1:

$$t = (-)\frac{\ln(2)}{m} \tag{1}$$

where m is the slope of linear regression.

For the evaluation of the treatment efficiency the bed volume (BV, equation 2) and empty bed contact time (EBCT, equation 3) were calculated:

$$BV_{treated} = \frac{V_{treated}}{V_{GAC}} = \frac{r \cdot t}{V_{GAC}} \tag{2}$$

where $V_{treated}$ is treated water volume during operation time [m^3], V_{GAC} is volume of the GAC (35 m^3), r is the average flow rate [m^3 s^{-1}] and t is the time [s].

$$EBCT = \frac{V_{GAC}}{r} \tag{3}$$

Results and discussion

Temporal trends of PFASs in the incoming raw water for the full scale DWTP

∑PFAS concentrations in the incoming raw water for the full scale DWTP were higher in well 1 which was located closer to the fire training facility (on average = 180 ng L^{-1}) compared to the groundwater well 2

which is located further away (on average = 36 ng L^{-1}) (Figure 1). Time trend analysis in well 1 showed significant decreasing concentrations of PFHpA and PFOS ($p < 0.05$) with half-times of 1650 ± 449 days (d) and 2210 ± 868 d, respectively. In well 2, PFBS, PFHxS and PFOS showed significant increasing concentrations with doubling times of 1820 ± 554 d, 1620 ± 456 d and 1270 ± 467 d, respectively. According to this analysis, PFHpA and PFOS concentrations will be decreasing to half in 5−7 years in well 1, whereas in well 2 concentrations of PFBS, PFHxS and PFOS will be doubled in 4−6 years. This indicates that the PFAS contamination originates from the fire training facility in the north of the city of Uppsala, Sweden, and is leading to a contamination plume from north to south in the main aquifer of the city, which is in agreement with a previous study [4].
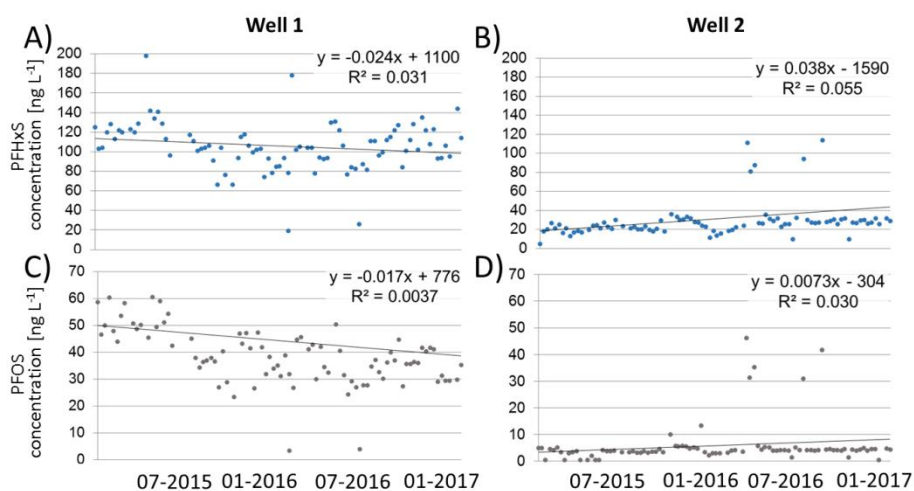

Figure 1. PFAS concentrations in the incoming raw water of the DWTP in Uppsala, Sweden, for A) PFHxS in well 1, B) PFHxS in well 2, C) PFOS in well 1, and D) PFOS in well 2 in ng L^{-1}.

Removal efficiency of PFASs using GAC in a full scale DWTP
PFASs were only removed using GAC filters, whereas no removal was observed after aeration, reactor, pH adjustment, and sand filtration. In general, the GAC Filtrasorb® 400 showed a slower decline in removal efficiency of PFASs compared to GAC AquaSorb® 2000 (Figure 2). For GAC Filtrasorb® 400, on average, PFHxA, PFOA, PFBS and PFHxS showed significant decreasing removal efficiencies ($p < 0.05$) with half-times of 257 ± 27 d, 783 ± 223 d, 390 ± 90 d and 1450 ± 138 d, respectively. This indicates that with longer chain-length the half-times were increasing and that PFCAs showed shorter half-times compared to PFSAs (PFHxA < PFBS < PFOA < PFHxS). However, no significant change was observed for PFOS (p-values > 0.05). For GAC AquaSorb® 2000 filter, PFHxA, PFOA, PFBS and PFHxS showed significant decreasing removal efficiencies ($p < 0.05$) with half-times of 174 ± 21 d, 640 ± 167 d, 262 ± 95 d and 1190 ± 139 d, respectively. This shows that the removal efficiency of PFASs declines faster using GAC AquaSorb® 2000 filter compared to GAC Filtrasorb® 400. For PFHxA, both GAC filter types showed a breakthrough with a removal efficiency < 0 % indicating desorption of PFHxA which has been also reported in GAC column sorption tests [7]. Furthermore, the breakthrough was much faster using GAC AquaSorb® 2000 (287 d, 26600 bed volumes treated) compared to GAC Filtrasorb® 400 (406 d, 33900 bed volumes treated) showing the higher sorption capacity of GAC Filtrasorb® 400 for shorter chained PFCAs.
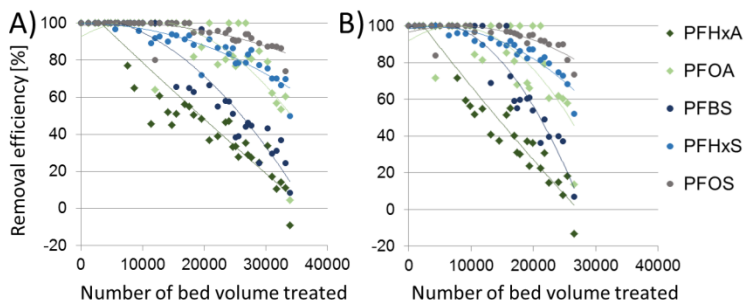
Figure 2. Removal efficiencies of GAC A) Filtrasorb® 400 and B) AquaSorb® 2000 in the full-scale DWTP.

Influence of flow rate on the removal efficiency of PFASs

To the author's knowledge, this is the first study investigating the influence of the flow rate on the removal efficiency of PFASs in a full scale DWTP. Significant changes (p-value < 0.05) for PFAS removal efficiencies with lower flow rates (thus, higher EBCT) were observed for PFHxA, PFOA, linear and branched PFHxS for the old GAC (in operation for 254 days) and for branched PFHxS for the newer GAC (58 days). Thus, an increase of the removal efficiency by lowering the flow rate from 45 L s^{-1} to 15 L s^{-1} is more apparent for GAC filters with long operation times and higher number of bed volumes treated. In general, with higher EBCT the water has more time to be in contact with GAC particles so that PFASs can have more time to get into pores and adsorb onto the surface of the GAC. This also seems to be the case for TOC which was better adsorbed with higher EBCT.

Overall, conventional treatment techniques were ineffective in removing PFASs. On the other hand, GAC filters were efficient in the removal of PFASs, but short chained PFASs are retained less effectively by GAC than long chained PFASs. The occurrence of PFASs in drinking water source areas leads to an urgent need for efficient treatment methods in DWTPs.

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