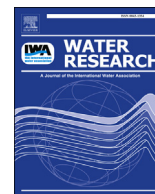


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Removal of per- and polyfluoroalkyl substances (PFASs) in a full-scale drinking water treatment plant: Long-term performance of granular activated carbon (GAC) and influence of flow-rate

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ARTICLE INFO

Article history:

Received 3 February 2020

Received in revised form

25 April 2020

Accepted 2 May 2020

Available online 22 May 2020

Keywords:

PFAS

PFOS

PFOA

PFC

Granular activated carbon

Drinking water treatment

ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) have been ubiquitously detected in drinking water which poses a risk for human exposure. In this study, the treatment efficiency for the removal of 15 PFASs was examined in a full-scale drinking water treatment plant (DWTP) in the City of Uppsala, Sweden, over a period of two years (2015–2017). Removal of the five frequently detected PFASs was influenced by the total operation time of granular activated carbon (GAC) filters, GAC type and surface loading rate. The average removal efficiency of PFASs ranged from 92 to 100% for “young” GAC filters and decreased to 7.0–100% for “old” GAC filters (up to 357 operation days, 29 300 bed volumes (BV) treated). Flow-rates were adjusted in two full-scale GAC filters of different operational age to examine the removal of PFAS and organic matter depending on GAC operational age and operating flow. The decrease in flow-rate by 10 L s⁻¹ from 39 to 29 L s⁻¹ led to an average increase of 14% and 6.5% in total PFAS removal efficiency for an “old” (264 operation days, 21 971 BV treated) and a “young” GAC filter (63 operation days, 5 725 BV treated), respectively. A cost-analysis for various operation scenarios illustrated the dominating effect of treatment goals and costs for GAC regeneration on overall GAC operation costs. The unit costs for GAC filters ranged from 0.08 to 0.10 € m⁻³ water treated and 0.020–0.025 € m⁻³ water treated for a treatment goal of 10 ng L⁻¹ and 85 ng L⁻¹, respectively, for \sum_{11} PFAS. Furthermore, it was concluded that prolonging the GAC service life by lowering the flow-rates after reaching the treatment goal could lead to a 26% cost-reduction. The results and methods presented in this study give drinking water providers valuable tools for the operation of a full-scale treatment train for the removal of PFAS in contaminated raw water.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are found ubiquitously in the abiotic and biotic environment (Ahrens, 2011). Due to their unique physico-chemical properties, PFASs have a wide range of applications and are for instance used in food packaging materials, textiles and in aqueous film forming foams (AFFFs) for firefighting (Buck et al., 2011; Appleman et al., 2014; Biegel-Engler et al., 2017). PFASs are highly persistent and many have half-lives of several years to decades in the human body (Lindstrom et al., 2011). Exposure to PFASs has been linked to adverse health

effects, e.g. increased risk of high cholesterol and blood lipid levels, decreased fertility and certain types of cancer (Lindstrom et al., 2011; Post et al., 2012; Biegel-Engler et al., 2017). PFASs have been detected in drinking water in several European countries and the USA (Ericson et al., 2009; Post et al., 2009; Ullah et al., 2011). In 2016, the US EPA therefore recommended a health advisory limit of 70 ng L⁻¹ for sum of PFOS and PFOA in drinking water (USEPA, 2016). The National Food Agency in Sweden recommends an action level of 90 ng L⁻¹ for the sum of 11 PFASs (i.e. C3–C9 perfluoroalkyl carboxylic acids (PFCAs): PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA; C4, C6, C8 perfluoroalkyl sulfonic acid (PFASs): PFBS, PFHxS, PFOS; 6:2 fluorotelomer sulfonic acid: 6:2 FTSA) in drinking water and advises the level should be reduced as low as possible (Ankarberg and Lindberg, 2016). In the future, the drinking water guidelines are becoming more strict (e.g. including a larger number of compounds and lower guideline

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levels) due to revised recommendations on the acceptable daily intake (ADI) value (Knutsen et al., 2018). PFAS emissions can occur through point sources such as wastewater treatment plants, landfill leachate, industries, and fire training facilities which have used PFAS containing AFFFs (Post et al., 2012). Nonpoint sources include surface runoff or precipitation (Ahrens, 2011). Once PFASs are released into the aquatic environment, they pose a risk for our drinking water, as conventional treatment processes such as sand-filtration, coagulation, flocculation, sedimentation, oxidation and disinfection are ineffective for the removal of PFASs during the treatment of contaminated ground or surface water (Rahman et al., 2014). The occurrence of PFASs in potable water at levels greater than regulatory limits therefore requires development and operation of efficient removal methods for drinking water treatment plants (DWTPs). Filtration through virgin or freshly regenerated (“young”) granular activated carbon (GAC) or ion exchange and membrane techniques like nanofiltration and reverse osmosis are effective methods for PFAS removal (Vecitis et al., 2009; Carter and Farrell, 2010; Eschauzier et al., 2012; Flores et al., 2013; Appleman et al., 2014; Chularueangaksorn et al., 2014; Rahman et al., 2014; Zhang et al., 2016; Zaggia et al., 2016; Franke et al., 2019). While it is recognized, that membrane filtration techniques like nanofiltration and reverse osmosis and adsorption to synthetic materials like anion exchange resins show superior PFAS removal compared to GAC, filtration through GAC remains a go-to method, as it is reliable, straight forward to operate and has been used in drinking water production for decades (Merino et al., 2016; Crittenden et al., 2012). GAC treatment also entails a commercially available method for regeneration without creating an additional waste stream. Today, filtration through GAC is commonly applied in DWTPs treating PFAS contaminated water. If deployed as a chemical barrier for the removal of PFASs, GAC filtration, however, needs to be closely monitored for PFAS breakthrough and regenerated or replaced relatively frequently. Short-chain PFASs (PFASs with ≤ 6 carbons and PFCAs with ≤ 7) break through rapidly (Flores et al., 2013; Zaggia et al., 2016) and even long-chain PFASs break through after a limited time (Takagi et al., 2011; Eschauzier et al., 2012; Rahman et al., 2014; Zaggia et al., 2016; McCleaf et al., 2017). Drinking water treatment and respective GAC filtration should therefore be optimized to the best extent, not the least in order to save costs arising due to the frequently necessary regeneration or exchange of filter material (Takagi et al., 2011; Rahman et al., 2014). Until this point, little is known concerning optimization and long-term removal efficiency of PFASs in full-scale DWTPs.

In this study, the removal of PFASs in a full-scale DWTP in the City of Uppsala, Sweden, was examined. PFAS contamination of groundwater in Uppsala was detected in 2012 and is likely linked to historic use of PFAS-containing AFFFs in the aquifer catchment (Gyllenhammar et al., 2015). Affected wells show sum concentrations of up to 250 ng L^{-1} PFASs. After process modifications, Uppsala's Bäcklösa DWTP began treating water from two contaminated wellfields in April 2015 using ten GAC gravity filters. PFAS concentrations were monitored throughout the full treatment train where evaluated treatment methods included aeration, softening and filtration, sand filtration, the plant's GAC filtration system and a disinfection step. The specific objectives of this study included to i) investigate the removal of PFAS in a full-scale DWTP, ii) evaluate the long-term performance of GAC for the removal of PFASs, iii) assess the impact of the GAC age and flow-rate on the removal of PFASs, and iv) to estimate the operations costs for the removal of PFASs using GAC at different treatment scenarios.

2. Materials and methods

2.1. PFAS analytes

In total, 27 PFASs were analyzed including C_4 , C_{6-8} , C_{10} PFASs (i.e. PFBS, PFHxS, PFHpS, PFOS, PFDS), C_{3-13} , C_{15} , C_{17} PFCAs (i.e. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrIDA, PFTeDA, PFHxDA, PFOcDA), perfluorooctanesulfonamide (FOSA), methyl- and ethyl FOSA (i.e. MeFOSA, EtFOSA), perfluorooctanesulfonamidoacetic acid (FOSAA), methyl- and ethyl FOSAA (i.e. MeFOSAA, EtFOSAA), methyl- and ethyl perfluorooctanesulfonamido-ethanol (MeFOSE, EtFOSE) and 6:2 FTSA (all > 98%, Wellington Laboratories, Canada). For internal calibration, 16 mass-labelled PFASs internal standards (IS) were used: $^{18}\text{O}_2$ -PFHxS, $^{13}\text{C}_4$ -PFOS, $^{13}\text{C}_4$ -PFBA, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_2$ -PFUnDA, $^{13}\text{C}_2$ -PFDoDA, $^{13}\text{C}_8$ -FOSA, d_3 -N-MeFOSA, d_5 -N-EtFOSA, d_3 -N-MeFOSAA, d_5 -N-EtFOSAA, d_7 -N-MeFOSE and d_9 -N-EtFOSE (all > 98%, Wellington Laboratories, Canada). In addition, a mass-labelled injection standard (InJS) (i.e. $^{13}\text{C}_8$ -PFOA: 97.9%, Wellington Laboratories, Canada) was applied. For details on PFAS analysis, see Tables S1 and S2 in the Supporting Information (SI).

2.2. Sampling

The DWTP contains five treatment steps: aeration, softening (fluidized bed pellet reactor type), dual media (granular carbon/sand) filtration, GAC filtration and disinfection with free chlorine. Samples were taken to investigate i) the full-scale treatment efficiency on November 24, 2016 (Table S4 in the SI), ii) the influence of flow-rate on the removal of PFASs between 28 November and December 21, 2016, and iii) long-term performance of granular activated carbon (GAC) between April 28, 2015 and February 7, 2017 (Fig. 1, Table S3 in SI). Samples taken for i) and ii) were analyzed at SLU, while samples for investigation of iii) were sent to the accredited commercial laboratories of ALS Scandinavia (see below). In all cases, samples were collected in clean 1 L polypropylene (PP) bottles and stored in the dark at 8°C until analysis. Evaluation of the PFAS removal performance of the full-scale DWTP is based on grab samples during one day and should not be considered representative of the PFAS concentrations over time.

PFAS concentrations were determined for samples taken after or just downstream of each respective process stage with the exception of the sample taken after the disinfection step, which was taken after free chlorine disinfection and after storage in an underground reservoir which has a residence time of approximately 6 h. The removal efficiencies of each GAC filter and of the whole DWTP are listed in Tables S5 and S6 in the SI.

The performance of one “young” GAC filter (GAC 10, 63 operation days, 5 725 bed volumes treated) and one “old” GAC filter (GAC 5, 264 operation days, 21 971 bed volumes treated) consisting of Filtrasorb® 400 were evaluated at full-scale. Flow-rates of initially 35 L s^{-1} to 45 L s^{-1} (1st sampling round, $n = 6$), were first adjusted to 30 L s^{-1} (2nd, $n = 12$) and then to 15 L s^{-1} (3rd, $n = 9$). The average flow-rates on the sampling days were calculated based on the following equation:

$$r = \frac{V_{\text{treated}}}{t} \quad (1)$$

where r [L s^{-1}] is the average flow-rate, V_{treated} [L] is the volume treated in the period between the sampling days and t [s] is the time in operation in the period between the sampling days. After each change of the flow-rate, the GAC filter adsorption process was allowed to stabilize. PFAS removal was assumed to stabilize when

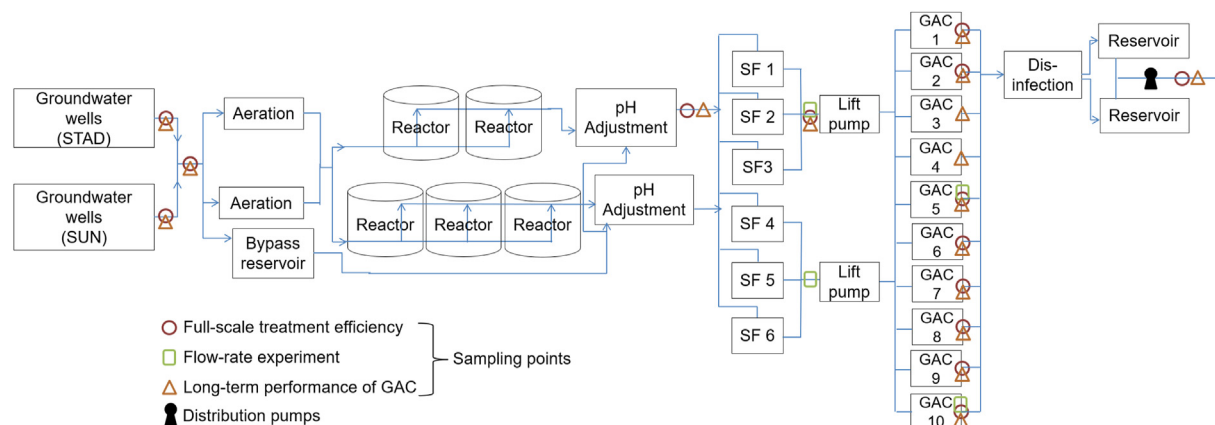


Fig. 1. Conceptual scheme of the drinking water treatment plant Bäcklösa in Uppsala, Sweden. Samples were taken to investigate the i) full-scale treatment efficiency (circles), ii) the influence of flow-rate on the removal of PFASs (squares) and iii) long-term performance of granular activated carbon (GAC) (triangles). SF = dual media filtration, GAC = granular activated carbon, STAD = Stadstädgården, SUN = Sunnersta.

Table 1

Specifications of the granular active carbon materials evaluated in this study, Filtrasorb® 400 (F400) (Calgon Carbon Corporation, 2004) and AquaSorb® 2000 (A2000) (Jakobi Carbons Group, 2012).

	F400	A2000
GAC ID number (Fig. 1)	1–6, 10	7–9
Iodine number [mg g^{-1}]	1050	1000
Surface area [$\text{m}^2 \text{g}^{-1}$] ^a	1050	950
MB number [mL g^{-1}] ^b	300	180
Effective size [mm]	0.6–0.7	0.6

^a Surface area analysis according to Brunauer, Emmett and Teller (BET) (Brunauer et al., 1938).

^b MB = Methylene blue.

UV adsorption stabilized. UV adsorption at 254 nm was utilized since it was a quick and accurate measurement technique. After stabilization was reached (varying between 3 and 7 days), water samples were collected and analyzed for PFASs.

2.3. Granular activated carbon (GAC) filters

The DWTP in Bäcklösa, Uppsala, Sweden has ten GAC filters with two different GAC types which are operated in parallel (Fig. 1). Six GAC filters are typically in operation at the same time. The types of GAC material applied during the course of this study were Filtrasorb® 400 and AquaSorb® 2000 (Table 1 (Calgon Carbon Corporation, 2004; Jakobi Carbons Group, 2012)).

GAC treatment efficiency was evaluated using the parameters bed volumes treated ($BV_{treated}$) and empty bed contact time (EBCT) according to Equations (2) and (3), respectively. EBCT indicates the residence or contact time of the water with the GAC granules (Applied Membranes Inc, 2020).

$$BV_{treated} = \frac{V_{treated}}{V_{GAC}} = \frac{r \cdot t}{V_{GAC}} \quad (2)$$

$$EBCT = \frac{V_{GAC}}{r} \quad (3)$$

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

Removal efficiency (RE [%], Equation (4)) of a GAC filter was calculated by considering the concentration of a substance after the dual media filtration step, i.e. before GAC filtration (incoming

water) and after GAC filtration (outgoing water):

$$RE = \frac{c_0 - c}{c_0} \cdot 100 \quad (4)$$

where c_0 [ng L^{-1}] is the concentration of the substance in the incoming water and c [ng L^{-1}] is the concentration of the substance in the outgoing water.

2.4. Sample preparation and analyses

2.4.1. PFAS analysis

Water samples sent to the commercial laboratory ALS Scandinavia were analyzed according to a method accredited for PFAS analysis. For more details, the authors refer to the laboratory (ALS Scandinavia Danderyd, 2017; ALS Scandinavia, 2017). Water samples processed at SLU were filtered through glass microfiber filters (47 mm diameter, Whatman™, China). After filtration, samples were extracted through solid phase extraction (SPE) cartridges (Oasis® WAX, 6 cc, 500 mg, 60 μm ; Waters, Ireland) using an established method described elsewhere (Ahrens et al., 2010). Briefly, the cartridges were preconditioned with 4 mL ammonium hydroxide solution (0.1% in methanol), 4 mL methanol and 4 mL Millipore water. Before loading the water samples, 100 μL of the IS mix (20 ng mL^{-1} for individual mass-labelled PFAS) were added to the samples in the PP bottles. 500 mL of the water samples were then loaded onto the cartridges with one drop per second. The cartridges were washed by adding 4 mL 25 mM ammonium acetate buffer in Millipore water. After drying the cartridges through centrifugation (3000 rpm, 2 min), the analytes were eluted from the cartridges by using 4 mL methanol and 8 mL 0.1% ammonium hydroxide in methanol. Finally, the samples were concentrated to 0.5 mL by evaporating with nitrogen (N-EVAPTM112; Organomation Associates, Inc., USA). Before injecting the samples into the LC-MS/MS, 10 μL of the InjS (200 ng mL^{-1}) were added. Blanks ($n = 7$) were processed in the same way as the natural samples but without loading the cartridge with any water. PFASs were analyzed using high performance liquid chromatography (HPLC) coupled to a triple quadrupole and an electrospray ionisation interface in negative-ion mode ((-)ESI-MS/MS, Agilent 6460 Triple Quadrupole System, Palo Alto, CA, USA) as described elsewhere (Ahrens et al., 2016). For HPLC (Agilent Technologies 1200 Series, Palo Alto, CA, USA), a Hypersil Gold pre-column (10 \times 2.1 mm, 5 μm particle size, Thermo Scientific, Waltham, MA, USA) connected to a Betasil C18 column (50 \times 2.1 mm, 5 μm particle size, Thermo Scientific,

Waltham, MA, USA) was used. For calibration, five standards with concentrations from 0.05 to 48 ng mL⁻¹ (injected absolute 0.5 pg–480 pg on column) were measured. PFHpS was semi-quantified using the response factors of PFHxS. The branched (B) isomers of PFHxS, PFOS and FOSA were semi-quantified using the response factor of the corresponding linear (L) isomer. Details for instrument parameters and transitions of the analytes can be found in Table S1 in the SI.

2.4.2. TOC and UV absorbance at 254 nm

For the TOC-analysis a catalytic combustion analyzer (TOC-VCPH with the autosampler ASI-V, Shimadzu, Japan) was used. Both, the total carbon (TC) and the inorganic carbon (IC) were measured after acidification (200 µL 2 M HCl in 20 mL) and purging with a carrier gas (purified air). Subsequently, the TOC concentration was calculated by subtracting the IC concentration from the TC concentration. Because of the purging step, the determined TOC is non-purgeable organic carbon (NPOC). In the following, NPOC will only be referred to as TOC as the amount of volatile OC is below the precision of the machine employed in this study (< 0.3 mg L⁻¹). UV absorbance at 254 nm was determined with a combined photometer-fluorometer (Aqualog, Horiba Scientific) following the method described previously (Lavonen et al., 2015). As particulate carbon in samples that have passed a GAC filter is usually very low, NPOC is considered equivalent to DOC. According to a method described by Eaton (1996), UV absorbance at 254 nm can be used to predict DOC concentrations, as it is highly proportional to DOC concentration. In this study, the correlation between UV absorbance at 254 nm and DOC concentrations was $\text{DOC} [\text{mg L}^{-1}] = 44 \cdot \text{UV} [\text{cm}^{-1}] + 0.22$ with $R^2 = 0.91$ (see Fig. S1 in the SI and for more details on TOC and UV absorption analysis, see text in the SI).

2.5. Quality control

The applied PP bottles used for PFAS analysis at SLU were machine washed and rinsed with methanol three times. All glassware and glass microfiber filters were heated at 400 °C and prior utilization, all glassware was rinsed with methanol. PFAS concentrations found in the blank samples were in the range of 0–8 ng L⁻¹. The method detection limit (MDL) was calculated based on the concentrations measured in the blanks (Equation (5)).

$$\text{MDL} = \bar{x}_{\text{blanks}} \cdot 3s \quad (5)$$

where \bar{x}_{blanks} [ng L⁻¹] is the average concentration found in the blank samples and s is the standard deviation. When a compound was not detected in the blanks, the lowest detectable calibration point (signal to noise ratio > 8) in the instrument was used as MDL (0.05 ng L⁻¹). The MDLs ranged between 0.05 and 15 ng L⁻¹. The recovery for the IS compounds ranged from 36% (Et-FOSA) to 135% (PFNA) (for details see Table S1 in the SI and Gobelius et al., 2018). Variations between the samples were calculated based on the collected duplicate or triplicate samples and are included in presented graphs. UV control analyses showed no variation and internal EDTA controls (nominal concentration 10 mg L⁻¹) during TOC analysis were in the range from 9.5 to 10 mg L⁻¹.

2.6. Statistical analysis

For statistical analyses, only PFASs with detection frequencies higher than 50% were evaluated. Concentrations below the MDL were set to 0.5 · MDL if not noted differently. Linear regression parameters were calculated with one-way ANOVA (analysis of variance). Pearson correlation was performed for correlation analysis between PFAS and TOC concentrations or UV absorbance

(254 nm). Half-times for GAC filters (half-time [BV_{treated}] until 0% removal of a respective compound can be expected) were calculated according to Ahrens et al. (2009) by performing a linear regression with the logarithmic values of removal efficiencies over BV_{treated} (Equation (6)):

$$t = -\frac{\ln(2)}{m} \quad (6)$$

where $-1/m$ is the slope of the linear regression. Significant changes were defined with $p < 0.05$ with a confidence level of 95%. Half-times in operating days were derived by converting BV_{treated} into days by multiplying with the average flow-rate (given in BV_{treated} per day). Generally, operation time was defined as the time filters produced > 500 m³ water per day in order to account for operation stops of the filters. Next to the operating half-times, treatment goals were defined as receiving an outgoing \sum_{11} PFAS concentration of 10, 25, 50 or 85 ng L⁻¹, respectively, for each filter. For deriving the amount of BV_{treated} when each of the treatment goals was reached, a linear regression was performed for the relationship of outgoing \sum_{11} PFAS concentration vs. BV_{treated}. Concentrations below MDL (removal efficiency near 100%) were disregarded in the two latter analysis as a linear regression for calculating the half-times and constant increase in outgoing concentrations should only be performed as soon as a decrease in performance is observed. Calculations and graphical visualizations were performed with the R software and the RStudio interface (R Development Core Team, 2016; R Studio Team, 2016). Smooth functions used for deriving the mean removal efficiency during GAC treatment applied the Local Regression (Loess) approach (Cleveland et al., 2017).

2.7. Economic analysis

Unit regeneration costs were calculated based on actual regeneration cost per Filtrasorb® 400 filter (i.e. 25 000 euro) divided by the volume of water treated by the filter up to each break through goal (10 ng L⁻¹, 25 ng L⁻¹, 50 ng L⁻¹, and 85 ng L⁻¹). Annual regeneration cost at Bäcklösa DWTP was calculated by multiplying unit regeneration costs by the actual annual volume of water treated at Bäcklösa DWTP (i.e. 7 million m³). Annual operations costs were defined as annual regeneration cost plus the uniform annual cost of the actual initial purchase cost of virgin GAC for one filter (40 000 euros) over 10 years with an interest rate of 5% per year. Calculations are based on an exchange rate of 1 euro = 9.86 SEK. Finally, annual unit operations costs (in the following simplified to *unit costs*) were calculated as annual operations cost as defined above divided by the actual annual volume of water treated at Bäcklösa DWTP (i.e. 7 million m³).

3. Results and discussion

3.1. Removal of PFASs in a full-scale DWTP

An evaluation of the full-scale treatment indicated that aeration, softening, pH adjustment and sand filtration did not decrease initial PFAS concentrations efficiently (Fig. 2). This was expected as it has been reported previously that these conventional treatment steps do not remove PFASs (Eschauzier et al., 2012; Appleman et al., 2014). However, GAC filtration (see Table 1 and Table S7 in the SI for individual filter characteristics) was effective in removing PFASs with removal efficiencies ranging from 67% to 100% (removal below MDL) depending on the filters' respective time in operation (BV_{treated}). This is also in agreement with previous studies (Eschauzier et al., 2012; Appleman et al., 2014; McCleaf et al., 2017).

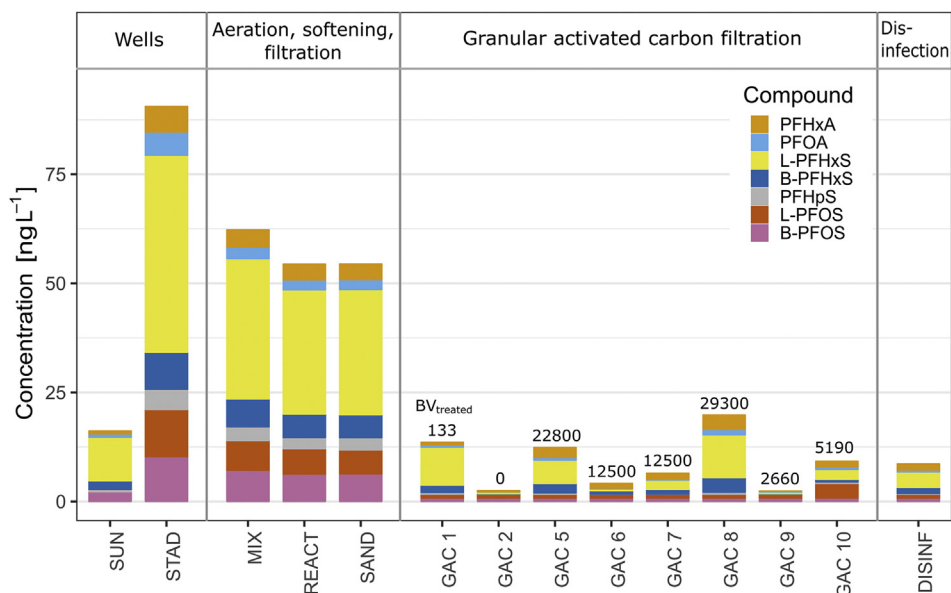


Fig. 2. PFAS concentrations detected in each step of the drinking water treatment plant (DWTP) Bäcklösa, Uppsala, Sweden. The incoming raw water from two wellfields SUN = Sunnersta, STAD = Stadsträdgården is mixed (MIX). The treatment involves aeration, softening and pH adjustment steps (REACT), followed by dual media filtration (SAND), several granular activated carbon filters (GAC) and finally a disinfection step (DISINF) (see also Fig. 1). GAC 1 and 2 were not in operation and the outgoing water of those filters was directed to the waste. Numbers on top of the bars indicate times in operation for the individual filters, expressed in bed volumes treated at the point of analysis ($BV_{treated}$).

Comparing the removal efficiency of individual PFASs, in particular the shorter chained PFCAs (i.e. PFHxA, PFHpA) showed lower removal efficiencies for GAC filters with large $BV_{treated}$ and PFASs were generally retained better than PFCAs. For example, GAC 9 (30 d; 2 660 $BV_{treated}$) removed > 99% of \sum PFAS as well as of short chained PFCAs (i.e. PFHxA, PFHpA), whereas GAC 8 (360 d; 29 300 $BV_{treated}$) removed 67% of \sum PFAS, where \sum PFCAs (i.e. PFHxA, PFHpA, PFOA) were removed to 22% (7.0% for PFHxA) and \sum PFASs (i.e. PFHxS, PFHpS, PFOS) to 72%. When comparing removal efficiencies for linear vs. branched isomers, it was found that the removal efficiency for L-PFHxS was higher (i.e. ranging from 66% for GAC 8–100% for GAC 9) compared to B-PFHxS (i.e. from 37% for GAC 8–100% for GAC 9). This is in agreement with previous studies which found that the removal of branched PFASs through GAC is less effective than for linear PFASs due to different adsorption strengths (Eschauzier et al., 2012; McCleef et al., 2017). McCleef et al. (2017) found that the branched isomers of PFHxS, PFOS and FOSA showed a 8–13% lower removal efficiency than the linear isomers during GAC treatment in pilot-scale. In summary, as shown in Fig. 2, “younger” GAC filters (smaller number of $BV_{treated}$ after regeneration) had greater total removal efficiencies compared to the “older” GAC filters and were more successful in removing short-chained PFCAs (i.e. PFHxA, PFHpA). When comparing the two different GAC materials applied in the plant, it was evident that water treated by Filtrasorb® 400 (GAC6) showed slightly lower outgoing \sum PFAS concentrations (2.1 $ng\ L^{-1}$) than the AquaSorb® 2000 material (GAC7; 4.9 $ng\ L^{-1}$) despite identical operation parameters. One explanation for this observation could be that the GAC material Filtrasorb® 400 has a more defined effective particle size and wider pore size distribution as well as a higher surface area of 1050 $m^2\ g^{-1}$ for enhanced PFAS removal compared to AquaSorb® 2000 with 950 $m^2\ g^{-1}$ (Table 1). An interesting finding was that \sum PFAS concentration in the full-scale treatment was significantly correlated with TOC concentration (Pearson correlation coefficient $r_p = 0.80$, $p < 0.05$) and UV absorption (254 nm) ($r_p = 0.82$, $p < 0.05$). More specifically, concentrations of individual PFASs were significantly correlated with TOC concentration and UV absorbance

($p < 0.05$) ranging from $r_p = 0.72$ (L-PFOS) to $r_p = 0.88$ (B-PFHxS) for UV absorbance and from $r_p = 0.73$ (L-PFOS) to $r_p = 0.85$ (PFHxA, B-PFHxS) for TOC concentration. This is similar to the correlation reported by Anumol et al. (2015) between PFOS and PFOA with UV absorbance (254 nm) ($r_p = 0.84$ and 0.93, respectively). Thus, removal of organic carbon as determined by TOC and UV absorbance (254 nm) could potentially be used as a temporal surrogate for measuring PFAS removal efficiency, as it is both more practical and economical to measure compared to PFAS analysis. It should be kept in mind, that the relationship between the adsorption of micropollutants and organic matter might be dependent on organic matter type and composition (Matsui et al., 2002; Zietzschmann et al., 2016). The relationship between PFAS removal and removal of TOC or UV absorbance (254 nm) should therefore be determined for local conditions. Generally, measurements of TOC or UV absorbance (254 nm) should only complement and not replace the analysis of PFASs. More details of UV and TOC concentrations from each treatment stage and GAC filter for the full-scale treatment can be found in Fig. S1 and Table S8 in the SI.

3.2. Long-term performance of GAC for the removal of PFASs in a full-scale DWTP

Fastest decreasing removal efficiencies were observed for PFHxA, which was the only substance showing complete breakthrough (removal efficiency < 0%) at a GAC treatment time between 20 000 and 30 000 BV for five of the six GAC filters monitored for this specific part of the study (Fig. 3). Rapidly decreasing removal efficiencies were also observed for PFBS with removal efficiencies of 20% at approximately 30 000 BV. The removal efficiency for PFASs with longer chains, i.e. PFOA, PFHxS and PFOS, did not decline as rapidly as the above-mentioned PFASs. This is in line with earlier studies and could be due to better adsorption capacity of the GAC material for long chained PFASs, replacement of shorter chained by long chained PFASs or general blockage of pores by organic matter or other micropollutants (Eschauzier et al., 2012; McCleef et al., 2017). PFOS was observed to

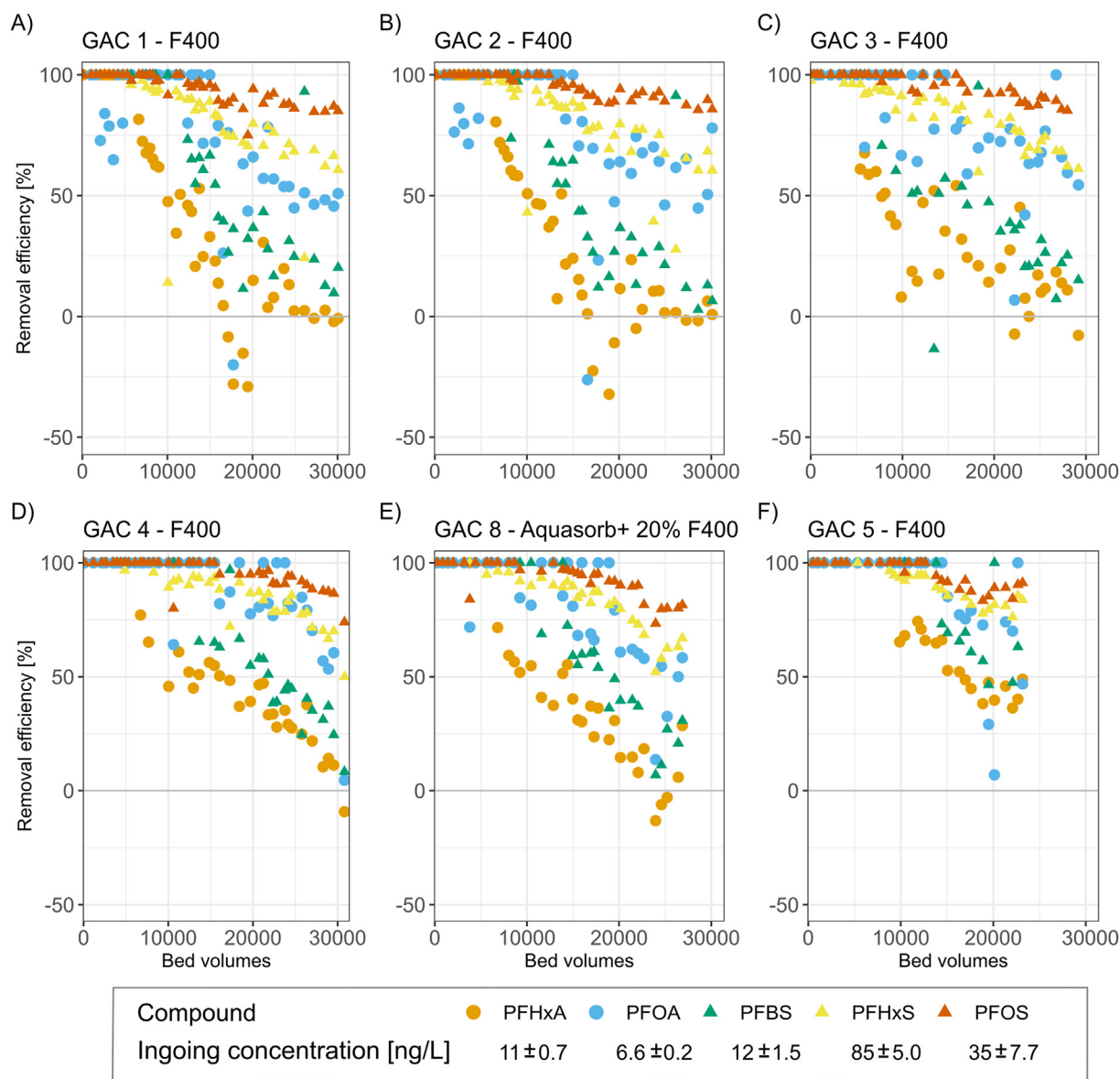


Fig. 3. PFAS removal efficiencies of A) GAC 1 (Filtrisorb® 400; “F400”), B) GAC 2 (F400), C) GAC 3 (F400), D) GAC 4 (F400), E) GAC 8 (80–90% AquaSorb® 2000 (“AquaSorb”) + 10–20% F400) and F) GAC 5 (F400) for individual PFASs (detection frequency > 50%) (circle: PFCAs, triangle: PFSAs) for the DWTP Bäcklösa, Uppsala, Sweden. Average concentrations going into the GAC filters are given in the legend (arithmetic mean ± standard deviation in ng L^{-1}).

be retained best of all frequently detected PFASs by all GAC filters and removal was at 80–100% even after 30 000 treated BV for all GAC filters. Despite lower initial concentrations, PFCAs showed faster decreasing removal efficiencies compared to PFSAs (e.g. PFHxA < PFBS and PFOA < PFHxS), which has been observed before and might be explained by Pearson’s concept of soft and hard acids or bases (Du et al., 2014). It can be argued that PFSAs (hard bases) are retained better than PFCAs (soft bases) by the oxide surface (hard acid) of the GAC (Du et al., 2014). Further adsorption mechanisms include the formation of hydrogen bonds between functional groups on the GAC surface (e.g. sulfides, halogenated hydrocarbons and non-aromatic ketones) and the hydrophilic group of PFCAs and PFSAs (Zhang et al., 2016a). For comparability, removal efficiencies at the greatest common $BV_{treated}$ of the six GAC filters studied are given in Table S9 in the SI. Generally, such comparisons should be made with care, as ingoing concentrations and water quality parameters like organic matter content are

known to experience seasonal changes and filters were operated during slightly different times (Table S9 in the SI). This is apparent when looking at the total PFAS loading individual filters experienced over time, where e.g. GAC 1 and GAC 2 experienced similar PFAS loadings (Fig. S2 in the SI), which reflects in the breakthrough curves, even on a concentration normalized basis as expressed by removal efficiency (Fig. 3). These findings suggests an influence of other water constituents, like organic matter loading, to be responsible for the observed performance differences (Corwin and Summers, 2010).

Individual estimated operation times at which the total removal efficiency reaches 50% (operation half-times) were calculated assuming a logarithmic decrease in removal efficiencies for individual PFASs and can be found in Table S10 in the SI. Operation half-times increased with increasing chain length for both PFCAs (i.e. PFHxA (20 300 BV) < PFOA (68 300 BV)) and PFSAs (PFBS (22 300 BV) < PFHxS (91 600 BV) < PFOS (284 000 BV)).

3.3. Influence of GAC flow-rate for removal of PFASs, TOC and UV absorbance

For the evaluation of the influence of the PFAS removal by the applied flow-rate through the full-scale GAC filters, flow-rate experiments were performed on one “old” (264 days of operation; 21 971 $BV_{treated}$) and one relatively “young” GAC filter (63 days of operation; 5 725 $BV_{treated}$), see also Table S11 in the SI. As expected, removal efficiencies increased with decreasing flow-rate and thus longer EBCT (Fig. 4). For instance, a decrease of 10 L s^{-1} from 39 to 29 L s^{-1} led to an average increase of 14% and 6.5% in total PFAS removal efficiency for the “old” and the “young” GAC filter, respectively. Greatest changes were observed for PFHxA, which showed a 15% and 25% better removal efficiency for the “old” and the “young” filter, respectively. For each 10 L s^{-1} decrease in flow-rate the removal efficiency for PFHxA increased by an average of 19% and 2.5% for the “old” and “young” GAC filter, respectively. The “young” GAC filter was generally less effected by the change in flow-rate compared to the “old” GAC filter. Both GAC filters showed high PFOS removal of $>98\%$, with the exception of the largest flow-rate tested in the “old” filter, where L-PFOS and B-PFOS were removed by 91 and 76%, respectively.

These results highlight a beneficial influence on adsorption kinetics on PFAS adsorption, where with higher EBCT the water spends more time in contact with GAC particles and thus PFASs and other substances have more time to diffuse into pores and adsorb onto sorption sites. This might further relate to diffusion limitations “older” GAC filters experience, due to the total organic matter loading. Longer contact times will allow for longer diffusion times thus creating a diffusion gradient beneficial for PFAS adsorption. Substantially lower flow-rates of 7.5 L s^{-1} for the “young” GAC filter showed no further increase in PFAS removal efficiencies, which indicates that PFAS adsorption is dominated by thermodynamic mechanisms, rather than kinetics at flow-rates of below 15 L s^{-1} for the “young” GAC filter. Naturally, operation flow-rates cannot be lowered indefinitely since at some point water production would be too low. Results of this study indicate however, that “older” GAC filters could be operated for a longer time than they commonly are by lowering the flow-rates, thus expand their service lifetime, and still provide sufficient PFAS removal.

The Swedish drinking water guideline is 90 ng L^{-1} for $\sum_{11}\text{PFAS}$, however drinking water providers in the City of Uppsala, Sweden, are setting even stricter treatment goals in their treatment plants. On average, the treatment goals of 25 and 50 ng L^{-1} were reached at 15 176 and 23 231 $BV_{treated}$, respectively. The average amount of $BV_{treated}$ when reaching the treatment goal of outgoing $\sum_{11}\text{PFAS} <$

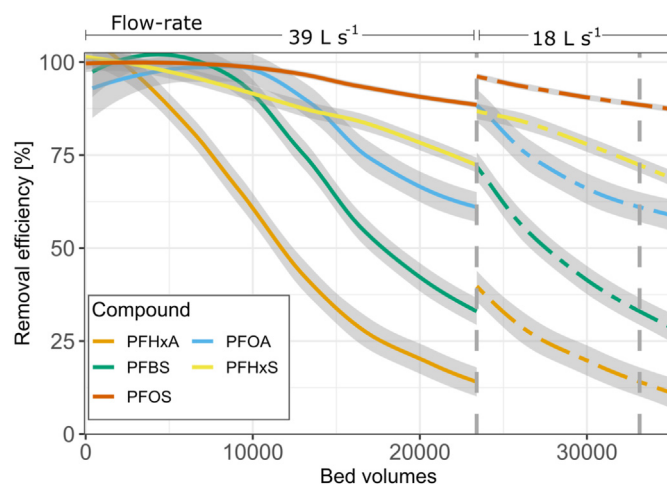


Fig. 5. Mean observed and predicted decrease in PFAS removal efficiency for all GAC filters monitored in this study. Grey shaded curves illustrate the 95% confidence intervals. Dashed lines depicted for bed volumes $> 23\ 200$ illustrate the expected behavior of removal efficiencies if flow-rates were decreased from 39 to 18 L s^{-1} at 23 200 $BV_{treated}$. Vertical dashed lines mark the average maximum amount of $BV_{treated}$ for reaching the treatment goal of outgoing $\sum_{11}\text{PFAS} < 50\text{ ng L}^{-1}$ for a flow of 39 L s^{-1} and a subsequent decrease in flow-rate to 18 L s^{-1} , respectively.

50 ng L^{-1} (23 231) is close to the $BV_{treated}$ of the “old” GAC filter examined in the flow-rate experiment discussed above (21 971). By decreasing the flow-rates from 39 to 18 L s^{-1} (Fig. 4), the average service lifetime of a GAC filter could potentially be extended from 23 231 to 32 976 $BV_{treated}$ targeting a treatment goal of 50 ng L^{-1} , assuming a similar decrease in removal efficiency as prior a decrease in flow-rate (Fig. 5). Based on this estimation, service life times of “old” GAC filters could potentially be increased by an additional 9 745 $BV_{treated}$ and thus expand the filter’s service lifetime by almost half for the treatment goal of outgoing $\sum_{11}\text{PFAS} < 50\text{ ng L}^{-1}$. Empirical data collected for one of the filters in the full-scale DTWP suggests this assumption to hold for certain PFAS compounds, see Fig. S3 in the SI. Similar estimations could be performed for other treatment goals, in case one would have data on the influence of flow-rate for different GAC operational ages at which those were reached. Takagi et al. (2011) proposed to renew GAC filters two or three times yearly. As shown in this work, estimation of when or how often to renew GAC filters should be based on $BV_{treated}$ in combination with the applied flow-rate and treatment goal rather than solely operational time. When looking at the influence of the operating flow-rate on other water quality

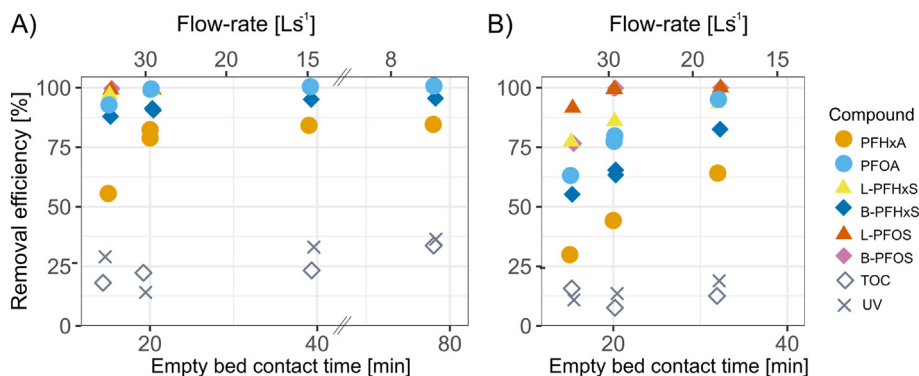


Fig. 4. Flow-rate experiment showing the removal efficiency of PFASs, total organic carbon (TOC) and UV absorption at 254 nm in % of A) a “young” GAC filter (63 operation days, 5 725 $BV_{treated}$) and B) an “old” GAC filter (264 operation days, 21 971 $BV_{treated}$) depending on the evaluated empty bed contact time (EBCT) in minutes (corresponding flow-rate in L s^{-1} shown on the upper axis). Duplicate samples were taken for each experiment with EBCT = 20 min and results from both samples are plotted.

parameters, it was found that lower flow-rates increased the removal efficiency not only for PFASs but also for organic carbon (Fig. 4). Significant changes ($p < 0.05$) in the removal of organic carbon (i.e. TOC) were observed when changing the EBCT in the “young” GAC filter from 39 to 7.5 L s⁻¹ ($p = 0.017$; $r_p = 0.94$). The removal of TOC and substances responsible for UV light absorption at 254 nm was generally lower for the “older” GAC filter, for which a change in EBCT did not have a significant effect on the removal efficiency for either of the parameters. This is most likely because the “old” GAC filter already was saturated with organic matter at the time of the flow-rate experiments.

3.4. GAC operations costs for the removal of PFASs

Operational parameters and costs were derived for GAC 1 at Bäcklösa DWTP, during operation from April 28, 2015 till June 7, 2016 (406 days). Operation of this GAC filter serves as an illustrative example and is summarized in Table 2 for four different treated water goals: 10, 25, 50 and 85 ng L⁻¹, respectively. At the Bäcklösa DWTP, approximately 7 million m³ drinking water are produced annually and distributed to about 80 000 consumers. The treatment goal for the plant is an average of 25 ng L⁻¹ ∑₁₁PFAS while the regulatory limit is 90 ng L⁻¹ for ∑₁₁PFAS. As shown in Table 2, the annual operation cost for the plant with a 25 ng L⁻¹ treatment goal is 0.058 euro per m⁻³ treated. Treatment goals were the key factor determining service volume as shown by the 75, 244, and 318% greater service volume with a treatment goals of 25, 50, and 85 ng L⁻¹, respectively, as compared to a 10 ng L⁻¹ treatment goal. Similarly, annual operations cost, which are dominated by regeneration costs, are lower if a higher treatment goal is adopted. Specifically, for treatment goals of 25, 50, and 85 ng L⁻¹, the annual operations costs are 42, 70, and 76% less, respectively, as compared to the cost with a treatment goal of 10 ng L⁻¹. This shows the impact of lowering or increasing regulatory levels for PFAS on operations costs.

Note that Table 2 costs are similar to those cited by McNamara et al., (2018) who estimated an operation cost of 0.025 euro m⁻³ (0.08 USD/1000 gal) for a simulated regenerated GAC filter, and estimated 0.038 euro m⁻³ (0.12 USD/1000 gal) for a simulated virgin GAC filter in order to achieve a water treatment goal of 70 ng L⁻¹ for combined PFOA and PFOS in the treated water for a dual vessel lead-lag treatment.

3.5. Optimization of treatment costs

As discussed earlier, a number of factors affects the length of

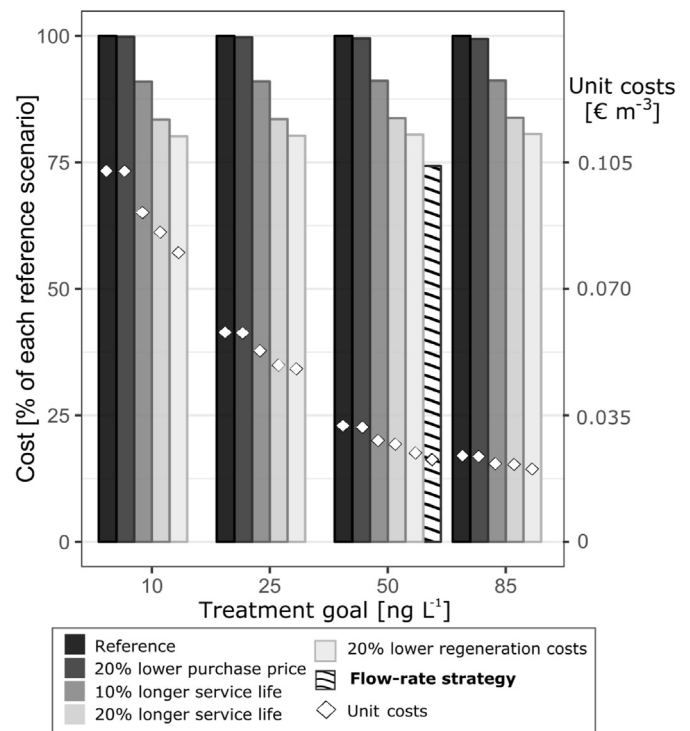


Fig. 6. Treatment costs for GAC 1 depending on treatment goal. Bars describe the relative costs for each cost scenario compared to the current (Reference) scenario. Diamonds illustrate estimations of the respective annual unit operations costs in the Bäcklösa drinking water treatment plant, i.e. unit costs.

service of a GAC filter, specifically the adsorption capacity of the GAC, the treatment goals, the flow operation of the filters (EBCT), initial PFAS concentrations in the raw water and general water quality. In order to explore the GAC 1 unit costs, various cost scenarios were calculated for different treatment goals assuming hypothetically 20% lower cost for virgin GAC, 20% lower GAC regeneration cost, 10 and 20% longer service life to treatment goal, and if the service life is extended using the low flow strategy depicted in Fig. 5. Relative cost savings for each treatment goal hypothetically achieved by the different scenarios are shown in Fig. 6. Absolute unit cost are depicted as diamonds in Fig. 6 and the results again illustrate the dominating effect of treatment goals on treatment costs.

For the specific treatment goal of 50 ng L⁻¹, it can be seen that

Table 2
GAC1 treatment operational parameters and costs for PFAS removal.

Parameter	GAC filter 1 Filtrasorb® 400			
Treated water goal [ng L ⁻¹ ∑ ₁₁ PFAS]	10	25	50	85
Average EBCT [min]	20	24	21	20
Inlet water average [ng L ⁻¹ ∑ ₁₁ PFAS]	216	189	160	159
Service volume treated [1000 m ³]	247	433	850	1034
BV _{treated}	7 070	12 400	24 300	29 600
Carbon use rate [dry kg m ⁻³ treated]	0.074	0.042	0.021	0.018
Total ∑ ₁₁ PFAS loading [μg PFAS g ⁻¹ dry GAC]	2.9	4.2	6.0	6.9
Unit regeneration costs [euros m ⁻³ treated] ^a	0.10	0.06	0.03	0.02
Annual regeneration cost at Bäcklösa DWTP (1000 euros year ⁻¹) ^b	707 000	404 000	206 000	169 000
Annual operations cost at Bäcklösa DWTP including regeneration and initial purchase of virgin GAC (1000 euro year ⁻¹) ^c	712 000	409 000	211 000	174 000

^a GAC regeneration cost 714 euro m⁻³ wet GAC.

^b GAC regeneration cost for treatment of 7 million m³ water per year at Bäcklösa DWTP.

^c Virgin GAC cost 1142 euro m⁻³ wet GAC and service life 10 years with interest rate 5%.

the greatest cost savings, 26%, appears to be provided by adopting a strategy of adjusting flow-rates to extend the service life of the filter without exceeding the treatment goal (Fig. 5). A 20% reduction in regeneration costs reduces the unit costs by 20% in the case of this specific study while a reduction in the cost of virgin GAC has little effect. Utilization of a more efficient GAC which provides a 10% longer service volume decreases unit costs by 9% while a GAC providing 20% greater service volume reduces unit costs by 16%. Thus, an initial greater cost for high quality virgin GAC can be offset if greater service volume is provided. Similarly, it is economically worthwhile to reduce the cost of regeneration by competitive bidding or even by cooperation between water producers to establish joint-owned regeneration facilities.

4. Conclusions

This study confirmed that conventional treatment techniques are not efficient for PFAS removal in a full-scale DWTP. However, GAC filters present a reliable treatment method for the removal of PFASs, which is straight forward to operate and can utilize the existing competitive GAC market to minimize operations costs. The removal efficiency for GAC filters evaluated in this study was higher for long chained PFASs than for short chained PFASs and PFASs were removed better than PFCAs. Adjusting the flow-rate through two full-scale GAC filters of different operational ages showed a positive correlation of PFAS removal with lower flow-rates (higher EBCT). The “young” GAC filter was less effected by the change in flow-rates, while the removal efficiency of the “old” GAC filter could be increased substantially by decreasing the flow. Estimations based on the six month data set for six GAC filters suggest that GAC service life could be prolonged by almost half if the flow-rate was decreased from the conventionally applied 39 to 18 L s⁻¹ after having reached the treatment goal of $\Sigma_{11}\text{PFAS} < 50 \text{ ng L}^{-1}$ in the outgoing water.

A subsequent cost analysis indicated an overwhelming effect of the treatment goals on unit cost. A decrease of Sweden's current regulatory guidelines of accepted 90 ng L⁻¹ in finished drinking water to 50, 25 or even 10 ng L⁻¹ would increase annual operations cost at the examined DWTP by 21, 135 and 314%, respectively. It was further shown, that regeneration cost is the dominant PFAS treatment cost factor at the Bäcklösa DWTP. Prolonging the overall service life time of the GAC filters by adopting a operations strategy of adjustment to low flow-rates at the end of service life could decrease operations costs. It is worth recalling that treatment performance of GAC is highly dependent on water quality and that there is a need for empirical studies for each raw water when comparing GAC filters in full-scale drinking water treatment plants. The tools and methods presented in this study can, however, easily be applied to other cases of full-scale operation and therefore provide valuable insights for drinking water providers worldwide. Future research should examine how to monitor the performance of GAC filters (i.e. good removal efficiencies for PFASs) and should attempt to quantify the influence of EBCT, ingoing PFAS concentrations and water quality parameters like organic matter concentrations for better performance and GAC service lifetime predictability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was partly funded by the Swedish Research Council Formas (PFAS-FREE, contract number 942-2015-1554). The authors would also like to thank Uppsala Water and Waste AB for the provided support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115913>.

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