

## REMOVAL EFFICIENCY OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN DRINKING WATER USING ADVANCED WATER TREATMENT TECHNIQUES

Ahrens L<sup>1\*</sup>, McCleaf P<sup>2</sup>, Lundgren S<sup>1</sup>, Englund S<sup>1</sup>, Östlund A<sup>1</sup>, Lindegren K<sup>1</sup>, Persson C<sup>1</sup>, Kothawala DN<sup>1</sup>, Köhler SJ<sup>1</sup>, Wiberg K<sup>1</sup>

<sup>1</sup> Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), Box 7050, 750 07 Uppsala, Sweden, <sup>2</sup> Uppsala Vatten, Box 1444, 751 44 Uppsala, Sweden

### Introduction

Per- and polyfluoroalkyl substances (PFASs) comprise a diverse group of chemicals that have been widely used as processing additives during fluoropolymer production and as surfactants in consumer applications for over 50 years. PFASs are persistent against typical environmental degradation processes and have been found ubiquitously in water, air, food, wildlife and humans<sup>1</sup>. As a consequence, perfluorooctane sulfonate (PFOS) and its precursors have been added to the persistent organic pollutants (POPs) list of the Stockholm Convention in May 2009, resulting in global restrictions on its use and production<sup>2</sup>. After the voluntary phase-out of PFOS, the production shifted to shorter-chained PFASs and PFAS precursors<sup>3</sup>. PFAS precursors can be degraded under aerobic and anaerobic conditions to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAAs) which are the final degradation products and extremely persistent in the environment<sup>4</sup>.

PFASs are prone to leach out to fresh water and groundwater systems due to their high persistence and mobility in the aqueous environment. Recently, several drinking water sources had to be restricted or even shut down because of chemical pollution from PFASs in Stockholm and Uppsala, Sweden. The aims of this study were *i*) to compare conventional and advanced treatment techniques for the removal of PFASs in lab-scale, pilot-scale, and full-scale studies, *ii*) to evaluate the removal efficiency of PFASs depending on their physicochemical properties (chain length and functional group), and *iii*) to examine the effect of the character of dissolved organic carbon (DOC) on the removal efficiency of PFASs.

### Materials and methods

The target analytes included C<sub>4</sub>–C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub> PFCAs (C<sub>n</sub>F<sub>2n+1</sub>COOH, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> PFSAs (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>3</sub>H, PFBS, PFHxS, PFOS, PFDS), perfluorooctanesulfonamide (FOSA, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>NH<sub>2</sub>), methyl and ethyl FOSAs (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)H), methyl and ethyl perfluorooctane sulfonamidoethanols (FOSEs, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)CH<sub>2</sub>CH<sub>2</sub>OH), perfluorooctanesulfonamidoacetic acid (FOSAA, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(H)CH<sub>2</sub>CO<sub>2</sub>H), methyl and ethyl FOSAAAs (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)CH<sub>2</sub>CO<sub>2</sub>H), and 6:2 FTSA (C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H) plus 16 isotopically-labeled internal standards (IS). An IS mix was spiked to the samples before extraction. The extraction of the water samples for PFASs was carried out using solid-phase extraction (Oasis WAX cartridges, Waters, 150 mg, 6 cm<sup>3</sup>, 30 μm) as described previously<sup>5</sup>. Duplicate samples, positive control, laboratory and field blanks were included for quality control. All extracts were analysed using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS)<sup>6</sup>.

In laboratory batch experiments, six different water types of varying DOC characteristics were used to investigate the removal efficiency of PFASs using different treatment techniques including nanofiltration (NF) membrane with a molecular weight cut-off (MWCO) of 500 D, magnetic ion-exchange resin (MIEX<sup>®</sup>), iron (III) chloride (FeCl<sub>3</sub>, 16%), and powdered activated carbon (PAC).

Pilot-scale column experiments were performed using two columns (diameter of 5 cm and length of 55 cm) filled with 100 g AE resin and GAC, respectively. Spiked drinking water (100 ng L<sup>-1</sup> for individual PFASs) was pumped from a reservoir into the two different columns with a constant flow rate at 37 mL min<sup>-1</sup> (5040 mL day<sup>-1</sup>).

<sup>1)</sup> for each column. Weekly samples were taken from the reservoir and the eluates after the AE and GAC columns over a period of 42 days.

In full-scale, the removal efficiency of PFASs was assessed in Stockholm drinking water treatment plant (DWTP). Water samples were collected in raw water, sand filtrate, granular activated carbon (GAC) filtrate, and drinking water. In addition, the removal efficiency of PFASs was investigated in pilot plant scale using nanofiltration (NF) techniques, anion exchange (AE) and GAC.

## Results and discussion

### Removal efficiency of PFASs in laboratory-scale using NF membrane, MIEX<sup>®</sup>, FeCl<sub>3</sub> and PAC

The results showed the best removal efficiency using NF membrane techniques (in average 51%), followed by MIEX<sup>®</sup> (33%), FeCl<sub>3</sub> (16%), and 20 mg L<sup>-1</sup> PAC (14%) (Figure 1).

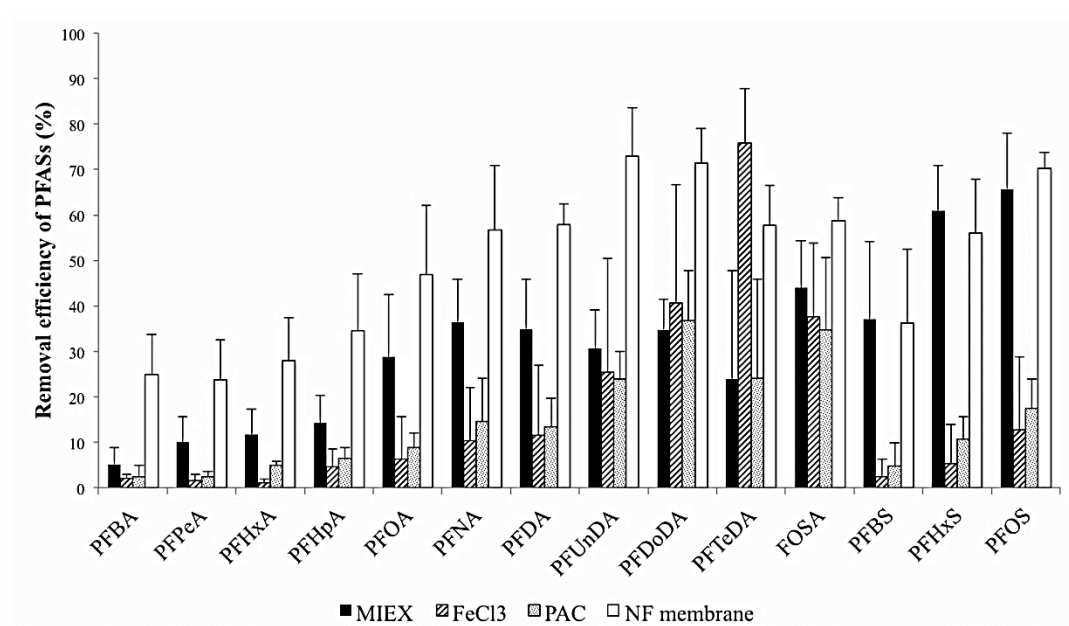


Figure 1. Comparison of the removal efficiency for individual PFASs using MIEX<sup>®</sup> ( $n=8$ ), FeCl<sub>3</sub> ( $n=8$ ), PAC 20 mg L<sup>-1</sup> ( $n=7$ ) and NF membrane ( $n=6$ ).

For NF membrane, the removal efficiency in correlation with molecular weight (MW) is shown in Figure 2. PFASs having a slightly higher removal efficiency compared to PFCAs. For example, PFOS (MW = 500.16 D) had a removal efficiency of 69±3.0 %, while PFDA (MW = 513.10 D) had a removal efficiency of 57 ± 11 %. However, there was no change at the MWCO of 500 D which indicates that there are other factors contributing to the removal of PFASs. One possible explanation could be the negatively charged and hydrophilic membrane surface. For PAC, the average removal efficiency of PFASs increased to 39% using 50 mg L<sup>-1</sup> PAC and 57% using 100 mg L<sup>-1</sup> PAC. The results showed that the removal efficiency of PFASs was dependent on the perfluorocarbon chain length and functional group of PFASs as was observed in previous studies<sup>7</sup>. Generally, this study showed an increasing removal efficiency with increasing perfluorocarbon chain length and a higher removal efficiency for PFASs and FOSA compared to PFCAs when comparing compounds with the same perfluorocarbon chain length. Different removal efficiencies were found for waters having widely different organic carbon compositions, indicating that the DOC characteristics (e.g. source, relative age and degree of humification (assessed though commonly used fluorescence indexes), pH and absorbance) have an influence on the removal efficiency of PFASs in water. An explanation could be that PFASs and DOC form colloids during the treatment process or the DOC promote the formation of a biofilm on the adsorbent surface<sup>8</sup>. Overall, comparing the four tested treatment techniques, NF membrane exhibits the best removal efficiency for the

investigated PFASs, however, the removal efficiency for the short-chained PFASs ( $C < 6$ ) was generally low (24-57%).

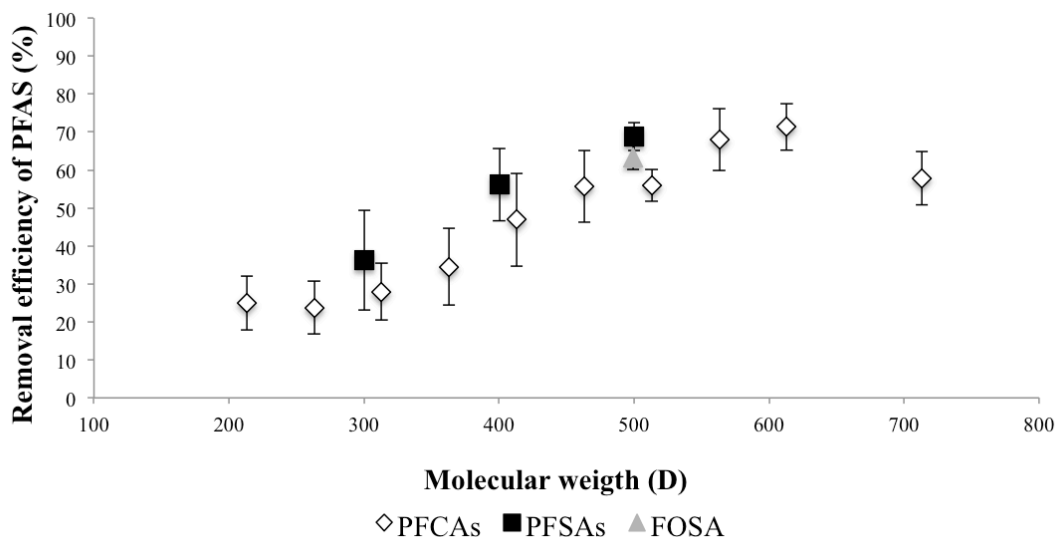


Figure 2. Average removal efficiency of individual PFASs using NF membrane (MWCO = 500 D) depending on the molecular weight (n=6).

#### Removal efficiency of PFASs in pilot-scale using AE and GAC

The bed volumes (ratio between the total volume of water that has passed through the AE and GAC, respectively, from  $t = 0$  to a given time) for the AE column and GAC column were 12 840 and 10 214 bed volumes, respectively for 42 days (Figure 3). The PFASs showed a high sorption potential to AE and GAC with an average removal efficiency of 86 % for both AE and GAC, respectively. The perfluorocarbon chain length and functional group of PFASs had an influence on the removal efficiency of PFASs. Comparing the same perfluorocarbon chain length, the removal efficiency for FOSA and PFASs was comparable whereas the PFASs showed slightly better removal efficiency compared to PFCAs. The lowest removal efficiency was observed for the shorter chained PFASs, on average, 46 % for  $\leq C_6$  PFCAs using AE and, on average, 75 % for  $\leq C_7$  PFCAs using GAC.

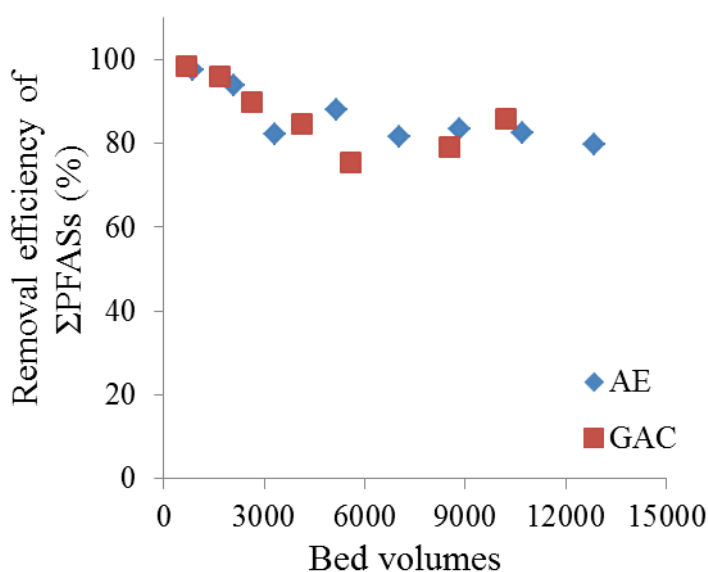


Figure 3. Average removal efficiency of  $\Sigma$ PFASs using AE and GAC.

#### *Comparison between conventional and advanced treatment techniques in full scale*

In a full-scale DWTP,  $\Sigma$ PFAS concentrations (i.e., PFBA, PFHxA, PFHpA, PFOA, PFNA, PFHxS, PFOS) ranged from 7.2–21 ng L<sup>-1</sup> in raw water and from 5.4–14 ng L<sup>-1</sup> in drinking water. The PFAS removal efficiency of sand filtrate and full-scale treatment was in average 7% and 25%, respectively. The PFAS removal efficiency of GAC and NF combined with GAC was in average 24% and 45%, respectively, in the pilot-scale plant connected to the DWTP. Results have shown a general increase in removal efficiency with increasing perfluorocarbon chain length for PFCAs and PFSAs. The removal efficiency depended also on the functional group with a higher removal efficiency for PFSAs compared to PFCAs.

The outcome of this study shows that short chain PFASs ( $C \leq 6$ ) are difficult to remove from drinking water using conventional as well as advanced treatment techniques. This is worrying since longer chained PFASs such as PFOS are replaced by (most often) shorter chained compounds<sup>9</sup> which has been shown in this study to have a low removal efficiency using conventional and advanced treatment techniques. Thus, more research is needed to develop treatment techniques regarding the removal of PFASs in drinking water. A combination of different treatment techniques could be an option to increase the removal efficiency. More research is also needed to understand the interaction between PFASs and DOC in water and how the removal efficiency is affected by the presence of DOC. Ultimately, it is crucial to work towards a more strict regulation regarding production and emission of short chain PFCAs and PFSAs and their precursors, as well as working toward a phase out of these compounds.

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