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Evaluation of the Removal Efficiency of Per- and Polyfluoroalkyl Substances in Drinking Water using Nanofiltration Membranes, Active Carbon and Anion Exchange

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ABSTRACT

Evaluation of the Removal Efficiency of Per- and Polyfluoroalkyl Substances in Drinking Water using Nanofiltration Membranes, Active Carbon and Anion Exchange

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Per- and polyfluoroalkyl substances (PFASs) is a group of man-made, highly persistent chemicals. Due to the specific surface-active attributes of these molecules, applications are numerous and feed an economically important industry. During the last decade, PFASs have been detected globally in the environment, living organisms and tap water. The combination of toxic properties and high bioaccumulative potential, together with the discovery that conventional water treatment methods do not remove PFAS, renders further research on purification methods highly needed.

Three techniques of purifying water from PFASs were examined. Nanofiltration technology (NF) is a membrane filtration technique, which produces a purified product (the permeate) by generating an effluent of high contaminant concentration (the reject water). To decontaminate the reject water, adsorption by granular activated carbon (GAC) or anion exchange (AE) have been proposed. The efficiency of these three technologies was studied at Bäcklösa drinking water treatment plant (DWTP) in Uppsala.

A nanofiltration pilot with two 270NF membranes (Dow Filmtech™), connected in series, was used. A high removal efficiency (>90%) was found for all PFASs. Furthermore, it was confirmed that the concentration in the permeate water was a function of the concentration in the incoming raw water; increased PFAS raw water concentration resulted in increased PFAS permeate concentration. Size-exclusion and electrostatic repulsion were deemed important mechanisms. For the comparison of GAC (Filtrasorb 400®) and AE (Purolite® A-600), a column experiment was set up. The perfluoroalkane (-alkyl) sulfonic acids (PFSAs) and perfluorooctanesulfonamide (FOSA) had similar removal efficiencies using both GAC and AE, and the efficiency increased with increasing chain length. AE was found to have a higher average removal efficiency of perfluoroalkyl carboxylic acid (PFCAs) (62-95%) than GAC (49-81%). In conclusion, longer chain length PFASs were removed more effectively than shorter-chained, and the PFSAs and FOSA showed higher removal efficiency compared to the PFCAs. Furthermore, linear isomers were removed more effectively than branched for GAC and AE. In contrast, the opposite was found for the NF membrane, where branched isomers were better retained.

Keywords: PFASs, perfluoroalkyl substances, removal efficiency, NF, nanofiltration, membrane, GAC, granular activated carbon, AE, anion exchange.

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REFERAT

Utvärdering av reningseffektiviteten av per- och polyfluorerade alkylsubstanser i dricksvatten med nanofiltrering, aktivt kol och jonbytarmassa
Klara Lindegren

Per- och polyfluorerade alkylsubstanser (PFAS) är en grupp syntetiska, ytterst persistenta kemikalier. På grund av deras ytaktiva egenskaper är de lämpliga för användning i många produkter och tillverkningsprocesser, och är således viktiga för en ekonomiskt betydande industri. Under det senaste årtiondet har PFAS påträffats i miljön, levande organismer och kranvatten världen över. Kombinationen av toxiska egenskaper, en hög bioackumuleringspotential och upptäckten att konventionella reningsmetoder inte avlägsnar substanserna från vatten, gör att vidare forskning av reningsmetoder för PFAS är mycket angelägen.

Tre reningsteknikers förmåga att rena vatten från PFAS undersöktes. Nanofiltrering (NF) är en membranfiltreringsteknik som utöver den renade produkten, permeatet, även framställer en biprodukt av hög föroreningsgrad, rententatet. För att rena rententatet har adsorption till granulärt aktivt kol (GAC) eller jonbytarmassa (AE) föreslagits. Teknikerna utvärderades på Bäcklösa Vattenverk i Uppsala.

Nanofiltreringen undersöktes i en pilotanläggning där två 270NF (Dow Filmtech™) membran var seriekopplade. En hög reningsgrad (>90%) konstaterades för alla typer av PFAS. Vidare visades PFAS-koncentrationen i permeatet vara en funktion av PFAS-koncentrationen i råvattnet; en ökad råvattenkoncentration gav en ökad permeatkoncentration. Storleksseparation och elektrostatisk repulsion befanns vara viktiga mekanismer som påverkade reningsgraden. För att undersöka de mekanismer som påverkar PFAS-adsorption jämfördes GAC (Filtrasorb 400®) och AE (Purolite® A-600) i ett kolonnexperiment. Reningsgraden för GAC och AE av perfluorerade sulfonsyror (PFSA) och perfluorooktan sulfonamider (FOSA) var lika hög och reningseffektiviteten ökade med ökande kolkedjelängd. AE återfanns ha en högre genomsnittlig reningsgrad av perfluorkarboxylsyror (PFCA) (62-95%) än GAC (49-81%). Sammanfattningsvis avlägsnades PFAS av längre kolkedjelängd mer effektivt än kortare kolkedjor, och PFAS med sulfonsyror och sulfonamider som funktionella grupper uppvisade en högre reningsgrad än karboxylsyrorna. Vidare renades linjära isomerer mer effektivt än grenade både genom GAC och AE. Däremot konstaterades det motsatta för NF-membranen, där grenade isomerer renades mer effektivt.

Nyckelord: PFAS, perfluorerade alkylsubstanser, reningeffektivitet, NF, nanofiltrering, membran, GAC, granulärt aktivt kol, AE, jonbytarmassa.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Utvärdering av reningseffektiviteten av per- och polyfluorerade alkylsubstanser i dricksvatten med nanofilter, aktivt kol och jonbytarmassa

Klara Lindegren

Per- och polyfluorerade alkylsubstanser (PFAS) är en grupp syntetiska kemikalier med unika, ytaktiva egenskaper. Dessa attraktiva egenskaper beror på PFAS-molekylernas uppbyggnad vilken förenklat kan liknas vid en svans kopplad till ett huvud. Svansen, eller *kolkedjan* som är dess vetenskapliga namn, är vattenskyende medan huvudet, eller den *funktionella gruppen*, gillar vatten. Olika funktionella grupper ger ämnena något skilda egenskaper. PFAS brukar därför delas in i grupper, varav perfluorerade karboxylater (PFCA), perfluorerade sulfonsyror (PFSA) och perfluoroktan sulfonamider (FOSA) är de mest studerade. De unika, ytaktiva egenskaperna gör ämnena både fett- och vattenavstötande, och kemikalierna ingår i kända produkter såsom GoreTex™ och Teflon™.

Det senaste årtiondet har PFAS påträffats på alla kontinenter, inklusive Arktis. Vilken påverkan exponering för ämnena har på människan och naturen är dock till stor del ännu okänd, men forskning har visat att ämnena kan orsaka skador på biologiskt liv såsom cancer och minskad fertilitet. Även kranvatten runt om i världen har visat sig innehålla koncentrationer av PFAS och eftersom intag av dricksvatten är en av de viktigaste exponeringsvägarna för PFAS är det av stor betydelse att det finns tekniker som kan avlägsna kemikalierna från vattnet. Tidigare försök har dock visat att konventionella reningsmetoder inte har någon större reningskapacitet för PFAS.

Tre olika reningstekniker undersöktes i syftet att studera metodernas förmåga att avlägsna PFAS. Försöken utfördes på Bäcklösa Vattenverk i Uppsala, där två pilotprojekt pågick. Nanofiltrering (NF) är en membranfiltreringsteknik som används i allt större utsträckning för dricksvattenrening. När vatten renas med denna teknik kan cirka 70 % av vattnet renas. De resterande 30 % innehåller det renade vattnets förorening och detta vatten är alltså mer förorenat än innan. För att rena dessa resterande 30 % har två andra reningstekniker föreslagits: granulärt aktivt kol (GAC) och jonbytarmassa (AE). Reningskapaciteten hos GAC och AE undersöktes genom att vatten spetsat med PFAS fick rinna genom två glascylindrar, en med GAC och en med AE.

Experimenten visade att NF renade bort alla PFAS till en tillfredställande hög nivå. De mekanismer som bestämde vilka PFAS som renades bäst visade sig bero på ämnets storlek och geometri, men också ämnets elektriska laddning och förmåga att på olika sätt interagera med membranet. Reningskapaciteten för GAC och AE var till en början mycket hög, men avtog hastigt med tiden för de flesta PFAS. Snabbast sjönk reningskapaciteten för de med kort kolkedja. De PFAS som hade en längre kolkedja hade en bättre genomsnittlig rening. Grupperna PFCA och FOSA renades ungefär lika bra med både GAC och AE, medan PFSA renades bättre med AE. En

slutsats är alltså att om kombinationen av NF med GAC eller AE ska användas, så kommer PFAS med kort kolkedja snabbt renas till en sämre grad. Vidare forskning på rening av korta PFAS bör därför utföras.

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ABBREVIATIONS

6:2 FTSA	6:2 fluorotelomer sulfonate
AE	Anion exchange
AFFF	Aqueous film-forming foam
BV	Bed volume
Da	Daltons (=g/mol)
DOC	Dissolved organic carbon
DWHA	Drinking water health advisory
DWTP	Drinking water treatment plant
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency (USA)
FOSA	Perfluorooctanesulfonamide
FOSAA	Perfluorooctanesulfonamidoacetic acid
FOSE	Perfluorooctanesulfonamidoethanol
FTSA	Fluorotelomer sulfonate
GAC	Granular activated carbon
IS	Internal standard
K_{OC}	Soil organic carbon-water partitioning coefficient
LOD	Level of detection
MDL	Method detection limit
MW	Molecular weight
MWCO	Molecular weight cut-off
N-EtFOSA	N-ethylperfluorooctanesulfonamide
N-EtFOSAA	N-ethylperfluorooctanesulfonamidoacetic acid
N-EtFOSE	N-ethylperfluorooctanesulfonamidoethanol
N-MeFOSA	N-methylperfluorooctanesulfonamide
N-MeFOSAA	N-methylperfluorooctanesulfonamidoacetic acid
N-MeFOSE	N-methylperfluorooctanesulfonamidoethanol
NF	Nanofiltration
PFAA	Perfluoroalkyl acid
PFASs	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoate

PFBS	Perfluorobutane sulfonate
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoate
PFDoDA	Perfluorododecanoate
PFDS	Perfluorodecane sulfonate
PFHpA	Perfluoroheptanoate
PFHxA	Perfluorohexanoate
PFHxDA	Perfluorohexadecanoate
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoate
PFOA	Perfluorooctanoate
PFOcDA	Perfluorooctadecanoate
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoate
PFSA	Perfluoroalkane (-alkyl) sulfonic acid
PFTeDA	Perfluorotetradecanoate
PFTriDA	Perfluorotridecanoate
PFUnDA	Perfluoroundecanoate
PP-bottle	Polypropylene bottle
rpm	revolutions per minute
SPE	Solid phase extraction
TDI	Tolerable daily intake
WWTP	Wastewater treatment plant

1. INTRODUCTION

In 2012, a study found young women in the city of Uppsala, Sweden, to have increased blood serum levels of PFASs; a group of chemicals, potentially harmful to health and environment. As these compounds have a half-life time of 26 days in the human body, the elevated blood serum levels indicated that the women were under continuous exposure (Glynn et al., 2012). Ingestion of tap water was the suspected exposure route due to detected levels on other locations (Rahman et al., 2013). In Uppsala, the PFASs were thought to originate from a military airport located north of the city, where aqueous film-forming foams (AFFF) used for fire drills contained the chemicals (Uppsala Vatten, 2013). Transported south by the groundwater movement, the contaminants were present in several of the city's water production wells, and subsequently distributed to the residents (Kemikalieinspektionen, 2013; Gyllenhammar, 2015). Levels of PFASs have been detected in tap water across the world (Rahman et al., 2013), and the need for appropriate treatment methods is prevailing.

1.1 PURPOSE

The purpose of this Master thesis was to examine the removal efficiency of PFASs using nanofiltration technology (NF), granular activated carbon (GAC) and anion exchange resin (AE).

1.2 HYPOTHESES

The nanofiltration technology will remove PFASs efficiently.
The removal efficiency of GAC and AE will decrease over time with increasing number of bed volumes.
The removal efficiency will be dependent on the perfluorocarbon chain length, type of functional group and molecular structure.

1.3 DELIMITATIONS

PFASs were the only compounds examined and the possible effect of DOC on removal efficiency was not evaluated in this work. The water used for the column study was spiked drinking water and hence not of the same composition as the untreated raw water used in the NF pilot plant.
As the aim was to study the quality of raw and drinking water and methods for drinking water purification, other forms of water and water treatments (such as waste water treatment) has not been included.

2. BACKGROUND

2.1 PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) belong to a large group of man-made chemicals, where some (poly-) or all (per-) of the hydrogen atoms attached to a carbon chain backbone are replaced by fluorine atoms, as described by the moiety C_nF_{2n+1}- (Buck et al., 2011; Rahman et al., 2014). PFASs are categorized after type of functional group, which give rise to different characteristics, including partitioning behavior (Wang et al., 2011). Two such groups of PFASs are the PFCAs and the PFSAs (Rahman et al., 2014). Congeners of environmental concern include PFOS (perfluorooctanesulfonic acid; Figure 1a), belonging to the PFSAs, PFOA (perfluorooctanoic acid; Figure 1b) and the related PFCAs (perfluorinated carboxylic acids), and FTOHs (fluorotelomer alcohols), which has the ability to degrade to PFCAs (Ellis et al., 2004; Lehmer, 2004). The PFASs are further categorized as longer chain and shorter chain compounds. For PFSA, the definition of a long chained molecule is a carbon chain exceeding C_6 and for PFCAs > C_8 (Butt et al., 2009).

a) **b)**

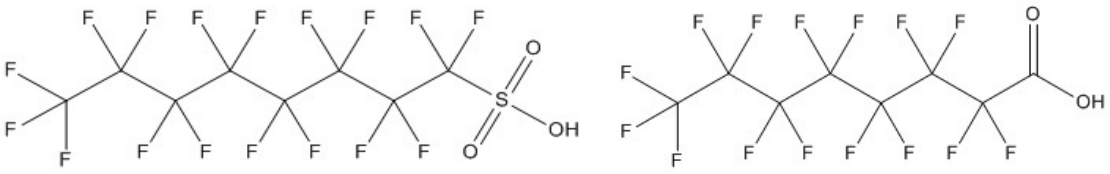


Figure 1 The chemical structures of two perfluoroalkyl substances; a) PFOS (perfluorooctane sulfonic acid) and b) PFOA (perfluorooctanioc acid). The functional groups are located in the right end of the molecules.

The strong polar covalent bond between the carbon and the fluorine make the molecules resistant to degradation from factors such as heat, acids, bases, and oxidizing agents. This resistance to degradation results in the compounds being persistent in the environment and practically biologically non-degradable (Smart, 1994; Butt et al., 2010). Following this, it has been shown that PFASs of longer chain lengths has a tendency to bioaccumulate and biomagnify in food webs due to, among other factors, its ability to covalently bond to proteins (Kannan et al., 2002, Lau et al., 2007).

2.2 PHYSICOCHEMICAL PROPERTIES

PFASs have low vapour pressure, which decrease with increasing chain length, and are stable even at high temperatures exceeding 150°C (Lau et al., 2007; Rayne & Forest, 2009). The combination of being hydrophilic through the acidic head group (differing in dissociation between homologues) and hydrophobic through the carbon

chain, grant the molecules surface tension lowering abilities, thereby acting as surfactants (Prevedouros, 2006; Rayne & Forest, 2009; Buck et al., 2011). The length of the carbon chain, and type of functional group gives rise to differences in properties; longer carbon chain length is for example associated with lower vapour pressure, rendering such homologues to foremost be transported by waterways (Ahrens, 2011).

2.3 MANUFACTURING, OCCURRENCE AND FATE

The chemicals have had numerous applications since the production started in the 1950s. Apart from being manufactured, PFASs can also be formed from precursors through degradation of other compounds (Rahman, et al., 2014). PFASs have been detected in human blood serum, biota, soils and waters across the globe, with geographically distant findings including the Canadian Arctic and Japan (Taniyasu et al., 2003). The widespread distribution of PFASs is thought to be due to long-range atmospheric transportation of volatile precursors and particle adsorbed PFASs, as well as by waterways in dissolved form (Dinglasan el al., 2004, Ahrens et al., 2009, Armitage et al., 2009). However, the highest PFAS concentrations are found in industrial discharges, in the vicinity of wastewater outlets and at fire-fighting training grounds (Valsecchi et al., 2015). The only sinks that have been identified are deep oceans and sediments, which in turn entail long resident times and further reinforce the chemicals' environmental persistency (Prevedouros et al., 2006). The synthesisation of PFASs gives rise to a range of congeners including linear and branched isomers and molecules of different carbon chain lengths (Prevedouros et al., 2006; Buck et al., 2011). This diversity, which increases exponentially with increasing homologue group (the C_{13} homologue has approx. 10, 000 congeners) complicate the analysis as isomers often are grouped, and attributes and effects of single isomers remain uninvestigated (Rayne & Forest, 2009). The percentage composition of linear/branched isomers differs between manufacturers, but a generally adopted proportion is, however, 70% linear and 30% branched (Benskin et al., 2010).

2.4 USE AND REGULATIONS

The simultaneous water- and oil repellent capacity of PFASs make the compounds versatile for a range of products, including textiles, fire fighting materials, cleaners, dirt-repellents (ScotchGard™) and Teflon™ coated cookware (Prevedorous et al., 2005; Benskin et al., 2010). The U.S. and Canada has passed legislations to decrease the production and import of PFOS and other long-chained PFASs (EPA, 2006; Environment Canada, 2010). For example, imports of PFAS treated mats has to be registered with the U.S. Environmental Protection Agency (EPA) 90 days in advance (EPA, 2013).

Since 2008, the manufacturing and use of PFOS and its precursors is banned in the European Union (European Union, 2008). In 2010, the European Union released the Commission Recommendation 2010/161/EU, where monitoring of PFASs in food in the member states was recommended. The legislations on longer-chained PFASs have induced a shift in production during the last decade, and PFASs of shorter chain lengths are being manufactured to an increasing extent (Butt et al., 2009).

There are drinking water guidelines for PFOS and PFOA. The 3M company, previously one of the largest manufacturers of PFAS in the world, has published a lifetime Drinking Water Health Advisory (DWHA) for PFOS of 0.1 μg/L (3 M, 2001). The U.S. Environmental Protection Agency (U.S. EPA) issued a short-term exposure provisional health advisory in drinking water of 0.2 μg/L for PFOS and 0.4 μg/L for PFOA (EPA, 2009). However, the state of New Jersey has set a considerably lower health-based guidance value of 0.04 μg/L for PFOS (State of New Jersey, 2013). In the U.K, the guidance levels are 0.1 μg/L for PFOS and 10 μg/L for PFOA (DWI, 2007). The Swedish National Food Agency has issued an action limit of 90 ng/L for Σ_7PFAS, which is the sum concentration of PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA and PFOA (Livsmedelsverket, 2014).

2.5 TOXICITY

The European Food Safety Authority (EFSA) recommends its members to collect and analyze food items since PFASs are suspected endocrine disruptors, and PFOS and PFOA have been found to accumulate in blood serum, liver and kidney after oral exposure (EFSA 2008, EFSA 2012). The most important exposure pathways for humans are hypothesised to be food intake, drinking water and indoor dust (Björklund, 2009; Gyllenhammar et al., 2015), further accentuating the need of monitoring levels in these mediums. La Rocca et al. published a report in 2012 as a part of a larger study issued by the Italian Environment Ministry, aiming to link environment and human health to endocrine disrupters. Examining fertile and infertile couples, most fertile couples had PFOS and PFOA levels below the limit of detection (LOD). Out of the infertile couples, 50% of the men and 37% of the females had levels exceeding the LOD >20 times. The study concluded elevated PFOS and PFOA levels being positively correlated to infertility. Prior to this, Joensen et al. (2009) associated men highly exposed to PFOS and PFOA with having impaired semen quality.

2.6 TREATMENT TECHNIQUES

2.6.1 Nanofiltration

Nanofiltration technology (NF) has been in use since the 1980's and is employed in several industries as well as in drinking water preparation and food production processes. For the production of drinking water, NF's ability to remove unwanted substances such as pesticides and endocrine disrupters, as well as lowering the hardness of the water without removing wanted salts, is beneficial (Mänttäri et al., 2013). NF membranes can be made of a variety of materials, such as organic polymers, ceramics or highly cross-linked polymers The highly cross-linked polymeric membranes are beneficial due to their ability to function under high pressures, and withstand high temperatures and pH (Van der Bruggen & Geens, 2008). Materials with different properties are however usually layered, forming a composite membrane. To reach the wanted purifying capacity within the set constraints (cost, pressure, power needed), the membranes can be connected and combined in various ways and thus form a plant. The design of a NF plant can differ in the number of stages used, in how the modules are configured and whether the plant operates continuously or in batch mode (Van der Bruggen et al., 2002).

Membranes are classified by their cut-off in Daltons, which for NF membranes is in the range 90-1,000 Daltons (g/mol). This is equivalent to a 90% removal of substances of that particular molecular weight. A molecule exceeding the cut-off (having a larger molecular weight) would hence be retained to a lager extent. However, the retention of a solute is reportedly foremost dependent on the size of the molecule (i.e. molecular length and width) (Van der Bruggen et al., 1999; Chen et al., 2004). Other factors influencing the retention are the hydrophobicity of the molecule, intermolecular forces and acting forces between the molecules and the membrane (Van der Bruggen et al., 2002; Braeken 2005). Studies have shown that it is important to maintain constant conditions in the membrane with regards to the flux, cross-flow velocity and the recovery (Appleman et al., 2013). With time, the membrane may be fouled by compounds present in the water, adsorbed or otherwise attached to the membrane surface. To prevent an increase in contaminant transport across the membrane due to fouling, the flux should be kept constant (Van der Bruggen et al., 2002; Appleman et al., 2013). However, in a study conducted by Appleman et al., (2013), an increase in removal efficiency was found for some PFASs when fouling was present. This further demonstrates the applicability of NF for PFASs-removal in drinking water production.

2.6.2 Granulated activated carbon (GAC)

Granular activated carbon is widely used in DWTP's for the removal of unwanted organic compounds, among others the taste-and-odour causing substance Geosmin

(O'Connor et al., 2008). The process that enables this is physical adsorption, in which certain substances from a solution bind to the surface of the adsorbent, in this case the carbon granules. Physical adsorption is a reversible process in which the GAC can be regenerated, meaning that the GAC is recyclable (Hung et al., 2005).

Studies have proven conventional water treatment techniques, such as sand filtration and ozonation, to be ineffective in the removal of PFASs (Quiñones & Snyder 2009; Takagi et al., 2011), why other techniques must be implemented. GAC has shown promising results in the retaining of unwanted pollutants, including PFASs (Hansen et al., 2010; Senevirathna et al., 2010; Appleman et al., 2013). However, PFASs of shorter carbon chain length (<C8) are not retained by the GAC to the same extent as fluorocarbons of longer chain length, due to lower adsorption capacity (Eschauzier et al., 2012). An increase in the outflow concentration of short chain PFASs has been observed for highly loaded (older, more used) GAC. In the competition of active sorption sites, less adsorptive compounds are desorbed and replaced by more sorptive PFASs of longer chain length (Eschauzier et al., 2012). Furthermore, studies have found branched isomers to be less retained than non-branched (Belford, 1979; Eschauzier et al., 2012; Östlund, 2015). This may be explained by the smaller Gibbs free energy gained by adsorption of branched PFASs, which have smaller molecule volumes (Wang et al., 2011).

2.6.3 Anion exchange (AE)

Anion exchange is a process in which certain matter in a liquid is adsorbed to an exchanger, i.e. the anion exchange resin. The matter being adsorbed is of negative charge, opposite to the charge of the ion exchanger (Dardel & Arden, 2012). Different types of exchangers are available on the market, including polystyrene and polyacrylic resins (Dardel & Arden, 2012). Due to the affinity of the resins to an ion, some ions are more readily adsorbed than others (Lampert et al., 2007). This result in individual breakthrough curves for each ion, where the most preferred ions break through last and the least preferred first, depending on the equilibrium between the ion and the resin (Lampert et al., 2007). Breakthrough curves can hence indicate what type of resin that should be used for removal of a certain ion/contaminant. AE has primarily been used in water treatment for its ability to soften and demineralize water (Crittenden et al., 2012), but according to bench and pilot scale studies, the method can successfully be used for the removal of PFASs (Senevirathna et al., 2010; Englund, 2015; Östlund, 2015).

3. MATERIAL AND METHODS

The PFAS removal efficiency using nanofiltration membranes was tested in a pilot plant, using groundwater as incoming raw water. An ongoing column experiment was used to evaluate the removal efficiency using GAC and AE as adsorbent. Here the incoming water was spiked drinking water. The nanofiltration pilot plant and the column experiment were set up at Uppsala Vatten AB's DWTP Bäcklösa, situated south of Uppsala city centre. The subsequent experimental work, including extraction and analysis, was performed at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU).

3.1 CHEMICALS AND MATERIAL

3.1.1 Chemicals

PFASs studied in this project were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoda, PFTriDA, PFTeDA, PFHxDA, PFOcDA, PFBS, PFHxS, PFOS, PFDS, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSA, N-EtFOSE, FOSAA, N-MeFOSAA, N-EtFOSAA and 6:2 FTSA. The spiking solution used for the tank contained the following 14 PFASs, obtained from the supplier Sigma-Aldrich (Sweden); PFBA (purity 98%), PFPeA (97%), PFHxA (≤ 97%), PFHpA (99%), PFOA (96%), PFNA (97%), PFDA (98%), PFUnDA (95%), PFDoDA (95%), PFTeDA (97%), FOSA (purity n/a), PFBS (98%), PFHxS (≤ 98%) and PFOS (98%).

Two internal standards (IS) were prepared with chemicals purchased from Wellington Laboratories (Canada); FXIS07 and FXIS11 (Lutz Ahrens, pers. comm., 2015). Both IS-solutions contained $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOS, all with a concentration of 20 pg/µL, and $^{13}C_8$-FOSA, d_3-N-MeFOSAA, d_5-N-EtFOSAA, d_3-N-MeFOSA, d_5-N-EtFOSA, d_7-N-MeFOSE and d_9-N-EtFOSE, all with a concentration of 50 pg/µL. FXIS07 was used until empty (2015-05-27), and thereafter FXIS11 was used.

To precondition the cartridges used in the solid phase extraction (SPE), 0.1% ammonium hydroxide (25%, Sigma-Aldrich, Spain) in methanol (LiChrosolv®, 99.9%, Merck K GaA, Germany), followed by unmixed methanol were used. The same methanol type was also used as final solvent for the samples and for cleaning all the equipment used during the experiments. A buffer solution containing acetic acid (>99.7%, Sigma-Aldrich, Netherlands), ammonium acetate (≥99.0%, Sigma-Aldrich, Netherlands) and Millipore water (Millipak® Express 20, 0.22 µm filter, Merck Millipore) was used for the extraction.

3.1.2 Nanofiltration membranes

Membranes of the type NF270 were purchased from Dow Filmtech™ Membranes. The expected removal efficiency of the NF270 membranes is a 90% removal of molecules with a molecular weight of 270 Da. These polypiperazine thin-film composite membranes are made of a combination of different materials, including the organic compound piperazine. The cylindrically shaped membranes have a diameter of 0.201 m and are 1.02 m long. A large active surface area of 37.0 m^2 contributes to the high productivity with a maximum feed flow (raw water flow) rate of 15.9 m^3/h. With a high removal capacity of organic compounds and a medium to high salt passage, it is stated as being ideal for purifying ground and surface water. The product sheet also holds several warnings and precise instructions that must be followed for the fragile membrane to function appropriately without being damaged (Dow, 2015).

3.1.3 Granular activated carbon

GAC of the type Filtrasorb 400®**,** manufactured by Calgon Carbon Corporation (Belgium), was used in Column 1 of the column experiment (section 3.3). The Filtrasorb 400® is made from bituminous coal (black coal), which has been agglomerated and activated. The effective size (i.e. 90%) of the granules is 0.55-0.75 mm. Filtrasorb 400® is suitable for drinking water treatment and has the ability to adsorb organic compounds of a broad range of molecular weights (Calgon Carbon Corporation, 2012).

3.1.4 Anion exchange

The AE resin used for Column 2 in the column experiment was Purolite A-600 (Purolite®, United Kingdom) (see section 3.3 for an explanation of the column experiment). With a functional group of Type I quaternary ammonium, the resin is strongly basic. The sizes of the spherical beads are in the range between 300-1200 μm. The resin's physical and chemical stability, together with a high operating capacity, makes the resin a suitable candidate for large-scale water treatment (Purolite, 2012).

3.2 NANOFILTRATION PILOT PLANT

Figure 2 displays a schematic picture of the NF-pilot plant, where two Dow Filmtech™ NF270 membranes were connected in series. Incoming raw water passed through a pre-filter, after which an internal pressure pump pushed the water to the membranes (at a pressure of 3 bars). Approximately 70% of the water volume passed though the membrane (permeate water, lower contaminant concentration), whilst 30% was rejected (reject water, higher contaminant concentration). The plant diverted the

correct volume reject water automatically, regulated by pressure gauges. Pressures and water flows were recorded every week (Table A1, Appendix).

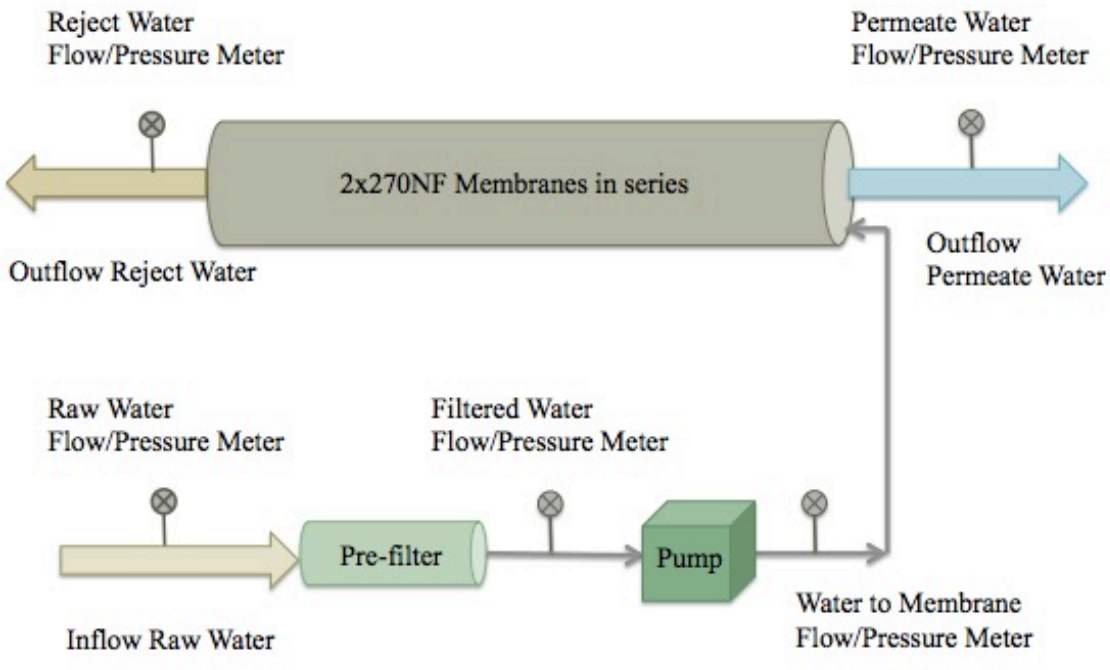


Figure 2 Schematic picture of the NF-plant showing raw water inflow, membranes, permeate and reject outflows and flow/pressure meters. The metal pipe holding the two membranes is 331 cm long and has a diameter of 20 cm.

Raw water, reject water and permeate water were sampled once every week during the time period 2015-05-11 to 2015-07-27 (12 weeks). The samples were labelled according to water type, date and sample number (T1-T12). The raw water was untreated water from the Stadsträdgården well field, obtained from an outlet at Bäcklösa DWTP. The reject water was taken from a tube, attached to the bottom of a small tank connected to the nanofiltration plant. Permeate water samples were carefully extracted from the plant in order to keep conditions in the membranes unchanged. Samples were collected into 1 L polypropylene bottles (PP-bottles), pre-rinsed 3 times with methanol, and transported directly to SLU.

On sampling occasion T4, the plant was off due to a clogged pre-filter. The gradual fouling of the filter is indicated in the collected data (prior to sample time T4) by decreasing flow rates and falling reject pressure (Table A1, Appendix).

3.3 COLUMN EXPERIMENT

Approx. 100 grams of each adsorbent was added separately to two glass columns (diameter 5.2 cm, length 55 cm) with a sintered glass filter (Saveen and Werner) at the bottom (Figure 3). This corresponded to 175 mL AE resin (Column 2), and 220 mL GAC (Column 1). A 1000 L polyethylene tank (Icorene™, France) was filled with drinking water from the DWTP and spiked with the 14 PFAS spiking solution (concentration 484.1 µg/mL, section 3.1.1) to maintain a concentration of 100 ng/L. By means of a peristaltic pump (Watson Marlow 520s), water was transported from the tank to the two columns at a speed of 20 revolutions per minute (rpm), aiming to keep a constant flow rate (Englund, 2015; Östlund 2015).

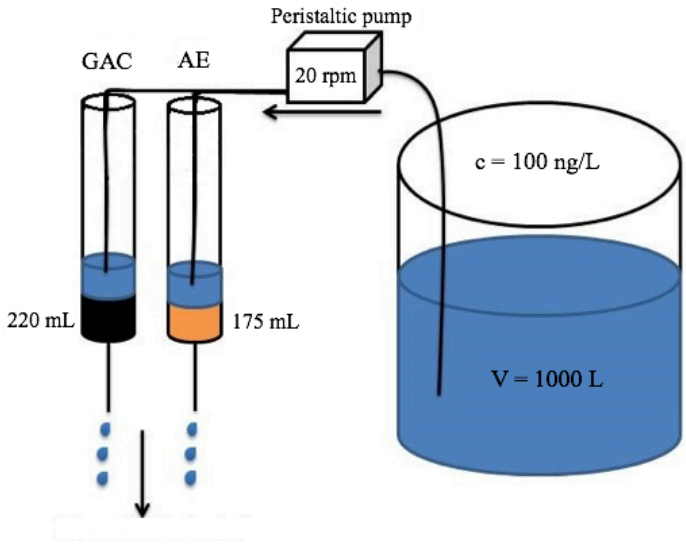


Figure 3 A schematic picture of the column experiment set up at Bäcklösa DWTP showing the 1000 L water tank, the peristaltic pump and the two columns (Englund, 2015).

Table 1 Summary of the column experiment with GAC (Column 1). Samples were collected at 30 sampling times, T1-T8 (Englund, 2015), T9-T25 (Östlund, 2015) and T28-T35 during the current project. The Tank and GAC DOC (mg/L) concentrations were analysed by another laboratory, on behalf of Uppsala Vatten. Duplicates were collected at sampling times T15, T20, T22, T24, and T30-T35. The blank samples, which were not taken at Bäcklösa DWTP, are not included in this table.

Sample	Day of collection	GAC Bed volume[a]	Tank DOC (mg/L)	GAC DOC (mg/L)	Column 1 water level (mL)	Duplicates collected
T1	3	693	1.78	0	300	-
T2	7	1661	1.77	0	230	-
T3	11	2629	1.73	0	260	-
T4	17	4106	1.8	0	330	-
T5	23	5588	1.56	0	300	-
T6	29	7035	1.62	0	340	-
T7	35	8533	1.74	0	330	-
T8	42	10214	1.86	0	340	-
T9	46	10594	1.74	1.03	340	-
T10	56	12750	-	-	360	-
T11	63	14351	-	-	410	-
T12	70	15952	1.67	0	420	-
T13	76	17386	1.95	1.05	440	-
T14	84	19154	1.99	1.02	450	-
T15	91	20759	1.88	1.05	360	Yes
T19	98	22360	1.79	0	455	-
T20	105	23966	1.99	1.04	Full	Yes
T21	112	25562	1.90	1.08	900	-
T22	119	27163	1.88	1.03	Full	Yes
T23	126	28764	1.62	1.01	Full	-
T24	133	30360	1.98	1.02	Full	Yes
T25	140	31966	2.23	1.04	580	-
T28	142	32407	-	-	340	-
T29	148	33774	-	-	350	-
T30	154	35113	-	-	340	Yes
T31	161	36704	-	-	380	Yes
T32	175	39908	-	-	790	Yes
T33	189	43110	-	-	560	Yes
T34	203	46307	-	-	590	Yes
T35	217	49523	-	-	880	Yes

[a] Bed volumes were calculated according to Equation (1), where V_a (GAC) = 220 mL.

Table 2 Summary of the column experiment with AE (Column 2). Samples were collected at 30 sampling times, T1-T8 (Englund, 2015), T9-T25 (Östlund, 2015) and T28-T35 during the current project. The Tank and AE DOC (mg/L) concentrations were analysed in another laboratory, on behalf of Uppsala Vatten. Duplicates were collected at sampling times T15, T20, T22, T24, and T30-T35. Samples not included in this table were blanks, and therefore not taken at Bäcklösa DWTP.

Sample	Day of collection	AE Bed volume[a]	Tank DOC (mg/L)	AE DOC (mg/L)	Column 2 water level (mL)	Duplicates collected
T1	3	871	1.78	0	310	-
T2	7	2088	1.77	0	300	-
T3	11	3305	1.73	0	310	-
T4	17	5162	1.8	1.04	330	-
T5	23	7025	1.56	1.07	310	-
T6	29	8844	1.62	1.16	280	-
T7	35	10727	1.74	1.22	260	-
T8	42	12840	1.86	1.26	270	-
T9	46	13318	1.74	1.51	270	-
T10	56	16199	-	-	250	-
T11	63	18233	-	-	250	-
T12	70	20267	1.67	1.44	280	-
T13	76	22089	1.95	1.59	280	-
T14	84	24335	1.99	1.52	240	-
T15	91	26375	1.88	1.46	235	Yes
T19	98	28409	1.79	1.46	235	-
T20	105	30449	1.99	1.46	235	Yes
T21	112	32477	1.90	1.53	270	-
T22	119	34511	1.88	1.53	310	Yes
T23	126	36545	1.62	1.37	340	-
T24	133	38573	1.98	1.46	340	Yes
T25	140	40613	2.23	1.43	315	-
T28	142	41173	-	-	370	-
T29	148	42910	-	-	500	-
T30	154	44611	-	-	470	Yes
T31	161	46633	-	-	450	Yes
T32	175	50704	-	-	475	Yes
T33	189	54772	-	-	405	Yes
T34	203	58834	-	-	420	Yes
T35	217	62920	-	-	485	Yes

[a] Bed volumes were calculated according to Equation (1), where V_a (AE) = 175 mL.

Sample collection was conducted in different campaigns, but executed in the same manner every time. Samples T1-T8 were collected and analysed by Englund (2015), T9-T25 by Östlund (2015) and T28-T35 during the current study. From the tank (spiked water, input) and each of the two columns (treated water, output), 1 L samples were collected. Duplicate samples from each of the columns were taken on ten occasions (Table 1-2). The samples were then directly transported in a sunlight-protected box to SLU for analysis. On two occasions (day 3 and day 48) 200 mL samples from each of the columns and from the tank, were collected and sent for analysis of parameters such as inorganic ion concentration. After sampling, using a pump (Watson Marlow Sci 323), a backwash was performed on each of the columns for two minutes to prevent the columns from clogging. For the GAC-column, a speed of 400 rpm (0.67 L/min) was deemed sufficient, and for the AE-column a speed of 220 rpm (0.37 L/min). Lastly, the tank was spiked with the standard mixture, kept in a refrigerator at the DWTP, and filled with drinking water from the plant.

At day 105 the GAC column overflowed, due to fine particles of GAC clogging the glass filter. The time of backwashing was increased to 4-6 minutes, but as this proved ineffective another pump (Masterflex® L/S®, easy-load 3, model 77800-62) was brought in. Operating at a higher speed of 600 rpm (1 L/min) for 4-6 minutes, the level of the GAC-column decreased with time (Table 1) (Östlund, 2015). The column experiment was paused for 42 days, from 2015-03-17 to 2015-04-27. Before resuming the experiment, the tank was washed out and Column 1 (GAC) was replaced with a new column of the same type. The original GAC was transferred into the new column.

The blockages in the GAC-column persisted during this study (day 142 to day 217). On day 175, due to a high water level in the column, the tubing was lowered 5 cm to increase the friction loss, and hence decrease the flow rate of the incoming water. On all sampling occasions following day 175, backwashing was performed for 6 minutes at 600 rpm. The water level in the column continued to increase, and reached a level of 820 cm on day 182. The tubing was lowered a further 5 cm, which kept the water level down until day 217 when an increase began. At the time the experiment was terminated (day 224), the column was again near overflowing, with a water level of 900 cm (Table 1).

To normalize the flow rate and the volume of the adsorbent, the bed volume (BV) was calculated for all times. The bed volume is proportional to the water flow rate and time, but is inversely proportional to the volume of the adsorbent.

$$\mathrm{BV} = \frac{f_r \cdot t}{V_a} \qquad \text{Equation (1)}$$

where f_r= flow rate (mL/h)
t = time (h)
V_a= volume of adsorbent (mL)

The removal efficiency, used to describe how well PFASs were removed by either adsorbent, was calculated according to the following formula:

$$\text{Removal efficiency} = 100 - \frac{C}{C_0} \cdot 100 \qquad \text{Equation (2)}$$

where C = contaminant concentration in the output (GAC/AE-column) water (ng/L)
C_0 = contaminant concentration in incoming (tank) water (ng/L)

The average concentration in the tank was used to calculate the removal efficiency for all PFASs, due to fluctuations in tank concentration (Table A1, Appendix). The amount of individual PFASs sorbed to the GAC and AE was calculated by subtracting the amount of PFASs in outflow from the amount of PFASs in the inflow (tank).

3.4 PFAS EXTRACTION

All equipment used for the PFAS extraction was rinsed 3 times with ethanol, dish washed and (if glassware or metal) burnt in an oven over night at 400°C. Prior to usage, the equipment was rinsed 3 times with methanol.

All water samples (both from the NF and column experiment) were filtered through glass fibre filters (Whatman™ Glass Microfiber Filters GF/C™, 47 mm diameter, 1.2 µm) with the aid of vacuum available in the fume hoods at the department laboratory. Samples were transferred back into their original PP-bottles, together with the subsequent 3x methanol rinse from the filtration equipment that had been in contact with the sample. The solid phase extraction (SPE) was assembled and the cartridges (Oasis® WAX 6 cc cartridges, 6 cm^3, 500 mg, 60 µm, Waters, Massachusetts, USA) preconditioned with 4 mL 0.1% ammonium hydroxide, proceeded by 4 mL methanol and lastly 4 mL Millipore water. The samples, extracted in batches of 12, were spiked with 100 µL IS mixture (50 pg of each compound per µL), and each loaded into one of the reservoirs. The flow was regulated to a flow of one drop per second, and the reservoirs were covered with aluminium foil to decrease the risk of contamination. Vacuum was used when the flow was slower than 1 drop per second or when blockages had occurred. When complete, each cartridge was washed with 4 mL of 25mM ammonium acetate buffer (pH 4) and dried in the centrifuge (eppendorf Centrifuge 5810, Hamburg, Germany) for 2 minutes at 3000 rpm. The samples were then collected into 15 mL PP-tubes by adding 6 mL methanol, followed by 6 mL 0.1% ammonium hydroxide in methanol, to the cartridges. The samples were placed under nitrogen evaporation (N-EVAP™ 112) for concentration. When the volume had decreased to 1 mL, samples were transferred into 1mL glass vials. The samples were concentrated to the exact volume of 1 mL, again using a gentle stream of nitrogen gas.

Finally, the samples were analysed using high performance liquid chromatography-mass spectrophotometry (HPLC-MS/MS) according to the method described by Ahrens et al. (2009).

3.5 QUALITY CONTROL

Due to the risk of contamination of the samples (e.g. indoor air and dust), 13 blank samples were analysed (one blank in this study and 12 blanks in the study by Östlund (2015)). The blanks were treated as the other samples, described in section 3.4. The average detected PFASs concentrations from the blanks (n=13) with standard deviation were used to calculate the method detection limit (MDL) for each individual PFAS:

MDL = Average blank concentration + (3 x Standard deviation) Equation (3)

The MDL ranged between 0.139 and 0.860 (Table A2, Appendix). Detected sample concentrations that were below the MDL were replaced by MDL/3. Because the MDL varies between the PFAS congeners, it was reduced by a factor of 3 to decrease its importance (for further explanation on this, see Figure 10 and corresponding text in the Method section).

The standard deviation of the duplicate samples ranged from 1.8% to 15% (Table A3, Appendix).

4. RESULTS

The results obtained from the NF pilot plant are presented in section 4.1 and the results from the column experiment in section 4.2. Data obtained by previous column experiments are also included in section 4.2 (samples T1-T25; Englund, 2015; Östlund, 2015).

4.1 NANOFILTRATION PILOT PLANT

The C_3-C_8 PFCAs were detected in varying concentrations in the incoming raw water, with highest levels of PFHxA, followed by PFOA (Figure 4a). PFBA, PFHpA and PFPeA were also present, but with lower concentrations (1.2-3.3 ng/L). Of the PFSAs (Figure 4b), PFHxS was found at high concentrations throughout the sampling time (on average 94 ng/L). PFOS was the PFAS with the second highest concentration (~20 ng/L). Lastly, PFBS was detected in increasing concentration between samples T7 (day 42) and T10 (day 63), from ~2.5 ng/L to ~9.3 ng/L. Thereafter the concentration decreased, and reached 8.6 ng/L in the final sample (T12, 77 days).

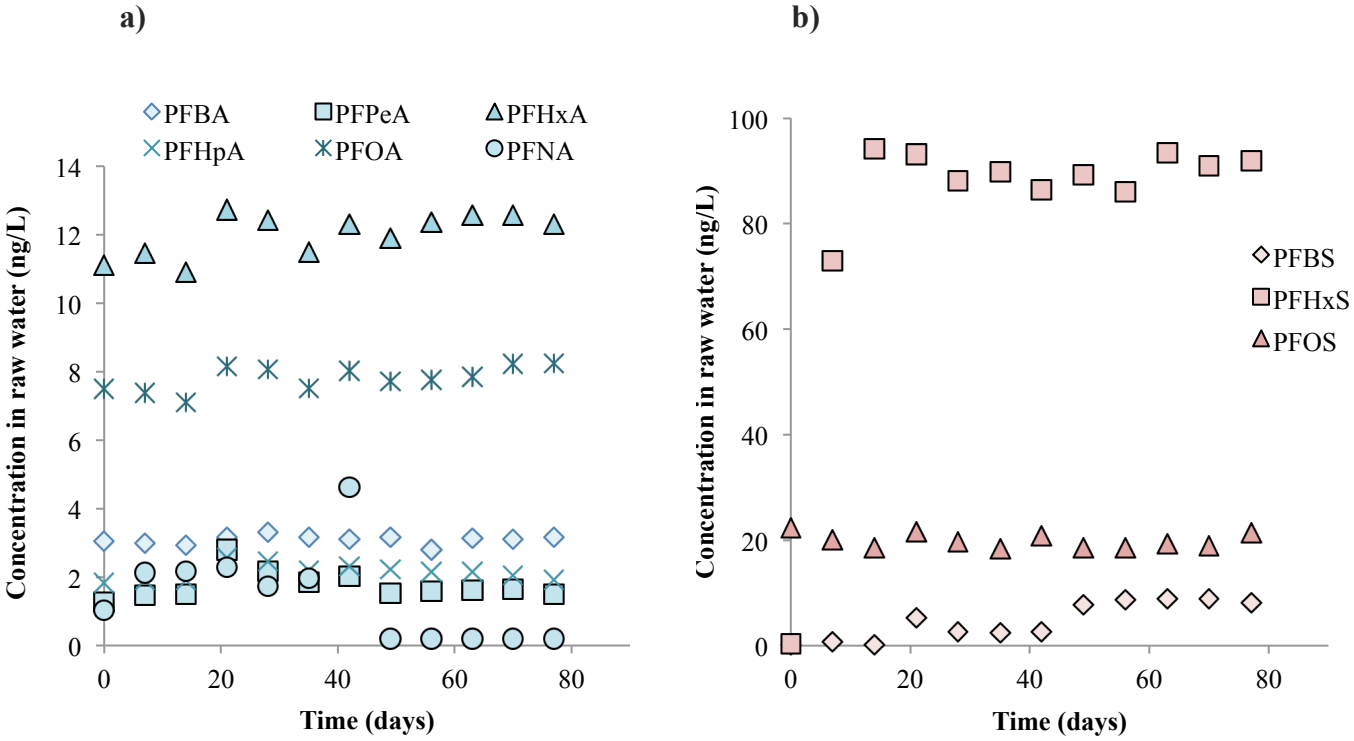


Figure 4 The concentrations (ng/L) of a) C_3-C_8 PFCAs and b) PFSAs in incoming raw water. Concentrations below MDL were replaced by MDL/3.

Short-chained PFCAs (C_3-C_7) were not detected in the permeate water (Figure 5a). However, PFNA (C_8) was found in increasing levels up until sample T7 (day 42), after which the concentration of PFNA was below the detection limit. Out of the examined PFASs, PFHxS was found at the highest concentration (6.3 ng/L). The level of PFOS remained constant at ~1 ng/L, whereas PFBS showed an increase after sample T7 (day 42). This increase coincided with the change of the pre-filter (which removed particles before the membrane process) in the NF plant. The PFAS concentration in sample T7 is shown in Table 3, but was removed from Figure 5 a-b in order to show the fluctuations in permeate concentrations when the plant was functioning.

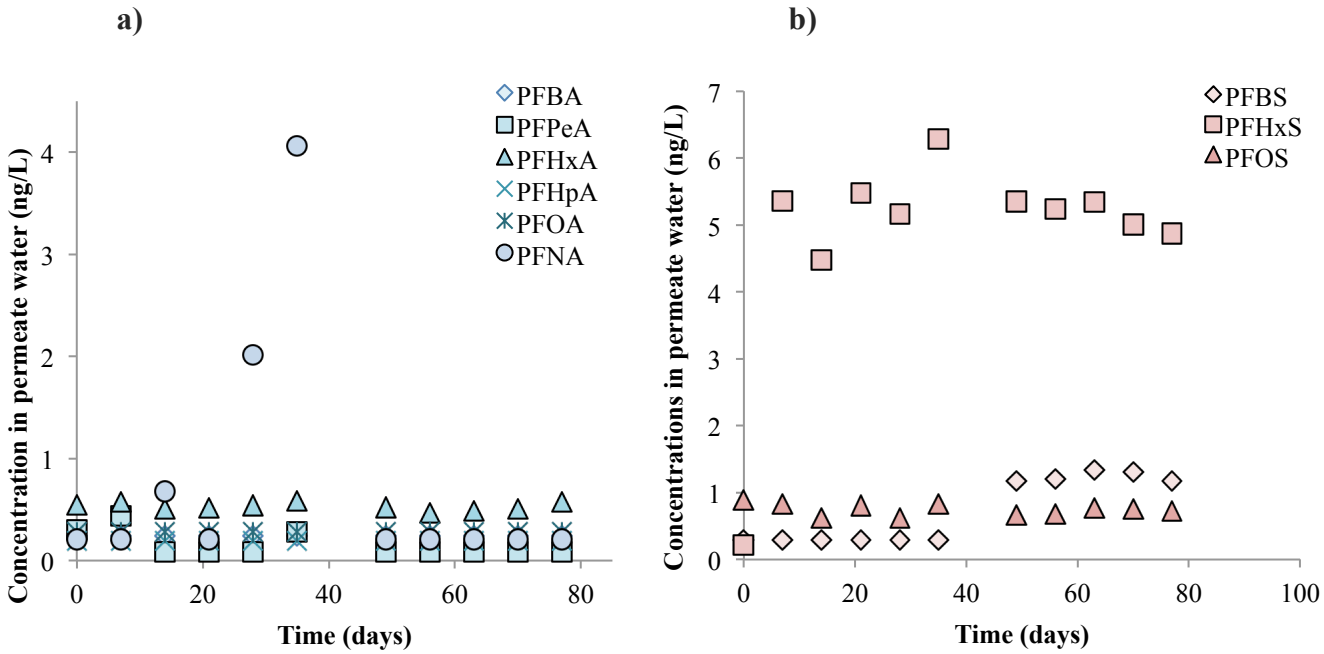


Figure 5 The concentrations (ng/L) of a) C_3-C_8 PFCAs and b) PFSAs in the permeate water. Sample T7 (day 42) is not shown since the NF-membrane was not functioning during this time. The PFAS concentration in sample T7 (day 42) are shown in Table 3. Concentrations below MDL were replaced by MDL/3.

Table 3 The concentrations (ng/L) of the different PFASs in the permeate water for day 42 (sample T7).

PFAS	Permeate concentration day 42 (ng/L)
PFBA	5.86
PFPeA	3.58
PFHxA	16.2
PFHpA	1.64
PFOA	4.21
PFNA	0.21
PFBS	1.54
PFHxS	64.2
PFOS	2.19

PFHxA showed the highest PFCA average concentration (55.1 ng/L) in the reject water, followed by PFOA (38.8 ng/L) (Figure 6a). PFOA was the PFAS that was concentrated to the highest degree for sample T7 (day 42; 71.3 ng/L). PFBA was present at an average of 13.7 ng/L, followed by PFHpA and PFPeA (averages of 7.5 ng/L and 5.3 ng/L). 50% of the PFNA samples were below the detection limit (0.625 ng/L). The highest PFAS concentration found was of PFHxS, reaching a maximum of 438 ng/L at day 70 (Figure 6b). However, for samples T2-T3 (7-14 days), the concentration of PFHxS, as well as PFBS and PFOS, was below the MDL. A fluctuation in PFOS concentration can be seen for samples 35, 42 and 49 days, which corresponds to the samples taken just before, during, and just after the NF-membrane was dysfunctional. PFBS had concentrations averaging 14.0 ng/L.

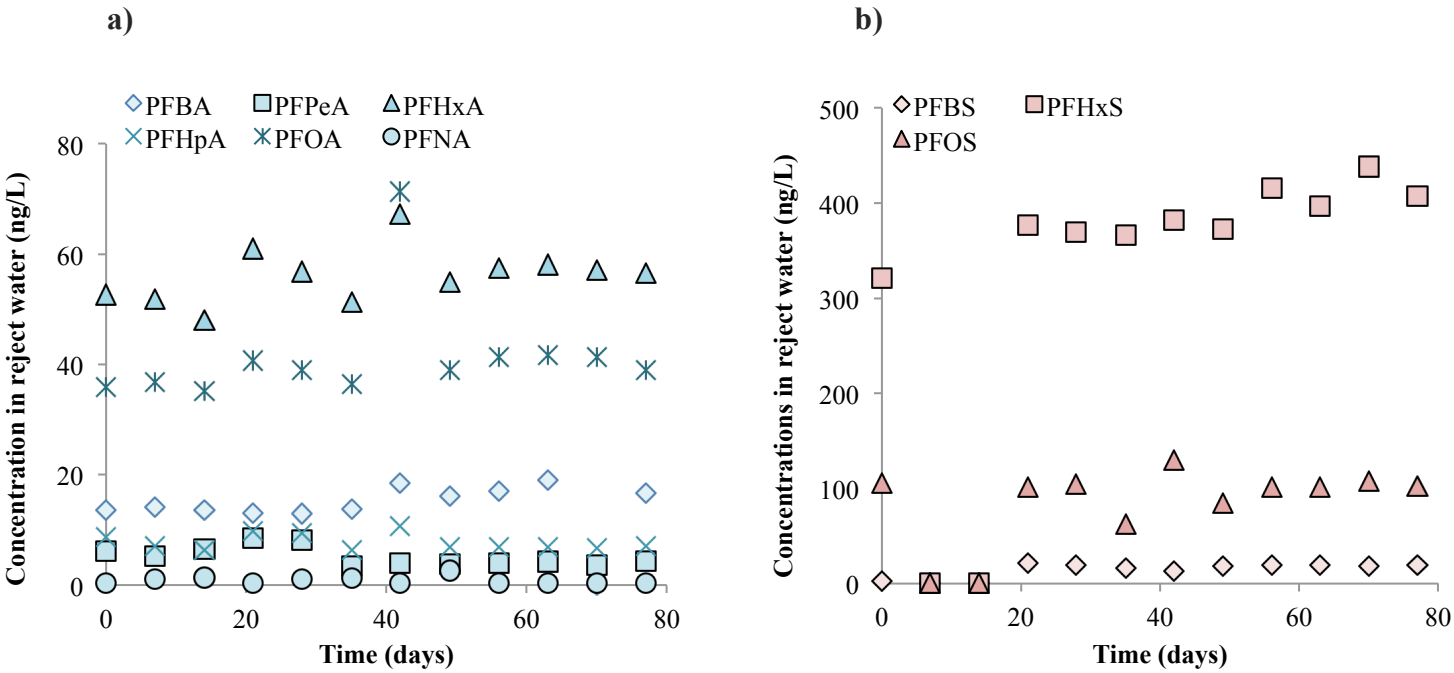


Figure 6 The concentrations (ng/L) of a) C_3-C_8 PFCAs and b) PFSAs in the reject water. Concentrations below MDL were replaced by MDL/3.

The total average PFAS concentration was 166 ng/L for the raw water, 679 ng/L for the reject water and 9.70 ng/L for the permeate (Figure 7a). PFHxS was the compound present in the highest concentration in all three water types, followed by PFOS (Figure 7a-b). Looking at the composition profile (Figure 7b), PFBS and PFNA showed a higher percentage in the permeate than in the raw and reject water (see Figure 5a and b for concentration in permeate water over time).

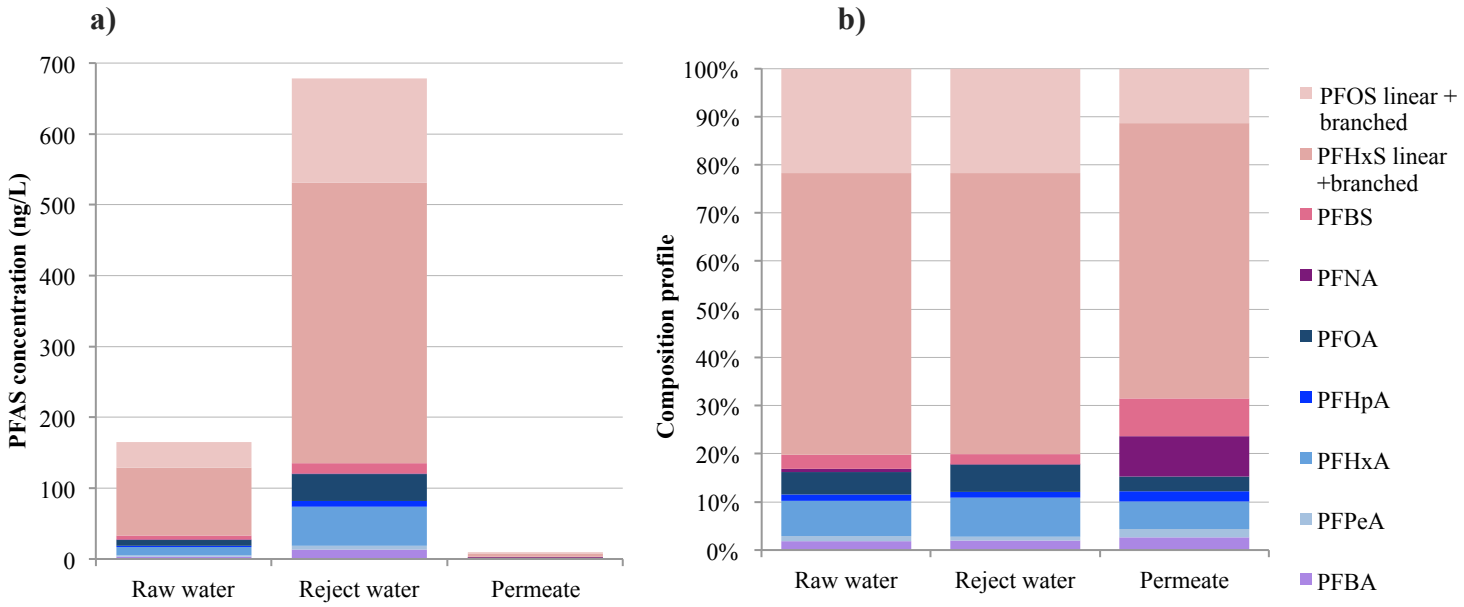


Figure 7 The average composition of PFASs in the raw water, reject water, and permeate water displayed as a) concentration in ng/L, and b) composition profile. Sample T7 (day 42) was excluded.

The concentration factor was calculated as the ratio between the total PFAS concentration in the reject water divided by the total PFAS concentration in the raw water. Sample T1 had a very low ΣPFAS concentration in the raw water (64 ng/L) compared to the total concentration in the reject water (688 ng/L), and hence the concentration factor was large. T2 and T3 had low reject water concentrations (116 and 111 ng/L, respectively), which resulted in low factors. The concentration factor of individual PFASs showed that the high variation in sample T1 was caused by PFHxS with a concentration factor of 1515 (compared to a concentration factor of ~5 for the other samples T4-T12, see Figure 8). The high concentration factor for PFHxS for sample T1 can be explained by the fact that the raw water concentration for PFHxS was below the MDL for this sample. The concentrations for PFHxS and PFOS for samples T2-T3 were below the detection limit in the reject water, explaining the low factors (0.002-0.008).

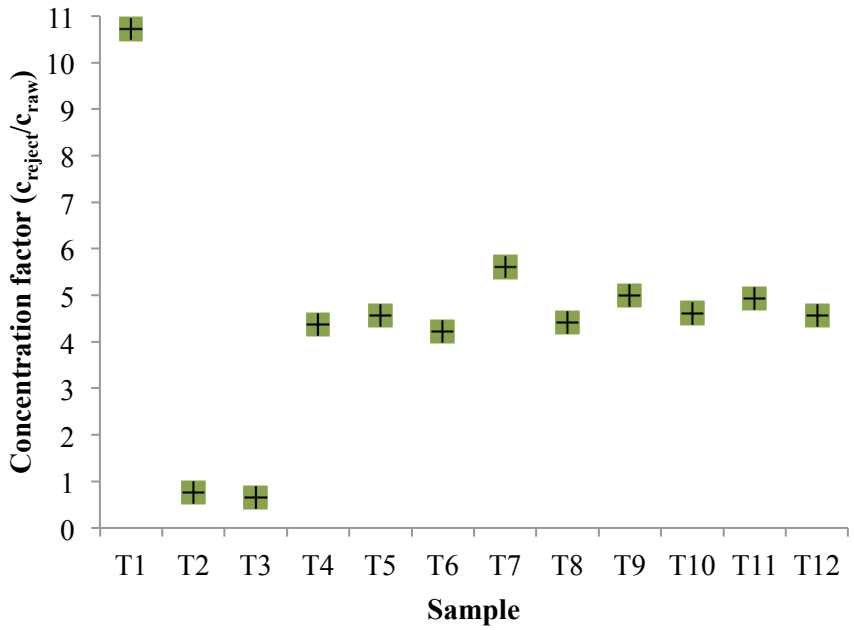


Figure 8 The calculated concentration factors of the reject water (c_{reject}) divided by the raw water concentration (c_{raw}) for the ∑PFASs for each sample time.

Disregarding samples T7, the removal efficiency (Equation 2) of PFBA, PFHxA, PFHpA and PFOA remained at high levels, close to 100% (Figure 9a). PFPeA fluctuated, with lower removal efficiency for days 0, 7 and 35. PFNA displayed a varying removal efficiency with negative values for days 28 and 35, which denotes higher concentrations in the permeate than in the raw water (compare Figures 5a and 4a). After sample T7 (day 42) PFNA's removal efficiency was zero. For sample T7 (day 42), PFBA and PFPeA were negative (~ -80%), and also PFHxA (-31%) (Figure 9a). For Figure 9b, the removal efficiency of PFBS was zero for the first three samples (days 0-14) due to concentrations below MDL for the raw water and the permeate water. For the next following sample day (day 21), the removal efficiency of PFBS was 100%, after which a slight decrease was seen. After 28 days, and prior to the pre-filter change, the removal efficiency was approx. 85% for PFBS. PFOS was well removed with an average removal efficiency of 96%. The removal efficiency of PFHxS was 0 for the first sampling time (day 0) due to a raw water concentration below MDL. For sample T7 (day 42), a small decrease was seen in the removal of PFOS (90% removed), whilst PFBS and PFHxS plunged (removal efficiencies of 42% and 26% respectively).

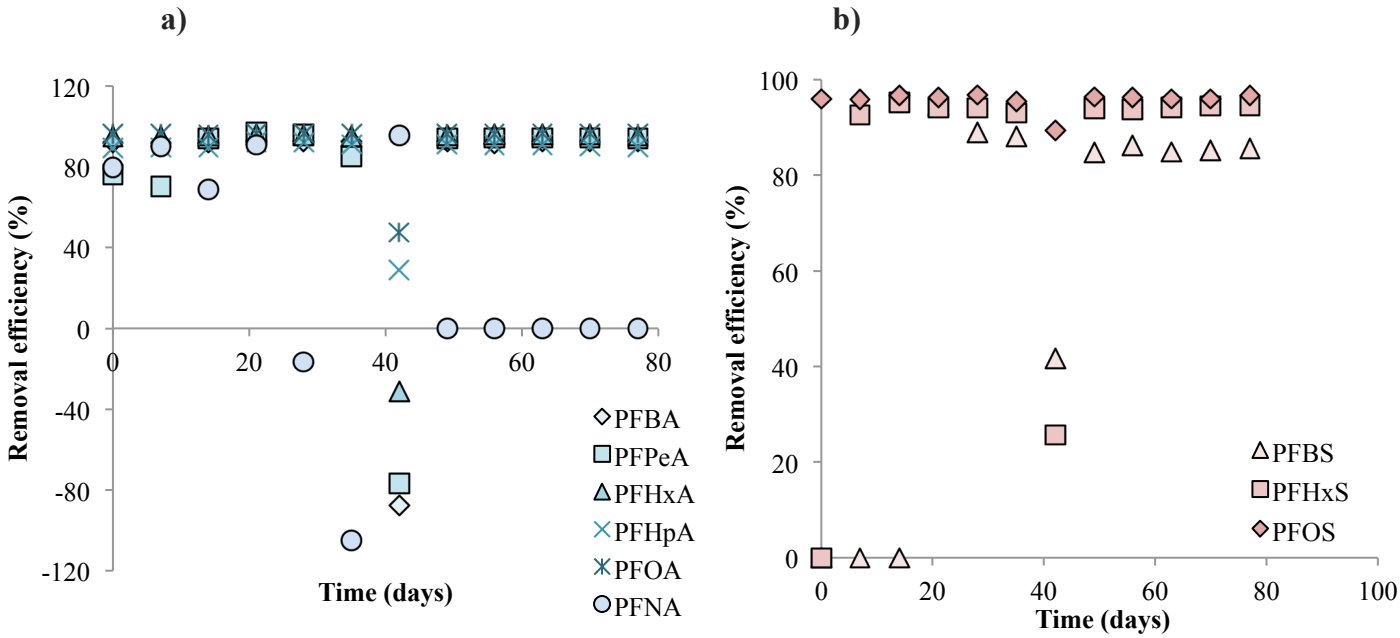


Figure 9 Removal efficiencies (%) of a) C_3-C_8 PFCAs and b) PFSAs. The data points at day 42 correspond to sample T7. Concentrations below MDL were replaced by MDL/3.

The permeate concentration of the PFCAs was below the minimum detection limit (MDL) for 76% of the samples, and set to 1/3 of the MDL's for these values. The MDL's were calculated for each PFAS individually and were of varying size, which results in fluctuating removal efficiency with molecular weight (Figure 10). Hence the removal efficiency for the PFCAs does not display the exact removal efficiency. The PFSAs showed an increasing removal with increasing molecular weight. The concentrations for sample T7 (day 42), when the plant was out of order, were removed to obtain the average removal efficiencies for a functioning NF-plan of this type.

The theoretical 90% cut-off for the membrane was obtained from the manufacturer (Dow, 2015) and is 270 Da (dark green dashed line, Figure 10). To determine the experimental 90% cut-off for PFSA, a linear regression was done for the first two data points (molecular weight 299 and 399 Da respectively). From this, the experimental 90% cut-off was found to be 340 Da (pink dashed line, Figure 10). No 90% molecular weight cut-off was sought for the PFCAs due to the ambiguity of the data (Figure 10).

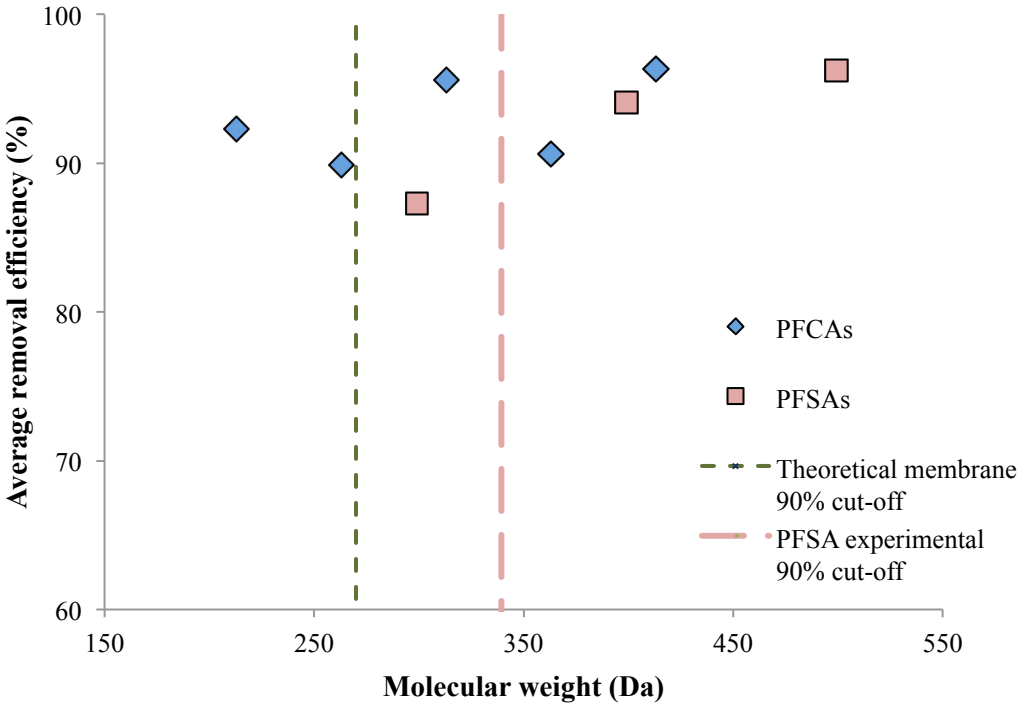


Figure 10 The correlation between the average removal efficiencies (%) of PFCAs and PFSAs is shown against their molecular weight (Da). The green dashed line represents the theoretical 90% cut-off of the membrane (270 Da), whereas the pink dashed line is the experimentally determined 90% cut-off for the PFSAs (340 Da). Sample T7 (day 42) is not included in the average removal efficiencies since the NF-membrane was not functioning during this time.

PFOS and PFHxS displayed a difference in removal efficiency between linear and branched isomers, where the linear molecules were less readily removed. For PFOS (Figure 11a), the removal efficiency for branched isomers was on average 1.9% higher than for linear isomers, when excluding sample day 42 (the removal is 1.6% better when including day 42). For PFHxS branched isomer were removed 3.0% better, when excluding sample day 42 (3.7% when including day 42) (Figure 11b). The removal efficiency for PFHxS at day 0 could not be calculated since both raw and permeate water concentrations were below MDL.

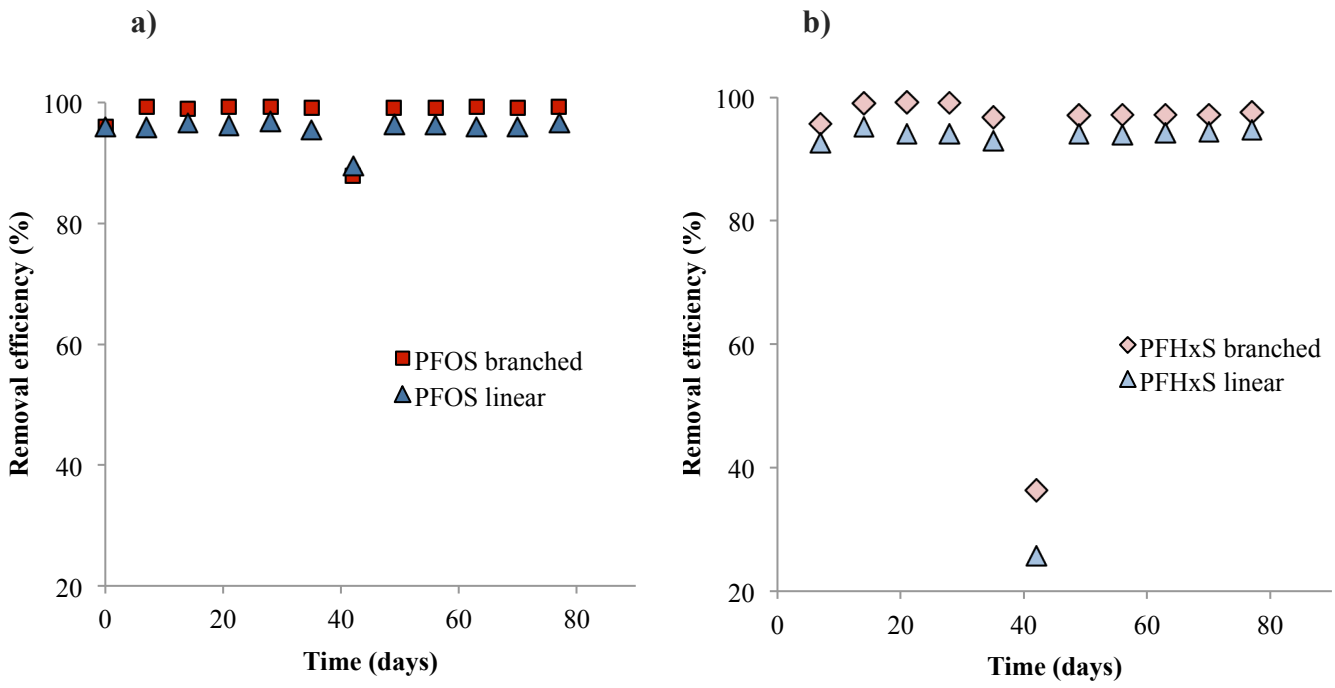


Figure 11 The removal efficiency (%) of branched and linear isomers of a) PFOS and b) PFHxS, with linear isomers pictured as triangles. The removal efficiency for sample time 0 days for PFHxS could not be calculated due to concentrations in raw and permeate water being below MDL.

4.2 COLUMN EXPERIMENT

In this section, the results from the column experiment at Bäcklösa Vattenverk, Uppsala, are presented focusing on granular activated carbon (section 4.2.1) and anion exchange (section 4.2.2). Furthermore, the removal efficiency of linear vs. branched isomers is compared (section 4.2.3).

4.2.1 Granular activated carbon

In the GAC experiment, the highest average removal efficiencies were found for PFTeDA (C_{13}, 81 ± 14%) and PFOS (C_8, 81 ± 13%) (Table 4). The lowest average removal was for PFBA (C_3) with 6.4 ± 40%. The standard deviation of the average removal of PFBA and PFPeA was high, and the last 15 sampling times (22,360 – 49,523 BVs) were negative (see Figure 12a). Samples T28 and T29 for PDPeA and PFHxA were removed due to contamination during sample preparation.

Table 4 The average removal efficiency ± standard deviation (%), and the removal efficiency at the final sampling day (T35; 49,523 BVs) for all detected PFASs using GAC as adsorbent.

PFAS	Average removal efficiency (%) (*n*=28)	Removal efficiency at final sampling day (T35) (%)
PFBA (C_3)	6.4 ± 40	-23
PFPeA (C_4)[a]	13 ± 41	-1.9
PFHxA (C_5)[a]	47 ± 28	4.9
PFHpA (C_6)	55 ± 28	19
PFOA (C_7)	65 ± 21	28
PFNA (C_8)	71 ± 18	40
PFDA (C_9)	75 ± 14	53
PFUnDA (C_{10})	79 ± 13	63
PFDoDA (C_{11})	79 ± 12	79
PFTeDA (C_{13})	81 ± 14	94
FOSA (C_8)	80 ± 13	64
PFBS (C_4)	49 ± 29	23
PFHxS (C_6)	69 ± 18	45
PFOS (C_8)	81 ± 13	66

[a]The data for sample times T28 and T29 were removed due to contamination of the sample during sample preparation.

The removal efficiency of all PFCAs exhibited a downward trend with increasing number of bed volumes. However, a levelling-out could be seen from ~40,000 BVs for short-chained PFCAs (Figure 12A), and from ~35,000 BVs for long-chained PFCAs (Figure 12b). PFTeDA (C_{13}), though being the least removed for samples 0-1,000 BVs, was on average the most efficiently removed PFCA (Figure 12b, Table 4). Out of the short-chained PFCAs, PFBA (C_3) and PFPeA (C_4) had negative removal efficiencies for 52% and 41% of their samples. Negative removal efficiencies are due to lower PFAS concentrations in the tank water than in the water that has passed through the column (outflow concentration > inflow concentration). PFOA (C_7) had the highest average removal efficiency of the short-chained PFCAs (Figure 12a).

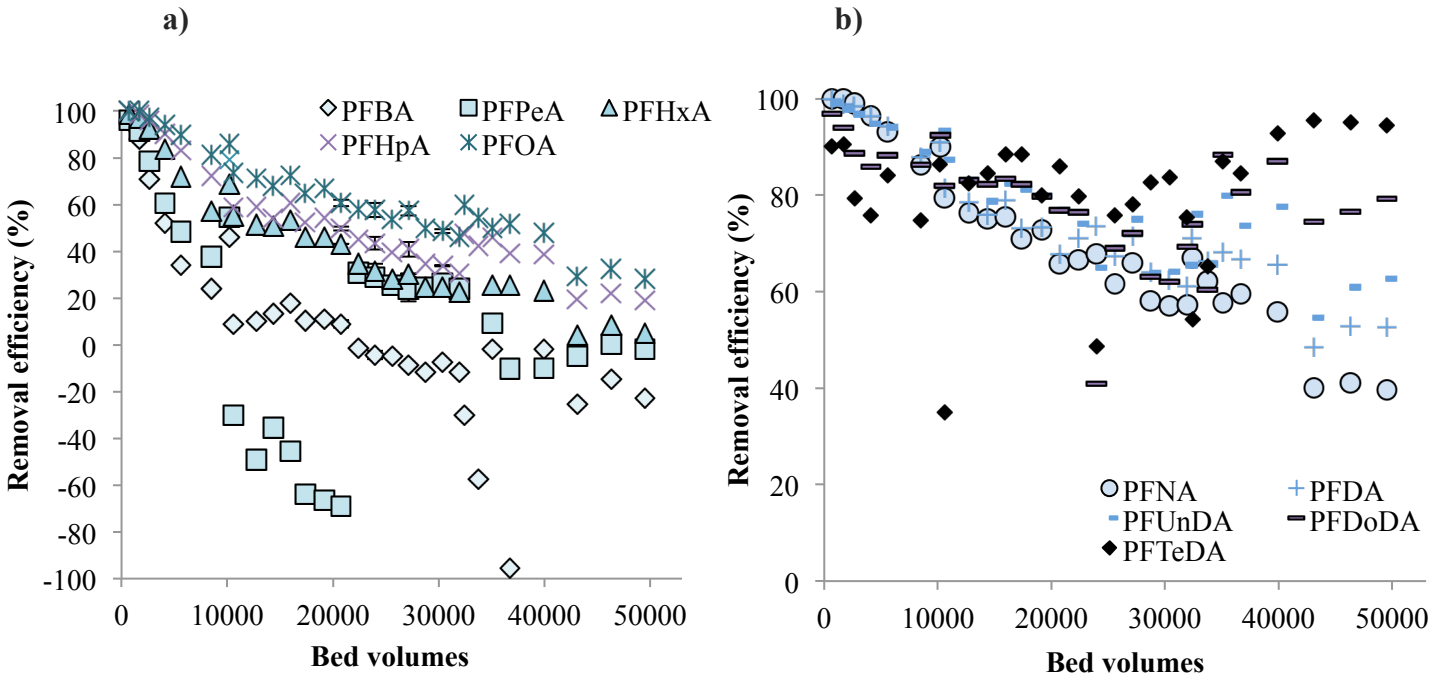


Figure 12 The removal efficiency (%) of a) short-chained (C_3-C_7) PFCAs, and b) long-chained (C_8-C_{11}, C_{13}) PFCAs, using GAC as adsorbent. The data for PFPeA and PFHxA for the samples T28 and T29 were removed from a) due to contamination during sample preparation.

FOSA and PFOS displayed high removal efficiency throughout the sampling time, averaging 80 ± 13% and 81 ± 13% respectively (Figure 13a and 13b, Table 4). PFHxS (C_6) was on average removed 69 ± 18%. PFBS had a fluctuating, low, removal efficiency after ~1,000 BVs and onwards, and is also the PFSA with the shortest carbon chain length (C_4), (Figure 13b, Table 4).

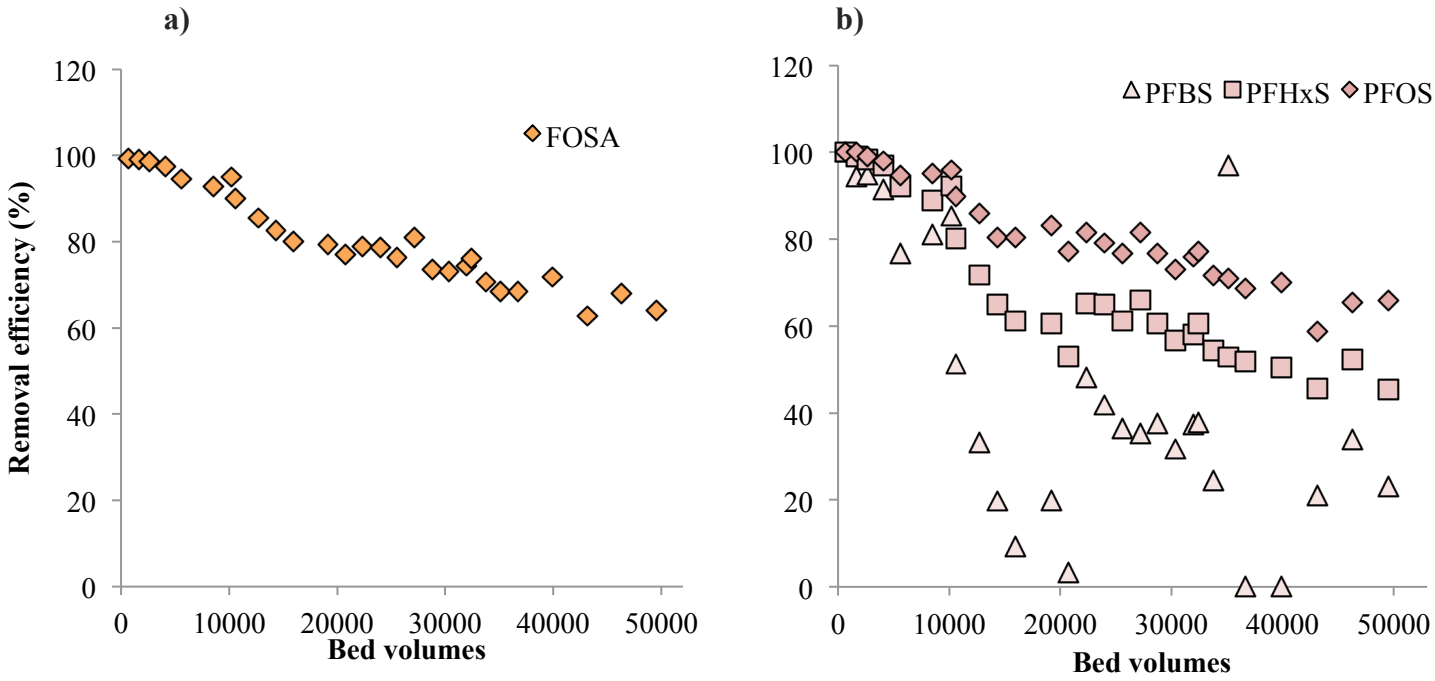
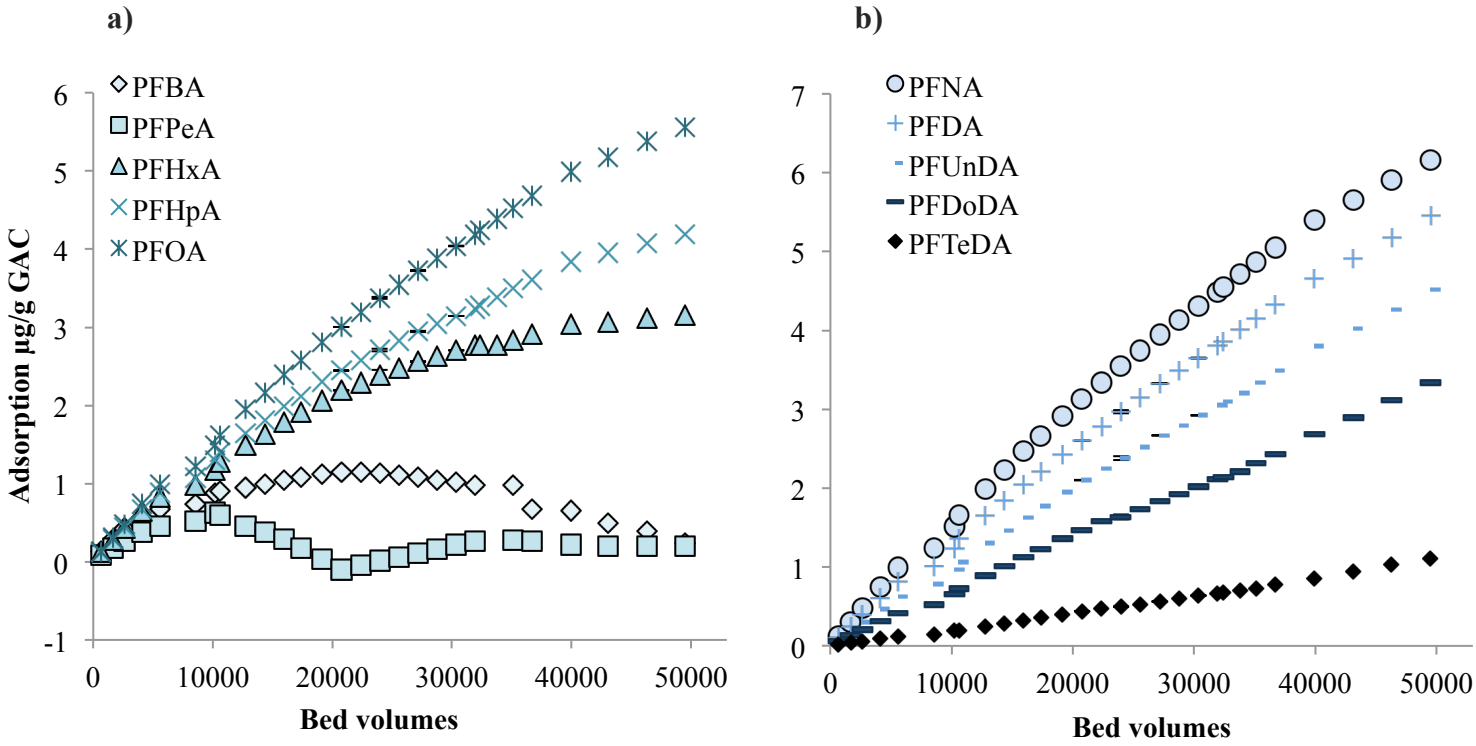


Figure 13 The removal efficiency (%) of a) FOSA and b) PFSAs using GAC as adsorbent.

The cumulative adsorption of PFASs, in microgram per gram (µg/g) GAC, provides information about GAC's sorptive process. For example, equilibrium is reached when a curve levels out and desorption occurs when a curve decreases. The C_3-C_5 PFCAs showed equilibrium (PFBA, PFHxA) or desorptive behaviour (PFBA, and PFPeA from 1,000-2,000 BVs) (Figure 14a), whilst the C_6-C_{11}, C_{13} PFCAs (PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA and PFTeDA) were continuing to adsorb (Figure 14b). This was also true for FOSA (Figure 14c) and the PFSAs except PFBS, showing equilibrium behaviour (Figure 14d).



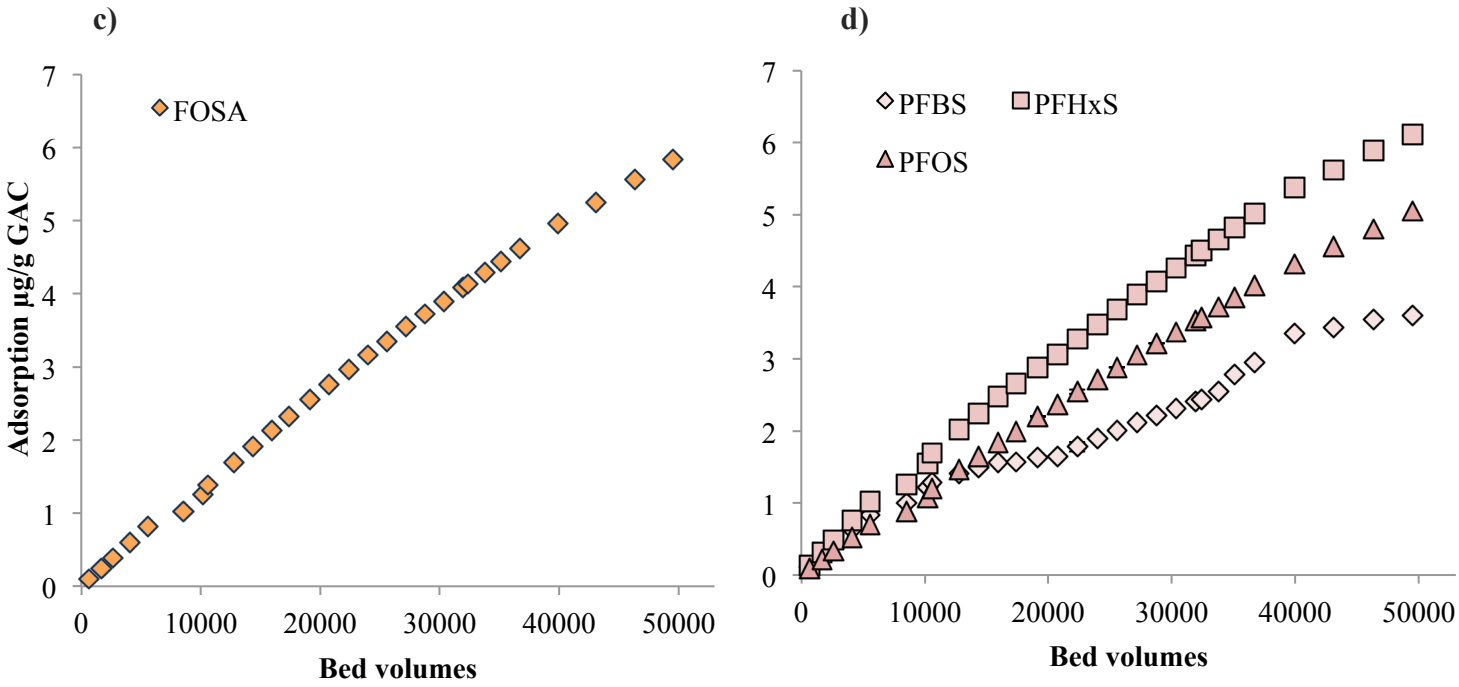


Figure 14 The cumulative adsorption of perfluoroalkyl substances to GAC (µg/g) for a) short-chained (C_3-C_7) PFCAs and b) long-chained (C_8-C_{11}, C_{13}) PFCAs, c) FOSA and d) PFSAs. The data for PFPeA and PFHxA for the samples T28 and T29 were removed from a) due to contamination during sample preparation.

The removal efficiency at the first sample time (T1; 871 BVs, Figure 15a) was 100% for FOSA, the PFSAs and PFCAs of perfluorocarbon chain length C_6-C_9. The least removed PFCA was the one with the longest chain length (PFTeDA, C_{13} of 90%).
For sample T15 (26,375 BVs) (Figure 15b), PFTeDA was removed to the highest extent (86%). A dependency between perfluorocarbon chain length and removal efficiency was also displayed, where longer chain length was associated with higher removal efficiency (Figure 15b). PFPeA, however, deviated from this pattern, and was negative (-69%). For sample T25 (40,613 BVs) (Figure 15c), PFBA (C_3), belonging to the PFCAs, showed negative removal efficiency (-12%). The PFAS with the highest removal efficiency was PFTeDA at 75%. Lastly, for sample T35 (62,920 BVs; Figure 15d), the perfluorocarbon chain length/removal efficiency dependence was the most pronounced. For all time points, the removal efficiency for PFOS and FOSA was similar but decreased over time from 100% (T1) to ~55% (T35). All PFCAs were initially well removed (90-100%, sample T1), however, for sample T35, the removal efficiency for the individual PFCAs was in the range of -23-95%. The C_4 PFCA (PFPeA) and C_4 PFSA (PFBS) were approx. removed to the same extent, except for T15, where PFPeA had a removal efficiency of -70% and PFBS 4.0%. The negative removal efficiency for PFPeA was due to the high PFPeA concentration at that time (95.6 ng/L). PFPeA and PFBS had removal efficiencies 24-32% at T25, decreasing to -1.9-10% at T35.

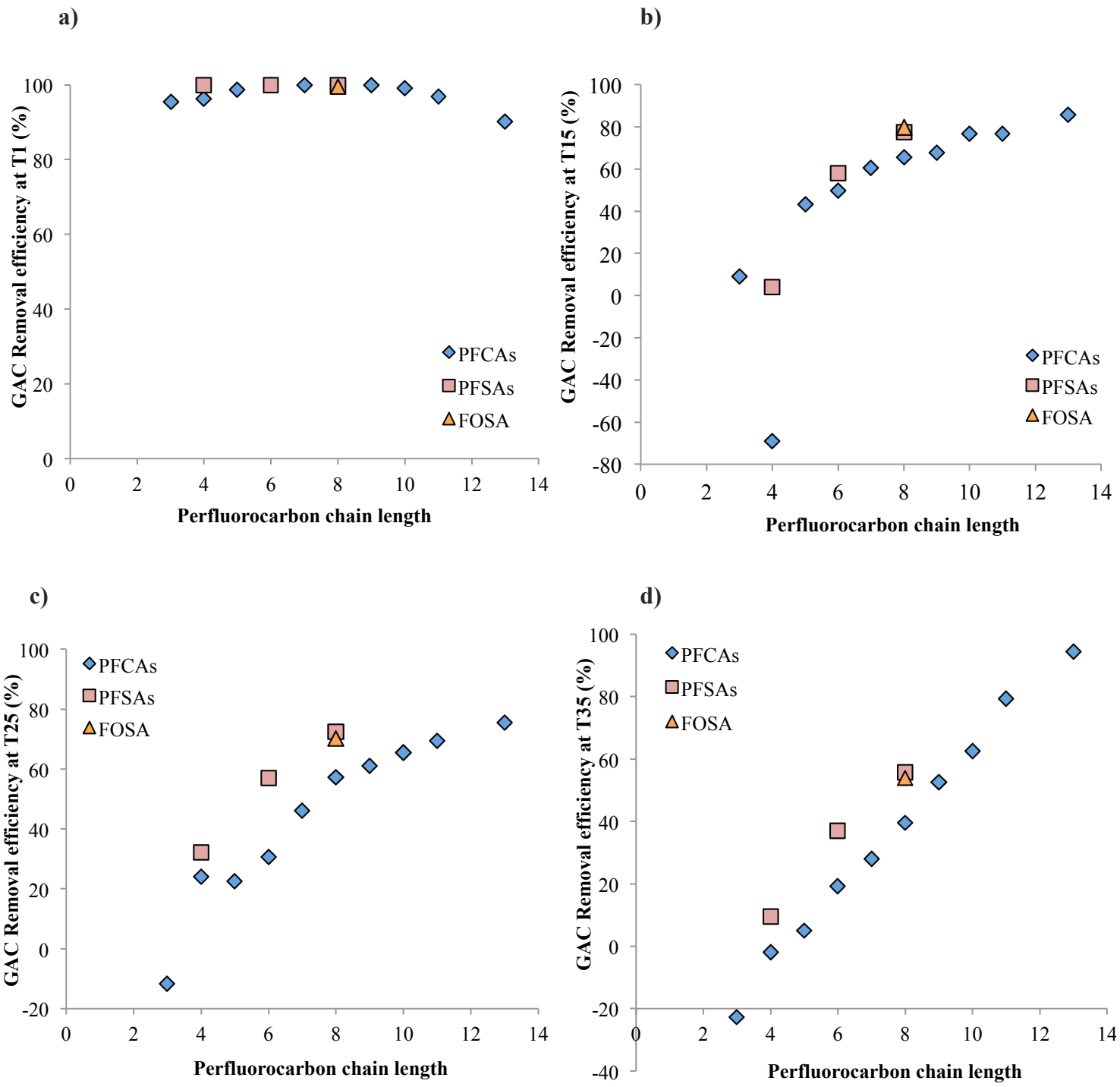


Figure 15 The removal efficiency (%) at sample times a) T1, b) T15, c) T25 and d) T35 for PFASs of different perfluorocarbon chain length and functional group.

4.2.2 Anion exchange

Using AE, the PFAS with the highest average removal efficiency was PFOS (C_8, 95 ± 5.4%) (Table 5). All short-chained PFCAs (PFBA, PFPeA, PFHxA, PFHpA and PFOA) had negative removal efficiencies on the last sampling day (T35; 62,920 BVs). PFPeA (C_4) had the lowest average removal efficiency and the highest standard deviation, -23 ± 78%.

Table 5 The average removal efficiency ± standard deviation (%), and the removal efficiency at the final sampling day (T35; 62,920 BVs) for all detected PFASs, using AE as adsorbent.

PFAS	Average removal efficiency (%) (*n*=30)	Removal efficiency at final sampling day (T35) (%)
PFBA (C_3)	0.6 ± 32	-22
PFPeA (C_4)[a]	-23 ± 78	-18
PFHxA (C_5)[a]	21 ± 38	-25
PFHpA (C_6)	37 ± 38	-30
PFOA (C_7)	59 ± 30	-5.9
PFNA (C_8)	73 ± 21	25
PFDA (C_9)	82 ± 13	52
PFUnDA (C_{10})	87 ± 8.9	70
PFDoDA (C_{11})	86 ± 9.3	84
PFTeDA (C_{13})	78 ± 16	94
FOSA (C_8)	83 ± 14	49
PFBS (C_4)	62 ± 28	9.8
PFHxS (C_6)	88 ± 11	74
PFOS (C_8)	95 ± 5.4	91

[a] The data from sample times T29 and T30 were removed due to contamination of the sample during sample preparation.

The removal efficiency decreased with increasing number of bed volumes for C_3-C_7 PFCAs. PFPeA (C_4) had negative removal efficiencies of -182- -116% for 13,318-26,375 BVs. However, after the next following sample time of 28,409 BVs, the removal efficiency was 20.3%. For samples after 54,772 BVs, the removal efficiency was negative for all but PFOA (C_7, 6.8% removal efficiency) (Figure 16a). The (C_8-C_{11}, C_{13}) PFCAs (Figure 16b) were more readily removed by AE. PFTeDA (C_{13}) exhibited an increase in removal efficiency between 46,633-58,834 BVs, reaching 100% removal at the latter. PFNA (C_8) had the lowest removal efficiency of 25% after the last sample time (T35; 62,920 BVs). Hence, the differences in removal efficiencies were prominent between the different long-chained PFCAs (e.g. 100% vs. 25.2% for PFTeDA and PFNA). Samples T29 and T30 were removed for compounds PFPeA and PFHxA due to contamination during sample preparation (Figure 16a).

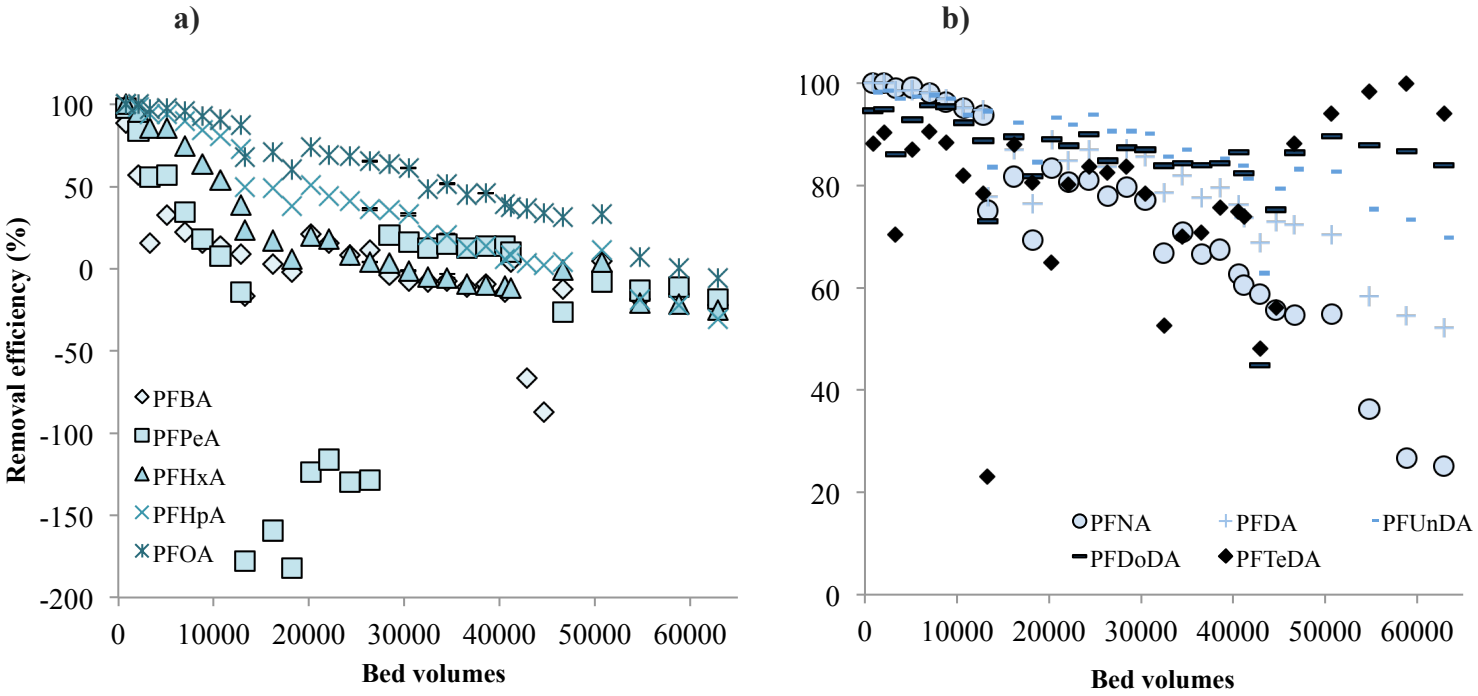


Figure 16 The removal efficiency (%) for a) (C_3-C_7) PFCAs and b) (C_8-C_{11}, C_{13}) PFCAs using AE resin as adsorbent. In a) data points for compounds PFPeA and PFHxA at sample times T29 and T30 were removed.

The removal efficiency of FOSA (C_8) (Figure 17a) was gradually decreasing, from 100% after 0 BVs, to 49% after the last sample (62,920 BVs). PFOS (C_8) was the best removed PFAS, with an average removal efficiency of 95 ± 5.4% (Figure 17b), followed by PFHxS, averaging 88 ± 11%. PFBS (C_4) had the lowest removal efficiency of the PFSAs, with 9.8% after 62,920 BVs.

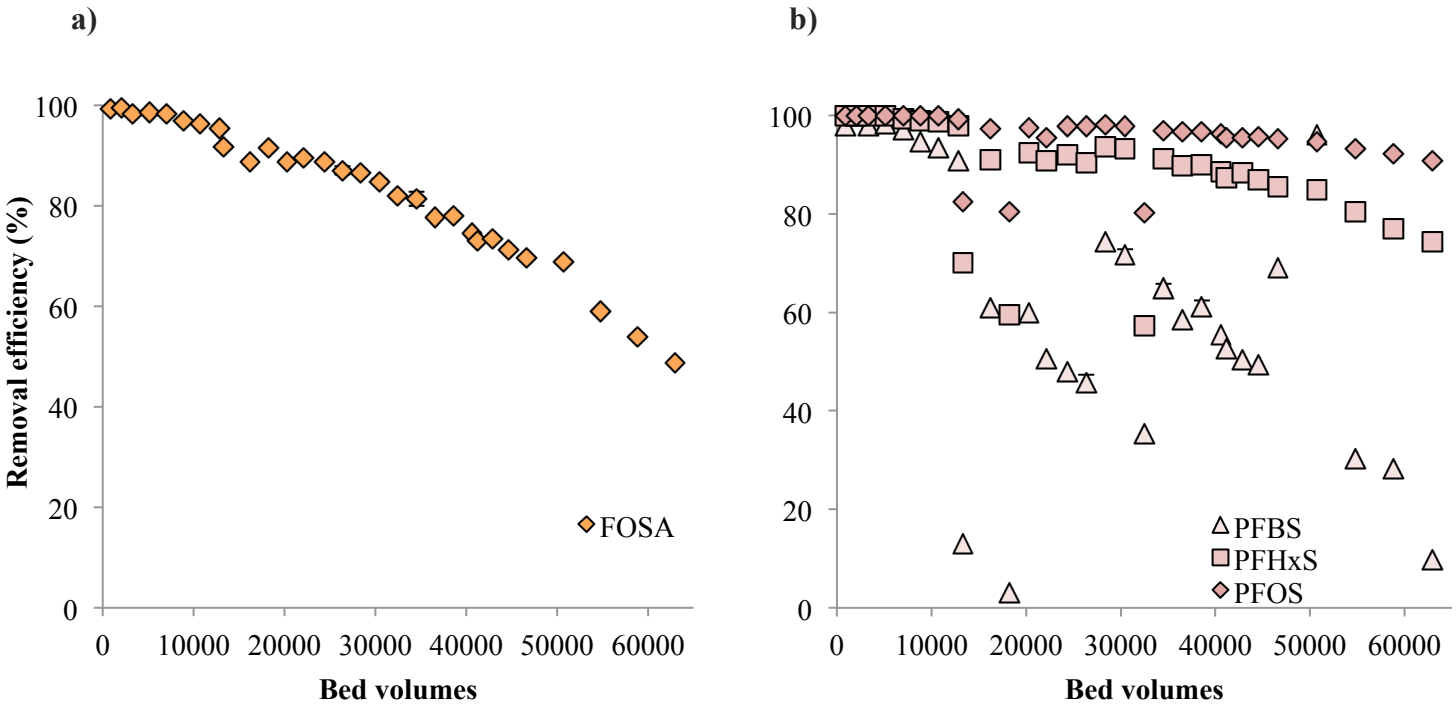


Figure 17 The removal efficiency (%) of a) FOSA and b) C_4-C_8 PFSAs using AE as adsorbent.

The C_3-C_7 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA) exhibited desorptive behaviour, with PFOA (C_7) being the last to start desorbing, after 50,704 BVs (Figure 18a). PFBA (C_3) was desorbing continuously from 26,375 BVs, and the adsorption was below zero from 54,772 BVs (-0.08 µg/g). The long-chained PFCAs (PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA) were continuing to be adsorbed throughout the experiment (Figure 14b). This was also true for FOSA (Figure 18c), and the PFSAs (PFHxS, PFOS and PFBS) (Figure 18d). However, PFBS displayed near-equilibrium behavior after 58,834 BVs.

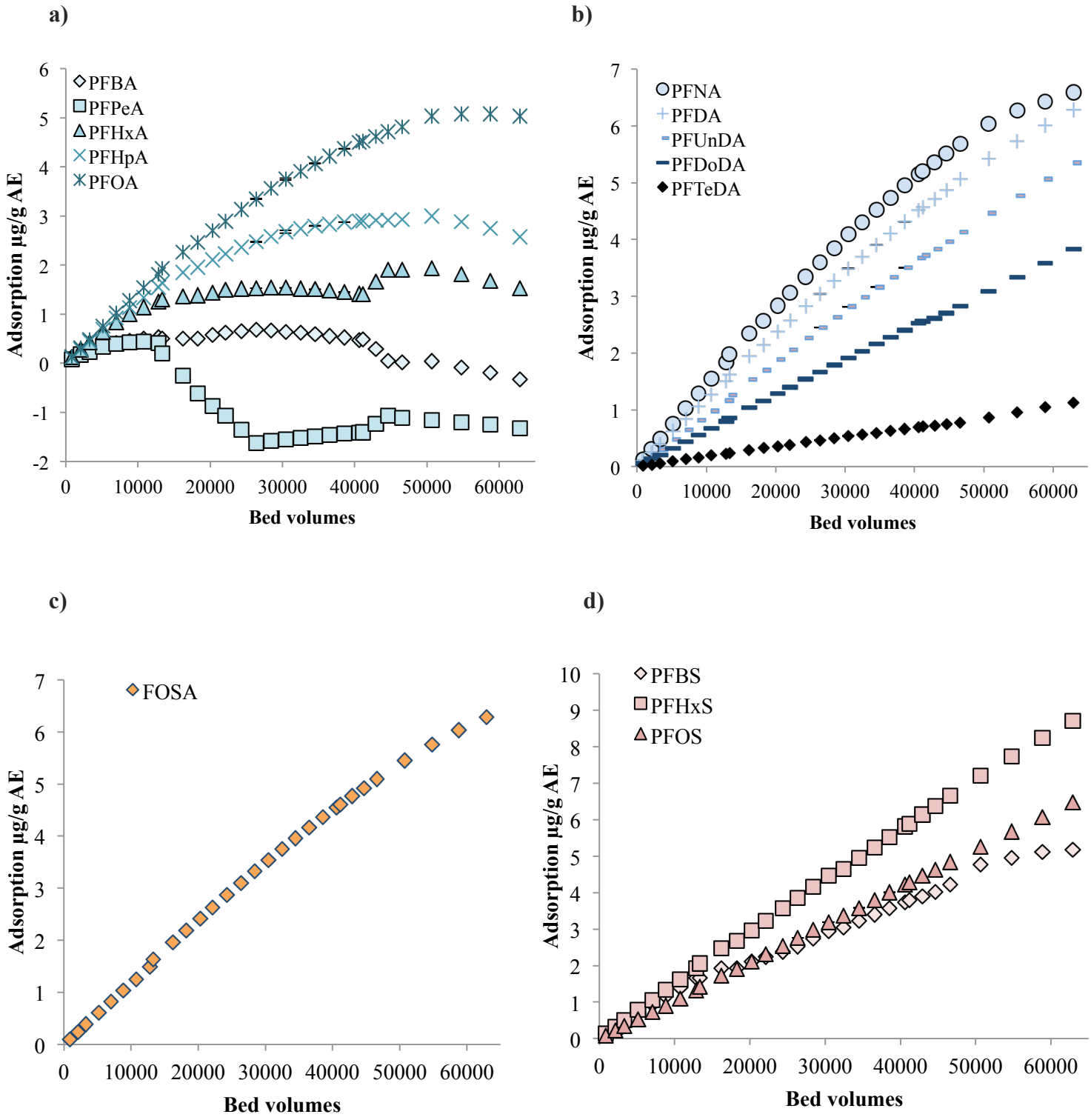
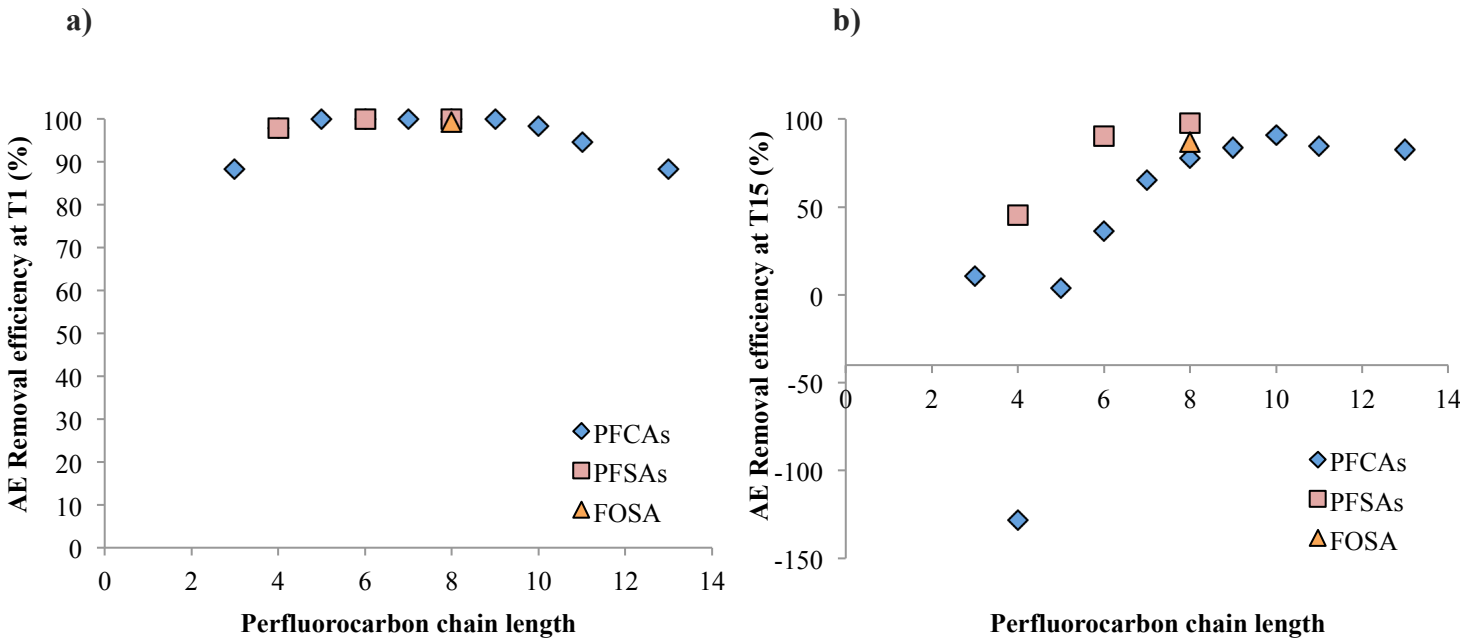


Figure 18 The cumulative adsorption of perfluoroalkyl substances to AE resin (µg/g), for a) short-chained (C_3-C_7) PFCAs and b) long-chained (C_8-C_{11}, C_{13}) PFCAs, c) FOSA and d) PFSAs. Samples T29 and T30 were removed for the compounds PFPeA and PFHxA due to contamination during sample preparation.

The removal efficiency at sample T1 (871 BVs) (Figure 19a) was 100% for FOSA, PFOS, PFHxS, and PFCAs of perfluorocarbon chain length C_5-C_9. Least removed were PFBA (C_3) and PFTeDA (C_{13}) of 88%. For sample T15 (26,375 BVs) (Figure 15b), PFOS (C_8) was removed to the highest extent (98%), followed by PFHxS (C_6, 89%), both PFSAs. The removal efficiency of PFOS, FOSA and PFNA was 98%, 87%, and 78% respectively. Having the same perfluorocarbon chain length (C_8), the difference between functional groups is displayed. This pattern, where PFOS was best removed and PFNA least removed, was also seen for samples T25 (Figure 19c) and T35 (Figure 19d). The removal efficiency of FOSA was decreasing; 99% at T1 (Figure 19a), 87%, T15 (Figure 19b), 75%, T25 (Figure 19c) and 49%, T 35 (Figure 19d). At the last sampling occasion (T35, 62,920 BVs), two PFCAs had negative removal efficiency; PFHxS of -10% and PFBS of -14%, the latter also being the least removed PFSA for this sample. Best removed at sample T35 was PFTeDA, 94%. FOSA (C_8) and PFOS (C_8, PFSA) were initially similarly removed (99-100%), with increasingly different removal for samples T15-T35: 87-98%, 75-96%, and finally 49-91%.



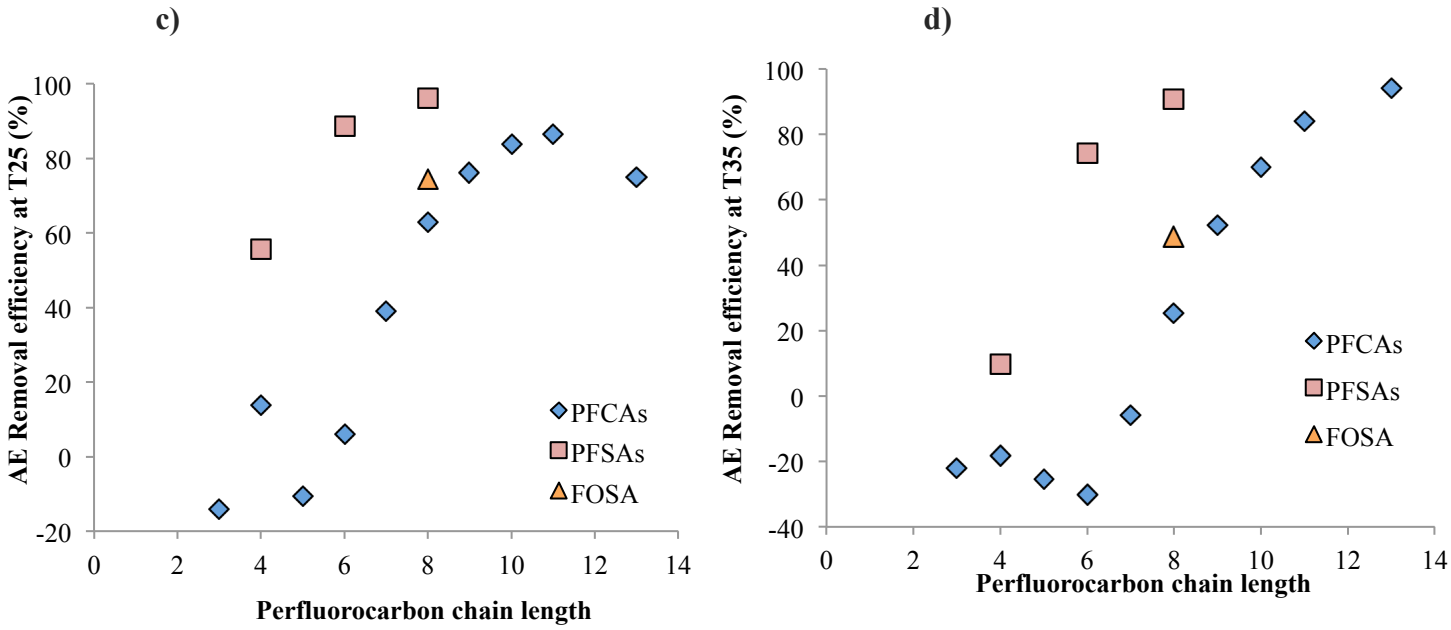


Figure 19 The removal efficiency (%) at sample times T1, T15, T25 and T35 for perfluoroalkyl substances of different perfluorocarbon chain length and functional group using AE resin as adsorbent.

4.2.3 Removal efficiency of linear and branched isomers of PFOS, FOSA and PFHxS

Using AE as adsorbent (Figure 20a), the average removal efficiency of PFOS for linear and branched isomers was 95±5.5% and 93±7.5%, respectively. A greater difference between removal efficiency of the two isomers was seen when using GAC as adsorbent; the linear isomer was on average removed 81±13% and the branched 71±18% (Figure 20b). On the last sampling occasion, the difference in removal efficiency was 2.1% for AE (62,920 BVs) and 20% for GAC (49,523 BVs), with linear isomers having higher removal efficiency for both adsorbents. Note that this is the opposite of the NF-membrane, where branched isomers of PFOS had higher removal efficiency than linear (Figure 11a).

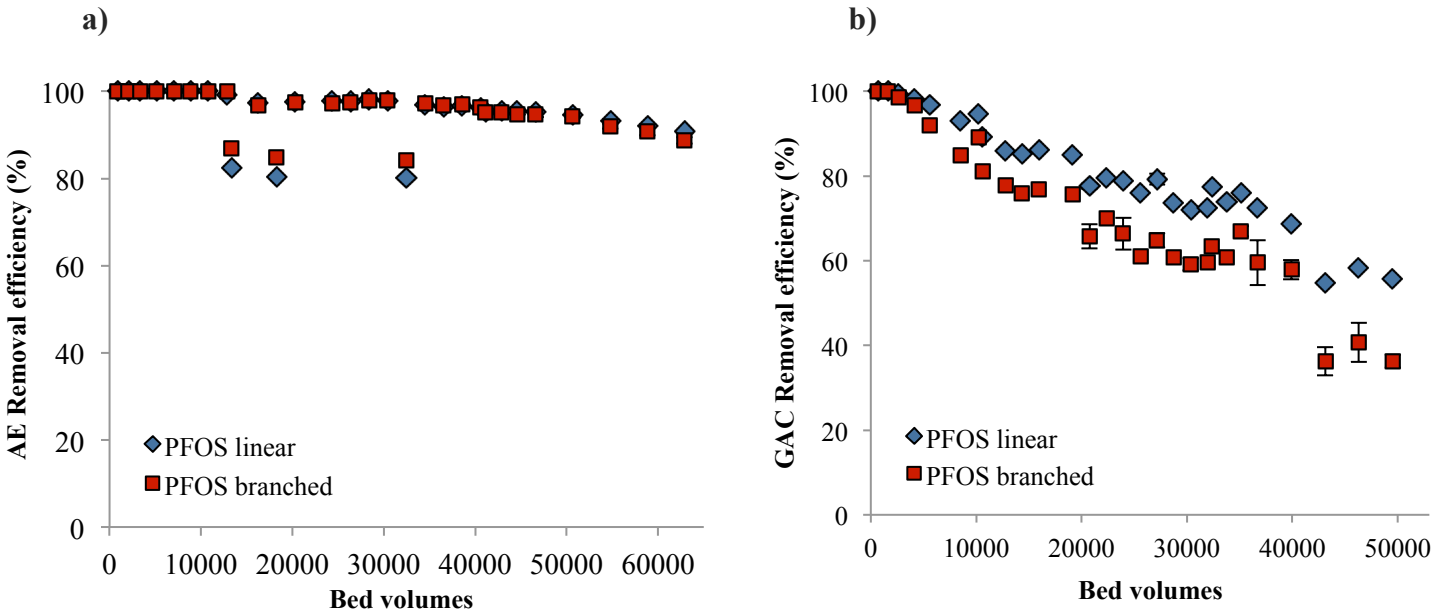


Figure 20 The removal efficiency (%) for a) AE and b) GAC for linear (blue) and branched (red) isomers of PFOS. Error bars show the standard deviation for the collected duplicate samples; T15, T20, T22, T24 and T30-T35.

Linear and branched isomers of FOSA were removed to the same extent when AE was used as adsorbent (83±14% removal efficiency for linear and 83±15% for branched, Figure 21a). A difference between the two isomers could, however, be seen for GAC (Figure 21b); the average removal efficiency of linear isomers was 80±13% and for branched 72±17%. For the last sampling occasion, the difference in removal efficiency was 8.0% for AE (62,920 BVs) and 14% for GAC (49,523 BVs), with linear isomers having higher removal efficiency for both adsorbents.

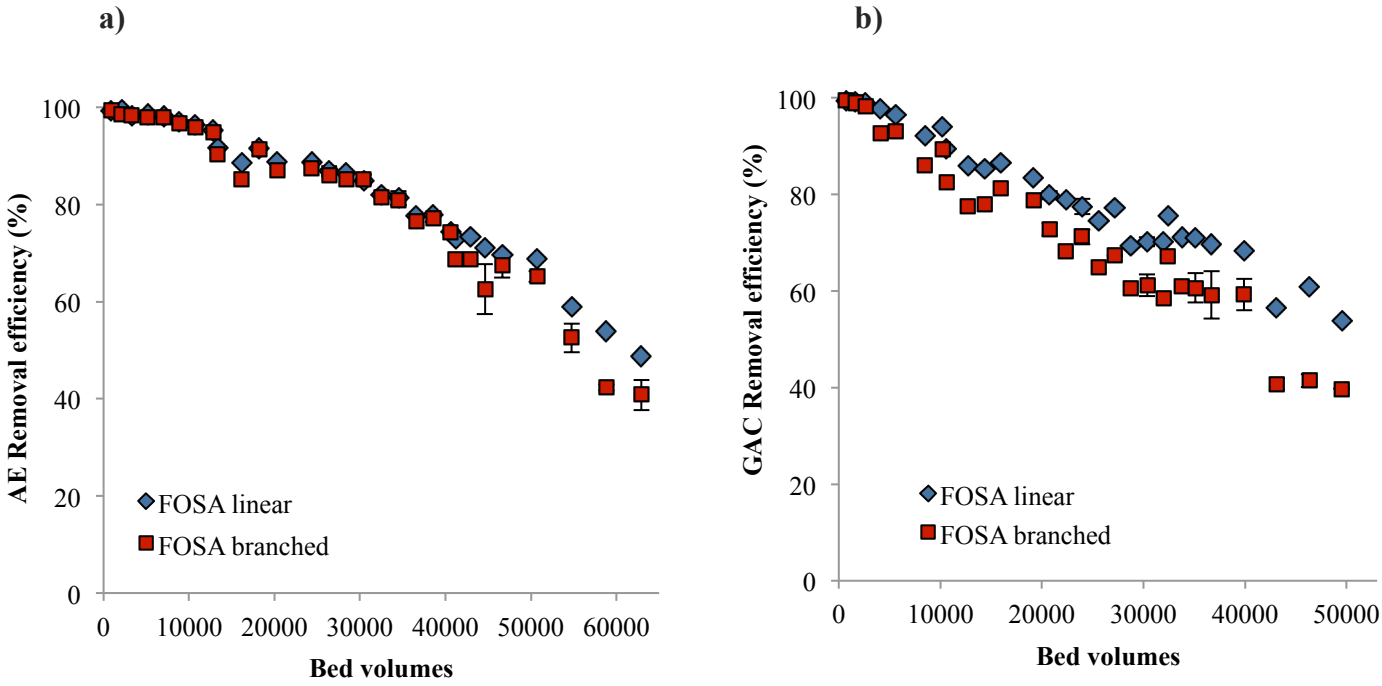


Figure 21 The removal efficiency (%) for a) AE and b) GAC for linear (blue) and branched (red) isomers of FOSA. Error bars show the standard deviation for the collected duplicate samples; T15, T20, T22, T24 and T30-T35.

Using AE as adsorbent (Figure 22a), the removal efficiency of PFHxS for linear isomers was 88±11%, and for branched 84±15%. A greater difference was seen when comparing the removal of the isomers using GAC as adsorbent; linear had a removal efficiency of 80±13% and branched 72±17% (Figure 22b). For the last sampling occasion, the difference in removal efficiency was 6.6% for AE (62,920 BVs) and 21% for GAC (49,523 BVs), with linear isomers having higher removal efficiency for both adsorbents.

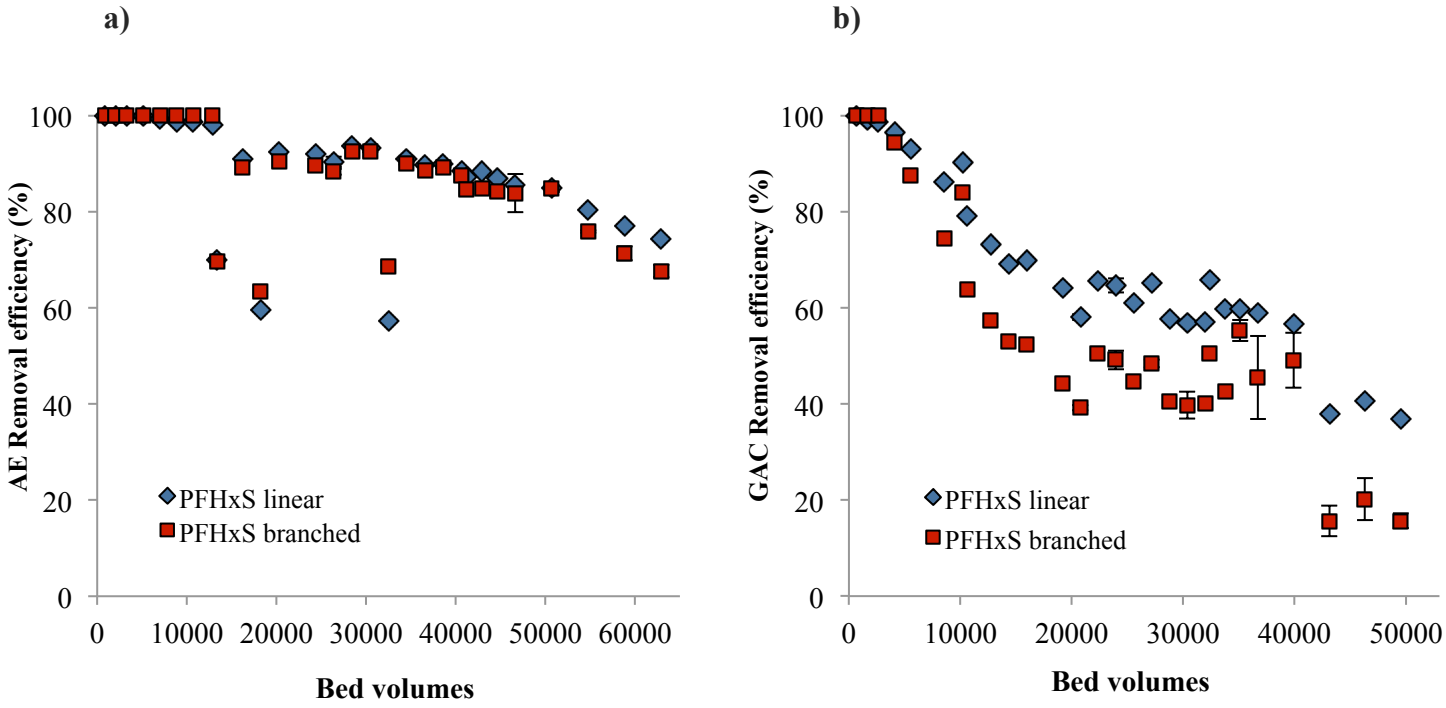


Figure 22 The removal efficiency (%) for a) AE and b) GAC for linear (blue) and branched (red) isomers of PFHxS. Error bars show the standard deviation for the duplicate samples that were collected; T15, T20, T22, T24 and T30-T35.

5. DISCUSSION

5.1 NANOFILTRATION MEMBRANE

After day 42, a 23% increase in the raw water concentration of PFBS occurred (Figure 4b), which ensued an increase in the permeate water concentration of a matching 23% (Figure 5b). As the removal efficiency of PFBS remained approx. constant at 92%, this demonstrates how the membranes remove a percentage of the concentration in the incoming water. The PFAS removal is hence dependent on the water quality, which also is supported by a previous study by Kimura et al. (2003). PFHxS had a high removal efficiency of 94±1.0% (Figure 9b), and was present in the highest concentration in the raw water (Figure 4b). The PFHxS concentration (in average 81.4±30.8 ng/L) was near the Swedish Σ_7PFAS (PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA) action limit for drinking water of 90 ng/L. No international guidelines were available for PFHxS, but the U.S. EPA has issued health advisory values for short-term exposure of PFOS and PFOA of 200-400 ng/L. In this study, PFOS and PFOA were detected at raw water concentrations of 19.9±6.78 and 7.79±4.52 ng/L, respectively (Figure 4a-b), which is well below these advisory values. It should however be noted that the EPA's health advisories are for short-term exposure. A continued oral intake should reasonably be compared to long-term exposure guidance levels, none of which the EPA has issued. The 3M Company has however determined a life time DWHA for PFOS of 100 ng/L. Suspicion regarding the bias of this advisory may arise when recalling that the company previously was one of the world's largest manufacturers of PFASs (Buck et al., 2011).

The concentrations of PFBA, PFHpA and PFOA in the permeate water were below MDL, and therefore considered well removed (Figure 5a). All the PFSAs had concentrations above MDL in the permeate water, resulting in removal efficiencies of 96±0.40%, 94±0.78% and 92±0.40% for PFOS, PFHxS and PFBS, respectively. Within this group of PFASs, the removal efficiency is evidently a function of molecular length. These results are in accordance of a bench-scale study by Appleman et al. (2013), who found permeate concentrations below MDL for all PFASs except PFBS and PFHxS (10-40 ng/L). PFOS, having the longest chain-length of the PFSAs, was not detected in the permeate in the Appleman et al. (2013) study, and the conclusion was drawn that size exclusion is an important retaining mechanism.

The PFNA concentration in the permeate was initially low (~0.3 ng/L for days 0 to 21). An increase was observed for sample T5 and T6 (day 28 and 35), reaching 2.02 ng/L, and then doubling to 4.06 ng/L (Figure 5a). The concentration of PFNA in the reject water was below the MDL for most sampling times, and in particular for sample T5 and T6. With low PFNA concentration in the reject water, and a relatively constant concentration in the raw water, the reason for the increase in the permeate for the two mentioned sample points is unclear. One explanation could be that the PFNA

diffused across the membrane. A study by Steinle-Darling & Reinhard (2008) examined the factors governing PFAS rejection using four different types of membranes, one of which being the same branded NF270 membrane as was used in this study. There, FOSA was the only PFAS found in the permeate. The plausible explanation given was that FOSA does not have a charged head group like the other PFASs, and therefore does not repel the negatively charged membrane surface to the same extent. Instead FOSA absorbs into the membrane and diffuse to the permeate side. The other PFASs were found to *ad*sorb to the membrane surface, with higher adsorption for increasing perfluorocarbon chain length. The authors hypothesised that electrostatic repulsion stops PFASs with charged head groups from diffusing to the permeate side.

In this study, where PFNA (having a charged head group) was found in the permeate, the question is whether some other mechanism could have induced the diffusion of PFNA. One such effect could be due to the hardness of the incoming raw water. Harder water contains more divalent cations (Ca^{2+} and Mg^{2+}), which in some cases have been shown to reduce the negative charge of the membrane surface, and hence inhibit the mechanism of electrostatic repulsion (Yoon et. al., 2002; Boussahel et al., 2002). Before undergoing softening processes, the water taken from Stadsträdgården well field in Uppsala is hard (>10 °dH) (Uppsala Vatten, 2015). Hypothesising that the presence of cations reduced the negative charge of the membrane, and further hypothesising that PFNA adsorbed in a larger extent than the other PFASs because of its longer perfluorocarbon chain length; one may speculate that PFNA diffused across the membrane (supported by Braeken et al., 2005 and Yoon et al., 2006).

The experimentally determined membrane cut-off for the PFSAs was 340 Da, which is considerably higher than the theoretical 270 Da (Figure 10). The membrane's retaining capacity of PFSAs was hence lower than the molecular weight-based retention capacity stated by the manufacturer, and the presence of cations could be a contributing factor to this. PFNA has a molecular weight of 463 Da, which is well above the experimentally determined PFSA cut-off of 340 Da. Despite the fact that its functional group is different than the PFSAs, it can be speculated that it could be retained by size exclusion. This is supported by a study by Bellona & Drewes (2005), which concluded that the retention lowering effect of cations decreased the retention only of ions with smaller molecular weight than the MWCO of the membrane. Furthermore, no changes in pressure or flow rate, corresponding to the increased PFNA concentration, were observed in the NF-plant (Table A1, appendix). Therefore, due to conflicting explanations and the small number of occurrence (n=2), it is difficult to draw any conclusion regarding the PFNA concentrations found in the permeate. The possibility of sample contamination during sample preparation is prevailing, and further samples should be studied to draw any conclusion regarding the above-mentioned scenarios.

The overall removal efficiency of the NF-pilot plant can, however, be considered sufficiently good when comparing the average Σ_7PFAS permeate concentration of 8.19±1.64 ng/L to the Swedish action limit of 90 ng/L.

The samples taken when the NF-plant was dysfunctional (after 42 days) are of interest since the conditions in the plant were different at this time. There was no water flow due to the pre-filter being clogged, and hence other mechanisms may influence the migration across the membrane. The highest permeate concentration was seen for PFHxS (64.2 ng/L), followed by PFHxA (16.2 ng/L) (Table 3). In the raw water, PFHxS was of the highest concentration (86.5 ng/L), followed by PFOS (20.8 ng/L) and then PFHxA (12.3 ng/L) (Figure 4b). As both PFHxS and PFHxA were present in high concentrations in the raw water, there was a concentration gradient over the membrane (i.e. a difference in concentration between the raw-and permeate sides). Diffusion of PFHxS and PFHxA across the membrane may hence have occurred, why concentrations were found in the permeate water. PFOS, which had a concentration of 2.19 ng/L in the permeate, did not diffuse in accordance with its raw water concentration (Table 3, Figure 4). One explanation could be that it has a larger molecular weight (499 Da) than PFHxS and PFHxA (399-313 Da), and hence size exclusion may hinder its diffusion. All PFASs had elevated concentrations in the permeate water at day 42, which is only to expect as concentration gradients over the membrane were present for all compounds. The concentration of PFASs in the permeate as a percentage of the concentration in the raw water was calculated, deducing size-exclusion as one factor governing this mechanism for the PFCAs (Table 6). PFHxS was an exception from this general rule for unknown reasons.

Table 6 The molecular weight (Da) and the accumulation in the permeate water expressed as permeate water divided by raw water concentrations (%) for the different PFASs for day 42.

PFAS	Molecular weight (Da)	Permeate concentration compared to the raw water concentration (%)
PFBA	213	190
PFPeA	263	180
PFHxA	314	130
PFHpA	363	71
PFOA	413	53
PFNA	463	4
PFBS	299	58
PFHxS	399	74
PFOS	499	11

The removal efficiency of PFOS and PFHxS was higher for branched isomers, meaning that the NF membrane retained branched isomers better (Figure 11a-b). Two molecular features may explain this: hydrophobicity and molecular volume. Branched isomers of PFOS are more hydrophilic, and therefore more water soluble, than linear

PFOS (Wang et al., 2011; Zhang & Qin, 2014). Hydrophobicity has been coupled to increased sorptive interactions (Steinle-Darling & Reinhard, 2008), and adsorbed molecules can diffuse across the membrane to the permeate side (Braeken et al., 2005; Yoon et al., 2006). Following this, hydrophilic molecules exhibiting *less* sorptive interactions, and hence adsorbing to the membrane to a smaller extent, would not diffuse to the same extent. One may speculate that the same is true for PFHxS, and that this is the reason why branched isomers of both compounds are better retained. However, as mentioned in the previous section, due to PFHxS and PFOS (MW 399-499 Da, respectively) both exceeding the MWCO of the membrane, the main mechanism of retention should be of the sieving type, such as size-exclusion (Boussahel et al., 2002). Branched isomers have smaller molecular volume than corresponding linear isomers (Wang et al., 2011). This may, however, be a somewhat misleading fact in this context. Picturing the membrane as a very fine sieve, with molecules being able to pass through the sieve by its pores; a long, thin object should pass through the pores more easily, even though it has a larger volume than a spherical object. Therefore, the relation between length and width plays an important role in the rejection process (Chen et al., 2004). However, no data on molecular sizes of PFASs was found. The combination of increased diffusion of linear isomers and a higher retention due to size-exclusion of branched isomers, must lead to the conclusion that the membrane remove branched isomers better than linear ones, in line with the results.

The concentration factor (Figure 8) is relatively constant for all samples except for the first three samples (0-14 days). Here, concentrations below MDL for PFOS and PFHxS in the raw or reject water resulted in large (day 0) and small (days 7-14) concentration factors. These low concentrations are most likely due to higher uncertainties at low concentration levels (close to the MDL).

The concentration in the reject water of PFHxS was approximately 400 ng/L, 4 times the life time advisory issued by the 3M Company of 100 ng/L (Figure 6b). Oral intake of untreated reject water is therefore strongly discouraged. The Σ_7PFAS for the reject water was approx. 600 ng/L, and hence well above the Swedish action limit for drinking water of 90 ng/L. As PFASs are very persistent in nature, and also bioaccumulative, the disposal of this reject water is a central question for water treatment plants implementing nanofiltration technology.

5.2 COLUMN EXPERIMENT

Due to the anionic nature of PFASs at environmentally relevant pH, adsorption to GAC or AE resin has been proposed as a purification method for reject water obtained from nanofiltration plants. Several experiments have been conducted on this subject, one of them being the column experiment at Bäcklösa DWTP. It was started by Englund in 2014 (Englund, 2015), continued by Östlund (2015), and finalized during this master's project. The following discussion reviews the results from the column experiment.

5.2.1 Comparison of the removal efficiency of GAC and AE

The PFCAs were similarly removed using GAC and AE, particularly for the long-chained C_8-C_{11}, C_{13} (Table 4, Table 5). At the last sampling occasion (T35), the removal efficiency of PFBA (C_3) was the same for both adsorbents (-22%) (Table 4, Table 5). Furthermore, the removal efficiency using AE was negative for all short-chained PFCAs (C_3-C_7) ranging from -30 to -6% (Figure 16a, Table 5). For GAC, removal efficiencies of PFBA (C_3) and PFPeA (C_4) were negative (-22 to -1.9%), whilst PFHxA, PFHpA and PFOA (C_5-$C_{7)}$ had positive removal efficiencies (4.9-28%) (Figure 12a, Table 5). Negative removal efficiencies are probably an indication of desorption. Longer-chained PFASs have been shown to dislodge shorter-chained ones and then adsorb to the material in their place (Higgins & Luthy, 2006; Eschauzier et al., 2012). This is further supported by the increase in removal efficiency of PFTeDA (C_{13}) on the one hand, and the simultaneous decrease in removal of PFNA (C_8) on the other, seen in this experiment (after 40,000 and 50,000 BVs for GAC and AE respectively) (Figure 12 a-b, Figure 16 a-b).

FOSA had similar average removal efficiency using GAC and AE (80-83%) (Table 4-5). At approx. 50,000 BVs, the removal efficiency was 69% for AE and 64% for GAC (Figure 13a, Figure 17a). After 50,000 BVs, the AE removal rapidly decreased from 64% to 49% (62,920 BVs). Because there is no data of the GAC removal efficiency after 50,000 BVs, it is still unknown whether the same drop would occur.

All PFSAs (PFBS, PFHxS, PFOS) had better average removal efficiencies using AE than GAC: (62%, 88%, 95% compared to 49%, 69%, 81%, respectively). This is in concurrence with a study conducted by Appleman et al. (2014), in which PFSAs were removed to a higher extent than PFCAs, using AE.

However, the above discussion concerns the removal efficiency when the same GAC and AE were used for 167 days, equalling 49,520 and 62,920 BVs, respectively. During this comparatively long time, the removal efficiency of individual PFASs was decreasing for most congeners, but increasing for some. To produce treated water of a uniform quality, the GAC and AE must hence be replaced periodically. How

frequently this replacement is required depends on which PFASs are desired to be removed, and to what level.

5.2.2 Influence of the perfluorocarbon chain length and functional group on the removal efficiency

When comparing GAC and AE, similarities in removal efficiency, linked to functional group and perfluorocarbon chain length can be seen. PFBS and PFPeA have the same perfluorocarbon chain length, viz. C_4. Using GAC as adsorbent, PFBS was removed to a higher extent, averaging 49% compared to 13% for PFPeA (Table 4). Likewise, PFBS had a higher average removal (62%) than PFPeA (-23%) when AE was used as adsorbent (Table 5). The average removal efficiency of PFHxS and PFHpA (both C_6) was 69% and 55% for GAC (Table 4). The removal efficiency for the same substances was 88% and 37% for AE (Table 5). Using GAC, the average removal efficiency of PFNA, FOSA, and PFOS, all of perfluorocarbon chain length C_8, was 71%, 80% and 81%, respectively (Table 4). After the last sample (49,523 BVs), the removal efficiency of PFNA, FOSA and PFOS was 40%, 64% and 66% using GAC. For AE, the removal efficiencies of the same compounds were 25%, 49% and 91% after the last sampling time (62,920 BVs). Consequently, the similarity in removal efficiency of PFASs of the same perfluorocarbon chain length was more evident for GAC than for AE, and for longer perfluorocarbon chain lengths than shorter (compare PFBS and PFPeA to PFNA, FOSA and PFOS).

The adsorption (as a percentage) increased with increasing perfluorocarbon chain length, in line with Ochoa-Herrera (2008) among others. The cumulative adsorption however, does not display this behaviour as PFOA, PFNA, FOSA and PFHxS reached the highest cumulative adsorption (5-6 µg/g GAC and 5-8 µg/g AE). PFTeDA with the longest perfluorocarbon chain length (C_{13}), had the lowest cumulative adsorption of the PFCAs (Figure 14b and 18b). However, this conforms to the incoming tank concentration of PFTeDA, which was lower compared to the other PFASs (Figure A1, Appendix).

The PFASs with the highest removal efficiency using GAC were PFTeDA (81%), PFOS (81%) and FOSA (80%) (Table 4, Figure 12b and 13a-b). These three PFASs have different functional groups, but the longest perfluorocarbon chain length of their respective group (C_{13}, C_8 and C_8). Lower sorption capacity of PFASs with longer chain length, indicated by decreasing log K_{OC} values, is one proposed explanation for the correlation (Ahrens, 2010). Three additional PFASs had longer perfluorocarbon chain length than PFOS and FOSA: PFDA (C_9), PFUnDA (C_{10}) and PFDoDA (C_{11}). Nevertheless, the removal efficiencies of these congeners were lower than that of PFOS and FOSA, indicating that the chain length is not the only attribute influencing the adsorption. PFDA, PFUnDA and PFDoDA have the same functional group as

PFTeDA, further displaying that the adsorbent also has an affinity for some functional groups over others.

5.2.3 Comparison of the removal efficiency for linear and branched PFASs

Linear isomers were better removed than branched, for both GAC and AE (~10% and ~2%, respectively, for the removal of PFOS). For the last sample, linear FOSA was removed 8.0% better than branched, when AE was used as adsorbent (62,920 BVs) (Figure 21a). For GAC, linear FOSA was removed 14% better than branched (after 49,523 BVs) (Figure 21b). The largest difference was seen when using GAC as adsorbent (Figure 20-22). For example, after 25,562 BVs (approx. halfway through the experiment) the removal efficiency of the linear isomer of PFHxS was 61%, compared to the branched removal efficiency of 45% (Figure 22b). PFHxS is of particular interest as it is the PFAS present at the highest raw, permeate and reject water concentrations (Figures 4b, 5b and 6b). Other studies have also found branched isomers to be less sorbable to GAC (Eschauzier et al., 2012). One explanation could be that branched molecules have a smaller molecular volume, and therefore the energy gain of Gibbs free energy, due to adsorption, is smaller (Wang et al., 2011).

According to Rahman et al. (2013), the sorption mechanisms for anion exchange resin are hydrophobic- and electrostatic interactions. Hence, the ionic strength and water solubility drives the adsorption of one ion over another. The average removal efficiency of branched and linear isomers was initially identical. With increasing number of bed volumes however, the difference became more apparent, and the average removal efficiency was better for linear isomers (Figures 20a, 21a, 22a). The initial similarity in removal suggests similar ionic strength and water solubility for the two isomers. Wang et al. (2011) have however shown branched isomers to have higher water solubility than linear, meaning that the sorptive interactions of branched isomers are somewhat weaker. This feature could explain the observed difference in removal efficiency between linear and branched isomers also in the GAC and AE experiment.

5.3 COMPARISON OF THE TREATMENT TECHNIQUES GAC, AE AND NF MEMBRANE

The column experiment was running for a total of 217 days (> 7 months), during which the PFOS removal efficiency using AE was 80-100% (averaging 95%) (Figure 17b). This demonstrates AE's high adsorption affinity of PFOS. Similarly, a high adsorption affinity was seen for PFHxS with a removal efficiency of 57-100% (averaging 95%), reaching a cumulative adsorption of 8.72 µg/g AE after 217 days (62,920 BVs) with no sign of reduction. GAC displayed a similar behaviour. Furthermore, all PFASs except the short-chained (C_3-C_7) PFCAs, continued to have an increasing cumulative adsorption for both GAC and AE. Hence the maximum

adsorption capacity of GAC and AE has not been reached within this experiment. However, the adsorption capacity of the five short-chained PFCAs (PFBS, PFPeA, PFHxA, PFHpA and PFOA), was exhausted because PFASs of longer chain length or different functional group replaced the short-chained PFCAs on the adsorbent.

The NF-plant removed the PFASs to a satisfactory high level (>90%) by producing reject water of considerably higher contaminant concentration (400-500%). How to dispose of, or purify, this reject water is a question that must be attended for the nanofiltration method to be environmentally sustainable.

According to the Swedish drinking water advisory, a maximum concentration of Σ_7PFAS 90 ng/L is acceptable. If GAC or AE would be implemented to remove PFASs from the reject water generated by the NF-plant, the question arises what a satisfactory removal efficiency would be. Comparing the acceptable drinking water level with the GAC/AE treated water, one finds that the GAC water exceeds the Swedish action limit after 5,588 BVs (23 days, 101 ng/L), and the AE water after 8,844 BVs (29 days, 102 ng/L). However, the incoming water used for the column experiment was spiked, aiming to keep a concentration of 100 ng/L, whereas the reject water for the NF-plant had a concentration of ~700 ng/L. The removal efficiency will therefore drop considerably faster for a concentration of this magnitude.

6. CONCLUSION AND FUTURE PERSPECTIVE

There are today no laws governing the allowed threshold PFAS concentration in drinking water, but the §7 regulation (Swedish law) states that drinking water should not contain substances of concentrations harmful to human health. However, the Swedish National Food Agency has issued an action limit for Σ_7PFAS (the sum concentration of PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA and PFOA) of 90 ng/L (Livsmedelsverket, 2014). In the raw water, this limit is well exceeded with Σ_7PFAS of 161±32.0 ng/L. The current Tolerable Daily Intake (TDI) value is set to 900 ng/L, which is considerably larger than the found concentrations. However, the long-term health effect of PFAS exposure is unknown and with ongoing research the TDI may be subject to change (Livsmedelsverket, 2014). The average Σ_7PFAS for the permeate water was found to be 8.2±2 ng/L, which is well below action limit of 90 ng/L, and hence the NF pilot plant meets the national requirements.

Both AE and GAC had high removal efficiency for small bed volumes. The Swedish drinking water advisory could be met for bed volumes less than 8,844 for AE and 5,588 for GAC. FOSA and long-chained PFSAs were removed to a similar extent for both adsorbents, whilst the PFCAs were better removed using AE than GAC. Best removed was PFOS, with an average removal efficiency of 95% using AE.

However, the production of reject water of high contaminant concentration (~700 ng/L) using NF membranes, is an issue that needs to be addressed. The column experiment had incoming PFAS concentrations of ~100 ng/L and it is unclear how the adsorption would behave for larger volumes and higher concentrations. Larger scale adsorption experiments with incoming water of higher concentration are needed to determine the most suitable technique. As branched isomers were better retained by the membranes than linear, an increased concentration of these was also present in the reject water. If GAC was to be used to purify the reject water, a problem would arise regarding the branched isomers due to the lower affinity of adsorption for branched isomers to GAC. The same would be true for AE, although the difference in removal efficiency of branched and linear isomers was smaller than for GAC.

Due to the difficulty in removing PFASs from water, and their highly persistent nature, the best solution would be if further manufacturing of the chemicals was stopped. Presently, this seems unlikely on account of the industry being economically prolific. However, Greenpeace and other NGO's may have an influence in this matter as press releases are used to black list companies and inform consumers of environmentally harmful chemicals in products (Greenpeace, 2015; Environmental Defence, 2015). If the manufacturing continues as now, with an increasing production of short-chained PFASs, the risk of contaminated water bodies and biota is impending. The water treatment plants would stand a real challenge, and potable tap water may be but a memory.

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8. APPENDIX

Table A1 Manually collected meter readings of physical parameters in the NF-plant. The clogging of the pre-filter was indicated by decreasing permeate and reject water flows (2015-05-04 to 2015-06-08), as well as reduced membrane and reject pressures. No flows or pressure values were collected when the pre-filter was clogged, as the NF-plant was not running during this time.

Date	Raw water flow (m^3/h)	Permeate water flow (m^3/h)	Reject water flow (m^3/h)	Recirculation (m^3/h)	Pressure membrane (bar)	Pressure reject (bar)	Temp. raw water (°C)	Frequency (Hz)
2015-05-04	2.25	1.87	0.45	3.1	3	1.9	8	24
2015-05-21	2.25	1.81	0.425	3.1	3	1.8	8	24
2015-05-26	2.25	1.8	0.425	3.1	3	1.8	8	24
2015-06-02	2.2	1.75	0.412	3.1	3	1.8	8	24
2015-06-08	2.2	1.7	0.4	3.1	2.9	1.7	8	24
2015-06-12	-	-	-	-	-	-	-	-
2015-06-22	-	-	-	-	-	-	-	-
2015-06-23	2.35	1.8	0.425	3.1	3	1.9	8	24
2015-06-30	2.35	1.8	0.42	3.1	3	1.8	9.5	24
2015-07-03	2.35	1.8	0.42	3	3	1.8	9.8	24
2015-07-14	2.35	1.75	0.42	3	3	1.8	9.8	24
2015-07-20	2.35	1.75	0.42	3	3	1.8	8	24

Table A2 The method detection limit (MDL) of the individual PFASs.

PFAS	MDL
PFBA	0.715
PFPeA	0.275
PFHxA	0.446
PFHpA	0.592
PFOA	0.845
PFNA	0.625
PFDA	0.570
PFUnDA	0.446
PFDoDA	0.724
PFTeDA	0.371
FOSA	0.139
PFBS	0.860
PFHxS	0.636
PFOS	0.437

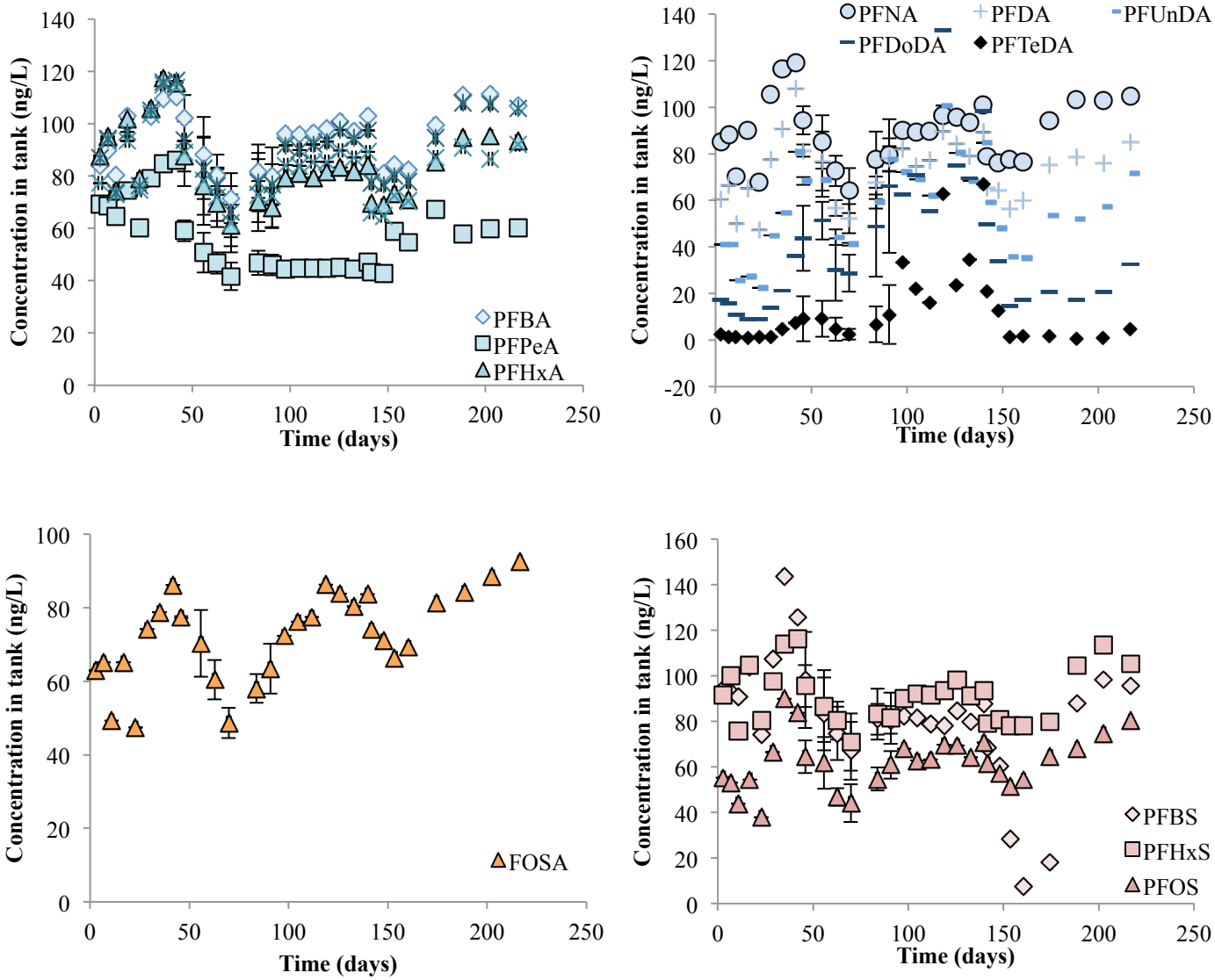

Figure A1 The concentration of the individual PFASs in the incoming tank water during the 217 days of the column experiment.

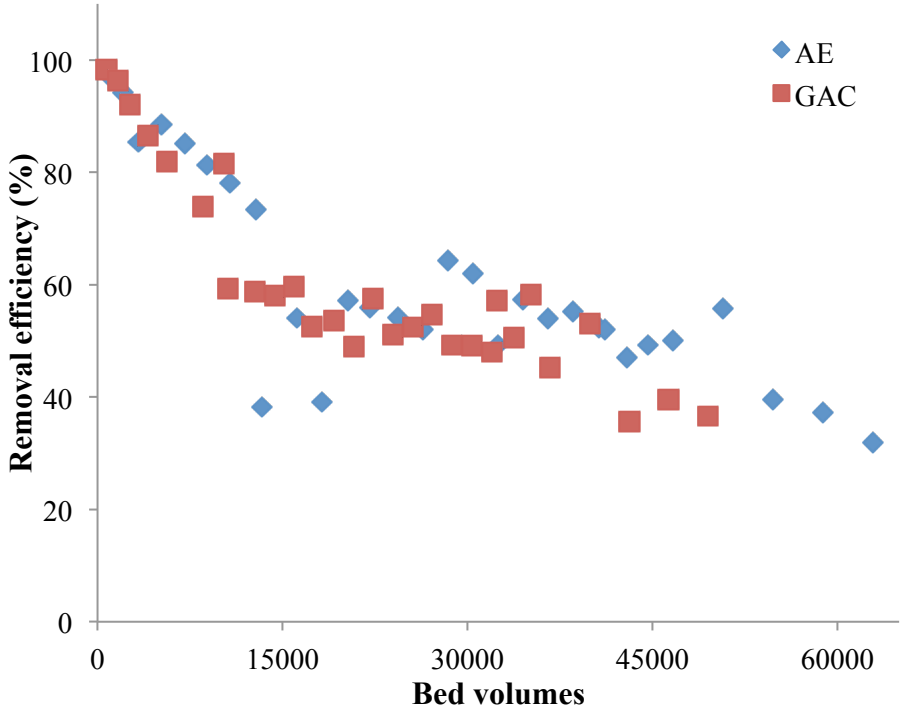

Figure A2 The total average removal efficiency of GAC and AE for all PFASs over the number of bed volumes.

Table A3 The standard deviation (%) of the total PFAS concentration of the duplicate samples.

Sample	Standard deviation (%)
AE-T30	2.0
AE-T31	9.1
AE-T32	2.5
AE-T33	1.8
AE-T34	5.6
AE-T35	3.1
GAC-T30	1.9
GAC-T31	15
GAC-T32	8.5
GAC-T33	2.9
GAC-T34	3.1
GAC-T35	2.2

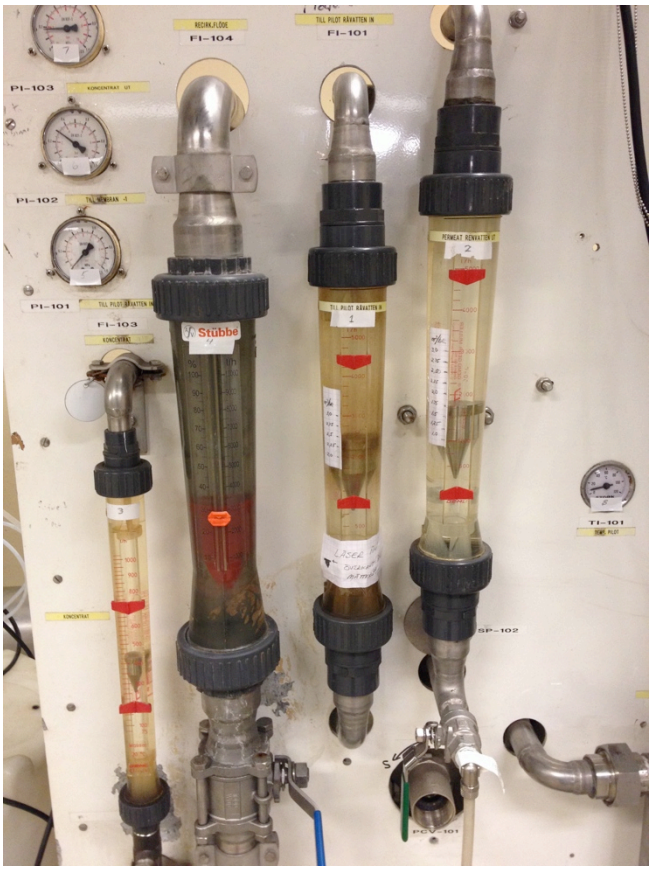

Figure A3 The NF-pilot, and the meters displaying pressures and water flows.

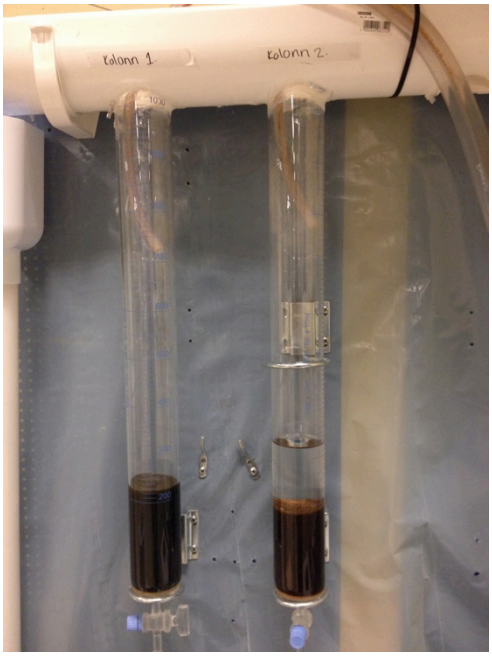

Figure A4 The experimental set up of the pilot scale column experiment at Bäcklösa DWTP, and the two columns with GAC (left) and AE (right).