

Screening of per- and polyfluoroalkyl substances (PFASs) in drinking water

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Abstract

Worldwide use of per- and polyfluoroalkyl substances (PFASs), both legacy and past, are problematic due to their persistent nature. To date, PFASs are of high concern since they have been found not only in the environment but also in animals, plants and humans. Therefore, the Swedish Food Agency has set a limit of 90 ng/L for \sum_{11} PFASs in drinking water. This study has assessed 47 drinking water plants (DWTP) in Sweden, where both in- and outgoing water was analyzed for 26 different PFASs during two different seasons (mid summer and late fall). The aim of this study was to assess the PFAS concentrations, removal efficiencies in DWTPs and seasonal trends. The maximum \sum_{26} PFAS concentrations were close or slightly over the limit of 90 ng/L in raw water at a few DWTPs during both seasons but the drinking water concentrations from both seasons were well below 90 ng/L. Most detected PFASs were included in the Swedish drinking water guidelines, except for FOSA. In early summer, the dominant PFASs in drinking water were PFOA (74%), FOSA (74%), PFHxS (48%), PFNA (48%) and PFBS (24%), while in the fall the dominant PFASs were that 6:2 FTSA (62%), FOSA (48%), PFBS (33%), PFHxS (31%) and PFOA (26%). Removal efficiencies showed efficient removal in the early summer for PFOA, PFBS, PFHxS, PFOS, and in fall the highest removal was observed for PFPeA, PFHpA, PFNA, PFBS, PFHxS, PFOS, 6:2 FTSA and FOSA, although the variations between the individual DWTPs was high. DWTPs which used granulated activated carbon (GAC) showed high removal of PFOA, PFNA and PFHxS in early summer and PFOA, PFNA, PFHxS and 6:2 FTSA in fall. Branched PFOS and PFHxS was detected only at a few DWTPs. Although the PFAS concentrations were slightly higher in early summer, there were no significant difference in the PFAS concentrations in raw water between summer and fall (Wilcoxon paired rank test, $p = 0.15$). Overall, the concentrations of PFAS at the investigated DWTPs were below the Swedish drinking water guidelines.

Populärvetenskaplig sammanfattning

PFAS, sv. *högluorerede ämnen*, eng. *per- and polyfluoroalkyl substances*, är en grupp av ämnen som har mycket speciella egenskaper. Alla PFAS-molekyler har en *funktionell grupp* som främjar vatten och en fluorerad *kolkedja* som är vattenavstötande, vilket gör PFAS både vatten och fettavvisande. PFAS används till en rad olika applikationer i samhället, bl. a. brandsläckare och ytbehandlingsmedel men återfinnes även i matförpackningar, smink och vissa kläder som skall ha vattenavstötande egenskaper. Föroreningar av PFAS är spridd över hela världen och ämnet är mycket svårnedbrytbart, till följd hittas det i stor utsträckning i samhället men även i dricksvatten, sediment, sjöar, djur och människor. PFAS har även länkats till bl.a. blodsjukdomar och hormonstörande effekter.

I dagsläget existerar det tusentals olika sorters PFAS och i takt med att vissa sorter förbjuds ersätts de med andra. Tidig forskning riktade in sig på typerna PFOA och PFOS, men på senare tid läggs även fokus på andra alternativa PFAS, i takt med att tidigare använda PFAS fasats ut. Eftersom PFAS är så pass välspridd har det blivit fokus för flertalet forskargrupper och idag anses PFAS vara en problematisk grupp av kemikalier. En stor oro ligger i att PFAS-ämnena är så långlivade i naturen. Vid misstanke av PFAS förorening i vatten eller mark undersöks 11 specifika PFAS och i Sverige ligger den s.k. åtgärdsgränsen för totalhalten av dessa 11 PFAS-ämnen på 90 ng/L i dricksvatten.

Denna studie undersökte dricksvatten i flera olika vattenverk i Sverige efter förekomst av PFAS, och fann att dricksvattnet höll god kvalitet med avseende på koncentrationen av alla undersökta PFAS. Koncentrationerna som hittades i dricksvattnet låg under åtgärdsgränsen. Däremot förekom olika PFAS i flertalet vattenverk i mindre halter och det specifika ämnet FOSA förekom även i större utsträckning än vad som förväntades. Huvudsakligen fanns de funna PFAS-ämnena inom den grupp av 11 PFAS-ämnena som vanligtvis undersöks. Det indikerar att Sverige hittar merparten av de olika PFAS-ämnena vid undersökningar. Däremot så ingår inte FOSA i dessa 11 PFAS-ämnena vilket kan vara problematiskt för framtida utvärderingar.

Studien kunde inte påvisa någon statistisk signifikant skillnad på koncentrationen av totalhalter av PFAS, sett mellan sommar och höst. Förekomsten av PFAS-ämnena i dricksvatten under sommaren var främst av typen PFOA, FOSA, PFNA, PFHxS, 6:2 FTSA, PFBS och PFOS, men under hösten var den huvudsakliga ämnena 6:2 FTSA,

FOSA, PFHxS and PFOA. Förekomsten av korta grenade PFAS var liten men hittades av typen PFHxS och PFOS.

Reningsgraden under sommaren för det inkommande råvattnet visade god rening av PFOA, PFBS, PFHxS, PFOS, men inte PFNA. Höstsäsongen visade en god rening av PFPeA, PFHpA, PFNA, PFBS, PFHxS, PFOS, 6:2 FTSA och FOSA. De vattenverk som använde *granulerat aktivt kol*, (GAC), visade hög reningsgrad av PFOA, PFNA och PFHxS under sommaren och PFOA, PFNA, PFHxS och 6:2 FTSA under hösten.

Sammanfattningsvis så är PFAS-situationen i Sveriges dricksvatten god, då PFAS-halterna ligger under de riktlinjer som är satta. De funna PFAS-ämnen som uppmättes i dricksvattnet var av den typ som förväntades men även en större del av proverna innehöll FOSA. Ingen signifikant säsongsberoende skillnad av uppmätta PFAS halter mellan sommar och höst kunde påvisas.

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Abbreviations

6:2 FTSA	6:2 fluorotelomer sulfonic acid
8:2 FTSA	8:2 fluorotelomer sulfonic acid
10:2 FTSA	10:2 fluorotelomer sulfonic acid
ADONA	ammounium-4,8-dioxa-3H-perfluorononanoate
AER	Aeration
AFFFs	Aqueous Film Forming Foam
AIX	Anion exchange
ARR	Aquifer recharge and recovery
ChlorineDiox	Chlorine Dioxide
HypCl	Hypochlor/hypoclorite
COAG	Coagulation
DAF	Dissolve air flotation
DI	Direct Injection
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DW	Drinking Water
DDWTP	Drinking Water Treatment Plant
FLOC	Flocculation
FOSA	perfluorooctanesulphoneamide
FOSAA	perfluorooctane-sulfonamidoacetic acid
GAC	Granulated Activated Carbon
Gen-X	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid
GFF	Glass Fibre Filter

HPLC-MS/MS	High-performance Liquid chromatography coupled to a tandem mass spectrometer
HFPO-DA	Gen-X, 2,3,3,3- tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
HFPO-TA	hexafluoropropylene oxide trimer acid
IS	Internal Standard
MF	Membrane Filtration
MST	Matix Standard
MDL	Method detection limit
N-MeFOSA	N-methyl- perfluorooctanesulfonamide
N-EtFOSA	N-ethyl- perfluorooctanesulfonamide
N-MeFOSAA	N-methyl- perfluorooctanesulfonamidoacetic acid
N-EtFOSAA	N-ethyl- perfluorooctanesulfonamidoacetic acid
N-MeFOSE	N-methyl-d7-perfluorooctane sulfonamidoethanol
N-EtFOSE	N-ethyl-d9-perfluorooctane sulfonamidoethanol
Ozone	Ozone
PFASs	Polyfluorinated Alkyl Substances (Full list of PFASs at Page 15, Table 1)
Σ PFASs ₁₁	Swedish guidelines for PFAS, sum concentrations of: <i>PFBS</i> , <i>PFHxS</i> , <i>PFOS</i> , <i>6:2 FTSA</i> , <i>PFBA</i> , <i>PFPeA</i> , <i>PFHxA</i> , <i>PFHpA</i> , <i>PFOA</i> , <i>PFNA</i> and <i>PFDA</i>
PFBA	perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorodeodecanoic acid
PFDS	perfluorobutanoic acid
PFHpA	perfluoroheptanoic acid

PFHxA	perfluorohexanoic acid
PFHxDA	perfluorohexadecanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOcDA	Perfluorooctadecanoic acid
PFOS	Perluorooctane sulfonic acid
PFPeA	perfluoropentanoic acid
PFTeDA	perfluorotetradecanoic acid
PFTriDA	perfluorotridecanoic acid
PFUnDA	perfluoroundecanoic acid
POP	Persistent Organic Pollutants
RO	Reverse Osmosis (water cleaning technique)
RBF	River bank filtration (water cleaning technique)
RW	Raw Water
SED	Sedimentation (water cleaning technique)
SOFT	Softening (water cleaning technique)
SPE	Solid Phase Extraction
SSC	Solids contact clarifier (water cleaning technique)
TFA	Trifluoroacetic acid
UV-AOP	UV photolysis with advanced oxidation (water cleaning technique)
WFD	Water Framework Directive
WWTP	Wastewater Treatment Plant

1. Introduction

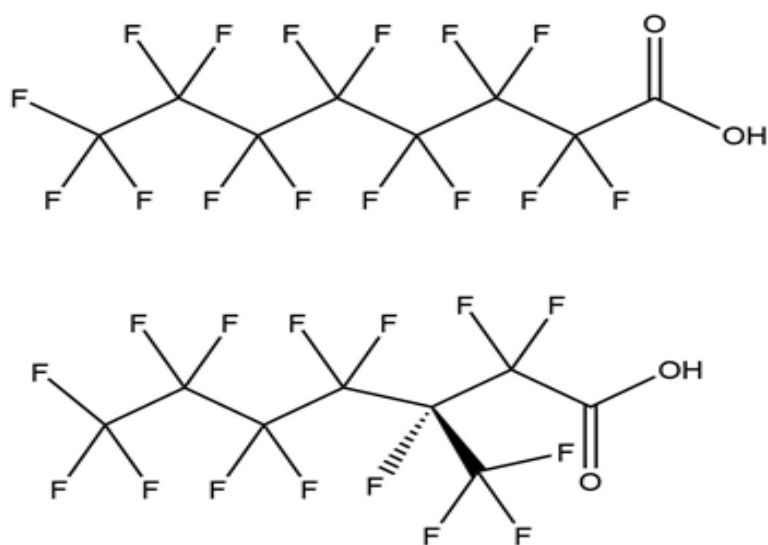
1.1 PFASs in the environment

The use of persistent organic pollutants (POPs) are of global concern due to their persistent nature and bioaccumulative properties (Buck et al. 2011). One group of POPs, named as per- and polyfluoroalkyl substances (PFASs), are of raising concern. These compounds originate from the 1950's and were used in several industrial applications but has largely been phased out or replaced by different PFASs. Today they can be used in a variety of different applications such as aqueous film forming foams (AFFFs), flame retardants, soil, grease and stain- repellent fabrics (Buck et al. 2011; Gobelius et al. 2018; Olsen et al. 2017; Stubleski et al. 2017). Research suggests that some PFASs are carcinogens and studies also show its link to diabetes, serum lipids, atherosclerosis, ulcerative colitis, early menopause, thyroid function in women, osteoarthritis, and immunological and developmental toxicity (Gobelius et al. 2018; Gyllenhammar et al. 2015; Stubleski et al. 2017; Wielsøe et al. 2015). Since 2009 some PFASs, more specifically perfluorooctane sulfonate (PFOS) and its precursors has been added to the Stockholm Convention (Ahrens et al. 2015) and is included in the Water Framework Directive, WFD (PFOS EQS dossier 2011) as a prioritized chemical.

Several Swedish studies investigated potential PFAS contamination from airfields where AFFFs have been used in the past and remain persistent in waterbodies affecting drinking water in the vicinity (Ahrens et al. 2015; Stubleski et al. 2017). Other countries also found contaminated drinking water from legacy use of PFASs (Takagi et al. 2008; Thompson et al. 2011).

The PFASs as a group is often referenced as \sum PFAS₁₁, which contain eleven PFAS used as indicators for PFAS contamination. In this study they are referred to \sum PFAS₁₁. The compounds included in the \sum_{11} PFASs are: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS and 6:2 FTSA (Table 1). In Sweden the guidelines states that the sum of \sum PFAS₁₁ should be below 90 ng/L and the LOQ, limit of quantification, should be in the 1 – 10 ng/L range (*PFAS in drinking water and fish - risk management*, 2018).

The structure of the PFAS molecule differs greatly, but at its core it is an alkyl that has its hydrogen atoms substituted by fluorine atoms and are thus considered a highly fluorinated aliphatic substance. The tail of the molecule is hydrophobic, and the ionic head is hydrophilic, giving the molecule both hydrophobic and hydrophilic properties. More specifically, for a molecule to be labeled as a PFAS, it has to contain the perfluoroalkyl moiety of C_nF_{n+1} - (Buck et al. 2011). A way to differentiate and sort the different PFASs is to look at the carbon chain length which makes it possible to consider them short- or long chained. The functional groups of the PFASs such as PFCAs and PFSA also make it possible to consider the PFASs by further grouping them into different functional groups (Table 1). For this thesis the PFAS nomenclature will be referenced as the way described in (Buck et al. 2011). Another group of PFASs that this study consider are the precursors (6:2 FTSA, 8:2 FTSA, 10:2 FTSA, FOSA, Me-FOSA, Et-FOSA, FOSAA, Me-FOSAA, Et-FOSAA, Me-FOSE and Et-FOSE, Table 1) which are volatile and can degrade to more stable PFASs such as polyfluorinated carboxylic acids, PFCAs, and polyfluorinated sulfonic acids, PFSA (Gobelius et al. 2018).



Picture 1. Example of a Linear PFOA (top) and branched PFOA (bottom).

Furthermore, the PFASs structure can be of branched (B) or linear (L) (Picture 1). A B-PFASs has similar molecular composition as one of its L-PFAS, but the structure differs, giving it different properties in the water-phase. A change of the structure that has the effect of the tail being shorter will make a molecule more mobile in the water

phase, thus B-PFASs are more mobile in the water phase than L-PFAS (Ahrens, 2011; Janousek et al. 2019).

Since the phase-out of different types of PFASs, others has taken their place. The shift is mainly from long-chained PFAS (PFOS, PFOA) to short-chained PFASs (PFBA and PFBS), and their branched counterparts, which makes it possible to consider the source of the PFASs, given the composition profile. Knowledge of the PFASs composition profile of the water body and also of B- and L-PFASs can indicate both source and or legacy use. Legacy use of PFASs is mainly attributed to ECF (electrochemical fluorination) and fluorochemicals (mixture of isomers) while latter sources consists of linear (telomer-derived products)(Ahrens, 2011; Janousek et al. 2019). Since the long-chained PFAS were voluntarily phased out in developed countries a shift might also take place where the developed countries use more short-chained PFASs than developing countries, which still use long-chained (Janousek et al. 2019).

The study of Janousek et al. (2019) compiled the academic PFAS progression between 1999 and 2015, and found that between 1999 and 2009 the focus was mainly on PFOA and PFOS, occurring in 92% of study topics, and PFHpA (76%), PFHxA (64%), PFHxS (60%), PFNA (60%) and PFDA (56%) of topics. Furthermore, other PFASs was only investigated in less than 52% of studies. After 2009 PFOS is listed in the Stockholm convention, and between 2009 and 2015 PFBA and PFBS (short-chained PFASs) was cited more often in studies (60 % and 75 %, respectively) than before 2009, where it was only cited in less than 56% cases. The studies mentioned in Janousek et al. (2019) are hard to compare with newer studies since the composition profiles differ in the sense that more compounds are monitored today. However, the period after 2009 detected PFOA, PFOS and PFNA in 95% of sites and PFDA, PFHxA in 90%, both PFPeA and PFHxS in 85% and PFBS in 79% of sites. Furthermore, after 2015 most long-chained PFASs are phased out and during this period PFBA and PFBS were analyzed in 80% of studies, PFOS has been measured between 80% of studies and PFOA in 100%. More compounds such as TFA and PFPrA are also investigated in newer studies together with compounds found in non-target analytical studies which conclude findings of Gen-X, TFMSA, HFPO-DA, HFPO-TA and ADONA (Pan *et al.*, 2018; Janousek, Mayer and Knepper, 2019). There seems to be a shift from both targets and

quantification of PFASs during the era of pre-2009 and post 2009 (Janousek et al. 2019). Comparing older studies of PFAS might be problematic due to this shift in use of PFAS.

The fate of PFASs in the environment are determined mainly by their functional group and chain length. The consensus is that the long chained sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$ PFASs) and perfluoroalkyl carboxylic acids ($C_nF_{2n+1}CO_2H$, $n \geq 7$ PFCAs) are more bioaccumulative in comparison to their short-chained counterpart, which are more water soluble and mobile in the environment. The short chained PFCAs has a chain length of $<C_7$ and the PFASs has a chain length of $<C_6$ (Ahrens, 2011; Buck et al. 2011; Gobelius et al. 2018; KEMI - Swedish Chemical Agency, 2019).

Studies which analyzed Swedish groundwaters for PFASs show a big contribution of PFCAs towards the \sum_{26} PFASs, and most of them are in the short C-range of C_4 - C_8 (Gobelius et al. 2018). Considering serum levels of population exposed to PFASs, significantly higher levels of PFHxS and PFOA were found in residents living at exposed areas over a longer time (Stubleski et al. 2017). Furthermore, these compounds are from the longer-C chains of PFASs and PFCAs, respectively. These studies are consistent with the reasoning that short-chained PFASs are found in the aquatic environment and long-chained PFASs are found bioaccumulated.

Seasonal parameters such as water fluxes, temperature and precipitation can affect the environmental factors for PFAS concentrations. Water temperature seems to promote higher concentrations of PFASs in the water phase due to less retention of PFAS to solids in the waterphase. A study in Japan (Takagi et al. 2008), concluded such variation between summer and winter while studying PFOA and PFOS, the differences in temperature shifted from 25 °C to 8 °C during the summer and winter periods, respectively. While temperature seems to play a role in seasonal patterns, other recent studies conclude no statistical trends between seasons, other than observed PFBS concentrations in the second half of the year, but could not link it to any seasonal variation since no other PFASs show this trend (Janousek et al. 2019). Other studies conclude higher concentrations of samples DWTPs in late summer and late early summer, than late fall and early early summer (Nguyen et al. 2019), but can not conclude any statistical significance of the observations. The study of Lee et al. (2020)

sampled PFASs from air, water, sediments, soils and species in Korea. The water samples show a trend of higher PFASs concentrations during autumn and early early summer, than in summer and late early summer.

Water fluxes is also a factor to consider since PFASs, as earlier stated, tend to be extremely mobile in the water phase. Even long-chained PFAS such as PFOS is mobile through soils and ground water to aquifers (McLachlan et al. 2007). The study further conclude that this behaviour of PFASs in soils will further reflect the watersheds riverine discharge, based on the hydraulic retention time. Thus the water flux is likely very much relevant when considering the PFASs concentrations and trends. The year of 2018 in Sweden was extreme, to say the least. Several climate stations measured extreme values in temperature and the rainfall was erratic. Average rainfall in Sweden is between 500 – 800 mm/year. Looking at data from SMHI (Swedish Meteorological and Hydrological Institute) some areas in the early summer had as low as 25% to 50% of the average rainfall, while most of Sweden had around 75%. The summer had similar values while autumn and winter show close to the average precipitation. The summer heat was around 4 degrees warmer on average through the summer. These conditions can lead to a lower flux in the early summer and summer due to lower rainfall and higher temperature, affecting the early summer values. The autumn fluxes appears to be closer to the average. An increased water flux can have the effect of dilution of PFASs which leads to a lower measured concentration (Zhang et al. 2013; Zhao et al. 2015) and altered water chemistry (base cations, pH, DOC) (Fölster and Wilander, 2002).

As mentioned above, the WFD only lists PFOS and its precursors as a prioritized chemical. As industries are phasing out PFOA and PFOS, the production shifts to more short-chained or alternative PFASs. PFAS present in the environment originate mainly from industrial sources, consumer products or biotic and or abiotic degradation from other PFASs precursors (Buck et al. 2011), although some fluorotelomers can originate from volcanic activity (Ahrens, 2011). A study conducted in Sweden conclude that landfills is a big contributor of PFASs having a lechate concentration of 487 ng/L, followed by STP effluent at 286 ng/L, surface waters at 112 ng/L and ground waters at 49 ng/L (Hedlund, 2016). Furthermore, the median concentration of surface waters

and ground in the study was much lower than average with 4.1 and 0.4 ng/L, respectively, indicating that PFASs can be very site specific.

1.2 Drinking water treatment techniques for PFASs

1.2.1 GAC, AIX and MF

The commonly tested and studied water treatment options to remove PFASs are granulated activated carbon (GAC), anion exchange (AIX) and membrane filtrations (MF) such as nano (NF) and reverse osmosis (RO) (Appleman et al. 2014; Eschauzier et al. 2012; Franke et al. 2019; Kothawala et al. 2017; McCleaf et al. 2017; Takagi et al. 2008).

GAC is charcoal derived from different wood components that is pretreated in order to increase the effective surface area. With an increased surface area the amount of substances that can bind to the surface is also increased, i.e. it has improved sorption and binding properties. The functionality of GAC can be varied by using different sizes of the granules which the GAC filter is comprised of, as they have different properties. In general, activated carbon is used not only for PFASs but as a catch-all for drinking water quality in removing pharmaceuticals and lessening the taste and odor-problems. When water is treated the water body is pushed through a bed of GAC which has different pore sizes ranging from micro 18-20 Å, transitional pores at 40-200 Å and macropores at 50-20 000 Å (*An Evaluation of Activated Carbon for Drinking Water Treatment*). GAC and PFASs removal is mainly tied to the long-chained PFASs. Its also limited as it needs to be refreshed over time as a lower removal of PFASs and desorption behaviour is seen with older GAC-batches (Franke *et al.* 2017; Takagi et al. 2008).

AIX is the practise of using resins or other materials which adsorb molecules to its structure. Depending on the target molecules the resins has different structures. In the case of PFASs, AIX is typically used and consists of a strong base and the functional groups of the resins are of quaternary amines. Since PFASs has many different functional groups and properties the resins need to be suited towards the removal of the specific substances present in the waterbody. The short chained PFASs mainly interact with electrostatic interaction and the longer chained PFASs are affected more of the resins hydrophobicity. Furthermore the mass of the resin can be manufactured

with different functional groups of quaternary amines, one short and one long alkyl chain, in order to more effectively target a wider range of PFASs (Franke *et al.* 2017). This is in line with a previous study, McCleaf *et al.* (2017), showing that GAC and AIX effectively remove PFASs from the water phase but differentiate between chain lengths. Towards the end of the study the short chained PFASs show desorption behavior and longer chained PFASs show increased removal (217 days). Furthermore, PFASs are more effectively removed in comparison to PFCAs. Other studies such as Takagi *et al.* (2008) show that AIX and GAC are viable options for the removal of PFOA and PFOS. This is in agreement with a previous study of Eschauzier *et al.* (2012) showing that GAC more easily remove long chained compounds such as PFNA and PFOS but shorter chained compounds such as PFBA and PFBS were not removed effectively.

Membrane filtration includes a type of different treatment options such as nano (NF) and ultra- filtration (UF) and reverse osmosis (RO). The membrane discriminates against the size of certain molecules, letting water molecules through the membrane but keeps larger molecules separated. In the case of NF which separates molecules with a size of 1 nm, (weight of 200 – 2000 Da) the pores are ranging from 0.5 – 2 nm. RO use a membrane which operates at 0.5 nm, separating salts effectively (<200 Da weight). Since the pores are very fine it has to be combined with other techniques to lessen the amount of particles needed to be separated. Otherwise the pores and the membrane gets clogged easily. NF operates at lower pressures and higher flowrates than RO which can make it a feasible cleaning method. After the water is treated a “concentrate” is left as a by-product. This concentrate has to be treated if it is used for PFASs removal (Franke *et al.* 2017).

1.2.2 Other treatment techniques

As stated above, the literature mainly suggests GAC, AIX and membrane-techniques but these treatment options are not implemented on a wide basis in today's water treatment plants (DWTP). Other techniques are commonly used such as aquifer recharge and recovery (ARR), aeration (AER), chlorine dioxide (ChlorineDiox), coagulation (COAG), dissolved air flotation (DAF), direct injection (DI), flocculation (FLOC), granular filtration (G-FIL, hypochlorous/Hypochlorite (HypCl), microfiltration (MF), Ozone(Ozone) river bank filtration (RBF), sedimentation (SED),

softening (SOFT), solids contact clarifier (SCC), UV photolysis with advanced oxidation (UV-AOP) and ultra-filtration (UF). However, COAG, FLOC, SED, and UV-AOP have been shown to be less efficient in removing PFASs (Dauchy, 2019).

1.2.3 Interaction of DOC on the removal of PFASs

Dissolved organic matter, DOM, is a catch-all phrase for different trace elements (C, H, O, N, P and S) in waterbodies. Often it is categorized as an organic material that can pass a filter size of 0.45 μm . Furthermore, this can be categorized into its nutrient fractions and DO, contains mostly of fulvic and humic acids. These two classes of organic acids has aromatic rings and are typically derived from microbial degradation of vascular plants. The DOM (fulvic and humic acids) is typically the major part of the carbon flux in streams. Common values found in nature for DOC are ranging from 1 – 5 mg/L for streams and can be tenfold for wetlands. DOM negatively affects the drinking water quality, since the organo-acid part can affect the color of the water and the smell. Furthermore, it can act as binding sites for rather insoluble organic compounds or metals and can also produce halogenated compounds if the water is chlorinated (Findlay and Parr, 2017).

Since DOM can interact with insoluble organic compounds its not unreasonable to assume they can interact with PFASs. The literature is rather limited on this subject but there are some studies that touch the subject. The removal of PFASs from the water phase can be disrupted by the interaction between PFASs and DOM. The DOM can also interact with the AIX and GAC, competing for the same sites where the PFASs would bind towards the GAC and by simply blocking the pores (Yu *et al.*, 2012). The AIX is less sensitive towards higher levels of DOM since the influence between the levels of DOM and recovery rates of PFASs were low, as in indicated in the study of Kothawala *et al.* (2017).

Indeed, the removal of PFASs is influenced by many factors such as PFASs chain length, functional group, water temperature, DOM and treatment method. When using GAC treatment the DOM should be considered as the DOM might clog up the filter bed and competes for the active sites on the material. A previous study show that the effectiveness of the GAC treatment decline over the period of the experiment and also suggest a replacement of GAC 2 – 3 times per year in a drinking water

treatment plant (Takagi et al. 2008) and other studies suggests that the removal efficiency is in direct relation to the lifespan of the filter (McCleaf et al. 2017)

1.3 Knowledge gaps

This study's scope is to fill knowledge gaps on PFAS-seasonality and add knowledge of the situation of Swedens drinking water supply. Sweden has historically conducted studies related to this specific topic in population studies (Gyllenhammar et al. 2015; Stubleski et al. 2017) contaminated sites (Ahrens et al. 2015) and drinking water techniques (Franke et al. 2019; McCleaf et al. 2017). However, meta-studies on a national scale has only been done on a few topics: surface and ground-waters (Gobelius et al. 2018), Swedish perch (Åkerblom et al. 2017) and sediments (Mussabek et al. 2019). In order to complement these topics seasonality was assessed and drinking water supplies were quantified for PFAS.

1.4 Aims of this study

This study aimed to investigate seasonal variation for PFASs (early summer vs. autumn). This was done by analyzing the concentration of 26 PFASs in both raw and drinking water from a total of 47 DWTPs in Sweden.

The research questions were:

- Which PFASs are found and at what levels?
- Are those detected PFASs included in the Swedish drinking water guideline?
- Are there any seasonal changes between early summer and autumn?
- How effective are water treatment plants in removing PFASs?

2. Material and method

2.1 PFAS target compounds

The target PFASs included C₃–C₁₃, C₁₅ and C₁₇ (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C₄, C₆, C₈ and C₁₀ PFASs (PFBS, PFHxS, PFOS, PFDS) and the PFAS precursors methyl- and ethylperfluorooctanesulfonamides (FOSAs: FOSA, MeFOSA, EtFOSA), methyl- and ethylperfluorooctanesulfonamidoethanols (FOSEs: MeFOSE, EtFOSE), methyl – and

ethylperfluorooctanesulfonamidoacetic acid (FOSAA: FOSAA, MeFOSAA, EtFOSAA) and 6:2 FTSA. Full list of compounds can be seen in Table 1.

Table 1. PFASs target compounds and their corresponding molecular formula

PFAS	Perfluoroalkyl carboxylates	Molecular formula
PFBA	perfluorobutanoic acid	C ₃ F ₇ CO ₂ H
PFPeA	perfluoropentanoic acid	C ₄ F ₉ CO ₂ H
PFHxA	perfluorohexanoic acid	C ₅ F ₁₁ CO ₂ H
PFHpA	perfluoroheptanoic acid	C ₆ F ₁₃ CO ₂ H
PFOA	perfluorooctanoic acid	C ₇ F ₁₅ CO ₂ H
PFNA	perfluorononanoic acid	C ₈ F ₁₇ CO ₂ H
PFDA	perfluorodecanoic acid	C ₉ F ₁₉ CO ₂ H
PFUnDA	perfluoroundecanoic acid	C ₁₀ F ₂₁ CO ₂ H
PFDoDA	perfluorodecaneanoic acid	C ₁₁ F ₂₃ CO ₂ H
PFTriDA	perfluorotridecanoic acid	C ₁₂ F ₂₅ CO ₂ H
PFTeDA	perfluorotetradecanoic acid	C ₁₃ F ₂₇ CO ₂ H
PFHxDA	perfluorohexadecanoic acid	C ₁₅ F ₃₁ CO ₂ H
PFOcDA	Perfluorooctadecanoic acid	C ₁₇ F ₃₅ CO ₂ H
PFASs	Perfluoroalkane sulfonates	Molecular formula
PFBS	Perfluorobutane sulfonic acid	C ₄ F ₉ SO ₃ H
PFHxS	Perfluorohexane sulfonic acid	C ₆ F ₁₃ SO ₃ H
PFOS	Perfluorooctane sulfonic acid	C ₈ F ₁₇ SO ₃ H
PFDS	perfluorobutanoic acid	C ₁₀ F ₂₁ SO ₃ H
FOSEs	methyl- and ethylperfluorooctanesulfonamidoethanols	Molecular formula
N-MeFOSE	N-methyl-d7-perfluorooctane sulfonamidoethanol	C ₈ F ₁₇ SO ₂ N(CH ₂) ₂ CH ₃ OH
N-EtFOSE	N-ethyl-d9-perfluorooctane sulfonamidoethanol	C ₈ F ₁₇ SO ₂ N(CH ₂) ₃ OH
FOSAAs (methyl- and ethylperfluorooctanesulfonamidoacetic acids)		Molecular formula
FOSAA	perfluorooctane-sulfonamidoacetic acid	C ₈ F ₁₇ SO ₂ N HCH ₂ CO ₂
N-MeFOSAA	N-methyl- perfluorooctanesulfonamidoacetic acid	C ₈ F ₁₇ SO ₂ N CH ₃ CH ₂ CO ₂
N-EtFOSAA	N-ethyl- perfluorooctanesulfonamidoacetic acid	C ₈ F ₁₇ SO ₂ N (CH ₂) ₂ CH ₂ CO ₂
FTSAs	fluorotelomer sulfonates	Molecular formula
6:2 FTSA	6:2 fluorotelomersulfonic acid	C ₈ H ₄ F ₁₃ SO ₃ H
FOSAs	methyl- and ethylperfluorooctanesulfonamides	Molecular formula
FOSA	perfluorooctanesulphoneamide	C ₈ F ₁₇ SO ₂ NH
N-MeFOSA	N-methyl- perfluorooctanesulfonamide	C ₈ F ₁₇ SO ₂ NHCH ₃

2.2 Sampling sites

In this study a total of 47 DWTPs (Table 2), was investigated, but not all plants was unisonally sampled between seasons or represented in both drinking and raw waters. Out of the 47 plants, 9 of those plants use GAC, GAC in combination of MF and one use GAC in combination with AIX. All plants have some kind of drinking water treatment, but as mentioned earlier, all treatment options are not relevant to PFAS removal. Plants without relevant or unique treatment options are defined as “Normal steps”. Containers of the size of 1 L were sent out to the different DWTPs, sampling was done by staff at the DWTP with a protocol provided. The samples were stored in a room with a constant temperature of 8 °C before analysis.

Table 2. DWTP sites screened in this study and their treatment steps for drinking water.

<i>Alelyckeverket</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Berggårdens vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Bingeby vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC+Ozone</i>
<i>Bjennberg vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Borgs vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Bua vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Bulltofta vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Bäcklösa vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Dalsjöfors vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Degerångets vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Finnsjöns vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Forslunda vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Fröfall vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Fågelbacken vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Gränby vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Gälleåsens vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Görvålverket</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Hovmantorps vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Hyndevads vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Hässlö vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Högby vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Högåsens vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Kärrgården vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Lackarebäckverket</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Lennhedens vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Lits vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Lockörns Vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>

<i>Lovös vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Lycksele centrala vv.</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Mariannelunds vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Norsborgs vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Näs vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Pagla vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Ringsjöverket</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Ryssby vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Råberga vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>GAC</i>
<i>Råssnäs vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Rökebo vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Sjöbo vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>AIX</i>
<i>Sörmons vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Tjärna vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Vagnhärads Vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Vombverket</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Västlands vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Nano Filtration</i>
<i>Åmåls vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Älmhults vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Normal Steps</i>
<i>Östersunds vattenverk</i>	<i>Early summer and autumn 2018</i>	<i>Ozone</i>

¹Normal steps include those that are not AIX, GAC or MF.

2.3. Sample preparation and analysis

PFASs were extracted and quantified in the POPs-lab at SLU, as described previously (Gobelius et al. 2018). The analysis of the samples were conducted in the following order; 500 mL ± 50 mL of water from the samples were filtered (1.2 µm glass fiber filter GFF, GE Healthcare Life Sciences, Whatman UK) and then spiked with 100 µL of internal standard (IS) mix of (20 ng /L for each of the 16 IS) and then extracted with solid phase extraction (SPE) using Oasis WAX cartridges (6 cc, 500 mg, 60 µm, Waters Corporation, USA). Before the SPE, the cartridges were preconditioned with 4 mL of 0.1 % ammonium hydroxide in methanol solution, 4 mL of methanol and 4 mL of Millipore water. After loading, the cartridges were buffered with 4 ml 25 mM ammonium acetate buffer in Millipore water and then dried in a centrifuge. Afterwards the cartridges were eluted with 4 mL of methanol and 8 ml of 0.1% ammonium hydroxide solution in methanol. The extracts were then concentrated to 1 ml. The analysis was performed using a high-performance liquid chromatography coupled to a tandem mass spectrometer (DIONEX UltiMate 3000 ultra-high pressure liquid chromatography (UPLC) system (Thermo Scientific, Waltham, MA, USA) coupled

to a triple quadrupole mass spectrometer (MS/MS) (TSQ QUANTIVA, Thermo Scientific, Waltham, MA, USA)).

In order to quantify the interactions of the PFASs towards the matrix, separate matrix spiked standards (MSTs) were prepared for both DW (n = 40) and RW (n = 41). These samples were prepared by taking 30 mL from each DWTP that has normal treatment procedures, yielding two MST mixes. In addition, separate MSTs for DWTPs using advanced treatment steps (Bingeby, Bäcklösa, Lackarebäck, Sjöbo, Västlands and Östersunds) were also prepared in order to compensate for matrix interactions.

To quantify and identify the compounds using the HPLC-MS/MS internal standard (IS), the following IS were used in this study; $^{13}\text{C}_4\text{PFBA}$, $^{13}\text{C}_2\text{PFHxA}$, $^{13}\text{C}_4\text{PFOA}$, $^{13}\text{C}_5\text{PFNA}$, $^{13}\text{C}_2\text{PFDA}$, $^{13}\text{C}_2\text{PFUnDA}$, $^{13}\text{C}_2\text{PFDoDA}$, $^{18}\text{O}_2\text{PFHxS}$, $^{13}\text{C}_4\text{PFOS}$, $^{13}\text{C}_8\text{FOSA}$, $d_3\text{-N-MeFOSA}$, $d_5\text{-N-EtFOSA}$, $d_7\text{-N-MeFOSE}$, $d_9\text{-N-EtFOSE}$, $d_3\text{-N-MeFOSAA}$, and $d_5\text{-N-Et-FOSAA}$. Some IS are used as surrogates for several compounds as there is no available IS for these compounds. Branched PFASs were quantified with the corresponding linear IS, the peak which elutes slightly before the linear peak is considered the intensity of the branched compound.

Quality control samples consisted of duplicate samples (n = 8), lab blanks where IS were spiked right before extraction (n = 10), and MQ blanks consisting of 500 mL Millipore water spiked with IS as a regular sample (n = 12).

2.4 Quality control

The blanks, i.e. the MQ samples, were extracted in the same way as the other raw and drinking water samples. The lab blanks (MQ 8 – 20) show a contamination of PFBA in 7 of the blanks samples (1.5 – 5.7 ng/L). Two out of 12 MQ-blanks contained traces of PFHxA (0.6 – 0.5 ng/L). Three show contamination of PFPeA (1.1 – 3.8 ng/L). PFHpA was also found in two samples (0.3 – 1.3 ng/L). Contamination of PFHxDA (0.2 – 6.2 ng/L) and PFOcDA (0.3 – 2.6 ng/L) were found in three samples. Almost all blanks show slight contamination of 6:2 FTSA (0.02 – 0.8 ng/L).

The drinking- and raw water samples are corrected as the amount found in the blanks are subtracted from these values found during quantification, when calculating the

concentrations. The average contamination and standard deviation can be seen in Table 3.

Table 3. Method detection limits (MDL) and lab blanks and MQ blanks. ND = not detected. Values presented in (ng/L).

	MDLs		MQ blanks		Lab blanks	
	MDL Fall	MDL early summer	Average	SD	Average	SD
PFBA	0.26	4.10	2.1	2.1	0.33	0.72
PFHxA	0.23	6.20	0.1	0.2	0.19	0.4
PFPeA	0.028	7.20	0.71	1.4	0.72	1.5
PFBS	0.028	1.10	0.02	0.05	ND	ND
PFOA	0.03	0.08	0.018	0.04	ND	ND
PFHpA	0.028	0.07	0.22	0.43	0.46	0.99
PFNA	0.032	0.07	ND	ND	ND	ND
PFDA	0.039	0.09	ND	ND	ND	ND
PFUnDA	0.019	0.14	0.0003	0.0017	ND	ND
PFHxS	0.28	0.83	0.06	0.19	ND	ND
PFOS	0.023	0.08	ND	ND	ND	ND
6:2 FTSA	0.22	0.84	0.16	0.24	0.51	0.92
FOSA	0.032	0.16	0.01	0.017	ND	ND

The method detection limits for individual PFASs range between 0.05 ng/L and 0.43 ng/L for the quantification done for the fall samples. The early summer samples show limits of detection between 0.06 ng/L and 7.2 ng/L (Table 3).

Considering the fortified samples, most compounds has a recovery rates within 60 – 140%, except for PFTriDA, PFDS, 10:2 FTSA, Me-FOSA, EtFOSA, FOSAA, MeFOSE, EtFOSE, PFDoDA, PFTeDA, PFHxDA, and PFOcDA, and thus were removed from the study.

2.5 Statistical method

In order to compare the two seasons for sample differences of \sum_{26} PFASs, matching pairs were constructed of the plants for RW, i.e. plants represented in both early summer and fall. Wilcoxon signed-rank test was performed on the RW datasets to assess if the \sum_{26} PFASs concentrations measured in early summer and fall come from different sampling population.

Removal efficiencies was evaluated by constructing matching pairs for the plants which were sampled unisonally, i.e. plants represented in both RW and DW. Plants were chosen by the highest \sum_{26} PFASs of RW concentrations (75th percentile and higher). Compounds assessed were chosen on the basis of availability, as they needed at least 3 datapoints for presentation. Drinking water treatment plants using GAC as a water treatment technique was also assessed seperately.

Linear and branched PFASs (PFOS and PFHxS) data are only presented as they were found (Figure 5 and 6).

3. Results

3.1 Occurrence of PFASs in raw and drinking water

All DWTPs showed drinking water concentrations below 90 ng/L. The RW had higher concentrations of \sum_{26} PFAS (Figures 1 and 2) than DW. Furthermore, the \sum_{26} PFASs mainly consisted of the \sum_{11} PFASs. The early summer campaign showed higher concentrations of PFASs in both raw and drinking waters when comparing average concentrations of \sum_{26} PFAS (Figure 2).

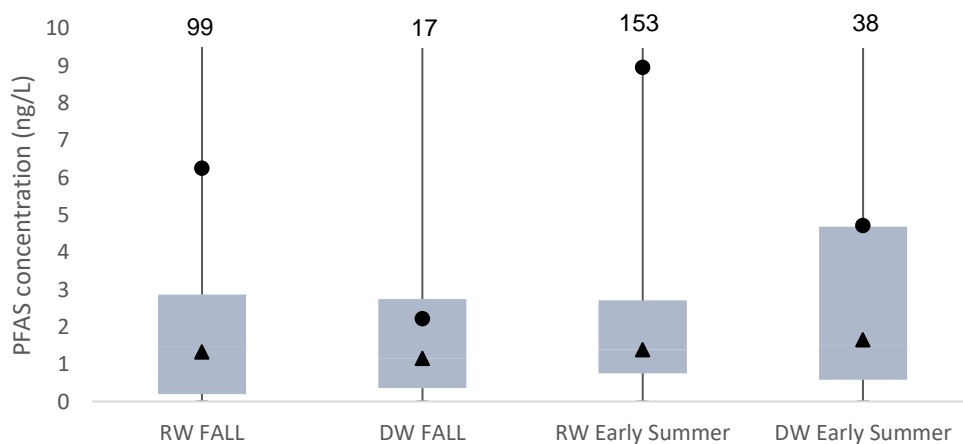


Figure 1. Box-Whisker plots of Σ PFASs₂₆ including all raw water (RW) and drinking (DW) samples ($n = 181$). The maximum values are included in the figure, circle representing the mean value and triangle the median.

However, comparing the raw waters between seasons, Wilcoxon rank test for paired samples show no evidence of a difference between mean concentrations of Σ_{26} PFAS between early summer and fall ($p = 0.15$). A few plants with excessive PFAS concentrations seem to contribute greatly towards the concentrations of Σ_{26} PFAS.

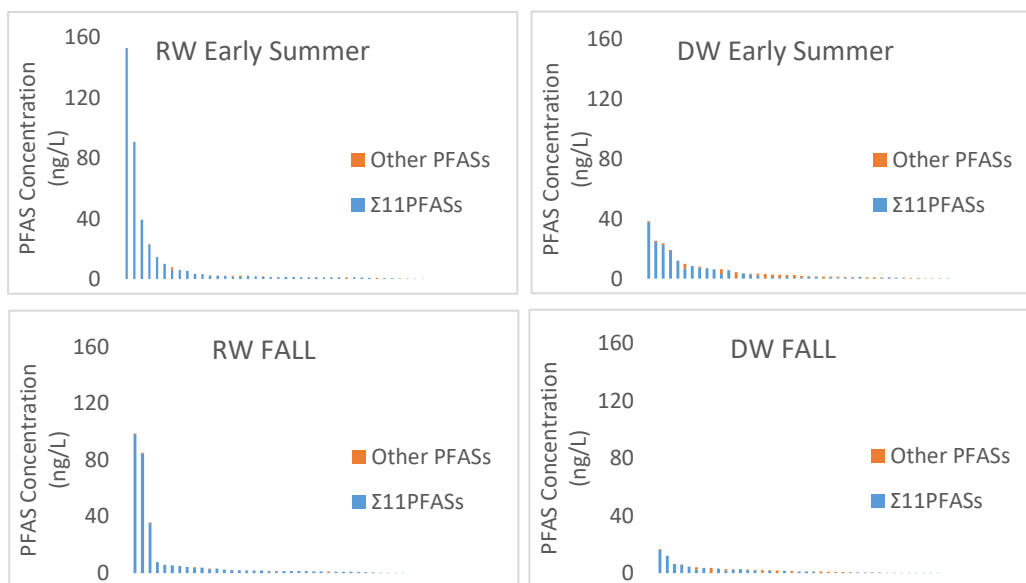


Figure 2. DWTPs are ranked on total amount of PFASs, y-axis show the PFAS concentrations in raw water (RW) and drinking water (DW) and the X-axis show the DWTPs.

The detection frequencies, i.e. how often a compound was found in the samples taken, of the different PFASs, can be seen in Figures 3 and 4. The raw waters contained 12 different PFASs; PFOA, PFHxS, PFBS, PFHpA, PFNA, FOSA, PFHxA, 6:2 FTSA, PFOS, PFBA, PFUnDA, and PFDA.

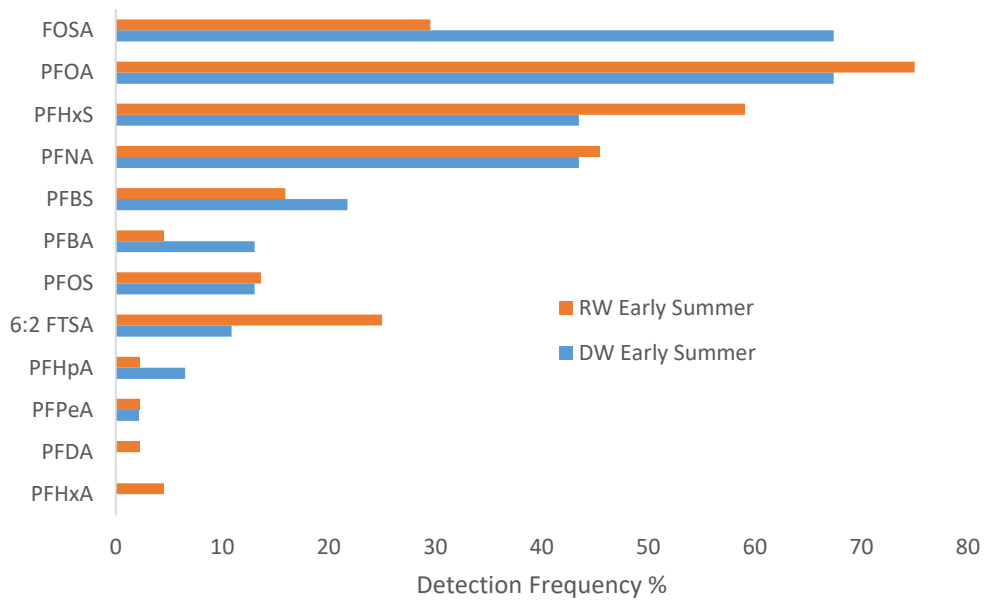


Figure 3. Detection frequency of individual PFASs in during the early summer (raw and drinking water).

The drinking water contained 11 different PFASs; FOSA, PFOA, PFHxS, 6:2 FTSA, PFNA, PFBS, PFOS, PFHpA, PFBA, PFHxA and PFPeA.

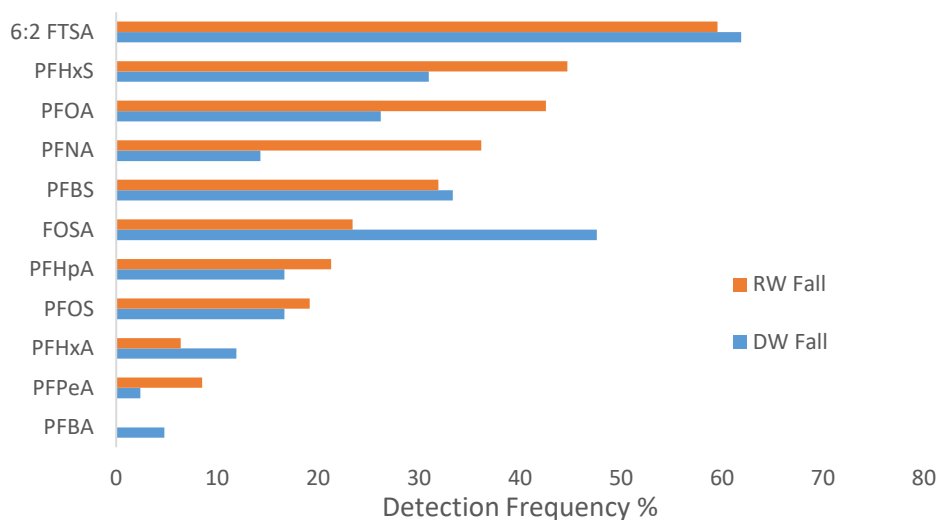


Figure 4. Detection frequency of individual PFASs in during the fall campaign (raw and drinking water).

The raw water profile of the early summer sampling campaign (Table 4) showed maximum values for PFBA, PFPeA, PFHxS, PFOS and 6:2 FTSA ranging between 14 ng/L – 66 ng/L. The most detected compounds were PFOA (79%), PFHxS (62%) and PFNA (48%) and 6:2 FTSA (26%) (Figure 3).

The raw water profile of the fall sampling campaign (Table 4) showed maximum values for PFHxS, PFOS, PFHxA and PFBS ranging between 8 ng/L – 60 ng/L. The most detected compounds were 6:2 FTSA (62%), PFHxS (45%), PFOA (43%), PFNA (36%) and PFBS (32%) (Figure 4).

Table 4, Raw water. Detection frequency (DF%), mean, median, min and max values for individual PFASs in early summer raw water (n=45) (RW) and fall raw water (n=47). Compounds marked with ND (not detected) had too low recoveries to be detected.

	RW early summer					RW Fall				
	DF%	Average	median	min	max	DF%	Average	median	min	max
PFBA	4.8	2.3	0	0	66	0	0	0	0	0
PFPeA	2.4	0.76	0	0	34	8.5	0.1	0	0	1.6
PFHxA	4.8	0.83	0	0	30	6.4	0.4	0	0	8.5
PFHpA	2.4	0.18	0	0	8.2	21	0.2	0	0	2.2
PFOA	79	0.88	0.7	0	5.7	43	0.52	0	0	5.3
PFNA	48	0.11	0	0	0.4	36	0.12	0	0	0.5
PFDA	2.4	0.01	0	0	0.3	0	0	0	0	0
PFUnDA	0	0	0	0	0	0	0	0	0	0
PFBS	17	0.27	0	0	5.7	32	0.73	0	0	8
PFHxS	62	2.2	0.24	0	60	45	3	0	0	57
PFOS	14	0.6	0	0	13	19	0.84	0	0	16
6:2 FTSA	26	0.45	0	0	14	62	0.26	0.1	0	2.5
FOSA	31	0.16	0	0	1.3	23	0.11	0	0	0.7

The drinking water profile of the early summer sampling campaign (Table 5) showed maximum values for PFBA, PFPeA, PFHxS, PFOS, 6:2 FTSA and FOSA ranging between 4.1 ng/L – 22 ng/L. The most detected compounds was PFOA (74%), FOSA (74%), PFHxS(48%), PFNA(48%) and PFBS (24%), (Figure 3).

The drinking water profile of the fall campaign (Table 5), contained relatively low concentrations of PFAS, in comparison to earlier sampling campaigns when considering PFBA, PFHxA, PFOA, PFBS, PFHxS, PFOS and FOSA. These maximum values were between 3 ng/L – 5.9 ng/L. The detection frequency revealed that 6:2 FTSA (62%), FOSA (48%), PFBS (33%), PFHxS (31%) and PFOA (26%) was found often in these compounds (Figure 4).

Table 5, Drinking water. Detection frequency (DF%), mean, median, min and max values for individual PFASs in early summer drinking water (n=48) (DW) and fall drinking water (n=42). Compounds marked with ND, not detected, had too low recoveries to be detected.

	DW early summer					DW Fall				
	DF%	Average	median	min	max	DF%	Average	median	min	max
PFBA	13	1.3	0	0	22	4.8	0.11	0	0	2.8
PFPeA	2.2	0.38	0	0	18	2.4	0.023	0	0	0.78
PFHxA	0	0	0	0	0	12	0.17	0	0	3.7
PFHpA	7.1	0.07	0	0	2.1	17	0.12	0	0	1.6
PFOA	74	0.43	0.35	0	1.9	26	0.23	0	0	2.5
PFNA	48	0.1	0	0	0.37	14	0.04	0	0	0.32
PFDA	0	0	0	0	0	0	0.001	0	0	0.03
PFUnDA	0	0	0	0	0	0	0.001	0	0	0.04
PFBS	24	0.25	0	0	2.9	33	0.3	0	0	3.1
PFHxS	48	0.46	0	0	7.9	31	0.37	0	0	5.9
PFOS	14	0.32	0	0	4.2	17	0.27	0	0	3
6:2 FTSA	12	0.54	0	0	17	62	0.11	0.06	0	1.4
FOSA	74	0.73	0.4	0	4.1	48	0.41	0	0	3.7

3.2 Branched and linear PFASs

Branched (B), and linear (L), isomers of PFASs was only found for two compounds (PFHxS and PFOS), between all the sampled plants. Furthermore, B-isomers were limited to a few plants and not found unisonally in both DW and RW.

The distribution of B and L-PFOS, (Figure 5), reveal that B-PFOS is found in greater extent in DW than in RW, in comparison to L-PFOS. Only four plants had sets with detection of B- or L in both DW and RW, and between those plants Norsborgs vattenverk and Lovös vattenverk showed a slight increase of B-PFOS in DW, in

comparison to L-PFOS. However, the plants are somewhat similar when comparing the percentages across the pairs. Plants without matching pairs of raw and drinking water show a wide range of distributions of either only B-PFOS, or similar distributions of PFASs as the matched pairs.

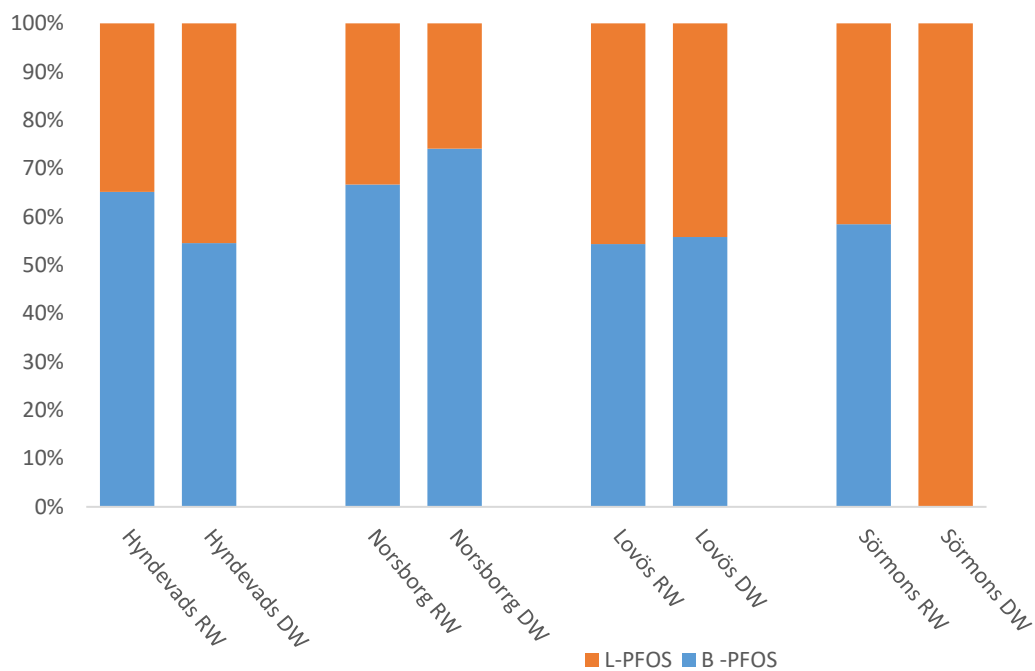


Figure 5. Distribution between branched and linear PFOS.

The distribution of B- and L-PFHxS, (Figure 6), reveal that the distribution is slightly favouring L-PFHxS, rather than B-PFHxS. Five plants had sets with detection of B or L-PFHxS in both DW and RW, and all those plants show an slight increase of B-PFOS in DW, in comparison to L-PFOS.

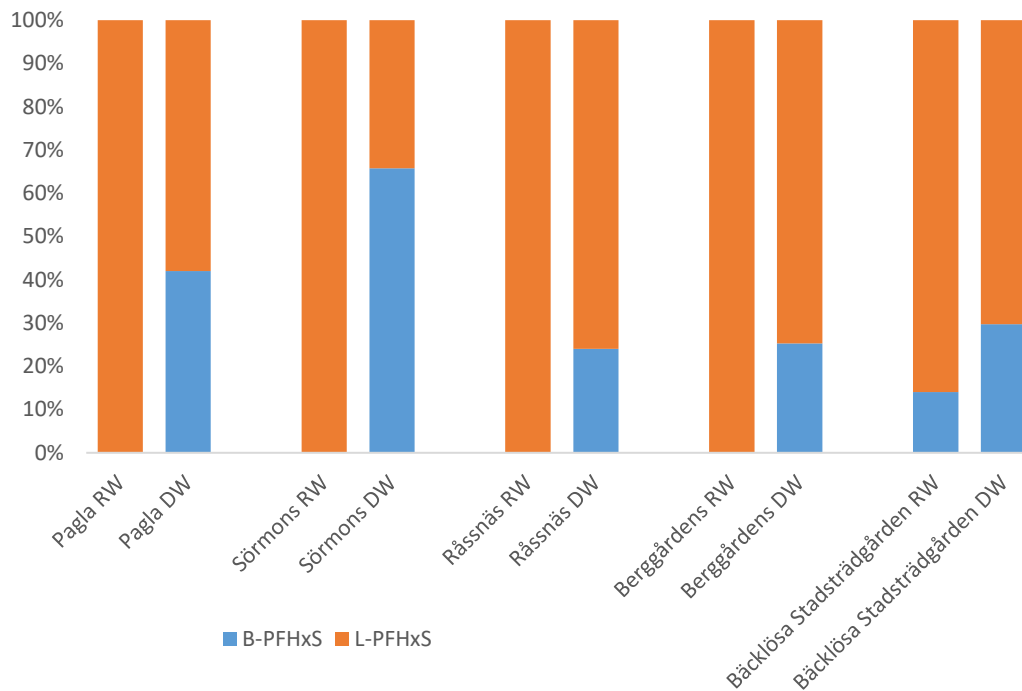


Figure 6. Distribution between branched and linear PFHxS.

Overall, the sets (Figure 5 and 6), indicates that B-isomers are contributing more towards the drinking water profiles than the raw water profiles.

3.3 Composition profiles of PFASs in raw and drinking water

The composition profiles of the major PFAS groups showed a unison distribution between the RW of early summer and fall with a shift of major groups between RW and DW. The DW had in general a higher contribution of precursors than PFCAs and PFASs (Figure 7).

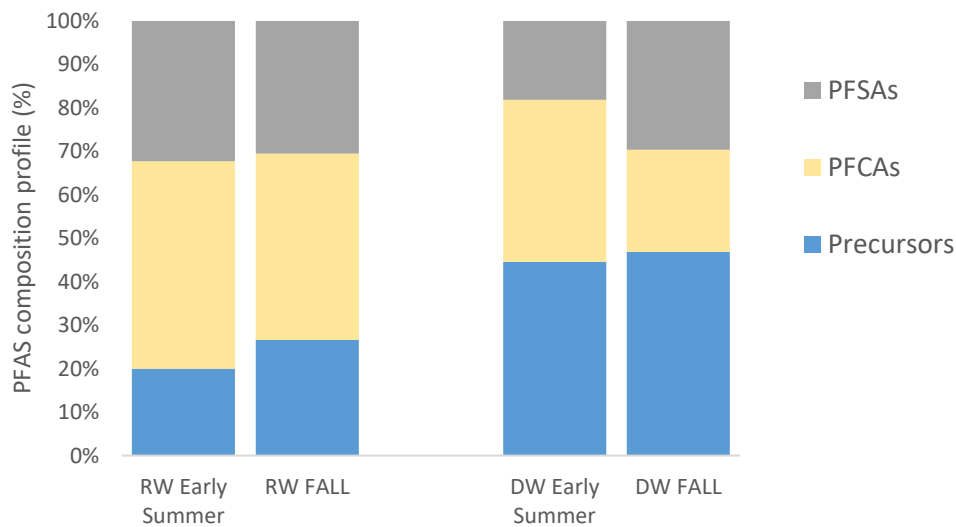


Figure 7. Major PFAS group distribution profile over the seasons.

Individual PFAS (Figure 8) showed a similar pattern as major groups (Figure 7). As stated before, the most common PFAS was from the Σ_{11} PFAS. Furthermore, FOSA was also contributing heavily towards the datasets, especially in DW.

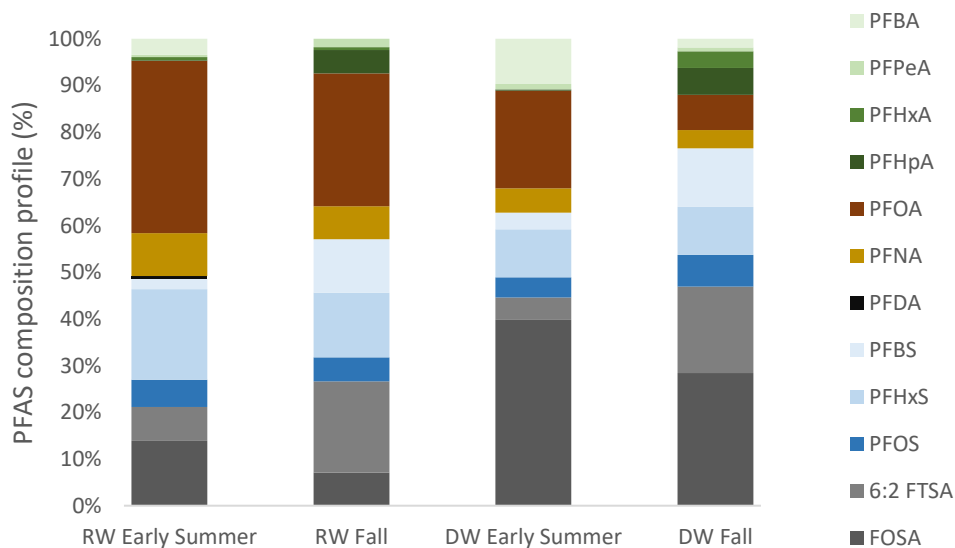


Figure 8. Composition profile in percentage for individual PFASs in raw water (RW) and drinking water (DW).

The reference site (Figure 9) showed a similar distribution profile between seasons for RW, with a shift in profile distributions between RW and DW.

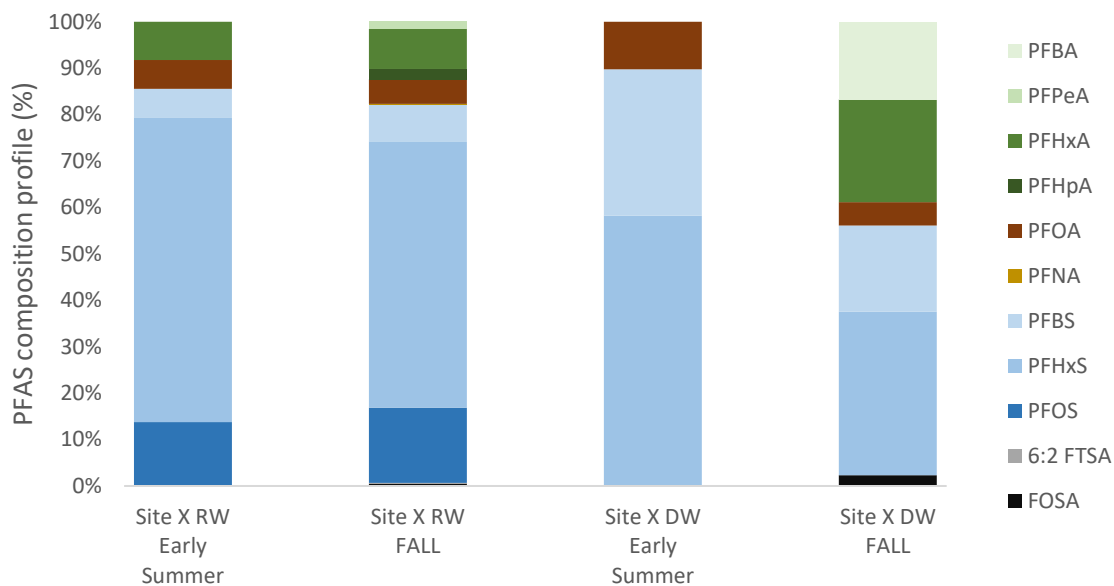


Figure 9. Composition profile of reference site with known high PFAS concentrations in raw water.

3.4 Removal efficiency of PFASs in DWTPs

The removal efficiencies contain many extreme values which can be misleading when presenting average values, thus the median values are presented (Figure 10, 11, 12 and 13).

The plants in the early summer with the highest concentrations of Σ_{26} PFASs, showed positive removal efficiencies for PFOA (55%), PFBS (57%), PFHxS (46%), PFOS (100%), 6:2 FTSA (100%) and negative removal efficiency for PFNA (-23%). All compounds except for 6:2 FTSA were covered in the drinking water guidelines (Figure 10).

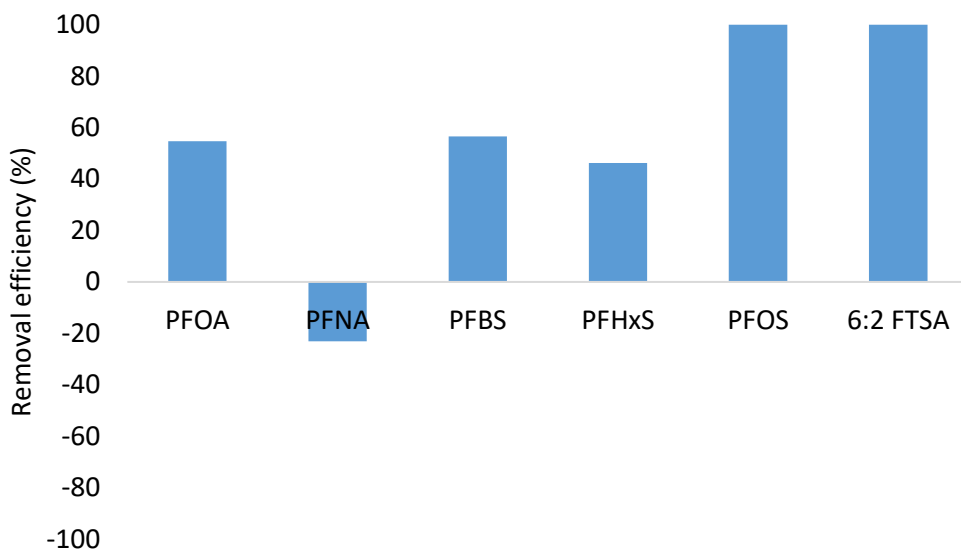


Figure 10. average removal efficiencies for selected DWTPs ($n = 11$) of all individual PFASs for early summer sampling. The selected DWTP represent plants with the highest measured concentrations of \sum_{26} PFASs from raw waters.

The removal efficiencies from the fall campaign from plants with highest concentrations of \sum_{26} PFASs showed a positive removal efficiency for PFPeA (100%), PFHpA (46%), PFNA (100%), PFBS (66%), PFHxS (84%), PFOS (35%), 6:2 FTSA (100%), and FOSA (100%) (Figure 11).

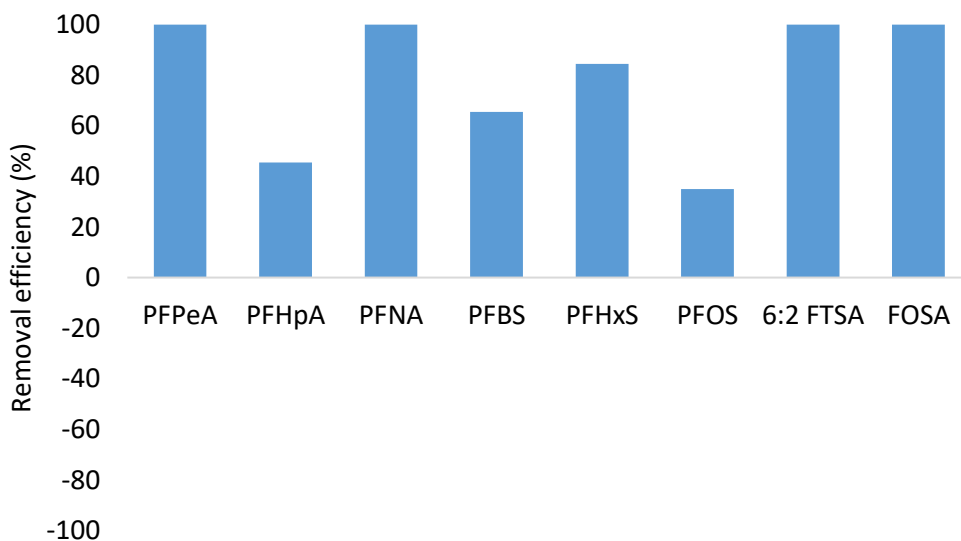


Figure 11. average removal efficiencies for the selected DWTPs ($n = 10$) of all individual PFASs for fall sampling. The selected DWTP represent plants with the highest measured concentrations of \sum_{26} PFASs from raw waters.

Early summer removal efficiencies for GAC plants showed consistent and positive removal of PFOA (50%), PFNA (37%), PFBS (56%) and PFHxS (45%) (Figure 12).

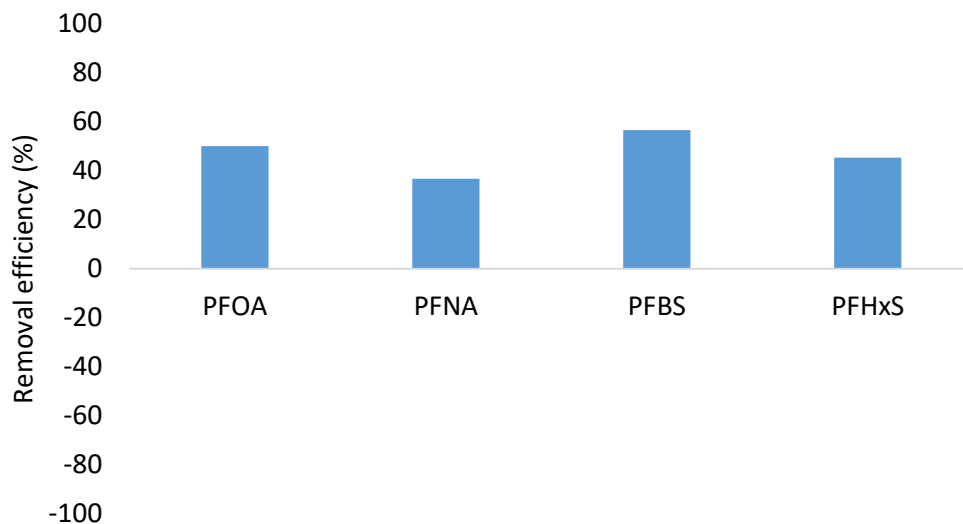


Figure 12. Removal efficiencies of DWTPs with GAC treatment ($n = 9$) during early summer season of plants with highest concentrations of Σ_{26} PFASs.

The fall campaign of the plants with specific treatment options (GAC) show consistent and positive removal efficiency for PFOA (63%), PFNA (100%), PFHxS (90%), and 6:2 FTSA (92%) (Figure 13).

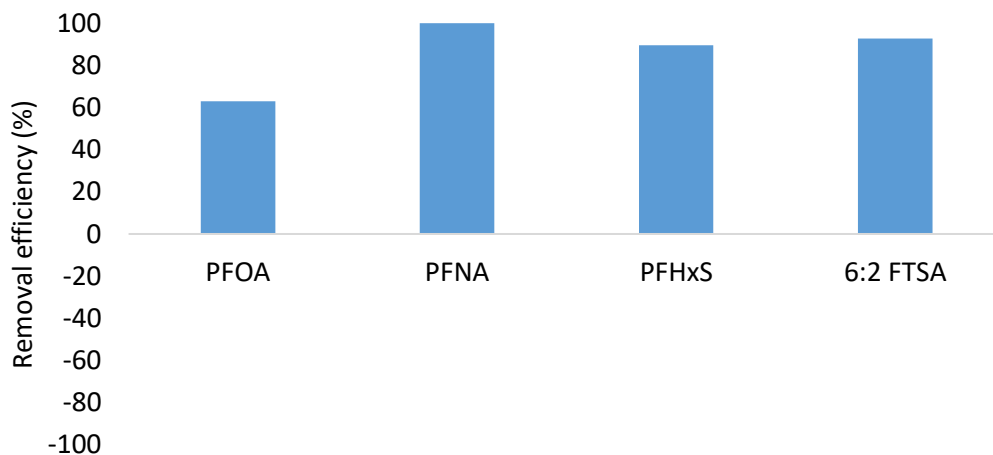


Figure 13. Removal efficiencies of DWTPs with GAC treatment ($n = 9$) during fall season.

4. Discussion

4.1 PFASs in raw and drinking water

As seen in the distribution profiles, the main contributing compounds of PFASs in raw and drinking waters were from the group of Σ_{11} PFASs (Figure 8), which are included in the Swedish drinking water guideline (*PFAS in drinking water and fish - risk management*, 2018). In addition FOSA was detected in samples during the fall campaign. This show that the Swedish drinking water guideline include the most common PFASs found in this study, which indicate that Sweden have robust monitoring practices in place for PFAS. Furthermore, the drinking waters in all DWTPs sampled were below the limit of 90 ng/L of Σ_{26} PFASs. The raw waters had an average Σ_{26} PFASs concentration of 8.8 ng/L (median 1.4 ng/L) in early summer and average Σ_{26} PFASs of 6.3 ng/L (median 1.3 ng/L) in fall (Figure 1). The drinking waters had an average Σ_{26} PFASs of 2.2 ng/L in the fall (median 1.16 ng/L) and an average Σ_{26} PFASs of 4.7 ng/L (median 1.7 ng/L) in the summer (Figure 1).

These values seen in the surface waters are resonable and in line with the study of (Hedlund, 2016) which report Swedish surface waters median of 4.1 ng/L and groundwaters of 0.4 ng/L. The affortmentioned study also had two extremely polluted sites which skews the average PFASs found (112 ng/L for surface and 49 ng/L for groundwaters).

The detection frequencies revealed that the following PFASs was found in many of the different fall water samples: 6:2 FTSA, PFHxS, PFOA, PFNA, PFBS, FOSA, and to lesser extent, PFHpA, PFOS, PFHxA, PFPeA and PFBA (Figure 4). The early summer campaign showed a different pattern of FOSA, which is found most times followed by PFOA, PFHxS, PFNA. Other compounds was found but to an lesser extent: PFBS, PFBA, PFOS, 6:2 PFHpA, PFPeA, PFDA and PFHxA (Figure 3). The differences between the detection frequencies of the two seasons were mainly the detection rates of three compounds: FOSA, PFOA and 6:2 FTSA. Looking at FOSA, the compound was found in greater extent during the fall season, in both raw and drinking waters. The compound PFOA was found to greater extent in both raw and drinking water during the early summer season. And lastly, 6:2 FTSA was found in greater extent during the fall season in both drinking and raw waters. This might be of concern since FOSA is not included in the

Σ_{11} PFASs and it is unclear how much FOSA could potentially contribute to future PFOS concentrations, since it is a precursor to this compound.

The composition profile of major groups revealed that the different Σ_{26} PFASs (Figure 7), is rather uniform across the season while considering the raw waters. Since the raw waters are not treated, it would make sense that they are unison when comparing between groups, compounds and composition. The differences between these group might stem from seasonal variation or the use- and disuse of different PFAS of industrial production. The drinking waters are expected to show bigger differences, the reason is the varying treatment options between all plants which not only affects the plants individual distribution profile but also removes certain compounds more effectively than others. Comparing between the raw and drinking waters, the shift towards a bigger contribution of precursors and a smaller contribution of PFASs and PFCAs, might indicate that PFCAs and PFASs are removed more efficiently from the raw waters.

Comparing between raw and drinking waters for individual compounds (Figure 8), there was an indication of a smaller contribution towards the drinking water profiles of PFOA and PFHxS. Furthermore, in raw waters PFNA had bigger contribution of the PFASs than in the drinking waters, indicating that this compound might be removed effectively. All of these compounds are long chained and the contribution shift makes sense since they should be removed more easily, and thus should contribute less in comparison to other shorter chained PFAS. The drinking waters had a higher contribution of FOSA, PFBS and PFBA. The PFBS distribution seems logical since it was higher in drinking waters profiles. The PFBA was fairly consistent through all waters, and had the same pattern through the seasons. The shift between RW and DW compositions are likely because of different treatment techniques, as the shorter chained PFAS are expected to be contributing more towards the distribution profile.

Since DWTPs take their water from ground or surface waters, it is reasonable to compare this studys concentrations of raw waters to surface and ground waters. However, as discussed before, drawing conclusions between drinking waters and raw waters can be optimistic at best due to the effects of treatment techniques.

The early summer raw waters of this study contained high proportions of PFOA, PFHxS and FOSA (Figure 8) and smaller contributions of PFBA, 6:2 FTSA, PFOS, PFNA while the study of Hedlund (2016) had the biggest contributions of FOSA and PFHxS in ground waters with lesser contribution of 6:2 FTSA, PFHxA, PFPeA, PFOA, PFNA, PFBS and PFOS. The surface waters of Hedlund (2016) is widely spread between PFHxA, PFHpA, PFOA, PFNA, PFHxS and PFOS. The similarities between early summer raw water profiles in this study and groundwaters of Hedlund (2016) are FOSA and PFHxS, contributing largely, and a smaller contribution of 6:2 FTSA, PFOS, PFNA. The biggest differences between raw waters of early summer and groundwaters of Hedlund (2016) are PFOA, which contribute more in this study. The reason for this might be the difference in targeted sites, as major point sources contribute greatly towards the distribution profiles. Comparing between raw waters of fall and ground waters of Hedlund (2016) are similar to the comparison between early summer raw water and groundwaters. Comparing between fall raw waters and surface waters of Hedlund (2016), the similarities are high contributions of 6:2 FTSA, PFHxS, PFBS and PFOA. However, the biggest differences are a higher contribution of the PFCAs (PFPeA, PFHxA, PFHpA and PFNA) in Hedlund (2016). The study of Janousek et al (2019) found the biggest contributions from the scope of 26 Hessian rivers between 2014 – 2016: 6:2 FTSA of 62% in 2014, PFOA 38% in 2015, PFBA by 65% in 2016 and PFOA 35% in 2017. The study also finds most of the PFASs from both this study and Hedlund (2016): (PFOA, PFOS, PFNA, PFDA, PFHxA, PFPeA and PFHxS and PFBS). The dominant PFASs in RW and DW were PFOA, PFNA, PFHxS, PFBS, PFOS, 6:2 FTSA and FOSA. While the compounds are similar to the compounds detected in this study, PFAS distribution in the German rivers might be vastly different from surface and ground waters of Sweden.

Considering the linear and branched PFASs, as they were only quantified for PFOS and PFHxS its hard to draw any conclusions on any seasonal trends. It is expected that the branched would show up more often in the drinking water due to the stronger sorption potential of linear PFASs in comparison to branched PFASs (McCleaf et al. 2017). This behaviour could explain what is seen for both PFOS, (Figure 5), and PFHxS, (Figure 6), where the amount of B-PFAS is greater in drinking water than in raw water, indicating that branched compounds was not removed from the raw water in the same extent that the L-PFAS was removed.

None of the plants which detected B- and L-PFOS in both RW and DW, (Figure 5), have relevant treatment options for PFASs removal, (GAC, AIX and or MF). As the proportions of B- and L-PFOS was somewhat unison between all plants this might be an indication that the PFAS is treated the same for both B- and L-PFOS.

Between the plants which found B- and L-PFHxS, (Figure 6), only one plant is using a relevant treatment technique (GAC). This plant show an increase of B-PFAS between RW and DW, which could further indicate that even with GAC the removal of B-isomers are not as efficient as L-isomers. However, the variance in the removal techniques was high and might contribute to uncertainty.

4.2 Removal efficiencies

The results, (Figure 10, 11, 12 and 13), indicate a high variation in the removal efficiency between the different plants and compounds. The median which was reported in this study was close to the mean in many cases, but ultimately a unison reporting of median was decided upon.

The removal efficiency from the DWTPs with the highest concentrations of \sum_{26} PFASs, revealed an average removal efficiency of 56% (n = 6) between all compounds in the early summer and 79% (n = 8) in the fall (Figure 10 and 11). In early summer, PFNA revealed a negative removal efficiency while all other compounds showed positive removal efficiency. A negative removal indicates that a higher concentration was found in the drinking water than in the raw water, which may indicate leeching or is attributed to variance. The fall sampling campaign revealed most removal efficiencies over 50% except two compounds, PFHpA and PFOS. However, none were negative. Both campaigns detected PFNA, PFBA, PFHxS, PFBs and 6:2 FTSA. Early summer campaign additionally detected PFOA and fall additionally detected PFHpA and PFPeA.

Considering the plants equipped with GAC treatment, the early summer plants showed an average removal of 48% (n = 4) and an average of 86% removal efficiency between all compounds in the fall. Both seasons report PFOA, PFNA and PFHxS, while early summer also reports PFBs and fall reports 6:2 FTSA. Furthermore, all plants show a positive removal efficiency of the detected PFASs(Figure 12 and 13).

The individual compounds will be discussed in greater depth in the next chapter.

4.3 Most occurring PFAS

PFOA had a high contribution towards the concentrations in both raw and drinking waters. The average amount of PFOA found in raw waters were between 0.88 ng/L in early summer and 0.52 ng/L in fall, with maximum values of 5.3 ng/L in fall and 5.7 ng/L in early summer. Drinking waters showed mean values of 0.43 ng/L in early summer and 0.23 ng/L in fall, with maximum values of 1.9 ng/L in early summer and 2.5 ng/L in fall. These values were low when comparing with other studies on rivers in Europe, but some plants has similar values as reported in McLachlan et al. (2007) and Möller et al. (2010). There seems to be an indication of PFOA contributing more towards the Σ_{26} PFASs in the raw waters than in the drinking water(Figure 8).

Furthermore, the early summer campaign showed a higher detection frequency of PFOA, than in the fall seasons. This was reflected in the average values found in the drinking waters. The DWTPs with the highest concentrations of Σ_{26} PFAS in the early summer removed PFOA with a median of 55% (n = 10, Figure 11), while the fall study did not detect PFOA enough to quantify removal. In comparison, DWTPs using GAC had a median removal efficiency of 63% (n = 6, Figure 13), and in the early summer a median of 50% (n = 7, Figure 12). Comparing DWTPs that had the highest concentrations of Σ_{26} PFAS with plants using GAC, the compound was removed effectively in most plants. Plants using GAC show similar removal efficiency in comparison to plants without a proper treatment technique. Other studies show similar removal efficiencies. The study of McCleaf et al. (2017) show an average removal efficiency of 64% with an initial removal efficiency of 100% and 28% at the end of the experiment. The study of Appleman et al. (2014) suggests a removal efficiency between 70% and 90 % for GAC, RO and AIX. Between the results of this study and cited literature this compound is effectively removed during the sampling campaign in this study. If the median removal efficiency from this study would be a true indicator of current removal efficiencies it could indicate that GAC filters are starting to wear out, since the range of McCleaf et al. (2017) was 100% to 28%, and current removal efficiency is 64%. However, the early summer study show a lower removal efficiency than fall, which may indicate variance in PFOA concentrations rather than removal efficiency.

PFNA showed high contribution towards the PFASs profile in raw water, but low in drinking water, and there seem to be efficient removal of this compound from the raw waters. The values of PFNA in the raw waters showed average values of 0.11 ng/L for early summer and 0.12 ng/L for fall with maximum values of 0.42 ng/L and 0.48 ng/L, respectively. These values are similar to McLachlan et al. (2007) for several rivers in Europe, but lower on average. Looking at the detection frequencies, the compound is only detected in raw waters in early summer and mostly in raw waters in fall. However, this compound showed high average values but did not contribute much towards the average composition profile. The removal efficiencies showed a median removal of 100% (n = 7, Figure 11) in fall and a median removal in early summer of -23% (n = 5, Figure 10). The plants with GAC showed a median removal of 100% (n = 5, Figure 13) in fall and a median removal of 37% (n = 4, Figure 12) in early summer. In both cases the removal was more effective in the fall than in early summer. This compound is a long chain PFCA and thus it should in theory show adsorption to sorbents such as GAC, which was expected for these plants. The plants which was utilizing GAC show high variance in the removal of this compound. However, this compound showed around 70% removal using GAC in the study of McCleaf et al. (2017) with a 10% removal at the end of the study's trial where the GAC show signs of saturation. The findings of McCleaf et al. (2017) contradicts the results of this study. Overall PFNA was removed extremely efficiently in the fall when critically reviewing the individual plants, but was removed poorly during the early summer. The negative removal and the range of removal efficiency from the study of McCleaf et al. (2017) suggests that results from this study might be uncertain.

PFHxS showed a large contribution towards the composition profile for raw water (Figure 8). The mean values found in the raw waters were 2.2 ng/L in early summer and 3 ng/L in fall with maximum values during early summer at 60 ng/L and fall at 57 ng/L. Drinking water results revealed a low average concentration of 0.46 ng/L in early summer samples and 0.37 ng/L in fall, maximum values in early summer concentrations of 7.9 ng/L and 5.9 ng/L for fall (Figure 1, Table 4 and 5). The contribution towards the distribution profile changed slightly with a higher contribution in the raw waters than in the drinking waters for \sum_{26} PFASs. The removal efficiencies show high variance and reveal that during the early summer this

compound had a median removal efficiency of 46% (n = 11, Figure 10) while the fall samples showed a median removal of 84% (n = 9, Figure 11). The GAC plants had a removal efficiency of 45% (n = 6, Figure 12) in the early summer and 90% in the fall (n = 3, Figure 13) in comparison to the study of McCleaf et al. (2017) which found average removal efficiencies of PFHxS of 63%, and 6% towards the end of trial. This study shows a high variance on PFHxS removal over the different plants and if the median is a true indicator of the removal efficiencies, it is within, or higher, than the study of McCleaf et al. (2017).

PFOS was found in all seasons and water sources with a small increase of PFOS concentrations in drinking water compared to raw water. The raw water reveals that on average PFOS concentrations were 0.6 ng/L in early summer and 0.84 ng/L in the fall, with maximum values of 13 ng/L and 16 ng/L, respectively. Furthermore, PFOS concentrations were on average 0.32 ng/L in the early summer drinking waters and 0.27 ng/L in the fall with maximum values of 4.2 ng/L and 3 ng/L, respectively (Figure 1, Table 4 and 5). The removal efficiencies of the plants with the highest concentration of Σ_{26} PFAS during early summer showed a PFOS median removal of 47% (n = 5, Figure 10). In the fall PFOS was removed by a median of 35% (n = 7, Figure 11). In the plants with GAC the detection of PFOS was low and could not be quantified. The study of McCleaf et al. (2017) showed an average removal of 81% using GAC with 47% removal at end of the trial. Other cited literature such as Appleman et al. (2014) show removal efficiencies of PFOS between 80% and 90% using GAC, AIX and RO. This could indicate that GAC removal effectiveness might be on the lower side for the DWTPs in this study, perhaps because their treatment technique is nearing its end-life. Since PFOS is a long-chained PFAS it is expected to be effectively removed, the source cited is in line with the findings of this study and the average values are close to the mean. Which may indicate strong data, and that this compound is readily removed from plants with the highest concentrations of the Σ_{26} PFAS.

6:2 FTSA showed higher contribution towards the profile of PFASs during the fall campaign than in the early summer campaign. Furthermore, they seem to contain roughly the same proportions if compared between raw and drinking water. The average concentrations in raw water were 0.45 ng/L during early summer and 0.26 ng/L during fall, with maximum values of 14 ng/L and 2.5 ng/L, respectively. The

drinking waters had average concentrations of 0.54 ng/L during the early summer and 0.11 ng/L during the fall sampling, with maximum values of 17 ng/L and 1.4 ng/L, respectively. This compound had a high variance in its removal efficiency between the different sampling campaigns. Early summer plants in the 75th percentile show 100%(n = 7, Figure 10) median removal efficiency with high variance, fall plants in the same category show a 100%(n = 10, Figure 11) median removal efficiency. The plants with GAC showed a median of 93%(n = 6, Figure 13) in fall while the early summer campaign could not be quantified due to the low detection frequency. Considering the extreme outliers which introduce uncertainties to the data, this compound should be further investigated if possible. The fall campaign seem to indicate more certain values for this compound.

FOSA was on average found in raw waters were between 0.16 ng/L in early summer and 0.11 ng/L in fall, with maximum values of 0.74 ng/L in fall and 1.3 ng/L in early summer (Table 4 and 5). The drinking water had a average FOSA concentration of 0.73 ng/L (early summer) and 0.41 ng/L (fall), with maximum values of 4.1 ng/L and 3.7 ng/L, respectively. This might be of concern since this compound is not in the scope of the Σ_{11} PFAS. The distribution profile of this compound showed a trend that the compound is contributing more towards the total drinking water profile than the raw water profile (Figure 8). Furthermore the compound show higher values in the early summer than in the fall. The MDL for FOSA was 0.16 ng/L in early summer and 0.032 ng/L in fall. Since the average FOSA concentration in the fall campaign was the same as the MDL of the early summer campaign, the vales might be uncertain. The removal efficiencies of FOSA was only quantified in the 75th percentile of fall plants with a median removal of 100% (n = 3, Figure 11). The plants with GAC treatments did not detect FOSA in in a high enough frequency. Since FOSA is a precursor to PFOS and is considered to bind strongly to particles (Ahrens. 2011), a high removal efficiency would be expected. Removal efficiencies for FOSA has been reported previously in McCleaf et al. (2017) which showed that FOSA was efficiently removed with fresh GAC or AIX materials but less over time. Furthermore, the study report an average removal efficiency of 80% with a spread of 99% at first day and a change of 54% removal at the last day from the initial removal. Since FOSA is a C₈ - PFAS, i.e. a long-chained PFAS, this compound should be excessively removed.

4.3 Seasonal variation of PFASs

The discussion will mainly focus on raw waters, since trends between seasons when comparing drinking waters can be problematic to assess due to removal techniques and treatment steps, which can affect PFAS concentrations.

Comparing between the two seasons the main parameters for seasonal variation is likely: water fluxes, temperature and DOM. As DOM was not sampled this variable is not discussed, as it would be speculative at best.

Water fluxes in the early summer can impact water contents and water quantity, which further can alter the water chemistry (Fölster and Wilander, 2002; Lee et al. 2020), and change PFAS concentration. As cited before, the temperature can also promote higher PFASs concentrations in the waterphase. This can also lead to altered PFASs fluxes since they are stipulated to not be retained in soils to great extent (McLachlan et al. 2007). This study sampled in July 2018 and October 2018, meaning summer and middle of fall. Since the early summer had a lower precipitation and higher evaporation compared to fall of 2018, the PFASs released from soils or other point sources could be staggered or delayed in the early summer due to no rain. Therefore, the year of 2018 in Sweden with extreme weather conditions may play a role in PFASs movement

In the even of lower precipitation, high temperature and higher evaporation, the total size of the waterbody would be smaller which could lead to higher PFAS concentrations in the waterbody. A normal year with average values of precipitation and temperature would most likely have a large flux of meltwater in the early summer which would carrying high volumes of PFAS from contaminated sites to watersheds. A constant but normal stream of water, seen in the summer and fall of 2018 would likely contribute to a dilution effect, lowering the PFAS concentrations (Zhang et al. 2013). The reasoning is that a larger volume of the waterbody, without addition of more PFAS, will lower the concentrations of PFAS (dilution). However, as major point sources of contaminated PFAS soils are likely affected, PFAS leeching due to rain can contribute to more PFAS in waterbodies but as the total volume rises, the concentration effect is hard to distinguish. While PFAS is detected in many surface

and ground waters, studies show extreme values from a few major point source (Ahrens et al. 2015; Gobelius et al. 2018; Gyllenhammar et al. 2015), which would greatly contribute towards PFAS concentrations in the case of rain. The result of such behaviour could mean that near major point sources a larger total PFAS load would be carried to the watershed, but overall the concentrations would be lower. Therefore the concentrations might be a weak indicator of the PFAS situation and instead the PFAS loads should be considered.

Looking at the results, some values in the early summer set, such as PFBA (66 ng/L), PFPeA (34 ng/L) and 6:2 FTSA (14 ng/L) was much higher in early summer RW than in fall RW, it might indicate that the individual PFAS are responding to water movements. The extreme values of the short-chained PFBA and PFPeA might also stem from water-flow, as these compounds are more water soluble than long-chained. Since this study only sampled in summer and fall, the differences between early summer, summer, fall and late fall can not be acknowledged. The extreme values seen in the early summer set might be attributed to the seasonal variation in the year of 2018. Comparing between the raw water of early summer and fall, which are the sets that should represent seasonal variation the most, show similar distributions. Main distributors are PFOA, PFNA, PFBS (more in fall), PFHxS, PFOS, 6:2 FTSA and FOSA. The early summer had more PFBA and fall had more PFHpA. Minor contributions of PFDA and PFPeA occurs in both sets. This might indicate that between the two seasons there is minor differences, i.e. they are almost the same. The reasons behind this trend can be that the two sampling points were too close in time, i.e. the sampling was too uniform between seasons. There are studies that indicate the same trends as this study, a higher concentration after potential influx of water in early summer and lower concentrations later in the fall. But the studies are not uniform, and comparing between them can be optimistic at best. Furthermore, this study does not find enough evidence to support a difference of PFAS concentrations (Σ_{26} PFAS) between the early summer and fall (Figure 1), Wilcoxon signed rank test ($p = 0.15$), between raw water sets. The main reason for this is likely a few select sites which contributes greatly to the total concentrations of Σ_{26} PFAS in both sets. As the sets are affected by outliers and not normally distributed, it seems to indicate that these few sites are major point sources for PFAS concentrations across the sampled sites. A comparison with tests against the means of both sets can also

indicate that two datapoints and one year of sampling is not enough for such analysis. Instead a campaign should be launched that target specific sites with known legacy PFAS contamination, sampled at a weekly or monthly basis, and evaluated over many years.

Seasonal variation of PFASs has been studied before. While no statistical significant results were concluded, the study of Nguyen et al. (2019), which sampled during two years between August 2016 and October 2017, show trends of lower PFASs concentrations during the late autumn (october) and higher concentrations summer and early early summer in WWTPs. The change in compounds was decreasing PFBS and PFOA, and increasing PFPeA, PFHxA, PFHpA, PFNA and PFHxS. Since this study did not specifically look at surface waters or drinking waters but WWTPs, it is hard to draw any meaningful conclusions between those and drinking waters. The reason is that WWTPs reflect not only seasonal distribution but also human consumption and behaviour, which can add uncertainties to the comparison. The study of Lee et al. (2020) conducted in South Korea conclude that the highest concentrations can be seen during the fall and early early summer, but lower values can be seen during summer and late early summer. They conclude a statistical significant difference between seasons but further point out that the concentrations might be diluted by the heavy rain seasons during summer, which is in line with Zhang et al. (2013) and Zhao et al. (2015) which finds statistical correlation between lower concentration of PFASs in waters with high water fluxes, i.e. a dilution effect.

One site in this study that is know to have legacy problems is located close to Uppsala, hereby referred as "Site X", which is contaminated by Ärna Airport with legacy sources of PFAS that stem from AFFFs. Concentrations are withheld from this thesis.

This is an environmental problem no doubt but can be of use to researchers for a number of reasons: the site has documented problems, the level of PFASs are way above MDL, the site is contaminated from a soil located upstreams and it is easier to focus one site locally with PFASs changes than comparing a whole country. The layout of the watershed can be seen in Gyllenhammar et al. (2015) and the distribution profile can be seen in Figure 9. Since these problems are known, it is also subject of

several cohort and environmental studies (Gyllenhammar et al. 2015; McCleaf et al. 2017; Stubleski et al. 2017).

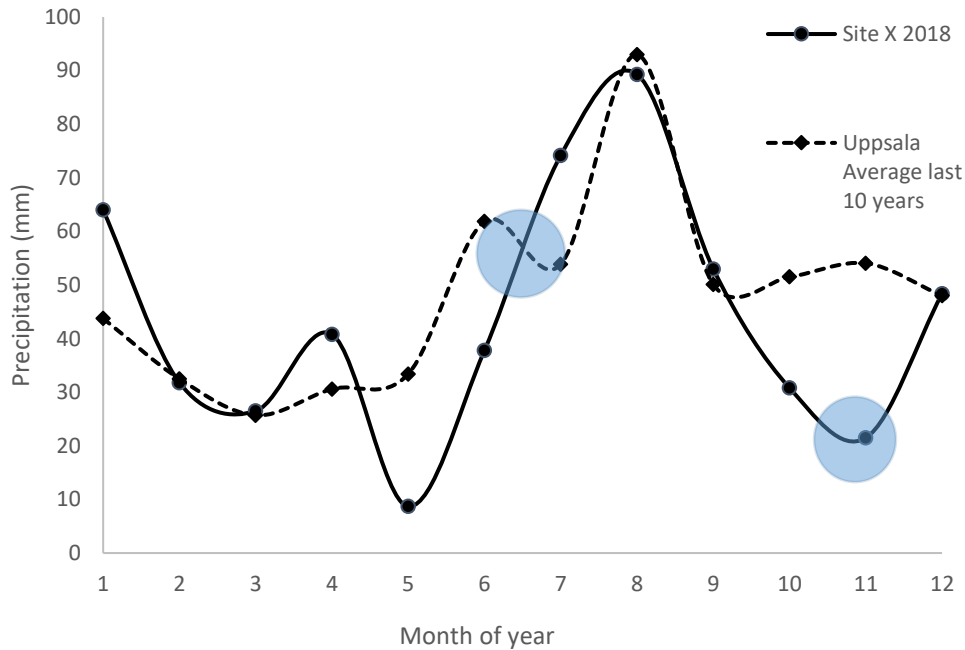


Figure 14 Mean precipitation in Uppsala for the last 10 years plotted against the precipitation at Ärna in 2018. Circles indicating sampling times for this study.

In the early summer season, the PFAS concentration has a higher percentage of PFASs in the drinking water than in the raw waters. All PFCAs except for PFOA was removed easily (Compared with anonymized removal efficiencies of this study), and the PFAS left in the drinking water are PFBS and PFHxS (Figure 9). The PFAS removed in the early summer were all long-chained, and what is left are mostly PFBS and PFHxS, which are short-chained. The fall season show a similar distribution profile comparing the early summer and fall raw waters. The fall drinking water show a removal of PFOS, PFOA and PFHxS. The remaining distribution profile consists mainly of short chained PFAS (PFBA, PFHxA, PFOA, PFBS and PFHxS) and to a lesser extent, PFOA and FOSA.

During early summer and fall there are fluctuations in precipitations at Ärna compared to the average of the last 10 years (Figure 14). Furthermore, there seems to be a higher precipitation around the summer sampling than in the fall. The autumn show lower precipitation than the mean going back 10 years. However, earlier precipitation leading up to the sampling date would likely matter in the case of this

PFAS flux, as the site has a soil profile which is contaminated by PFAS. The precipitation need to leach through the site and transport the PFAS to the recipient (Site X).

At Ärna airport during early summer in June and July there were reports of 38 mm and 74 mm precipitation respectively, while September and October the precipitation was reported at 53 and 31 mm, respectively. On the other hand, the early summer will provide with stored precipitation from melt water, which can mean that these effects are somewhat negated, as there was hardly any precipitation prior to the summer. If the precipitation would be the main parameter in the PFAS flux from this site, the summer would likely show higher concentrations. However, the rain is ongoing during the summer months leading up to the fall sampling, which might yield the same results of the fall sampling. Furthermore, when comparing the concentrations of Σ_{26} PFAS between the sample points, there is minor differences. It might be the case that the stored meltwater at the site in early summer and the dilution effect of upstreams meltwater together yielded concentrations in early summer, similar to of the rain leading up to the sampling date in fall.

This could explain some of the trends seen, where the concentrations between the two seasons are almost the same. Indicating that if there's no difference in water fluxes the leaching from a site would be the same.

The distribution profile is further indicating that the parameters of PFAS fluxes in and around Ärna airport and the recipient are controlled to such degree that it can be used in future studies to assess trends between other parameters. Those parameters could be rainfall, DOM, suspended particles, water chemistry parameters and water fluxes. As the incoming raw waters in both early summer and fall are fairly similar, both composition-wise and concentration-wise, the site is relevant for future studies. What goes out of the DWTP is on the other hand affected by its treatment options. However, incoming water seem to have no difference between seasons. Comparing these findings at Site X (Figure 9) and the overall profile (Figure 8), similar pattern is observed between the raw waters of all sampling sites. The biggest differences are the big contribution of PFBA, which is contributed by one plant. Also 6:2 FTSA and PFBS which are found more often in fall. However, the sets are similar (Figure 8 and 9).

There seem to be no distinct differences between the sampled periods when looking at the contribution profiles. However, it should be noted that this site has a specific profile of contamination since the source is known, and the overall profile of the seasons are a average value from all of Sweden. This comparison can introduce uncertainty in comparison.

Since PFASs is widely spread in society from products and industry applications, the phase-out, or use- and disuse of PFASs components vary. It can further become problematic to attribute seasonal variations to PFAS changes in the environment if they originate from point sources or consumption patterns. These behaviours in society as a whole is therefore adding uncertainties when attributing PFAS variation to seasonal changes. Especially if studies are conducted over several years or samples are taken where anthropogenic activity is high. The study of Janousek et al. (2019) tried to tie consumption patterns to PFAS concentrations but did not find any significant findings.

The use- or disuse of PFASs may be attributed to phase-outs or shifts in industries the uncertainties need to be accounted for. To eliminate this factor a site or stream that is free of industries which currently use PFAS in their production line has to be chosen, and if there are contaminated sites, these has to be pin-pointed and accounted for. This is problematic in streams, as seen in (Janousek et al. 2019; Lee et al. 2020) where uncertainty arose due to PFASs shifts or WWTP discharge. Furthermore, sampling WWTPs is not ideal to assess seasonal variation since those reflects the PFASs use in consumer products from cities, which are subject to anthropogenic behaviour. The same uncertainty can be introduced in this studys whole dataset as there is no information about industrial use and emissions of PFAS. While some sites are recognized as legacy source, there has to be a more thorough inventory of all sites and sources.

5. Conclusions

All drinking waters had levels below \sum_{26} PFAS 90 ng/L at all investigated DWTPs. The main PFAS detected were reflected in the Swedish drinking water guidelines (\sum_{11} PFASs), except for FOSA. There was no significant difference of \sum_{26} PFAS

concentrations between seasons when comparing the raw waters of the sampled DWTPs. Some sites showed elevated levels of PFAS concentrations in the raw water. However, more studies are needed to trace potential sources. The removal techniques show a high variation. Generally, highest removal of PFASs was found for the long-chained PFAS, as reflected in the literature cited.

No significant differences were observed for seasonal variation of PFASs at the investigated DWTPs. More studies with more frequently sampling is needed at the individual sites to explain seasonal difference. In addition to water samples, precipitation should be collected in order to assess how precipitation is contributing to the PFASs in the aquatic environment.

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