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Mass flows of per- and polyfluoroalkyl substances (PFASs) in a Swedish wastewater network and treatment plant

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Linda Glimstedt

ABSTRACT

Mass flows of per- and polyfluoroalkyl substances (PFASs) in a Swedish wastewater network and treatment plant

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Per- and polyfluoroalkyl substances (PFASs) are man-made substances that hold unique properties. They are not only oil- and water repellants but also very resistant to degradation. Due to these properties, the applications are endless and PFASs can be found in a wide range of industrial applications and commercial products. The effluents of wastewater treatment plants (WWTPs) have been pointed out as one of the major sources of PFASs in the environment.

The main aim of this project was to evaluate the sources and the occurrence of PFASs in a wastewater network in a Swedish city and in the different treatment steps at the connected WWTP. Another objective was to use these data to calculate mass flows and to investigate the fate of PFASs within the WWTP. The city of Uppsala and the WWTP *Kungsängsverket* were selected as study objects. Both wastewater and sludge were sampled and analyzed. In the wastewater network, a total of 15 pumping stations (PSTs) were sampled for wastewater, and at the WWTP, a total of 10 wastewater and 10 sludge samples were taken. The samples consisted of grab samples ($n = 24$), time-integrated samples (100 mL every 20 min during 24 hours, $n = 2$) and flow proportional samples (24 hours, $n = 9$). The aqueous and sludge samples were prepared for analysis using solid-phase and solid liquid extraction, respectively, and then analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

The PFAS concentrations and composition profiles varied greatly in the network. High concentrations of 6:2 fluorotelomer sulfonate (6:2 FTSA) were generally found in the wastewater, which indicates increased usage of 6:2 FTSA in industrial processes and applications as replacement for perfluorooctane sulfonate (PFOS) and/or leaching from fire-training sites. A hot spot was detected (Sågargatan PST: ΣPFAS = 55,000 ng L^{-1} = 110,000 mg d^{-1}) with elevated discharges of $C_3 – C_8$ perfluoroalkyl carboxylates (PFCAs).

The studied WWTP was ineffective in removing C_4, C_6, C_8 perfluoroalkyl sulfonates (PFSAs), $C_3 – C_8$ PFCAs and 6:2 FTSA from wastewater. Longer chained $C_9 – C_{17}$ PFCAs tended to partition to sludge more effectively than shorter chained $C_3 – C_8$ PFCAs, where PFCAs with an even amount of perfluorated carbon atoms had a higher affinity for sludge than those with an odd amount. The PFAS concentrations and mass flows tended to increase across the second clarifier in both wastewater and sludge, probably due to precursor degradation.

PFSAs and PFCAs tended to be at similar or lower concentrations in the effluent compared to the influent. This shows that these substances enter the WWTP from an upstream source and are not formed or added in the WWTP. The transformation of precursors is therefore not the most important source of PFASs in *Kungsängsverket*. PFASs in wastewater at a large scale municipal WWTP may origin to a large extent from both industrial applications and domestic sources, such as daily life products. The new knowledge generated within this project will help Uppsala Vatten to protect drinking water supplies and the receiving aquatic environment from PFAS contamination.

Keywords: per- and polyfluoroalkyl substances, PFAS, 6:2 FTSA, wastewater, wastewater network, wastewater treatment, WWTP, Uppsala, Kungsängsverket.

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REFERAT

Massflöden av per- och polyfluoralkylerade substanser (PFAS) i ett svenskt ledningsnät och reningsverk

Linda Glimstedt

Per- och polyfluoroalkylerade substanser (PFAS) är konstgjorda ämnen som har unika egenskaper. De är inte bara fett- och vattenavvisande utan är även mycket resistenta mot nedbrytning. På grund av dessa egenskaper är applikationerna med PFAS oändliga, och de används i en lång rad industriella applikationer och kommersiella produkter. Renat vatten från avloppsreningsverk har pekats ut som en av de största källorna av PFAS i miljön.

Syftet med det här projektet var att undersöka källorna och uppkomsten av PFAS i ett ledningsnät i en svensk stad och även före/efter de olika reningsstegen i det största reningsverket. Ett annat mål var att använda dessa data för att beräkna massflöden och att studera ödet för PFAS i reningsverket. Uppsala stad och reningsverket Kungsängsverket valdes som studieobjekt. Både avloppsvatten och slam provtogs och analyserades. I ledningsnätet provtogs totalt 15 pumpstationer (PST) med avseende på avloppsvatten och i reningsverket togs det totalt 10 avloppsvatten- och 10 slamprover. Proverna bestod av stickprover ($n = 24$), tidsintegrerade prover (100 mL var 20 min under 24 timmar, $n = 2$) och flödesproportionerliga prov (24 timmar, $n = 9$). Vatten- och slamproverna preparerades för analys med hjälp av fastfas- respektive fast-vätske-extraktion, och analyserades därefter med vätskekromatografi kopplat till tandem-mass-spektrometri (LC/MS/MS).

PFAS koncentrationerna och sammansättningsprofilerna varierade mycket i ledningsnätet. Koncentrationerna av 6:2 fluorotelomersulfonsyra (6:2 FTSA) var generellt höga i avloppsvattnet, vilket tyder på en ökad användning av 6:2 FTSA i industriella processer och applikationer som ersättningssubstans för perfluorooktansulfonsyra (PFOS) och/eller urlakning från brandövningsplatser. En så kallad hot spot detekterades i ledningsnätet (Sågargatan PST: ΣPFAS = 55 000 ng L^{-1} = 110 000 mg d^{-1}) med punktutsläpp av $C_3 – C_8$ perfluoroalkylerade karboxylsyror (PFCA).

Det studerade reningsverket var inte effektivt för rening av C_4, C_6, C_8 perfluoroalkylsulfonsyror (PFSAs), $C_3 – C_8$ PFCAs och 6:2 FTSA. PFAS av typen $C_9 – C_{17}$ PFCA (långa kolkedjor) tenderade att fördela sig till slamfasen mer än $C_3 – C_8$ PFCA (kortare kedjor), där PFCA med ett jämnt antal perfluorerade kolatomer hade större affinitet för slam än de med udda. PFAS koncentrationerna och massflödena tenderade att öka från första till andra sedimentations-tanken, både i avloppsvatten och i slam, troligtvis som en följd av degradering av prekursorer.

PFSA och PFCA tenderade att ha likvärdiga eller lägre koncentrationer i ut- jämfört med inflöde. Detta tyder på att huvudkällorna för dessa substanser i avloppsvatten finns uppströms och uppkommer inte genom bildning eller tillsats i reningsverket. Nedbrytning av prekursorer är därför inte den viktigaste källan av PFAS i Kungsängsverket. Det visades tydligt att PFAS i ett kommunalt avloppsvatten kan ha sitt ursprung såväl i både industriella produkter och processer som produkter från hushåll, som t.ex. dagligvaruprodukter. Den nya kunskapen som genererats i detta projekt kommer att hjälpa Uppsala Vatten att skydda dricksvattentäkter och den mottagande akvatiska miljön för PFAS förorening.

Nyckelord: per- och polyfluoroalkylerade substanser, PFAS, 6:2 FTSA, avloppsvatten, ledningsnät, avloppsnät, avloppsvattenrening, reningsverk, Uppsala, Kungsängsverket.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Massflöden av per- och polyfluoralkylerade substanser (PFAS) i ett svenskt ledningsnät och reningsverk

Linda Glimstedt

Per- och polyfluoroalkylerade substanser (PFAS), även kallade högfluorerade ämnen, utgör ett hot mot människors hälsa och miljön. De är konstgjorda ämnen som har skapats för att ha unika egenskaper. De är inte bara fett- och vattenavvisande utan är även väldigt stabila, dvs. tåliga mot nedbrytning. På grund av dessa egenskaper har de använts i många olika produkter, allt från brandskum till smutsavvisande ytor på smartphones. PFAS har även visat sig vara giftiga och anrikas lätt i levande organismer.

Den mest kända substansen är perfluorooktansulfonsyra (PFOS). Den har använts i brandskum på olika brandövningsplatser runt om i landet. Ett flertal svenska dricksvattentäkter har nyligen fått stängas på grund av PFOS-förorening, vilket har lett till ombyggnation och installation av nya reningssteg i flera vattenverk för att kunna säkerställa dricksvattenkvalitén. Förutom användning av PFAS i brandskum har även utsläpp från avloppsreningsverk visat sig vara en stor källa till PFAS i miljön. I den här studien undersöktes källorna till PFAS i Uppsalas avloppsvatten. Detta gjordes genom att ta prover både i ledningsnätet och i Uppsalas största reningsverk, Kungsängsverket.

En av de 26 olika PFAS som undersöktes (6:2 fluorotelomersulfonsyra: 6:2 FTSA) dominerar i ledningsnätet med upp till 96 % av den totala PFAS koncentrationen. Sedan PFOS förbjöds i EU har nya substanser börjat användas. Det finns dock ingen substans som är så effektiv som PFOS, vilket gör att ersättningsämnena måste användas i tre till tio gånger så stora mängder som PFOS för att samma effekt ska uppnås. 6:2 FTSA är en sådan substans och den används numera som ersättning för PFOS i brandskum. Att 6:2 FTSA är den mest dominanta substansen i Uppsalas avloppsvatten tyder alltså på att användningen av brandskum är en källa till PFAS-förorening. Ökad användning av 6:2 FTSA i andra produkter kan vara en annan trolig orsak.

En så kallad hot spot i ledningsnätet hittades vid en pumpstation som tar emot avloppsvatten både från hushåll och från industrier (Sågargatan). Vid denna hot spot uppmättes värden som var mer än 20 gånger så höga än andra uppmätta värden i ledningsnätet. Hushållsavloppsvatten hade stundtals högre totalkoncentrationer av PFAS än industriellt eller blandat avloppsvatten. De högsta halterna i hushållsavloppsvatten hittades vid en pumpstation (Bärby hage) som även tar emot avloppsvatten från en av brandövningsplatserna i Uppsala.

Kungsängsverket kunde inte rena bort de flesta PFAS substanserna från avloppsvattnet, vilket var förväntat på grund av PFAS extremt persistenta egenskaper i kombination med relativt hög vattenlöslighet. Eftersom det i stort sett är samma PFAS-halter i in- och utflöde i reningsverket kan man dra slutsatsen att källorna för PFAS i Uppsalas avloppsvatten kommer från industrier och hushåll, och att eventuell bildning och tillsats av PFAS i reningsprocessen är obetydlig.

ABBREVIATIONS

PFBS – perfluorobutane sulfonate
PFHxS – perfluorohexane sulfonate
PFOS – perfluorooctane sulfonate
PFDS – perfluorodecane sulfonate

PFBA – perfluorobutanoate
PFPeA – perfluoropentanoate
PFHxA – perfluorohexanoate
PFHpA – perfluoroheptanoate
PFOA – perfluorooctanoate
PFNA – perfluorononanoate
PFDA – perfluorodecanoate
PFUnDA – perfluoroundecanoate
PFDoDA – perfluorododecanoate
PFTriDA – perfluorotridecanoate
PFTeDA – perfluorotetradecanoate
PFHxDA – perfluorohexadecanoate
PFOcDA – perfluorooctadecanoate
FOSA - perfluorooctane sulfonamide
***N*-MeFOSA** – *N*-methyl perfluorooctane sulfonamide
***N*-EtFOSA** – *N*-ethyl perfluorooctane sulfonamide
***N*-MeFOSE** – *N*-methyl perfluorooctane sulfonamido-ethanol
***N*-EtFOSE** - *N*-ethyl perfluorooctane sulfonamido-ethanol
FOSAA – perfluorooctane sulfonamido acetic acid
***N*-MeFOSAA** – *N*-methyl perfluorooctane sulfonamido acetic acid
***N*-EtFOSAA** – *N*-ethyl perfluorooctane sulfonamido acetic acid
6:2 FTSA – 6:2 fluorotelomer sulfonate

ASP – activated sludge process
KV – Kungsängsverket
MDL – method detection limit
LC/MS/MS – liquid chromatography tandem mass spectrometry
SLE – solid liquid extraction
SPE – solid-phase extraction
PBT – Persistent Bioaccumulative Toxic
PFAS – per- and polyfluoroalkyl substance
PFCA – perfluoroalkyl carboxylate
PFSA – perfluoroalkyl sulfonate
POP – Persistent Organic Pollutant
WWTP – wastewater treatment plant

CONTENTS

1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) have received large attention both in politics and science during the recent decade (Clara et al., 2008). PFASs have been detected all over the world, in both developed and developing countries, in humans, biota and in the abiotic environment (Boulanger et al., 2005; Kunacheva et al., 2012; Naturvårdsverket, 2012). PFASs are man-made substances that hold unique physical and chemical properties. They are not only oil- and water repellant but also extremely resistant to degradation, due to the strong strength of the carbon-fluorine bond. Because of these properties, PFAS have been used as surfactants, or as constituents in surfactants, in a wide range of industrial applications and commercial products, from aqueous film forming foams (AFFFs) to dirt repellant coatings (Naturvårdsverket, 2012; Kemi, 2015). Because of its wide range of applications, PFASs have been detected in many different water matrices such as rainwater, groundwater, surface water and in the oceans. They have also been found in both waste- and drinking water (Clara et al., 2008; Willach et al., 2016). PFASs can enter the environment through the emissions from industries, the usage of AFFFs, the consumer's use of products, leakage from waste disposals or landfills and from the effluents from wastewater treatment plants (WWTPs) (Naturvårdsverket, 2012; Willach et al., 2016). The effluents from WWTPs are seen as a major source for the emissions of PFASs and other hazardous xenobiotic substances into the aquatic environment. Since drinking water is one of the major pathways in which PFASs can reach humans, the presence of PFASs in the aquatic environment becomes a threat to human health, biota and the environment (Clara et al., 2008; Kunacheva et al., 2012).

1.1 Objectives and hypotheses

The objective of this project was to evaluate the sources and the occurrence of PFASs in Uppsala's wastewater network and main WWTP, *Kungsängsverket*, in order to provide new knowledge that will help protecting the environment from PFAS contamination and thereby improve the quality of Uppsala's drinking water supplies and human health. It also aimed to investigate the removal efficiency and fate of PFASs within the WWTP.

The following hypotheses were investigated:

- The sampling locations in the wastewater network that receive wastewater from industries will hold higher concentrations of PFASs compared to wastewater dominated by domestic waste.
- The composition profile of PFASs and the mass flow data can be used to pinpoint PFAS contamination sources for wastewater.
- The concentrations of perfluoroalkylated sulfonic acids (PFSAs) and perfluoroalkylated carboxylic acids (PFCAs) will be similar or higher in the effluent compared to the influent due to poor removal efficiency in the wastewater treatment plant and degradation of PFAS precursors.

1.2 Focus and delimitations

An overview on the current situation of the mass flow and removal efficiency of PFASs in Uppsala's wastewater network and main WWTP is presented. It is thereby not intended to optimize the current treatment process in the WWTP.

The pollutants evaluated include 26 different substances belonging to the compound group of PFASs. It is restricted to the wastewater network and main WWTP of Uppsala, *Kungsängsverket*, and to approximately 60 samples.

2 BACKGROUND

2.1 Site description

2.1.1 Kungsängsverket

The largest WWTP in Uppsala, *Kungsängsverket* (KV), receives wastewater from households, businesses and other operators in *Uppsala*, *Bälinge* and *Lövstalöt*. The WWTP is capable of treating wastewater corresponding to 200,000 person equivalents (pe), which approximately translates to 286,000 persons. In the beginning of 2016, there were 162,000 persons connected to the wastewater network. In 2014, KV treated around 18.4 million m^3 of water, which has been a normal amount during the past years (Uppsala Vatten och Avfall, 2014, 2016a).

The wastewater network receives blackwater (feces, urine and flush water), greywater (water from sinks, showers, baths, washing machines and dish washers) and stormwater (run-off-water from roofs, roads etc. during precipitation). The black- and greywater are separated from the stormwater using a duplicate system. In *Bälinge* the blackwater is further separated from the greywater with a vacuum system. In total, the wastewater network consists of 52 pumping stations (PSTs), where 43 are located in Uppsala with two additional vacuum PSTs for greywater (UNEP, n.d.; Uppsala Vatten och Avfall, 2014, 2016a). The PSTs investigated receives domestic, industrial or mixed wastewater (Table 1).

***Table 1** Who is connected on the different pumping stations (PSTs) in the wastewater network of Uppsala (Uppsala Vatten och Avfall, 2016b)*

PST	Information
Bärby hage	Domestic and fire-training site
Ekeby bruk	Domestic (school)
Falebro	Domestic and some agriculture
Flogsta	Domestic
Kumlagatan	Industry (car services, timber trade) and fire-training site
Norra Librobäck	Industry (land processing, remediation, real estate and damage service)
Seglarvägen	Domestic
Seminaregatan	Industry (medical devices)
Skarholmen	Domestic and small boat harbor
Strandbodgatan	Domestic/Industry (Eastern Uppsala)
Sundby	Domestic
Sågargatan	Domestic/Industry (medical devices)
Sävja	Domestic
Tullgarn	Domestic/Industry (Northwestern Uppsala)
Ultuna	Domestic and laboratories

2.1.2 Kungsängsverket's treatment processes

Figure 1 shows a schematic process diagram of KV's current treatment processes concerning both wastewater and sludge. KV is divided into three sections: A, B and C, where each section represents different expansions that have been performed during the years. Section A, when KV was initially constructed, was built in 1957, while section B was built in 1967 and section C in 1999 (Uppsala Vatten och Avfall, 2016a).

The treatment steps at KV are as following:

- **Primary mechanical treatment** including grids and screening (to remove rags, paper, plastics, pieces of wood and other larger pollutants), aerated sand traps (to remove sand, coffee grounds and other heavier particles) and primary sedimentation basins (to remove lighter particles that can disturb the following biological treatment).
- **Biological treatment** of the type activated sludge. Includes aerated and anoxic basins for nitrogen reduction, followed by another sedimentation basin (to remove sludge). Pollutants are degraded with the aid from microorganisms, mostly bacteria; it is they who constitute the activated sludge. A fraction of the sludge from the sedimentation is returned to the beginning of the biological treatment, maintaining the microorganisms within the process.
- **Chemical treatment** with ferric chloride ($FeCl_3$). $FeCl_3$ is added to the water in two steps, after the sand trap in the primary treatment and before the chemical treatment in order to achieve a phosphor reduction that is fully effective. With $FeCl_3$ so-called flocks are produced; agglutinated particles and pollutants, which is removed from the water in a lamina sedimentation basin (Svenskt Vatten, 2013; Uppsala Vatten och Avfall, 2016a, 2016c).

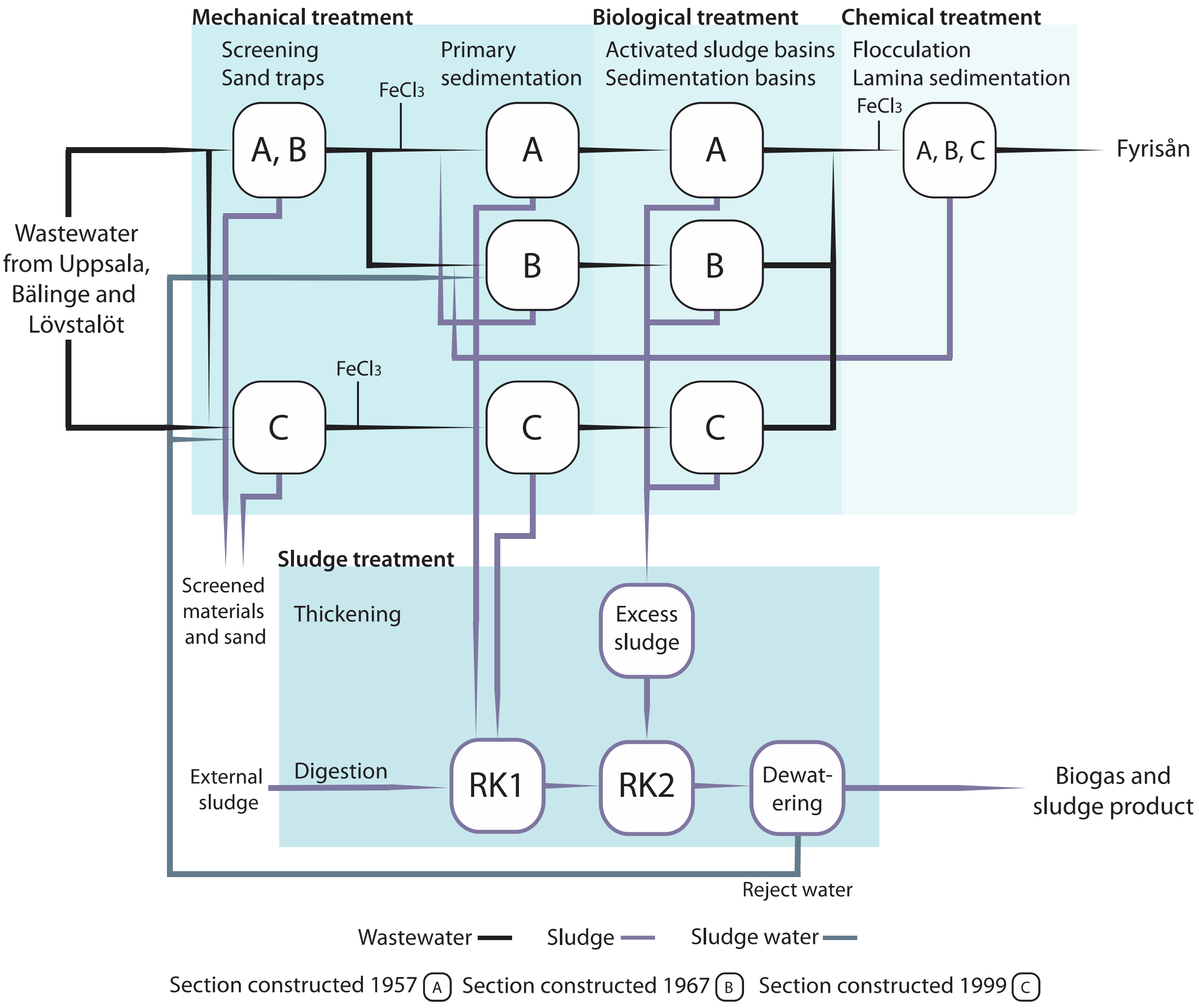

Figure 1 *Schematic process diagram of the wastewater and sludge treatment at Kungsängsverket, sketched from available information (Uppsala Vatten och Avfall, 2014, 2016c), with permission from Uppsala Vatten och Avfall AB.*

The wastewater is treated with, as explained above, mechanical, biological and chemical treatment. The sludge that is created from each treatment goes into a digestion chamber, creating biogas and a sludge product. The sludge holds different properties depending from which treatment step it was created. The different sludge's are: primary, secondary and final clarifier sludge (Uppsala Vatten och Avfall, 2016a, 2016c).

Sludge contains a lot of water, which can be removed by different processes, for example, by a sludge thickener or a centrifuge. At KV the primary clarifier sludge is thickened in their respective primary sedimentation basins, while the secondary and final clarifier sludge are thickened in the sludge thickener. After thickening the sludge continues to an anaerobic digester, creating biogas and a sludge product. This sludge product is today used, after further treatment, to cover up landfills. In the long-run Uppsala Vatten hopes to have their sludge certified and used as a fertilizer in agriculture (Uppsala Vatten och Avfall, 2016a, 2016c).

2.1.3 Kungsängsverket's recipient

KV is located near the river *Fyrisån,* which is its recipient and receives the effluents from the WWTP. When the WWTP was constructed in the early 1940s it was located near the outskirts of Uppsala. Since then the city has grown and nowadays the nearest residential buildings are only 250 meters away from the WWTP (Uppsala Vatten och Avfall, 2014).

Fyrisån flows through Uppsala and plays, in many ways, an important role. It does not only work as a drinking water supply, but also as a recipient, a medium for communication and as an important element in the urban environment. The management and land use in Fyrisån's catchment area, which is almost one third of Uppsala County, has become a major issue. Emissions from industries affect the water quality, despite them being controlled by *Miljölagstiftningen.* As well as leakage of nitrogen and phosphor from agriculture, which contributes to eutrophication (Vattenmyndigheten, n.d.).

2.1.4 PFASs in drinking water

Most people in Uppsala receive their drinking water from groundwater in the Uppsala ridge. In order to keep the groundwater level steady, the ridge is filled with water from *Fyrisån*. The surface water enters the ridge and, by the ridge itself, is treated naturally for six to eight months. In *Almunge* and *Länna*, the drinking water comes from *Östra Långsjön*, a lake located to the north of Uppsala (Uppsala Vatten och Avfall, 2015). Due to the water cycle in society, where purified drinking water is used, enters the drain and flows to Uppsala's WWTPs (Uppsala Vatten och Avfall, 2016d), purified drinking water can work as background levels of PFASs in untreated wastewater. Several drinking water supplies was shut down in Uppsala in 2012 due to detected levels of PFASs. The most probable reason is the usage of AFFFs. The situation regarding the drinking water in Uppsala had to be investigated and measurements had to be taken. This led to reconstruction and installation of new alternative treatment processes in Uppsala's water purification plants (Naturvårdsverket, 2016; Uppsala Vatten och Avfall, 2016e), which resulted in low PFAS concentrations in purified drinking water (Table 2).

There are today no legally binding limits for PFASs in drinking water. However, the National Food Agency has established an action threshold (90 ng $PFAS_{11}$ L^{-1}) and a health based guideline value (900 ng $PFAS_{11}$ L^{-1}) for the sum of 11 different PFASs. The action threshold is to be used by drinking water producers to decide whether the occurrence of PFASs in drinking water can pose a threat to human health. If the PFAS levels exceed the threshold, measurements are to be taken promptly (Naturvårdsverket, 2016).

Table 2 *PFAS concentrations (ng* L^{-1}*) in purified drinking water in southern, central and northern parts of Uppsala (Uppsala Vatten och Avfall, 2016f)*

Analyte / Region	South (ng L^{-1})	Center (ng L^{-1})	North (ng L^{-1})
PFBS	3.7	1.9	nd
PFHxS	5.0	11	nd
PFOS	5.0	2.5	nd
PFDS	nd	nd	nd
PFBA	nd	nd	nd
PFPeA	nd	nd	nd
PFHxA	5.2	2.6	nd
PFHpA	nd	nd	nd
PFOA	1.1	0.56	nd
PFNA	nd	nd	nd
PFDA	nd	nd	nd
PFUnDA	nd	nd	nd
PFDoDA	nd	nd	nd
FOSA	nd	nd	nd
6:2 FTSA	nd	nd	nd

nd = not detected.

2.2 Per- and polyfluoroalkyl substances

This section gives an overview of the physical, chemical and biological properties of PFASs, the effect they have on the environment and the production, usage and regulation of PFASs in society. The section also explains why and how PFASs are present in wastewater and presents possible removal techniques.

2.2.1 Physicochemical and biological properties

PFASs are complex substances that involve many different groups and congeners. They are man-made substances that, deliberately, carry many useful properties. They are repellant to fat, dirt and water, are non-sensitive to temperature and hold film-forming properties. Due to these properties the applications are endless and an immense variation of PFASs occur in both industrial applications and commercial products (Kemi, 2015; Svenskt Vatten, 2015). However, it is not as good as it sounds; the tremendously strong and stable carbon-fluorine bond makes PFASs extremely resistant to any type of degradation. PFASs can therefore be found all over the world in humans, biota and in the environment (Buck et al., 2011; Naturvårdsverket, 2012).

The PFAS family consists of a copious number of members and can be divided into several subfamilies. There are in fact 3,000 different variations of PFASs known to circulate the global market (Buck et al., 2011; Svenskt Vatten, 2015). The first primal distinction is between polymers and non-polymers; further distinction is between the degrees of fluorination. For the non-polymers the distinction is between per- and polyfluoroalkyl substances, while the polymers distinct between fluoropolymers, perfluoropolymers or side-chain fluorinated polymers (Buck et al., 2011).

PFASs are a group of aliphatic substances, where the H atoms have been partially (poly) or fully (per) substituted by F atoms. All PFASs are therefore, to different degrees, fluorinated aliphatic substances. They follow the general formula C_nF_{2n+1}-R, where n refers to the number of carbon atoms and R to the functional group. The functional group can, for example, be a sulfonic acid (SO_3H) or a carboxylic acid (COOH) (Buck et al., 2011). Two examples of PFASs, which are the most studied ones, are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). PFOS consists of the functional group SO_3H and belongs therefore to the group of perfluoroalkyl sulfonates (PFSAs), while PFOA has COOH as the functional group and belongs to the group of perfluoroalkyl carboxylates (PFCAs) (Table 3). This kind of characterization of PFASs, who share the same functional group, are called homologues (Buck et al., 2011; Naturvårdsverket, 2012).

PFASs consist of two parts: the hydrophobic tail and the hydrophilic functional group. In some cases a coupling is used to link these two parts together and in other cases the functional group consists of several functional groups. The functional group can consist of anions (e.g., carboxylates, sulfonates or phosphates), cations, non-ions and ampholytics (both anion and cation). Production of highly fluorinated substances mainly involves the processes electrochemical fluorination and telomerization. These substances can react further and create polymers and other derivatives (Kemi, 2015).

PFOS and PFOA are the substances in the PFAS family that has received most of the attention. They are also the most studied PFASs (Naturvårdsverket, 2012). PFOS has been characterized as a Persistent Organic Pollutant (POP), which refers to organic compounds capable to long-range transportation that are persistent, bioaccumulative and toxic to humans and wildlife (Kunacheva et al., 2012). According to the Swedish EPA, Naturvårdsverket, PFSAs and PFCAs are strong acids present in the environment and wildlife mostly in their non-volatile forms. Fluorotelomers are, in contrast to PFSAs and PFCAs, volatile and can undergo long-range transport via the atmosphere (Naturvårdsverket, 2012).

Similar to PFOSs' POP-characteristics to be persistent, extensively biomagnifying and bioaccumulative, toxic and capable to long-range transportation, other PFASs have shown similar properties. PFAS congeners have been found in the highest levels of the food chain in polar bear, otter, seal and mink, showing the biomagnifying potential. Also, PFASs, like PFOS, bind to proteins in liver, eggs and plasma and to fatty acid binding proteins in cells. This differ to the classical POP, such as chlorinated and brominated compounds, which usually partitions into fatty tissues in living organisms ("Stockholm Convention on Persistent Organic Pollutants (POPs)", 2009; Naturvårdsverket, 2012).

2.2.2 Production and use in society

PFASs are man-made substances that, due to its unique properties, are present in many different types of products in both industrial applications and in commercial products (Buck et al., 2011; Naturvårdsverket, 2012; Glynn et al., 2013). They can be created in two different ways, either by electrochemical fluorination (ECF) or by telomerization, where the latter is the most common process today (Kemi, 2015). PFASs are mainly produced in China, Japan, USA, Germany, Italy and Russia (possibly). A few big companies are dominating the production and all together they stand for 90 % of the total (Glynn et al., 2013; Svenskt Vatten, 2015).

Investigations and surveys have been made during 2015 regarding PFASs in consumer products that are normally occurring in Sweden and in other Nordic countries. From these investigations it was found that PFASs are present in many different products, products that were not unusual to be in contact with food. For example, PFOS could be found in microwave popcorn paper and PFOA in rinsing agents for dishwashers. PFASs are widely used and there are probably more than 3,000 PFASs circulating on the global market. PFASs was found in the following products: AFFFs, bags, baking paper, baking tins, cardboard, carpets, car seat covers, car wax, casual clothing, coating materials, color for printers, cooling liquid, cosmetics, cupcake molds, dental floss, dental restorative materials, floor polish, impregnation of glass and plastics, insecticide, lubricant, photo materials, pizza boxes, popcorn-paper, rinsing agents for dishwashers, ski wax, surface treatment for smartphones, table cloths, tents and umbrellas (Kemi, 2015; Svenskt Vatten, 2015). In AFFFs, PFASs are used for their film-forming properties and high resistance to temperature. The usage of PFASs in AFFFs have led to contamination of groundwater and drinking water in Sweden, which have brought great attention to the problematic properties of PFASs (Naturvårdsverket, 2016). There is lacking information about many of these substances since, due to their effective properties, they are used in low enough concentrations to escape the information requirements controlled by REACH (See ‘Regulations concerning PFASs’) (Kemi, 2015).

Due to the phase-out of PFOS, other PFASs have started to emerge as replacement substances (Naturvårdsverket, 2012; Glynn et al., 2013). The production of fluorotelomers and other shorter PFSAs increased while the production of PFOS decreased. Perfluorobutane sulfonate (PFBS) is an example of such a substance that works as a replacement substance for PFOS (Glynn et al., 2013). In AFFFs and in metal industries, PFOS is today replaced by 6:2 fluorotelomer sulfonate (6:2 FTSA). No alternative substance has an efficiency comparable to PFOS; it is therefore needed three to ten times more of the substance in order to fully replace it (Kemi, 2015).

The fluorinated substances that enter the EU come in different consumer products at low concentrations, since most applications with PFOS are forbidden in the EU and are therefore not imported as a pure substance. Besides import, PFASs can also reach Europe, and Sweden, via long-range air and water transportation (Svenskt Vatten, 2015). PFASs can enter environmental matrixes, such as soil, air, groundwater, surface water and drinking water, via WWTP effluents from production in goods and products. These matrixes work as PFAS exposure pathways for aquatic organisms, fish and humans (as shown in Figure 4 in Naturvårdsverket, 2016). Establishments that produce products containing PFASs (AFFFs, textile and detergent production) and establishments where PFAS containing products are used in industrial processes (metalworking industries) can act as direct sources of PFASs into the environment. However, usage of commercial products containing PFASs can also act as a direct source. The PFAS discharges via waste can therefore act as a secondary source of PFASs into the environment, where WWTPs and waste treatment plants plays an important role (Naturvårdsverket, 2016).

2.2.3 Regulations concerning PFASs

PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) has been listed as a POP in the Stockholm Convention (2009). This means that they shall be eliminated by all parties except those that produce and/or use PFOS for acceptable purposes (“Stockholm Convention on Persistent Organic Pollutants (POPs)”, 2009; Kunacheva et al., 2012). Examples of acceptable purposes are the photo and metal industry or in hydraulic oils and electronic products, where PFOS is still used in the absence of acceptable replacements (Glynn et al., 2013). The restriction on the usage of AFFFs containing PFOS, that were still kept in stock, did not come into effect until 2011 (Naturvårdsverket, 2016).

The US Environmental Protection Agency (USEPA) launched the 2010/2015 PFOA Stewardship Program in 2006. This is a voluntary agreement between the industry and the USEPA with the purpose to reduce and eliminate industrial emissions and products containing PFOA and PFOA related substances. This program has created a significant decrease of PFOA. However, at the same time as PFOA has been decreasing in the industry, other shorter chained PFASs have been increasing instead (Kemi, 2015; Svenskt Vatten, 2015), similar to the situation with the phase-out of PFOS (See 'Production and use in society').

In a recent report from Svenskt Vatten (2015), the authors demanded a prohibition on all PFASs in society. This can be possible by a so-called group prohibition of PFASs within EU. Prohibiting every single substance in the PFAS family would take decades. The prohibition would start with consumer products since the use of these contribute to an uncontrollable and diffuse dispersion of PFASs to the aquatic environment.

Within EU, the most important regulation for chemical substances is REACH. PFOS and the substances that can be degraded to PFOS are today the only PFASs that are controlled by REACH. In Sweden, if an additive is less than five percent of the total product it does not need to be reported to the Swedish products register. This is the case for most PFASs; because of their high efficiency little is needed to achieve the desired effect, causing problems and difficulties controlling them. Information requirements within REACH are very low for substances in low volumes; below 100 ton year^{-1} no information at all is required from producers and importers. From June 8 2018, this limit will be lowered to 1 ton year^{-1}. Many PFASs enter the EU and Sweden without control, making it difficult for individual importers or consumers to access information about the product contents (Kemi, 2015; Svenskt Vatten, 2015).

There are today no limit values for PFASs that are legally binding, explicitly, for wastewater.

2.2.4 Health and environmental risks

In the beginning, PFOS was found in the blood of people working with PFOS production in USA. When research began regarding the occurrence of PFOS in the environment, PFOS was found in almost all investigated species, even in arctic environments (Naturvårdsverket, 2016). The National Food Agency is regularly collecting serum samples from primiparae (women who give birth for the first time) in Uppsala with regard to PFASs and other pollutants. The population of Uppsala was until 2012 exposed to high levels of perfluorohexane sulfonate (PFHxS) in drinking water, which resulted in increasing PFHxS levels in blood samples from primiparae during the test period (6 % per year). The levels of $C_9 – C_{17}$ PFCAs were increasing during the test period as well (3 % per year). However, the increase of these substances seems to level out, which indicates that the exposure of PFASs to the Swedish population is no longer increasing (Naturvårdsverket, 2016).

The Swedish EPA, Naturvårdsverket (2012), did an environmental and health risk assessment of PFASs in Sweden, the first one to investigate a large number of PFASs. PFASs were analyzed in human tissues and in biota. The general population, consisting of individuals who are exposed indirectly in everyday life, has in general low ppb (ng mL^{-1}) concentrations of PFASs in serum compared to the population exposed through their occupation, such as professional ski-waxers. A correlation was found between the number of working years and serum levels.

Many species have been investigated for PFASs, e.g. seal, otter, peregrine falcon egg, herring, freshwater perch, moose and reindeer. PFASs were present in all investigated species, except for moose and reindeer, the terrestrial species. Common for the species in which PFASs were present are that they are associated to the aquatic environment in some way, illustrating the impact of aquatic food chain accumulation (Naturvårdsverket, 2012). In a risk characterization of PFASs in food and drinking water it was found that regular intake of fish with high-contaminated levels of PFOS can cause high intake levels. It was also found that a high intake of PFOS contaminated drinking water can contribute to higher levels than from food consumption, e.g. fish, especially if the water is used in preparation of breast milk formulas (Glynn et al., 2013). However, no correlation has been found between PFAS levels and birth defects, birth weight or other pregnancy outcomes, for populations exposed to PFAS contaminated drinking water or for industrial workers producing PFASs (Naturvårdsverket, 2012). Despite this, PFASs have been connected to cases with endocrine disruption, developmental and reproductive toxicities such as lower birth weight and miscarriages. PFASs have also been connected to increasing risks of breast cancer (Bjerregaard-Olesen et al., 2016).

Little is known about the health risks associated with PFASs other than PFOS and PFOA (Svenskt Vatten, 2015). Due to the phase-out of PFOS and PFOA, the levels of these two substances are decreasing in humans (Glynn et al., 2013). However, other PFASs have started to emerge as replacements. In the textile industry, PFASs with shorter carbon chains are used as a replacement to PFOS. These PFASs are not as bioaccumulative as PFOS, however, due to their extreme persistency they can still be accumulated in the environment (Svenskt Vatten, 2015).

The highest health and environmental risks have been identified to occur in connection to areas contaminated by AFFFs, which mostly consists of training areas for fire-fighting. It is not possible to evaluate the risks concerning areas where larger fires have been contested, since both measurements and information about the localization of the fire are to a large extent missing. However, the possibility that PFASs are being transported to groundwater and drinking water from these individual areas is high, which have been confirmed by a few studies (Naturvårdsverket, 2016). The science regarding the environmental and health effects due to high levels of PFASs is still under development (Anderson et al., 2016). More research in form of risk assessments and toxicological studies is therefore needed.

2.2.5 PFASs fate in wastewater treatment plants

Many studies have evaluated the occurrence and fate of PFASs in WWTPs, in particular for PFOS and PFOA. However, also for other PFASs, such as perfluorobutanoate (PFBA), PFBS, PFNA, perfluorodecanoate (PFDA), perfluoroheptanoate (PFHpA), perfluoroundecanoate (PFUnDA), perfluorohexanoate (PFHxA) and precursors to PFASs such as *N*-ethyl perfluorooctane sulfonamido-ethanol (*N*-EtFOSE), *N*-ethyl perfluorooctane sulfonamido acetic acid (*N*-EtFOSAA), perfluorooctane sulfonylfluoride-based perfluorochemicals (POSF) and fluorotelomer alcohols (FTOHs) (Lange, 2000; Schultz et al., 2006a, 2006b; Sinclair and Kannan, 2006; Bossi et al., 2007; Loganathan et al., 2007; Yu et al., 2009; Guo et al., 2010; Ma and Shih, 2010; Kunacheva et al., 2011; Chen et al., 2012; Kim et al., 2012; Sun et al., 2012; Zhang et al., 2013). Loos et al. (2010) carried out an European-wide survey consisting of 90 WWTPs and 156 organic substances, amongst them PFASs. The effluents of WWTPs have been pointed out as a main source for micropollutants such as hormones, personal care products (PCPs), pharmaceuticals and PFASs to the aquatic environment. The cause to this is the progressive implementation of water treatment across Europe, both municipal and industrial, using technology meeting current water quality standards whilst new non-regulated pollutants continue to emerge (Loos et al., 2013). The WWTPs of today are designed to reduce levels of carbon, nitrogen, phosphorous, coliforms and pathogens. They are therefore not designed to remove organic micropollutants. Despite this, some are removed by the conventional WWTP, mostly those that are sorbed to the solid phase. Some can also be biodegraded, biotransformed or volatized (Radjenović et al., 2007).

An increase of PFOS and PFOA have been found in WWTP effluents, due to precursor degradation (Schultz et al., 2006a; Sinclair and Kannan, 2006; Loganathan et al., 2007; Yu et al., 2009; Guo et al., 2010; Chen et al., 2012; Sun et al., 2012; Zhang et al., 2013). Precursors to PFASs can be biodegraded into different PFASs, mostly PFOS and PFOA, contributing to an increase in mass flow. *N*-EtFOSE, *N*-EtFOSAA, POSF and FTOH are examples of such precursors. PFOA mostly originates from fluorotelomer-based compounds, such as FTOH, and PFOS from *N*-EtFOSAA, while *N*-EtFOSE is an important precursor to both PFOS and PFOA (Lange, 2000; Schultz et al., 2006b; Bossi et al., 2007; Loganathan et al., 2007; Yu et al., 2009; Ma and Shih, 2010; Kunacheva et al., 2011; Chen et al., 2012; Sun et al., 2012; Zhang et al., 2013).

The precursor *N*-EtFOSE can be emitted into the atmosphere when entering the WWTP, during aeration, or be generated by hydrolysis of monomers within the aeration basin in the activated sludge process (ASP) (Lange, 2000). *N*-EtFOSE has been found to only undergo transformation under aerobic conditions (Boulanger et al., 2005), where the main part is being stripped into the atmosphere when the basin is open to the atmosphere. WWTPs can therefore be seen as a source of atmospheric *N*-EtFOSE (Rhoads et al., 2008). It has also been found that the source of PFCAs, such as PFOA, PFDA and PFUnDA, in the Arctic originates from the atmospheric oxidation of precursors. These precursors mainly consists of FTOHs (Young et al., 2007). The presence of not highly used longer chained PFCAs (e.g. PFDA, PFUnDA PFTriDA and PFTeDA) in the Arctic, indicates that volatile precursors have been exposed to atmospheric oxidation, which later are deposited (Stock et al., 2007; Young et al., 2007).

Another route for PFASs to reach the atmosphere could be through incineration of sludge, which enhances the possibility of residues entering the atmosphere via flue gas and being remobilized into the environment. Further, if PFAS contaminated sludge is used as fertilizer on agricultural crops, remobilization is possible here as well due to their extreme persistency (Schröder and Meesters, 2005). Once emitted into the environment, PFCAs and PFSAs can undergo long-range transport to remote locations, such as the Arctic and Antarctic, either via the aquatic environment or the atmosphere (Martin et al., 2004; Stock et al., 2007; Young et al., 2007; Butt et al., 2010; Benskin et al., 2012; Cai et al., 2012). Neutral PFASs, in comparison to ionic PFASs like PFCAs and PFSAs, have been shown to have higher tendency to undergo long-range transport via the atmosphere (Ellis et al., 2004; Martin et al., 2006). The shorter chained PFASs have, on the other hand, higher tendency for long-range transport via the aqueous environment (Ahrens, 2010). This kind of transportation is an important source of PFASs to remote locations (Armitage et al., 2006).

As reported from various studies, the effluents of WWTPs are a major source of PFASs into the aquatic environment (Boulanger et al., 2005; Schultz et al., 2006a; Becker et al., 2008; Clara et al., 2008). With exposure to wildlife, the PFAS levels in biota will continue to increase even if the levels at the source has been radically reduced (Armitage et al., 2006). The fate of PFASs in WWTPs seem to be related to their influent concentrations (Kim et al., 2012) as well as to how large the industrial wastewater fraction is to the total (Becker et al., 2008). Their fate also seems to be related to the WWTPs treatment processes (Zhang et al., 2013), the functional group and the chain-length (Kissa, 2001). The distributions in the WWTPs differ for different PFASs (Guo et al., 2010). Longer chained PFCAs carry a higher tendency to sorb to the solid phase and PFCAs with an even number of carbon atoms (even-chained) are more likely for sorption than those with an odd number (odd-chained) (Bossi et al., 2007). With regard to industrial or mixed wastewater, these holds in general higher concentrations of PFASs than domestic (Sinclair and Kannan, 2006; Bossi et al., 2007; Becker et al., 2008; Kim et al., 2012), where PFOS is more prevalent in domestic wastewater and PFOA in industrial wastewater (Loganathan et al., 2007; Chen et al., 2012).

2.2.6 Treatment techniques for PFASs in wastewater

Since WWTPs are seen as one of the main sources of PFASs to the aquatic environment, it is important to investigate and understand the PFASs path through the different treatment steps and how these affect their removal (Schultz et al., 2003). Biological treatment has been ineffective in removing PFASs. Some of them, e.g. PFOS, have been proven to sorb onto sludge to some extent (Boulanger et al., 2005; Schultz et al., 2006a; Loganathan et al., 2007; Yu et al., 2009; Kunacheva et al., 2011; Chen et al., 2012; Kim et al., 2012; Sun et al., 2012; Zhang et al., 2013). As mentioned earlier, PFASs can be partly eliminated through sludge incineration. However, it is possible for the residues to be remobilized into the environment via flue gas (Schröder and Meesters, 2005). Therefore, it is needed to investigate which other treatment techniques that can remove PFASs from wastewater (Schultz et al., 2003).

Activated carbon comes in two forms: granular (GAC) and particulate activated carbon (PAC). They have mainly been used for drinking water purification to reduce smell and odor. The main difference between PAC and GAC is that GAC is a filter, on which contaminants adsorb to, whereas PAC (and the contaminants adsorbed to it) ends up in the solid phase together with the sludge (Svenskt Vatten, 2010a). This is not desirable if the sludge is to be used in agriculture (Schröder and Meesters, 2005). However, PAC is more effective in adsorbing PFASs and does not demand as high flow rate as GAC, while GAC is a more practical solution in order to avoid clogging (Hansen et al., 2010). Both GAC and PAC can be integrated in WWTPs without significant changes in construction (Meinel et al., 2014).

With 100 mg L^{-1} added PAC in a membrane bio-reactor (MBR), a 90 % removal of PFASs from wastewater was achieved. Both PAC and sludge was present in the solid phase, where most of the PFASs seemed to be adsorbed to PAC. PAC adsorption is therefore more effective than adsorption to sludge for PFASs. This indicates that PAC adsorption can be an important removal mechanism for PFASs from wastewater (Yu et al., 2014). The chemical structure of PFASs has influence on their sorption affinity to GAC. Since PFOS was found to have stronger sorption affinity to GAC than the other substances, the functional group and carbon chain length may have influenced the sorption. A PFSA would have higher affinity than a PFCA, and a longer carbon chain than a shorter (Ochoa-Herrera and Sierra-Alvarez, 2008). In a comparison with other sorptive mediums, PFOS was found to have higher affinity for GAC, followed in decreasing order by: hydrophobic zeolite, anaerobic granular sludge and activated sludge. PFOS should therefore be expected, to some extent, be removed by sorption to sludge in the biological treatment. It has also been shown that the sludge type will significantly affect the sorption degree of PFOS to the sludge (Ochoa-Herrera and Sierra-Alvarez, 2008).

Membrane filtration has since the 1990s been developed into a competitive separating technique for drinking water. The basic principle is feed water being pressed or drawn through a thin membrane while the pollutants remains on the feeding side, creating clean water called permeate (Steinle-Darling and Reinhard, 2008). In Sweden, membranes are mainly used for: softening or fluoride separation of groundwater, color removal from surface water or removal of particles and microorganisms. The pore size of the membranes decides what can be removed, the different types of membranes are therefore called: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Svenskt Vatten, 2010b). NF membranes have been reported to remove PFASs to more than 95 % with molar weight larger than 300 g mole^{-1} (PFOS and PFOA) (Steinle-Darling and Reinhard, 2008). RO-membranes on PFAS contaminated wastewaters could remove 99 % PFOS or more. The removal increased with increasing feed concentration. Indicating that commercially available RO-membranes are capable to effectively remove PFOS (Tang et al., 2006).

3 MATERIAL AND METHODS

In this chapter, the material and methods used in this thesis is explained. These involve: chemicals and materials, sampling, sample preparation and extraction, quality assurance and quality control and lastly, methods for statistical data analysis.

3.1 Chemicals and materials

In total, 26 PFASs were analyzed (Table 3) using an internal standard (IS) mix (FXIS11) for quantification (Table 4).

***Table 3** Analyzed per- and polyfluoroalkyl substances*

Name	Abbreviation	Molecular formula
PFSAs (perfluoroalkane sulfonates)		
perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$
perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_3^-$
PFCAs (perfluoroalkyl carboxylates)		
perfluorobutanoate	PFBA	$C_3F_7CO_2^-$
perfluoropentanoate	PFPeA	$C_4F_9CO_2^-$
perfluorohexanoate	PFHxA	$C_5F_{11}CO_2^-$
perfluoroheptanoate	PFHpA	$C_6F_{13}CO_2^-$
perfluorooctanoate	PFOA	$C_7F_{15}CO_2^-$
perfluorononanoate	PFNA	$C_8F_{17}CO_2^-$
perfluorodecanoate	PFDA	$C_9F_{19}CO_2^-$
perfluoroundecanoate	PFUnDA	$C_{10}F_{21}CO_2^-$
perfluorododecanoate	PFDoDA	$C_{11}F_{23}CO_2^-$
perfluorotridecanoate	PFTriDA	$C_{12}F_{25}CO_2^-$
perfluorotetradecanoate	PFTeDA	$C_{13}F_{27}CO_2^-$
perfluorohexadecanoate	PFHxDA	$C_{15}F_{31}CO_2^-$
perfluorooctadecanoate	PFOcDA	$C_{17}F_{35}CO_2^-$
FOSAs (perfluorooctane sulfonamides)		
perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$
N-methyl perfluorooctane sulfonamide	*N*-MeFOSA	$C_8F_{17}SO_2N(CH_3)H$
N-ethyl perfluorooctane sulfonamide	*N*-EtFOSA	$C_8F_{17}SO_2(C_2H_5)H$
FOSEs (perfluorooctane sulfonamidoethanols)		
N-methyl perfluorooctane sulfonamido-ethanol	*N*-MeFOSE	$C_8F_{17}SO_2(CH_3OH)H$
N-ethyl perfluorooctane sulfonamido-ethanol	*N*-EtFOSE	$C_8F_{17}SO_2(C_2H_5OH)H$
FOSAAs (perfluorooctane sulfonamidoacetic acids)		
perfluorooctane sulfonamido acetic acid	FOSAA	$C_8F_{17}SO_2NH_3CH_2CO_2H$
N-methyl perfluorooctane sulfonamido acetic acid	*N*-MeFOSAA	$C_8F_{17}SO_2NCH_3CH_2CO_2H$
N-ethyl perfluorooctane sulfonamido acetic acid	*N*-EtFOSAA	$C_8F_{17}SO_2N(CH_2)_3CH_3CO_2H$
FTSAs (x:2 fluorotelomer carboxylates)		
6:2 fluorotelomer sulfonate	6:2 FTSA	$C_8H_4F_{13}SO_3^-$

***Table 4** Internal standards used (FXIS11), with corresponding PFASs*

Internal Standard	Corresponding PFASs
$^{18}O_2$ PFHxS	6:2 FTSA, PFHxS
$^{13}C_4$ PFOS	PFBS, PFDS, PFOS
$^{13}C_4$ PFBA	PFBA
$^{13}C_2$ PFHxA	PFPeA, PFHxA
$^{13}C_4$ PFOA	PFHpA, PFOA
$^{13}C_5$ PFNA	PFNA
$^{13}C_2$ PFDA	PFDA
$^{13}C_2$ PFUnDA	PFUnDA
$^{13}C_2$ PFDoDA	PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA
$^{13}C_8$-FOSA	FOSA
d_3-*N*-MeFOSA	*N*-MeFOSA
d_5-*N*-EtFOSA	*N*-EtFOSA
d_3-*N*-MeFOSAA	FOSAA, N-MeFOSAA
d_5-*N*-EtFOSAA	*N*-EtFOSAA
d_7-*N*-MeFOSE	*N*-MeFOSE
d_9-N-EtFOSE	*N* -EtFOSE

The chemicals used in the experiments were: methanol (≥ 99.9 %, Lichrosolv®, Merck KGaA, Darmstadt, Germany), acetone (≥ 99.8 %, Suprasolv®, Merck KGaA, Darmstadt, Germany), ethanol (≥ 95 %, Solveco, Rosenberg, Sweden), Millipore water (Merck Millipore), glacial acetic acid (≥ 99.7 %, Sigma-Aldrich, Steinheim, Germany), ENVI-carb (120/400, Supraclean ENVIcarb SupELCO), ammonium acetate (≥ 99.0 %, Sigma-Aldrich, Steinheim, Germany), ammonium hydroxide (28 – 30 %, Sigma-Aldrich, Steinheim, Germany), sodium hydroxide (≥ 99.9 %, Merck, Darmstadt, Germany) and hydrochloric acid (30 %, Merck KGaA, Darmstadt, Germany).

3.2 Sampling

In total, 35 wastewater samples were collected, including 15 in the wastewater network of Uppsala and 20 samples in the WWTP, KV (Figure 2 and Table A1 in the Appendix). The wastewater samples at the PSTs ($n = 13$) were collected on the 26th of January 2016 using grab sampling. Some water samples at the PSTs ($n = 2$) were collected during the 28th of January 2016 using time-integrated sampling (100 mL every 20 min during 24 hours) (Table A2 in the Appendix). In KV, the sludge samples ($n = 10$) and a reject water sample from sludge dewatering ($n = 1$) were collected on the 20th of January 2016 using grab sampling. The water samples in KV ($n = 9$) were collected on the 25th of January 2016 using flow proportional sampling (during 24 hours) (Table A3 in the Appendix). After sampling, the water samples were stored in a fridge (4.5 °C) and the sludge samples in a freezer (-18.5 °C) until further analysis.

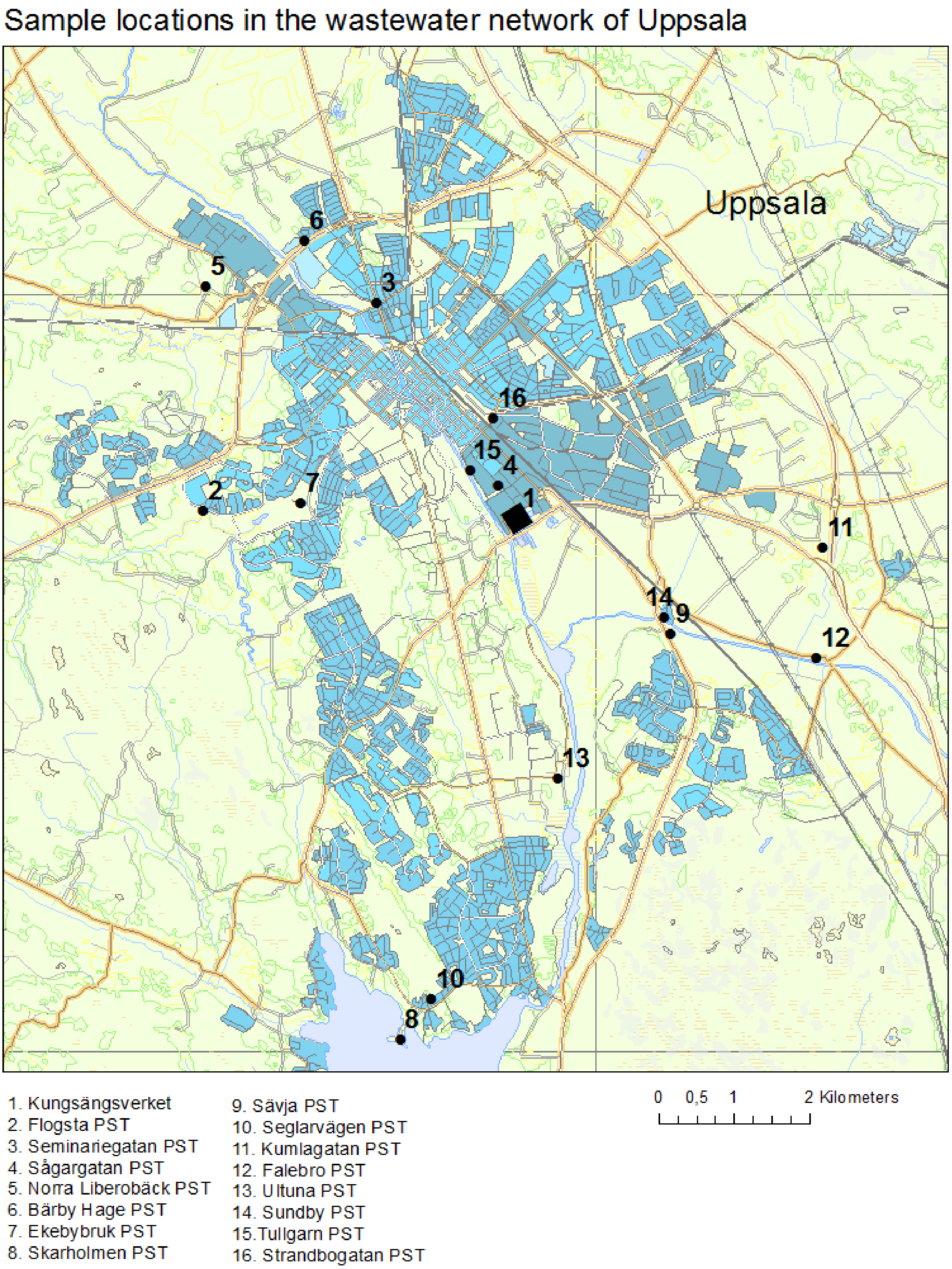

Figure 2 *The sample locations in Uppsala, showing the wastewater treatment plant, Kungsängsverket, and the pumping stations (PSTs) in the wastewater network of Uppsala © Lantmäteriet [I2014/00764].*

3.3 Sample preparation and extraction

3.3.1 Wastewater samples

As preparation for the solid-phase extraction (SPE), the water samples were first sonicated in a sonication bath (Branson 5510) for five minutes. After the sonication, they were filtered through a GFF-filter (Whatman™ glass microfiber filters, GE Healthcare, 47 mm in diameter), to remove large particles, using Werner Glass Filtration equipment and vacuum. Since PFASs are surfactants, the equipment walls were rinsed with methanol and the subsequent was added to the filtered water sample. The filtered water samples were spiked by adding 100 µL FXIS11 (500 pg µL^{-1}) to each sample (Table 4).

The solid phase extraction was used for the filtered water samples (300 mL) using cartridges (Oasis® weak anion exchange (WAX) 6 cc cartridge, 500 mg, Waters). The cartridges were preconditioned, in the following order, with 4 mL 0.1 % ammonium hydroxide in methanol, 4 mL methanol and 4 mL Millipore water. Using vacuum and a stopcock, the flow through the cartridges was regulated to one drop per second. During the extraction, the cartridges were covered with aluminum foil to decrease the risk of contamination. After extraction, the cartridges were washed with 4 mM ammonium buffer and dried in a centrifuge (5810, Eppendorf) at 3000 rpm for two minutes. The cartridges were eluded with 4 mL methanol and 8 mL 0.1 % ammonium hydroxide in methanol, enabling the samples to be loaded into 15 mL PP tubes. The solid phase samples were concentrated under nitrogen stream (N-Evap™112, Organomation Associates Inc, Berlin, USA) to exactly 0.5 mL in 1 mL glass-vials. The glass-vials were vortexed (Heidolph, REAX 2000) and stored in a freezer (- 18.5 °C) until PFAS analysis using liquid chromatography tandem mass spectrometry (LC/MS/MS) (Ahrens et al., 2009).

In total there were 27 samples analyzed with SPE: 25 wastewater samples and two blanks.

3.3.2 Sludge samples

The sludge samples were divided into two parts, one part for PFAS analysis using solid liquid extraction (SLE) and the other to determine the dry weight (TS), organic matter (OM) and moisture content.

For TS, OM and moisture content, the sludge samples were burned in two steps, first in 105 °C to determine TS and moisture content and then in 550 °C to determine OM, both overnight (Table A4 in the Appendix).

For PFAS analysis, the samples were freeze-dried (Edwards) during 7 days. Each sample (1–2 g) was homogenized in a homogenizer (Bertin Technologies, Precellys Evolution) and then transferred into 50 mL polypropylene (PP) tubes (1). Then, 2 mL of 100 mM sodium hydroxide in 80 % / 20 % methanol/Millipore water was added and soaked for 30 min before 20 mL methanol and 100 µL FXIS11 was added. The samples were placed on a wrist-action shaker (Gerhardt) at 200 rpm for 60 min and centrifuged at 3000 rpm for 15 min to separate the solid and liquid phase. The supernatants were transferred into new 50 mL PP-tubes (2). This procedure was repeated two times in PP-tube (1), but with 1 mL sodium hydroxide in 80 % / 20 % methanol/Millipore water, 10 mL methanol and 30 min on the wrist-action shaker instead. The supernatants were transferred each time into the same 50 mL PP-tube (2). 0.1 mL 4 M HCl were added into the PP-tubes (2) before they were shaked by hand and centrifuged at 3000 rpm for five minutes. A part of each sample (8.3 mL) was transferred into 15 mL PP-tubes and concentrated under nitrogen stream to 1 mL. With 25 mg ENVI-carb and 50 µL glacial acetic acid, the samples were vortexed and centrifuged in centrifuge tubes (Eppendorf micro centrifuge tubes) at 4000 rpm for 15 min. The supernatants were transferred into glass-vials and stored in a freezer (- 18.5 °C) until PFAS analysis using LC/MS/MS (Ahrens et al., 2009).

In total there were 22 samples analyzed with SLE: 10 original samples, where three of these were triplicated and one was duplicated for quality control, and three blanks.

3.4 Quality assurance and quality control

To assure the quality and to prevent contamination from other sources in the laboratory, all equipment was rinsed three times with methanol prior to usage. After usage, all equipment used for the PFAS extraction was rinsed three times with ethanol, dish washed and burnt in an oven overnight (400 °C) (glassware).

The quality control was made in order to calculate the standard deviations (SD) and method detection limits (MDL, Equation 1).

$$MDL = \bar{C}_{blanks} + 3 \times SD_{blanks} \qquad (1)$$

$\bar{C}_{blanks}$ is the mean PFAS concentration in the blanks and SD_{blanks} is the standard deviation of the blank concentrations. If no PFASs were detected in the blanks, the MDL is set to the lowest calibration standard concentration.

As part of the quality control, the recoveries of the ISs were calculated (Equation 3).

$$Recovery\ IS\ (\%) = \frac{Area_{IS(sample)}}{\overline{Area}_{IS(calibration)}} \times 100 \qquad (3)$$

Where $Area_{IS(sample)}$ is the IS area beneath the chromatography curves for the samples and $\overline{Area}_{IS(calibration)}$ the mean IS area beneath the calibration curves.

3.5 Methods for statistical data analysis

3.5.1 *Pearson correlation*

Pearson correlation is used to establish connections between two variables (Grandin, 2003). Here, Pearson correlation was used in order to evaluate if the PFAS concentrations at the different PSTs in the wastewater network of Uppsala were correlated to each other.

The Pearson correlation coefficient, called Pearson's r, can vary between - 1 and + 1 and describes how heavily two variables are correlated to each other (Equation 4) (Grandin, 2003).

$$r = \frac{\Sigma XY/N - \bar{X}\bar{Y}}{\sigma_X \sigma_Y} \qquad (4)$$

$\Sigma XY/N$ is the sum of concentration of analyte X multiplied by the concentration of analyte Y, divided by the sample size (N). This term is subtracted by the sample mean factor ($\bar{X}\bar{Y}$) and divided by the covariance ($\sigma_X\sigma_Y$). The covariance is the term that describes how the two variables tend to vary together (Cohen, 2013).

The next step in the Pearson correlation is to test the Pearson's r for significance. The t-value is calculated from Pearson's r and N (Equation 5) (Cohen, 2013).

$$t = \frac{r\sqrt{N-2}}{\sqrt{1-r^2}} \qquad (5)$$

Using the Student's t-distribution, a *p*-value can be obtained from the t-value and $(N-2)$ in Equation 5 (Cohen, 2013).

With this *p*-value it can be determined whether the correlation is significant or not by studying its value. The Null hypothesis about that no correlation exists can be rejected if the *p*-value is less than 0.05 (Cohen, 2013).

3.5.2 Linear regression

The R^2-value, the coefficient of determination, describes how much of the variation in Y can be explained by the variation in X. The higher the R^2-value, the greater the connection is between the two variables (Grandin, 2003).

The Pearson correlation was analyzed together with the linear regression. This was done in order to determine the data sets variety, while observing its significance. A correlation can therefore have a low R^2-value while still being significant (Norman and Streiner, 2008).

4 RESULTS

In this section, the results from the quality assurance and quality control are presented and then the PFAS concentrations, composition profiles, mass flows and statistical analysis of PFASs in the wastewater network of Uppsala are reported. Lastly, the concentrations, composition profiles, mass flows and removal efficiencies of PFASs in the WWTP are presented.

4.1 Quality assurance and quality control

In order to assure the quality of the analysis, average blank concentrations with standard deviations, MDLs (Table 5), IS recovery (Table 6) and percentage difference of the duplicates and triplicate samples used in the SLE analysis (Table 7) were calculated for each PFAS. A total of 5 blanks were used.

***Table 5** Average PFAS concentrations with standard deviations and method detection limits (MDL) for the blank samples from wastewater (ng L^{-1}) and sludge (ng g^{-1}) analysis*

	WATER		**SLUDGE**	
Analyte	**Average blank concentrations (n = 2) (ng L^{-1})**	**MDL**	**Average blank concentrations (n = 3) (ng g^{-1})**	**MDL**
PFBS	nd	0.19	0.037 ± 0.011	0.069
PFHxS	nd	0.19	0.021 ± 0.019	0.077
PFOS	nd	0.19	nd	0.044
PFDS	nd	0.19	nd	0.044
PFBA	nd	0.19	0.86 ± 0.14	1.3
PFPeA	nd	0.19	0.58 ± 0.0071	0.60
PFHxA	nd	0.19	0.21 ± 0.018	0.26
PFHpA	nd	0.19	0.17 ± 0.032	0.27
PFOA	nd	0.19	0.12 ± 0.0079	0.14
PFNA	nd	0.19	0.032 ± 0.016	0.079
PFDA	2.3 ± 0.54	3.9	0.059 ± 0.044	0.19
PFUnDA	nd	0.19	0.047 ± 0.035	0.15
PFDoDA	nd	0.19	0.037 ± 0.014	0.080
PFTriDA	nd	0.19	nd	0.044
PFTeDA	nd	0.19	nd	0.044
PFHxDA	nd	0.19	nd	0.044
PFOcDA	nd	0.19	0.025 ± 0.023	0.095
FOSA	nd	0.19	nd	0.044
N-MeFOSA	nd	0.19	nd	0.044
N-EtFOSA	nd	0.19	nd	0.044
N-MeFOSE	nd	0.19	0.079 ± 0.14	0.49
N-EtFOSE	nd	0.19	nd	0.044
FOSAA	nd	0.19	0.014 ± 0.024	0.084
N-MeFOSAA	nd	0.19	nd	0.044
N-EtFOSAA	nd	0.19	nd	0.044
6:2 FTSA	nd	0.19	0.0066 ± 0.011	0.041

nd = not detected.

Overall, the blank concentrations in wastewater ranged between not detected and 2.3 ng L^{-1} (PFDA) and the MDL between 0.19 and 3.9 ng L^{-1}. The blank concentrations in sludge varied between not detected and 0.86 ng L^{-1} (PFBA) and the MDL between 0.044 and 1.3 ng L^{-1} (Table 5).

Table 6 *Internal standard recoveries with standard deviations (%) in wastewater and sludge*

Internal Standard	**Wastewater recovery (n = 25) (%)**			**Sludge recovery (n = 17) (%)**			**Corresponding PFASs**
$^{18}O_2$ PFHxS	150	±	58	110	±	9.7	6:2 FTSA, PFHxS
$^{13}C_4$ PFOS	170	±	54	240	±	210	PFBS, PFDS, PFOS
$^{13}C_4$ PFBA	30	±	23	97	±	12	PFBA
$^{13}C_2$ PFHxA	100	±	53	98	±	8.2	PFPeA, PFHxA
$^{13}C_4$ PFOA	140	±	73	92	±	9.5	PFHpA, PFOA
$^{13}C_5$ PFNA	160	±	67	86	±	10	PFNA
$^{13}C_2$ PFDA	110	±	73	87	±	16	PFDA
$^{13}C_2$ PFUnDA	91	±	68	76	±	23	PFUnDA
$^{13}C_2$ PFDoDA	71	±	53	58	±	26	PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA
13C$_8$-FOSA	83	±	69	56	±	29	FOSA
d$_3$-*N*-MeFOSA	70	±	50	84	±	23	*N*-MeFOSA
d$_5$-*N*-EtFOSA	74	±	39	36	±	33	*N*-EtFOSA
d$_7$-*N*-MeFOSE	57	±	41	42	±	46	*N*-MeFOSE
d$_9$-*N*-EtFOSE	66	±	31	28	±	28	*N*-EtFOSE
d$_3$-*N*-MeFOSAA	130	±	90	74	±	42	FOSAA, *N*-MeFOSAA
d$_5$-*N*-EtFOSAA	96	±	110	93	±	46	*N*-EtFOSAA
Average recovery (%)	100	±	59	84	±	35	

The recovery for IS in wastewater were generally high, with an average on 100 ± 59 %, but with a high variation between the different samples. The recovery in sludge was lower, with an average on 89 ± 37 %. The variation between sludge samples was also lower than for the wastewater, except for $^{13}C_4$ PFOS, which had the highest recovery and standard deviation of both wastewater (170 ± 54 %) and sludge samples (220 ± 190 %). Overall, the recoveries were all in acceptable range (Table 6).

***Table 7** Percentage difference in concentration between duplicate (primary clarifier sludge A) and triplicate (final clarifier sludge, digested sludge RK2 and dewatered sludge) sludge samples*

	Difference in concentration (%)			
Analyte	**Primary clarifier sludge A (n = 2)**	**Final clarifier sludge (n = 3)**	**Digested sludge RK2 (n = 3)**	**Dewatered sludge (n = 3)**
PFBS	nd	nd	130	nd
PFHxS	7.2	33	130	6.0
PFOS	33	20	23	6.8
PFDS	nd	nd	nd	nd
PFBA	nd	70	9	18
PFPeA	nd	nd	nd	nd
PFHxA	8.0	44	36	12
PFHpA	31	140	28	nd
PFOA	7.7	30	8.0	3.7
PFNA	25	130	10	2.1
PFDA	12	12	6.0	4.8
PFUnDA	30	21	14	14
PFDoDA	11	16	4.8	7.4
PFTriDA	0.82	61	7.4	9.3
PFTeDA	2.5	22	4.2	13
PFHxDA	nd	nd	2.2	10
PFOcDA	nd	nd	nd	nd
FOSA	nd	nd	nd	nd
N-MeFOSA	nd	nd	nd	nd
N-EtFOSA	11	nd	nd	nd
N-MeFOSE	nd	nd	nd	nd
N-EtFOSE	nd	nd	nd	nd
FOSAA	nd	130	28	20
N-MeFOSAA	nd	85	3.9	13
N-EtFOSAA	2.0	5.5	4.5	11
6:2 FTSA	29	0	96	76
Min	0.82	5.5	2.2	2.1
Max	33	140	130	76
Median	1.4	14	5.4	5.4
Average	8.0	32	21	8.7
Overall average	17			

nd = not detected.

The percentage difference was highest for the final clarifier sludge (Average = 32 %) and lowest for the primary clarifier sludge (Average = 8.0 %). The overall average was 17 % (Table 7).

4.2 PFASs in the wastewater network

In the wastewater network of Uppsala, 21 out of 26 PFASs were detected (PFBS, PFHxS, PFOS, C_3 – C_8 PFCAs, C_9 – C_{17} PFCAs, FOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA and 6:2 FTSA) (Table A4 in the Appendix) (Figur 6). In the wastewater at KV, 13 out of 26 PFASs were detected (PFBS, PFHxS, PFOS, C_3 – C_8 PFCAs, PFTeDA, FOSA, *N*-EtFOSAA and 6:2 FTSA).

The PFAS concentrations and composition profiles varied greatly in the network. The highest ∑PFAS concentration was found at Sågargatan PST (∑PFAS = 55,000 ng L^{-1}), which is a value that is more than 20 times higher than the ∑PFAS concentration at Norra Librobäck PST (∑PFASs = 2,100 ng L^{-1}). Whether the PST received domestic, industrial or mixed wastewater had an impact on the ∑PFAS concentration levels. Overall, the PSTs receiving mixed wastewater had the higher ∑PFAS concentrations (average = 19,000 ng L^{-1}, median = 180 ng L^{-1}), followed by industrial (average = 1,000 ng L^{-1}, median = 730 ng L^{-1}) and domestic wastewater (average = 290 ng L^{-1}, median = 150 ng L^{-1}). However, several PSTs receiving domestic wastewater had higher ∑PFAS concentrations (i.e. Bärby hage and Flogsta PST) than those receiving industrial or mixed (i.e. Seminaregatan, Strandbodgatan and Tullgarn PST) (Table 1). For example, Flogsta (∑PFASs = 570 ng L^{-1}) and Bärby hage PST (∑PFASs = 1,100 ng L^{-1}) had higher ∑PFAS concentrations than Seminaregatan (∑PFASs = 120 ng L^{-1}), Strandbodgatan (∑PFASs = 90 ng L^{-1}) and Tullgarn PST (∑PFASs = 180 ng L^{-1}) (Figure 3).

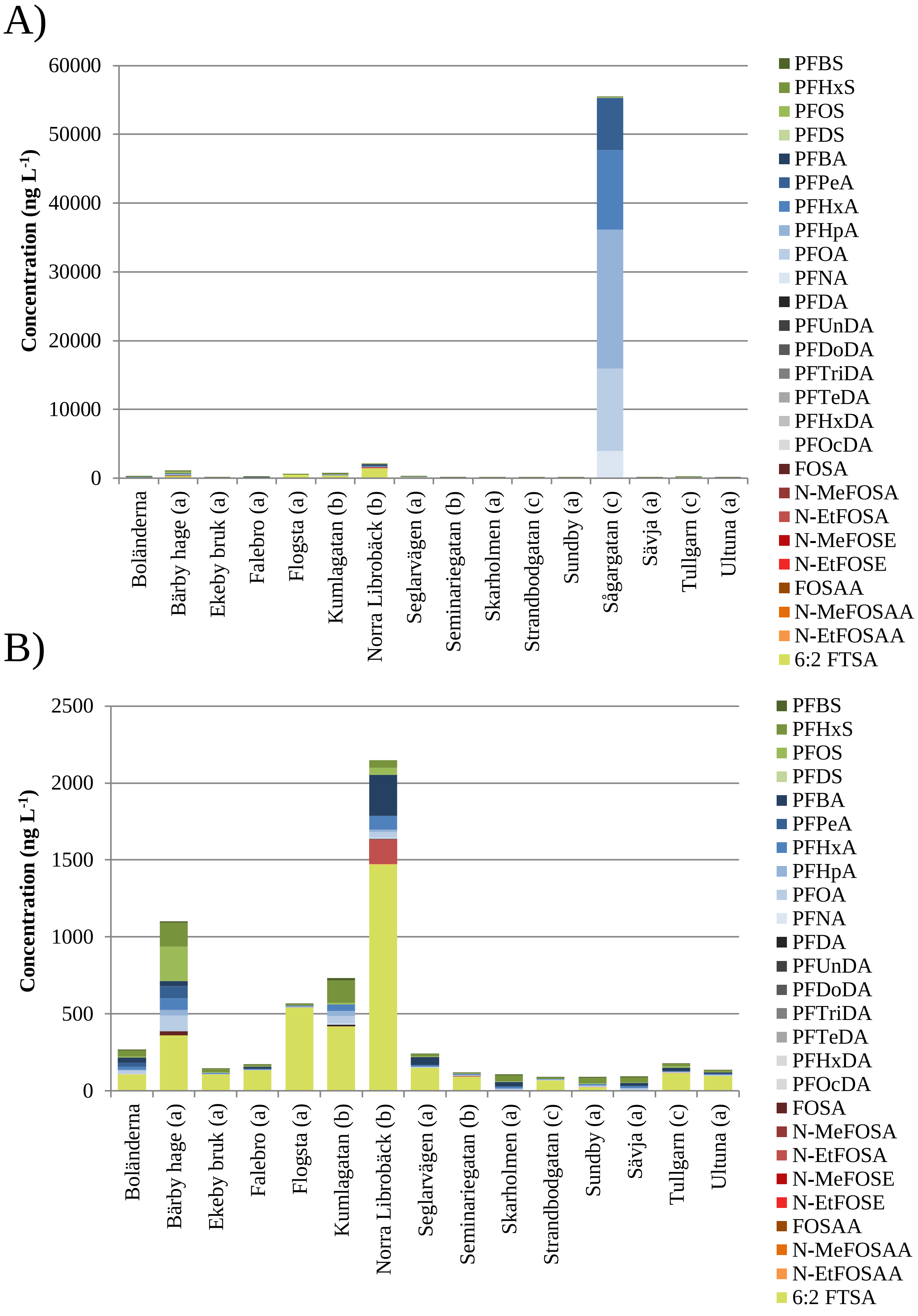

***Figure 3** A) PFAS concentrations (ng L^{-1}) at the different pumping stations (PSTs) in the wastewater network of Uppsala and B) excluding Sågargatan PST. The indexes refer to PSTs receiving (a) domestic, (b) industrial or (c) mixed wastewater.*

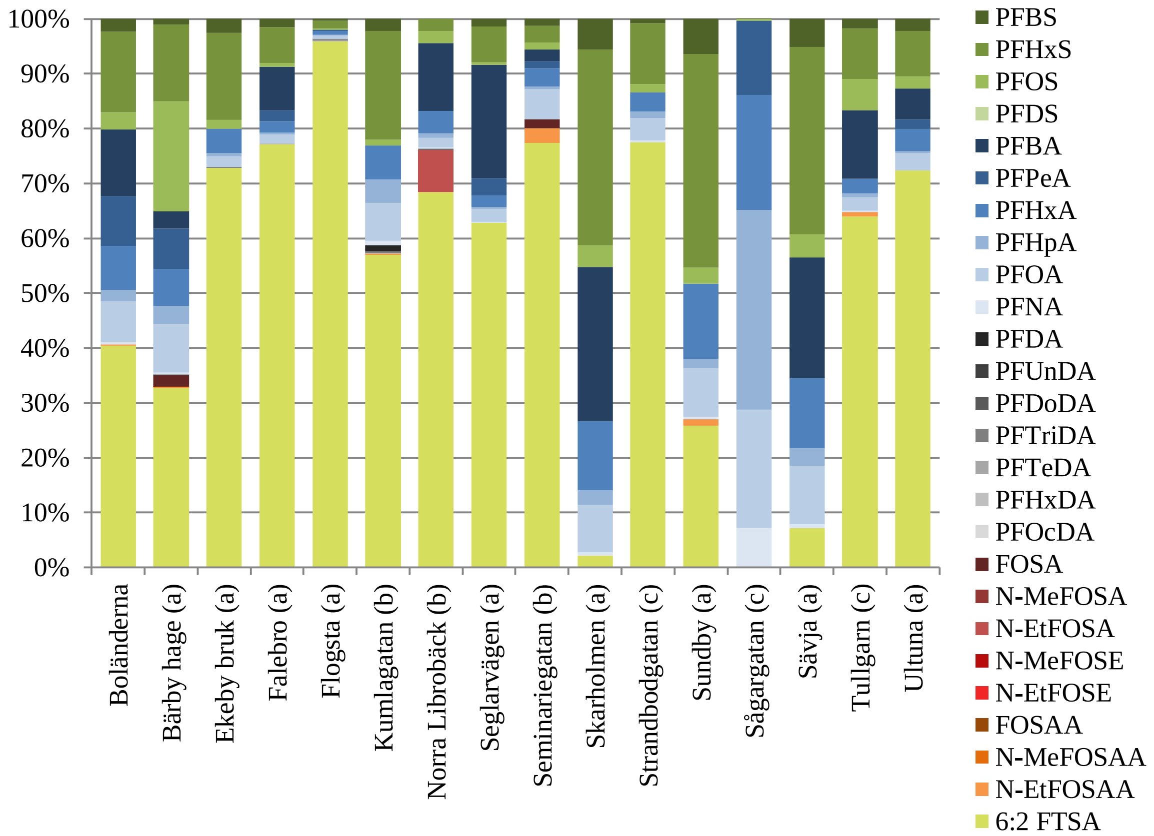

***Figure 4** PFAS composition profile in the different pumping station in the wastewater network of Uppsala. The indexes refer to PSTs receiving (a) domestic, (b) industrial or (c) mixed wastewater.*

6:2 FTSA is the dominating substance in the wastewater network of Uppsala. 6:2 FTSA was the most dominating substance at all PSTs besides Skarholmen, Sundby, Sågargatan and Sävja PST, ranging from 40 to 96 % of the ∑PFAS concentration (average = 230 ng L^{-1}, median = 110 ng L^{-1}). The highest concentration could be found at Norra Librobäck PST (1,500 ng L^{-1}), followed by Flogsta PST (540 ng L^{-1}). The PST with the highest amount of 6:2 FTSA, to the ∑PFAS concentration, was Flogsta PST (96 %). High amounts were also found for Ekeby bruk (73 %), Falebro (77 %), Seglarvägen (63 %), Strandbodgatan (77 %), Tullgarn (64 %) and Ultuna PST (72 %). All of these receive domestic wastewater. However, Strandbodgatan and Tullgarn PST also receive industrial wastewater. 6:2 FTSA was not only detected in domestic wastewater, but also at PSTs receiving solely industrial wastewater, such as Kumlagatan (57 %), Norra Librobäck (68 %) and Seminaregatan PST (77 %) (Table 1, Figure 3, 4 and 5).

Other dominating PFASs in the wastewater network were PFHxS and PFHpA. PFHxS (average = 37 ng L^{-1}) could be found at most PSTs (*n = 15*), being the most dominant compound in Skarholmen (36 %), Sundby (39 %) and Sävja PST (34 %), while PFHpA (average = 1,300 ng L^{-1}) was most dominant in Sågargatan PST (36 %). Skarholmen, Sundby and Sävja PST all receive domestic wastewater. Sågargatan PST receives both domestic and industrial (medical devices) wastewater and C_3 – C_8 PFCAs are the completely dominating PFASs. Skarholmen and Sävja PST also consist of a high amount C_3 – C_8 PFCAs, 53 % and 49 % respectively. However, these both receive domestic wastewater. C_9 – C_{17} PFCAs was found at several PSTs, receiving both industrial (*n = 3*) and domestic wastewater (*n = 5*), ranging from 0.011 to 1.1 % (Figure 4).

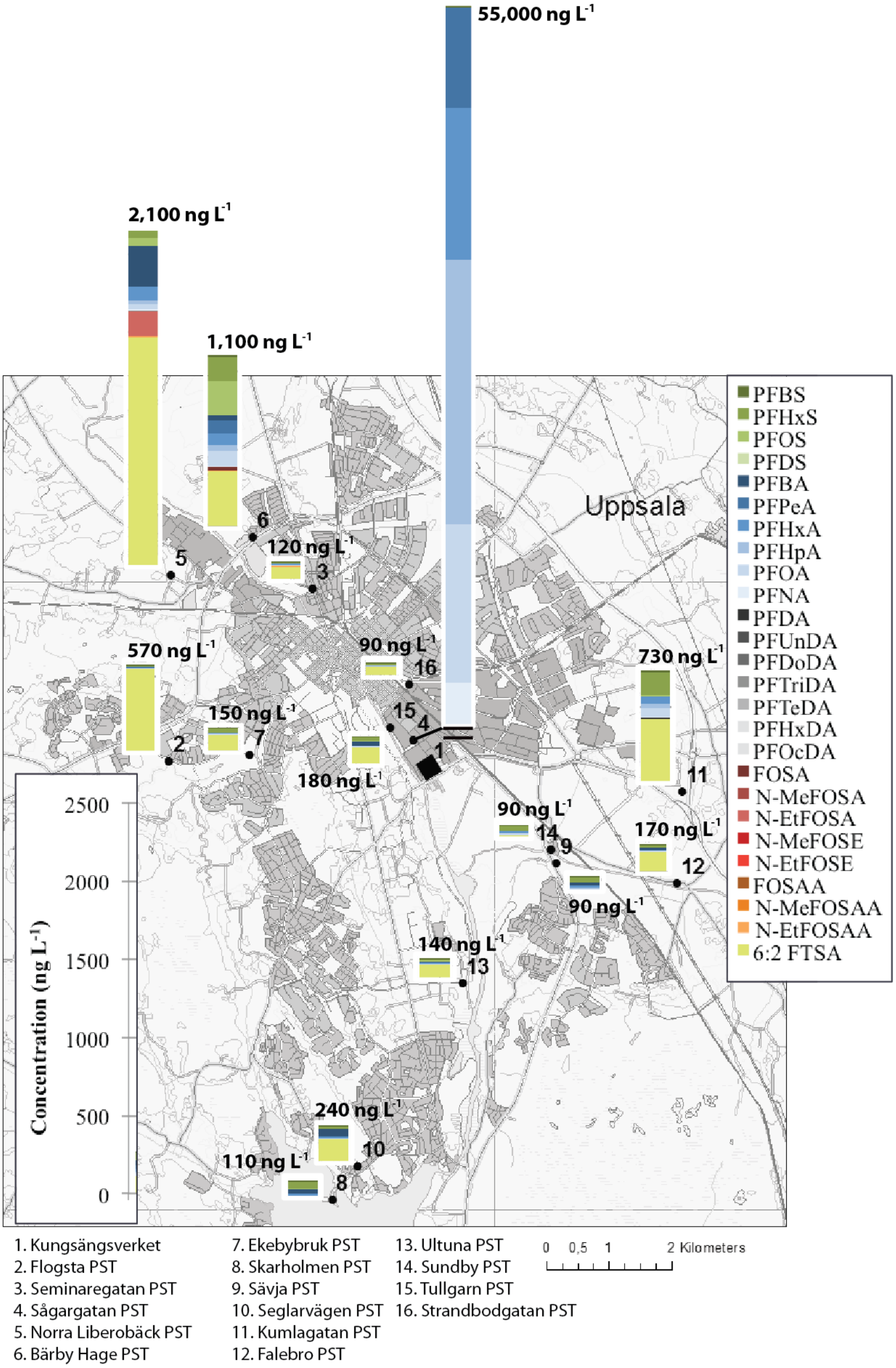

Figure 5 *A map of PFAS concentrations (ng L^{-1}) at the different pumping stations in the wastewater network of Uppsala. Due to its size, the bar for Sågargatan PST (site 4) is not according to scale © Lantmäteriet [I2014/00764].*

FOSAs and FOSAAs occurred in both domestic and industrial wastewater. The PSTs with wastewater containing FOSAs was Bärby hage (FOSA: 2.2 %), Norra Libroback (*N*-EtFOSA: 7.5 %) and Seminaregatan PST (FOSA: 1.6 %). *N*-EtFOSAA could be found at several PSTs (average = 0.74 ng L^{-1}), which receives industrial (*n = 3*) and domestic wastewater (*n = 3*). *N*-MeFOSAA was detected at Bärby hage PST (0.028 %). The PST with the highest amount of PFOS was Bärby hage PST (20 %), receiving domestic wastewater but also wastewater from a known fire-training site (Table 1). The highest amount of PFOA was found at Sågargatan PST (22 %).

4.2.1 Mass flow

The mass flows and standard deviations (mg d^{-1}) for PFSAs, C_3 – C_8 PFCAs, C_9 – C_{17} PFCAs, FOSAs, FOSAAs and FTSAs (Table A7 in the Appendix) in the wastewater network of Uppsala are presented in the figures below (Figure 6, 7, 8 and 9). The mass flows for wastewater and sludge were calculated according to Equation 6. The PFASs that were not detected are left out in the mass flow figures. For a more detailed map of the PST locations, see Figure 2 or 5.

$$\dot{m}\ (mg\ d^{-1}) = Concentration\ (ng\ L^{-1})\ \times\ Flow\ (m^3\ d^{-1})\ \times\ 10^{-3} \qquad (6)$$

Varied mass flows across the wastewater network was seen, where the highest mass flow in the entire wastewater network came from Sågargatan PST (∑PFAS = 110,000 mg d^{-1}), followed by Tullgarn PST (∑PFAS = 4,300 mg d^{-1}) and Flogsta PST (∑PFAS = 1,200 mg d^{-1}). The highest mass flow from Tullgarn and Flogsta PST was found for 6:2 FTSA (2,800 mg d^{-1} and 1,100 mg d^{-1}, respectively) and the highest from Sågargatan PST was found for PFHpA (39,000 mg d^{-1}), which is the highest out of all PFASs in the wastewater network.

Several PSTs were contributing to the mass flow of PFSAs. The ones with the highest mass flows were Sågargatan (PFOS: 280 mg d^{-1}), Tullgarn (PFHxS: 400 mg d^{-1}), Bärby hage (PFOS: 130 mg d^{-1}) and Strandbodgatan PST (PFHxS: 98 mg d^{-1}). The highest mass flow amongst PFSAs was found at Tullgarn PST (400 mg d^{-1}). For PFSAs overall, PFOS contributed to the highest mass flows (∑PST = 690 mg d^{-1}), followed by PFHxS (∑PST = 680 mg d^{-1}) and PFBS (∑PST = 130 mg d^{-1}) (Figure 6).

Sågargatan, Tullgarn, Strandbodgatan and Bärby hage PST contributed with the highest mass flows of C_3 – C_8 PFCAs, ranging from not detected to 39,000 mg d^{-1}. Sågargatan PST excluded, which had the highest mass flows of C_3 – C_8 PFCAs, Tullgarn PST contributed with the highest mass flows (PFBA: 540 mg d^{-1}), followed by Bärby hage (PFOA: 57 mg d^{-1}) and Strandbodgatan PST (PFOA: 37 mg d^{-1}). For C_3 – C_8 PFCAs, PFHpA contributed to the highest mass flows (∑PST = 39,000 mg d^{-1}), followed by PFOA (∑PST = 23,000 mg d^{-1}), PFHxA (∑PST = 22,000 mg d^{-1}), PFPeA (∑PST = 14,000 mg d^{-1}), PFNA (∑PST = 7,500 mg d^{-1}) and PFBA (∑PST = 620 mg d^{-1}) (Figure 7).

C_9 – C_{17} PFCAs were not as evident as C_3 – C_8 PFCAs, ranging from not detected to 11 mg d^{-1}. The PSTs contributing with C_9 – C_{17} PFCAs were Flogsta (PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA and PFOcDA: 0.6 – 0.9 mg d^{-1}) and Sågargatan PST (PFDA: 11 mg d^{-1}). For C_9 – C_{17} PFCAs overall, PFDA contributed to the highest mass flows (∑PST = 11 mg d^{-1}), followed by PFUnDA (∑PST = 1.2 mg d^{-1}), PFDoDA (∑PST = 0.90 mg d^{-1}), PFHxDA (∑PST = 0.84 mg d^{-1}), PFTriDA (∑PST = 0.79 mg d^{-1}), PFTeDA (∑PST = 0.78 mg d^{-1}) and PFOcDA (∑PST = 0.57 mg d^{-1}) (Figure 8).

High mass flows were coming from several PSTs with regard to 6:2 FTSA, such as Tullgarn (2,800 mg d^{-1}), Flogsta (1,100 mg d^{-1}), Strandbodgatan (690 mg d^{-1}) and Bärby hage PST (210 mg d^{-1}). For other PFAS precursors, it was either one or two PSTs contributing with mass flows. The highest mass flow among these was found at Tullgarn (*N*-EtFOSAA: 36 mg d^{-1}), Bärby hage (FOSA: 14 mg d^{-1}) and Norra Librobäck PST (*N*-EtFOSA: 5.2 mg d^{-1}). Overall, 6:2 FTSA contributed to the highest mass flows of PFAS precursors ($\sum$PST = 5,000 mg d^{-1}), followed by *N*-EtFOSAA ($\sum$PST = 38 mg d^{-1}), FOSA ($\sum$PST = 15 mg d^{-1}), *N*-EtFOSA ($\sum$PST = 5.2 mg d^{-1}) and *N*-MeFOSAA ($\sum$PST = 0.18 mg d^{-1}) (Figure 9).

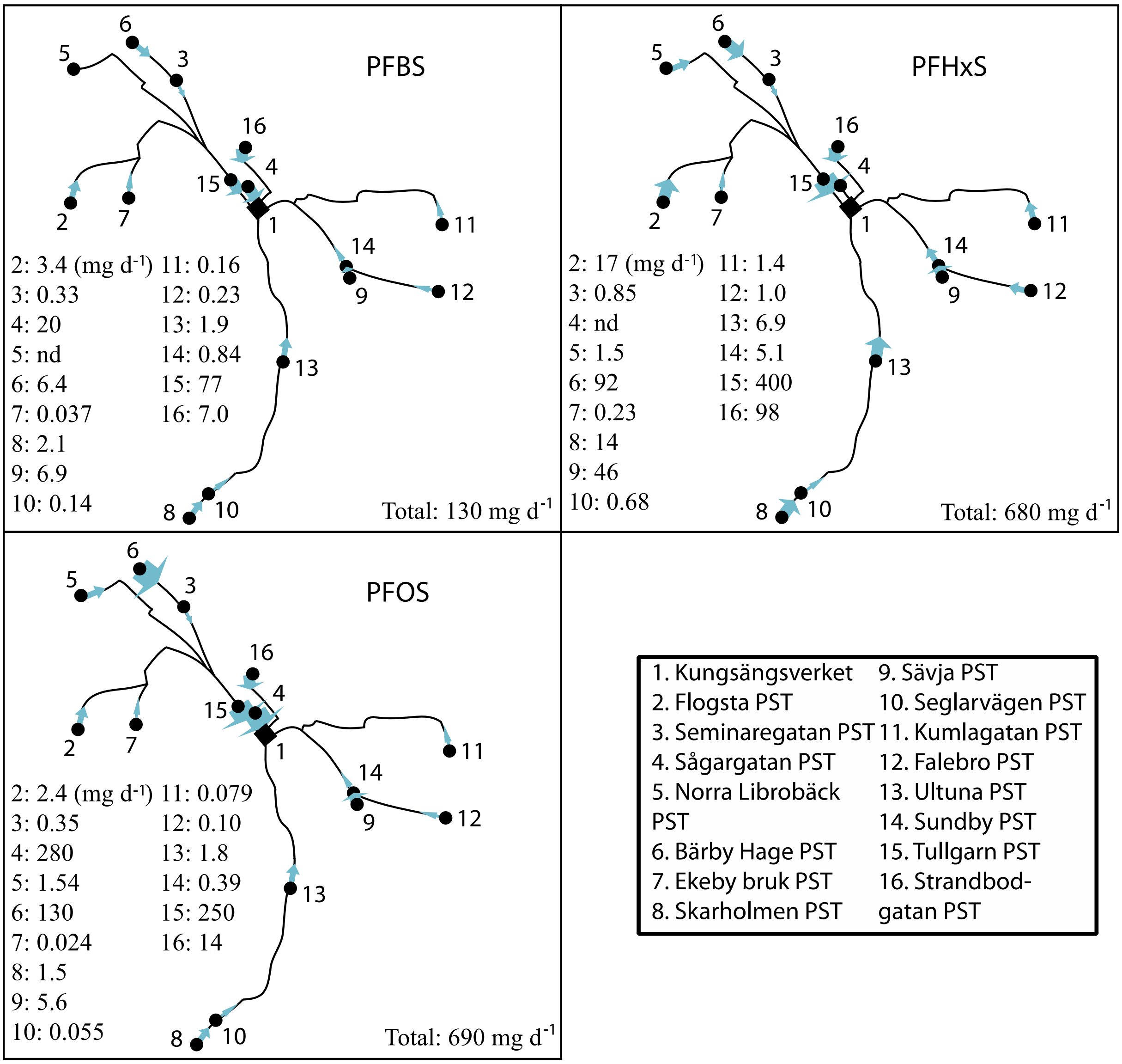

***Figure 6** Mass flows (mg d $^{-1}$) of the PFSAs PFBS, PFHxS, PFOS and PFDS at the different pumping stations in the wastewater network of Uppsala. "nd" = not detected.*

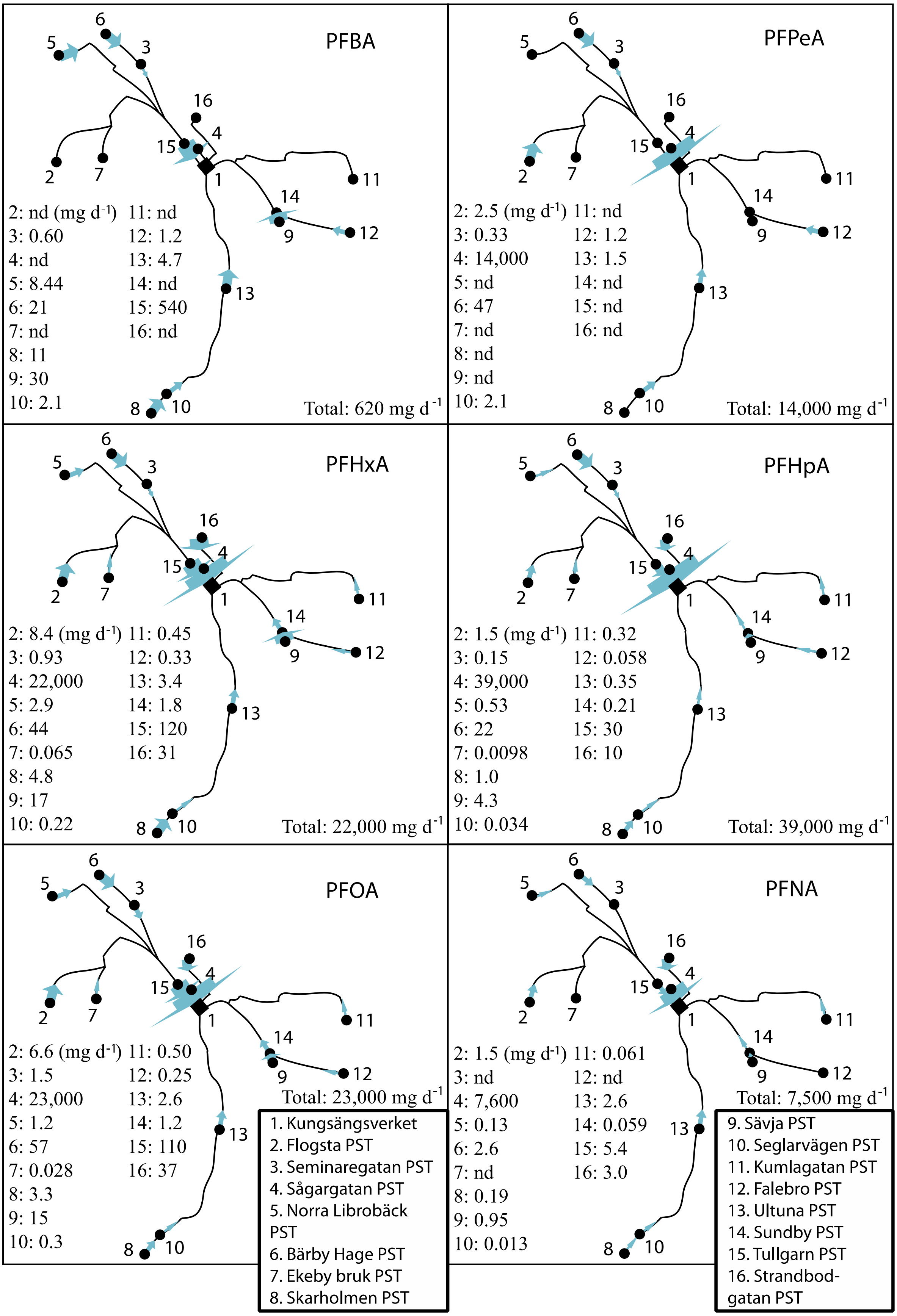

Figure 7 *Mass flows (mg d^{-1}) of the C$_3$ – C$_8$ PFCAs PFBA, PFPeA, PFHxA, PFHpA, PFOA and PFNA at the different pumping stations in the wastewater network of Uppsala. "nd" = not detected.*

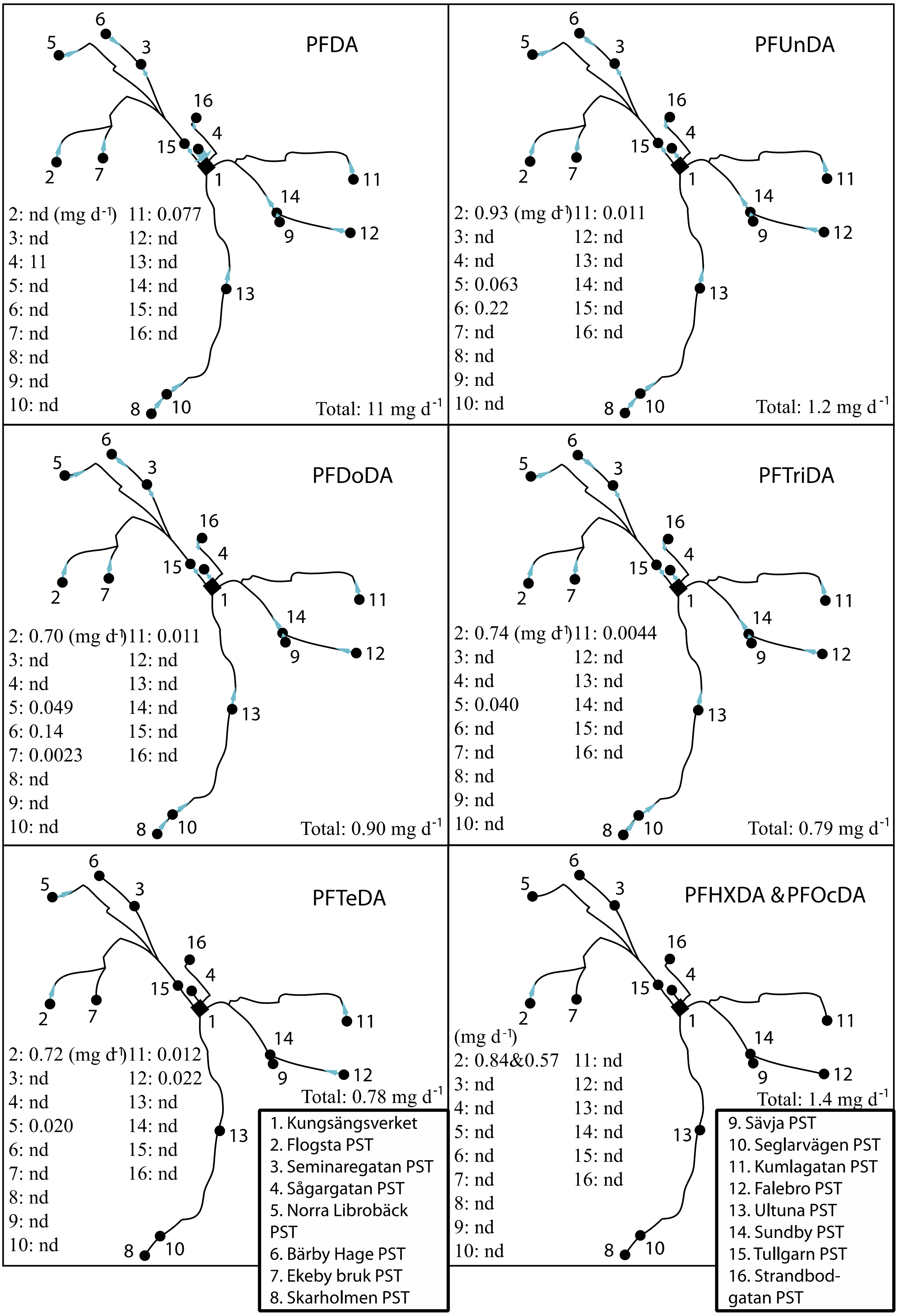

Figure 8 *Mass flows (mg d* $^{-1}$*) of the* $C_9 - C_{17}$ *PFCAs PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA and PFOcDA at the different pumping stations in the wastewater network of Uppsala. "nd" = not detected.*

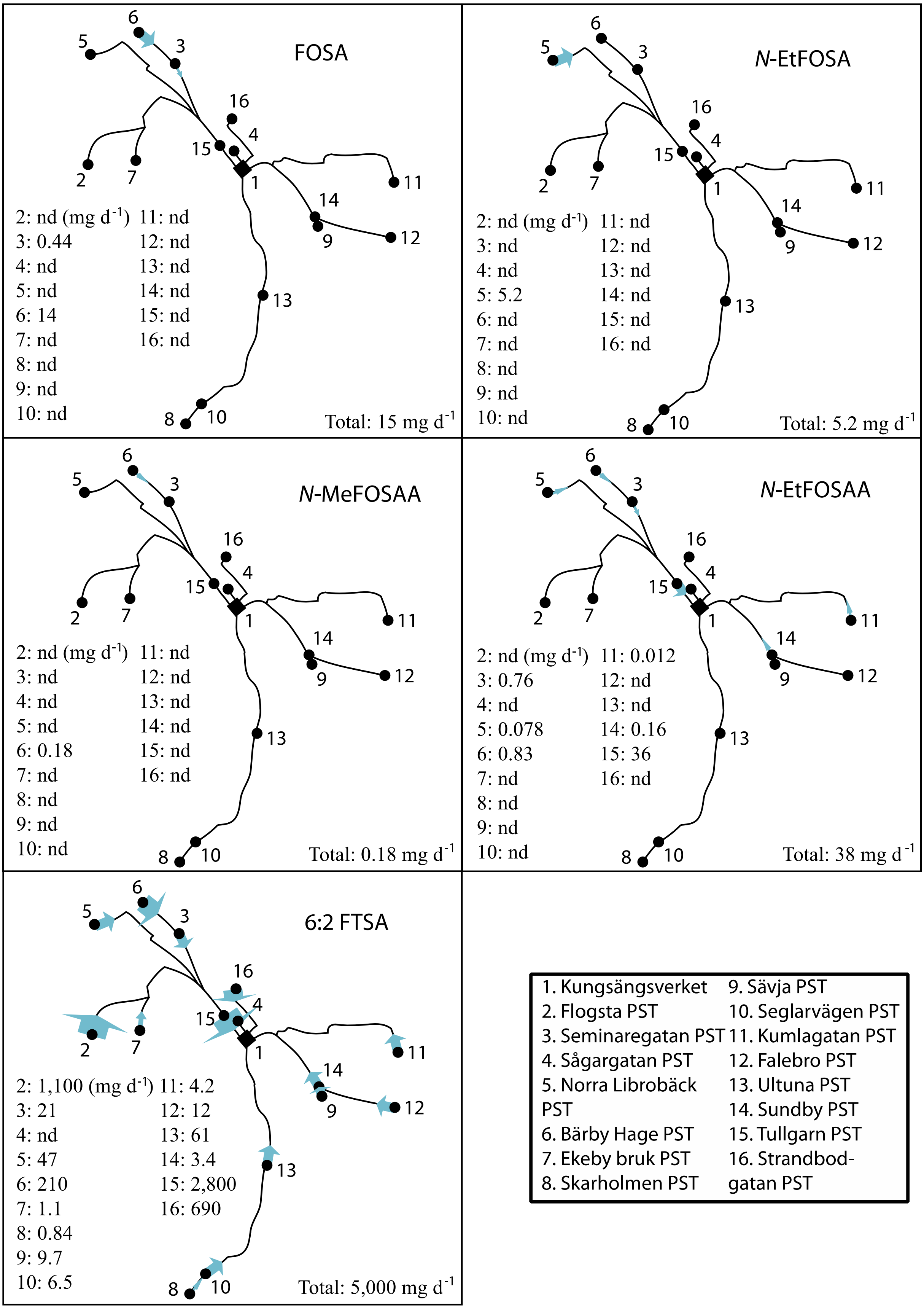

Figure 9 *Mass flows (mg d $^{-1}$) of the PFAS precursors FOSA, N-EtFOSA, N-MeFOSAA, N-EtFOSAA and 6:2 FTSA at the different pumping stations in the wastewater network of Uppsala. "nd" = not detected.*

4.2.2 Correlation analysis for PFASs

A Pearson correlation was made, together with linear regression, in order to evaluate if the PFAS concentrations at the different PSTs in the wastewater network of Uppsala have any connection to each other. The correlations were categorized by degree of correlation (R^2), positive or negative correlation (Pearson's r) and significance (p-value). Only the PFASs with a detection frequency larger than 50 % were analyzed (Table 8).

Table 8 *Correlations between PFASs in the wastewater network of Uppsala. The correlations are categorized by* $* = p < 0.5$, $** = p < 0.01$, $*** = p < 0.001$ *and* $**** = p < 0.0001$

		PFBS	**PFHxS**	**PFOS**	**6:2 FTSA**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**
PFBS	R^2									
	Pearson's r									
PFHxS	R^2									
	Pearson's r									
PFOS	R^2									
	Pearson's r									
6:2 FTSA	R^2		**0.40							
	Pearson's r		0.63							
PFBA	R^2									
	Pearson's r									
PFPeA	R^2		*0.33	*0.26						
	Pearson's r		-0.57	0.51						
PFHxA	R^2			****0.68	*0.29		**0.41			
	Pearson's r			0.82	-0.53		0.64			
PFHpA	R^2			***0.67	*0.28		**0.41	****0.97		
	Pearson's r			0.82	-0.53		0.64	0.99		
PFOA	R^2			***0.67	*0.29		**0.49	****0.97	****0.98	
	Pearson's r			0.82	-0.54		0.70	0.98	0.99	
PFNA	R^2			***0.58	*0.26		**0.40	****0.93	****0.96	****0.94
	Pearson's r			0.76	-0.51		0.63	0.97	0.98	0.97

The correlation analysis showed varying correlation strengths between different PFASs, where, in total, 21 significant correlations were found. The correlations between these PFASs were both negative (Pearson's $r < 0$) and positive (Pearson's > 0). The correlations between 6:2 FTSA and PFHxS, PFOS and $C_3 – C_8$ PFCAs (PFHxA, PFHpA, PFOA and PFNA) and amongst $C_3 – C_8$ PFCAs (PFPeA, PFHxA, PFHpA, PFOA and PFNA) were positively correlated. While the correlations between PFPeA and PFHxS and between 6:2 FTSA and $C_3 – C_8$ PFCAs (PFHxA, PFHpA, PFOA and PFNA) were negatively correlated. The $C_3 – C_8$ PFCAs PFHxA, PFHpA, PFOA and PFNA showed significant strong correlations to each other ($p < 0.0001$). The same $C_3 – C_8$ PFCAs showed significant correlations with PFOS ($p < 0.001$) and significant weak correlations to PFPeA ($p < 0.01$). PFPeA also showed a significant weak correlation to PFHxS ($p < 0.05$) and PFOS ($p < 0.05$). Significant weak correlations could be found between 6:2 FTSA and $C_3 – C_8$ PFCAs (PFHxA, PFHpA, PFOA, PFNA) ($p < 0.05$) and PFHxS ($p < 0.01$).

4.3 PFASs in Kungsängsverket

In total, 13 out of 26 substances were detected in wastewater (PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFTeDA, FOSA, *N*-EtFOSAA and 6:2 FTSA) and 21 out of 26 in sludge (PFBS, PFHxS, PFOS, FFDS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, *N*-EtFOSA, FOSAA, *N*-MeFOSAA, *N*-EtFOSAA and 6:2 FTSA). Perfluorodecane sulfonate (PFDS), PFDA, PFUnDA, PFDoDA, PFTriDA, PFHxDA, *N*-EtFOSA, FOSAA and *N*-MeFOSAA were not detected in wastewater, but detected in sludge. FOSA was not detected in sludge, but detected in wastewater (Table A6 in the Appendix).

4.3.1 Wastewater

Most substances were primarily detected in the influent (*n = 10*), but some substances were not detected until after the primary clarifier (i.e. PFPeA and PFTeDA) or after the secondary clarifier (i.e. FOSA). One substance, which was detected in the influent, was not detected in the effluent (i.e. *N*-EtFOSAA). The other PFASs that were detected earlier were all detected in the effluent (i.e. PFBS, PFHxS, PFOS, PFBA, PFHxA, PFHpA, PFOA, PFNA and 6:2 FTSA). Most of the detected substances in wastewater increased in concentration after the biological treatment (i.e. PFBS, PFHxS, PFOS, $C_3 – C_8$ PFCAs, FOSA and 6:2 FTSA), while the rest decreased (i.e. PFTeDA and *N*-EtFOSAA). The only exception is PFHxS, which increased at all treatment lines except for one (Figure 10).

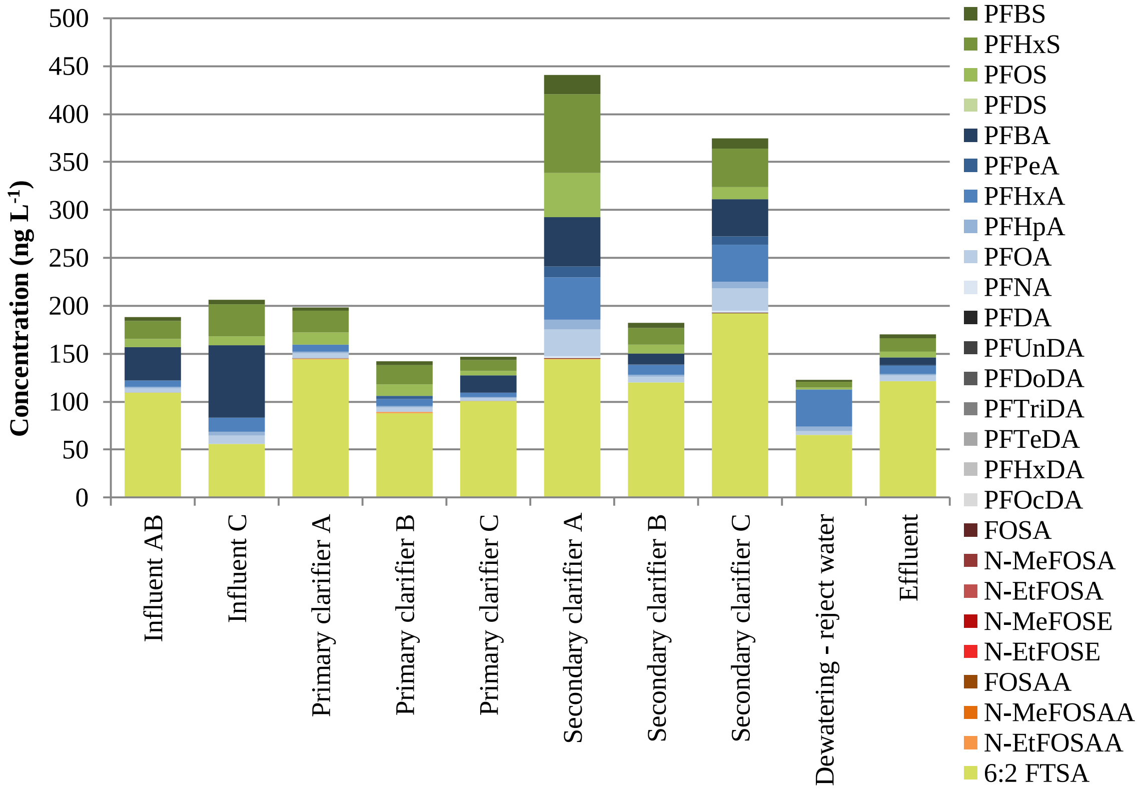

***Figure 10** PFAS concentrations (ng L^{-1}) at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket: A, B and C. "Influent" refers to the influent channels before the grid at rough treatment, "Primary clarifier" to the effluent water from the settling basin after the mechanical treatment, "Secondary clarifier" to the effluent water from the settling basin after the biological treatment, "Dewatering – reject water" to the reject water created from sludge dewatering and "Effluent" to the treated wastewater leaving Kungsängsverket.*

The PFAS concentrations after the secondary clarifier (A: ∑PFAS = 440 ng L^{-1}, B: ∑PFAS = 180 ng L^{-1}, C: ∑PFAS = 370 ng L^{-1}) were generally higher than after the primary clarifier (A: ∑PFAS = 200 ng L^{-1}, B: ∑PFAS = 140 ng L^{-1}, C: ∑PFAS = 150 ng L^{-1}). The concentrations in the effluent (∑PFAS = 170 ng L^{-1}) were lower than in the influent (AB: ∑PFAS = 190 ng L^{-1}, C: ∑PFAS = 210 ng L^{-1}). However, some substances increased in concentration between influent and effluent (i.e. PFNA and 6:2 FTSA). The lowest concentration could be found in the reject water from sludge dewatering (∑PFAS = 120 ng L^{-1}) and the highest after the secondary clarifier A (∑PFAS = 440 ng L^{-1}).

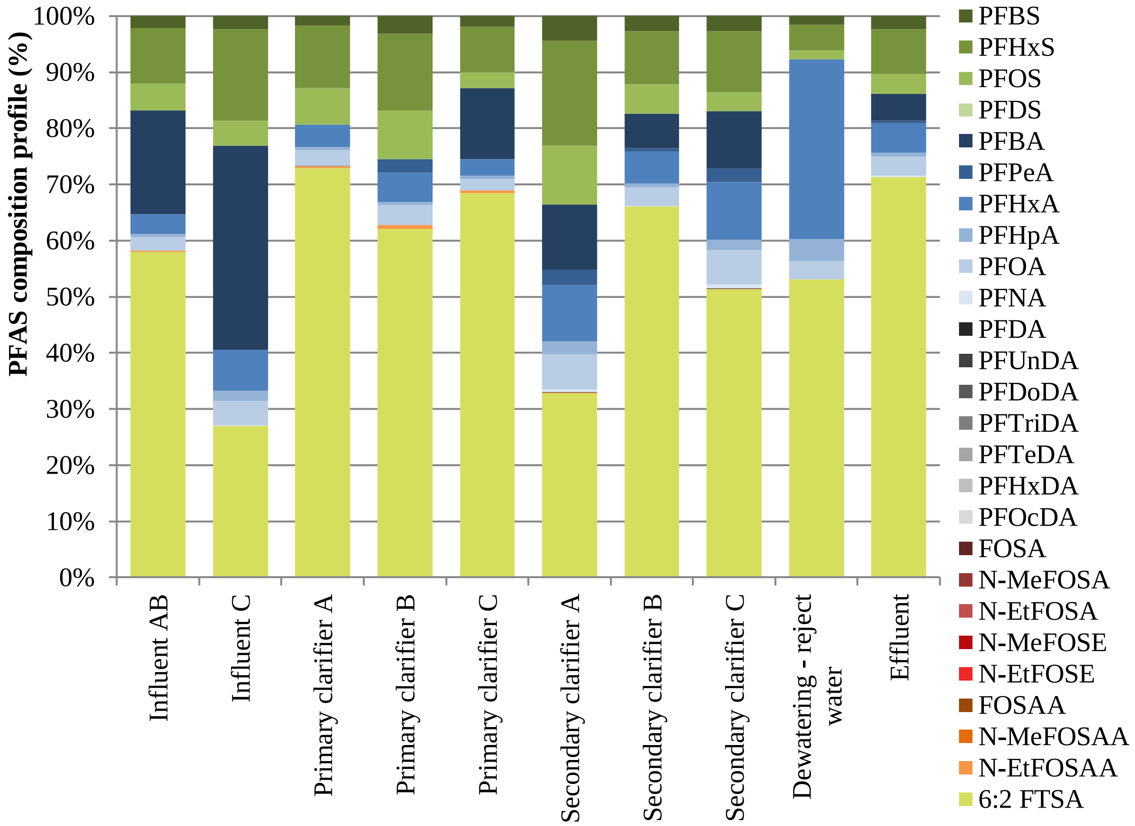

Figure 11 *PFAS composition profile at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket: A, B and C. "Influent" refers to the influent channels before the grid at rough treatment, "Primary clarifier" to the effluent water from the settling basin after the mechanical treatment, "Secondary clarifier" to the effluent water from the settling basin after the biological treatment, "Dewatering – reject water" to the reject water created from sludge dewatering and "Effluent" to the treated wastewater leaving Kungsängsverket.*

PFAS precursors and $C_9 – C_{17}$ PFCAs were either not detected or detected at very low concentrations. $C_9 – C_{17}$ PFCAs, except PFTeDA (average = 0.031 ng L^{-1}, median = 0 ng L^{-1}), were not detected in wastewater at all. The only precursors detected in wastewater were FOSA (average = 0.13 ng L^{-1}, median = 0 ng L^{-1}), *N*-EtFOSAA (average = 0.30 ng L^{-1}, median = 0.20 ng L^{-1}) and 6:2 FTSA (average = 110 ng L^{-1}, median = 110 ng L^{-1}). 6:2 FTSA had the highest concentration (190 ng L^{-1}) and median value (110 ng L^{-1}) out of all detected PFASs in wastewater, making it the most dominant substance, ranging from 27 to 73 % of the ∑PFAS concentration. However, at Influent C and secondary clarifier A this was not the case. At Influent C, $C_3 – C_8$ PFCAs was the most dominant group (PFBA: 37 %) and at secondary clarifier A PFSAs was most dominant (PFHxS: 19 %). But although PFSAs was the most dominant group, 6:2 FTSA was still the most dominant substance at secondary clarifier A (33 %) (Figure 11).

4.3.2 Sludge

4.3.2.1 Moisture, dry and organic matter

The highest moisture content in sludge from KV was found in the final clarifier sludge (97 %) and the lowest moisture content was found in the dewatered sludge (69 %). Leading to that the highest TS content was found in the dewatered sludge (32 %) and the lowest in the final clarifier sludge (3.5 %). The highest OM content was found in primary clarifier sludge A (90 %) and the lowest in the final clarifier sludge (50 %). A high TS content was found for primary clarifier sludge A, primary clarifier sludge C, secondary clarifier sludge A, digested sludge RK1, digested sludge RK2 and dewatered sludge. A high OM content was found for all sludge's except final clarifier sludge (Table A4 in the Appendix).

4.3.2.2 PFASs in sludge

Most substances were primarily detected in primary clarifier sludge (i.e. PFHxS, PFOS, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, *N*-EtFOSA, *N*-EtFOSAA and 6:2 FTSA). If not, they were either detected in secondary clarifier sludge (i.e. PFBS, PFDS, PFPeA, PFHxA, FOSAA and *N*-MeFOSAA) or digested sludge (i.e. PFBA and PFHpA). In the sludge treatment, the primary clarifier sludge is sent to digestion chamber 1 (RK1) and the secondary clarifier sludge to chamber 2 (RK2). Some of the substances detected in digested sludge RK1 were not detected in primary clarifier sludge (PFHpA, FOSAA and *N*-MeFOSAA) and vice versa (PFHxS and *N*-EtFOSA). The same trend could be seen for secondary clarifier sludge and digested sludge RK2, where some substances were detected in digested sludge RK2 but not in secondary clarifier sludge (PFBA and PFHpA) and vice versa (PFDS and PFPeA). Most PFASs detected in sludge were also detected in dewatered sludge (i.e. PFHxS, PFOS, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, FOSAA, *N*-MeFOSAA, *N*-EtFOSAA and 6:2 FTSA), some of them were also found in the reject water from the dewatering (i.e. PFHxS, PFOS, PFHxA, PFOA and 6:2 FTSA), However, some of the PFASs found in the reject water were not detected in the dewatered sludge (i.e. PFBS and PFHpA) (Figure 12).

The concentrations in dewatered ($\sum$PFAS = 33 ng g^{-1} dw) and digested sludge (RK1: $\sum$PFAS = 12 ng g^{-1} dw, RK2: $\sum$PFAS = 36 ng g^{-1} dw) were generally higher than in the primary clarifier sludge (A: $\sum$PFAS = 34 ng g^{-1} dw, B: $\sum$PFAS = 16 ng g^{-1} dw, C: $\sum$PFAS = 7.0 ng g^{-1} dw). The lowest concentration could be found in primary clarifier sludge C ($\sum$PFAS = 7.0 ng g^{-1} dw) and the highest in secondary clarifier sludge A ($\sum$PFAS = 61 ng g^{-1} dw).

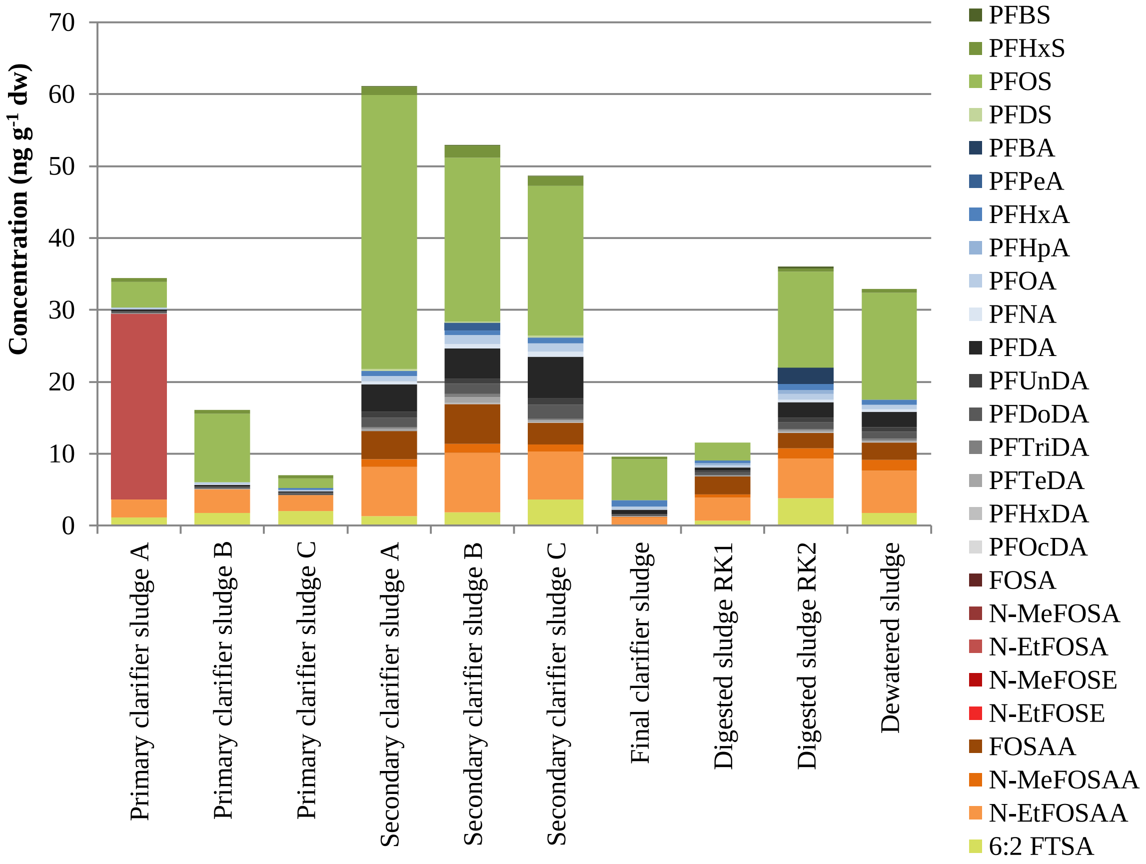

Figure 12 *PFAS concentration (ng g^{-1} dw) in the different sludge's at Kungsängsverket. There are three treatment lines at Kungsängsverket: A, B and C. "Primary clarifier sludge" refers to the sludge created at the primary clarifier, "Secondary clarifier sludge" to the sludge created at the secondary clarifier, "Final clarifier sludge" to the sludge created at the final clarifier, "Digested sludge" to the fully digested sludge from the two digestion chambers RK1 and RK2 and "Dewatered sludge" to the sludge created from sludge dewatering.*

Secondary clarifier sludge A, together with digested sludge RK2, had the highest number of PFASs ($n = 18$). For most PFASs, an increase in concentration could be detected between primary clarifier sludge (A: ∑PFAS = 34 ng g^{-1} dw, B: ∑PFAS = 16 ng g^{-1} dw, C: ∑PFAS = 7.0 ng g^{-1} dw) and secondary clarifier sludge (A: ∑PFAS = 62 ng g^{-1} dw, B: ∑PFAS = 53 ng g^{-1} dw, C: ∑PFAS = 49 ng g^{-1} dw), but a decrease or sudden drop in concentration in the final clarifier sludge (∑PFAS = 9.6 ng g^{-1} dw). This was true for ∑PFAS, but more specifically for PFSAs, C_3 – C_8 PFCAs, FOSAAs and 6:2 FTSA ($n = 14$). Meaning that the treatment step with the highest efficiency to transfer PFASs to the solid phase is the biological treatment. However, this does not mean that the biological treatment is successful in removing PFASs.

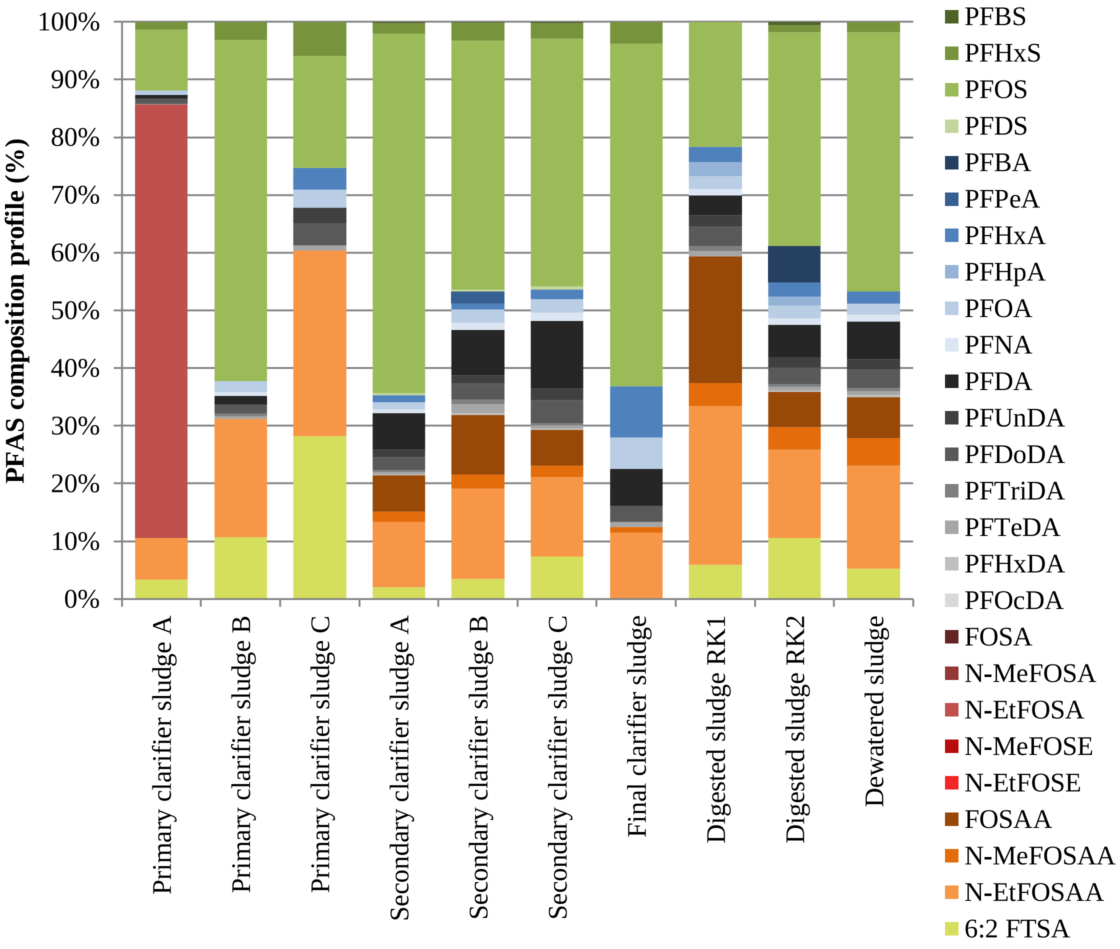

Figure 13 *PFAS composition profile in the different sludge's in Kungsängsverket. There are three treatment lines at Kungsängsverket: A, B and C. "Primary clarifier sludge" refers to the sludge created from the primary clarifier, "Secondary clarifier sludge" to the sludge created from the biological treatment, "Final clarifier sludge" to the sludge created from the chemical treatment, "Digested sludge" to the fully digested sludge from the two digestion chambers RK1 and RK2 and "Dewatered sludge" to the sludge created from sludge dewatering.*

The only PFAS precursors detected in sludge were *N*-EtFOSA (average = 2.6 ng g^{-1} dw, median = 0 ng g^{-1} dw), FOSAA (average = 1.9 ng g^{-1} dw, median = 2.3 ng g^{-1} dw), *N*-MeFOSAA (average = 0.69 ng g^{-1} dw, median = 0.71 ng g^{-1} dw) and *N*-EtFOSAA (average = 4.6 ng g^{-1} dw, median = 4.4 ng g^{-1} dw). PFOS (average = 13 ng g^{-1} dw, median = 11 ng g^{-1} dw) had the highest maximum (38 ng g^{-1} dw) and median concentration (11 ng g^{-1} dw) out of all PFASs detected in sludge, making it the most dominant substance ranging from 11 to 62 % of the ∑PFAS concentration. However, this was not true for primary clarifier sludge A, primary clarifier sludge C and digested sludge RK1, where PFAS precursors was the most dominant group. In primary clarifier sludge A, *N*-EtFOSA was the most dominant substance (75 %), while *N*-EtFOSAA was the most dominant in primary clarifier sludge C (32 %) and digested sludge RK1 (27 %) (Figure 13).

4.3.3 Mass flow

The mass flows and standard deviations (mg d^{-1}) for PFSAs, C_3 – C_8 PFCAs, C_9 – C_{17} PFCAs, FOSAs, FOSAAs and FTSAs in KV (Table A7 in the Appendix) are presented in the figures below (Figure 14, 15, 16 and 17). The PFASs that were not detected in either wastewater or sludge are left out in the mass flow figures. For a more detailed schematic of the different treatment steps, see Figure 1. The mass flows for wastewater and sludge were calculated according to Equation 6 and 7, respectively (Table A5 in the Appendix).

$$\dot{m}\ (mg\ d^{-1}) = Concentration\ (ng\ g^{-1}\ ww) \times\ Density\ (g\ mL^{-1}) \\ \times\ Flow\ (m^3\ d^{-1}) \qquad (7)$$

The mass flows were fluctuating between the different PFASs. In total, the highest mass flows were coming from digested sludge RK2 (∑PFAS = 13,000 mg d^{-1}), followed by second clarifier sludge B (∑PFAS = 12,000 mg d^{-1}) and C (∑PFAS = 12,000 mg d^{-1}). In wastewater, the highest mass flows were coming from the secondary clarifier C (∑PFAS = 7,700 mg d^{-1}), followed by effluent (∑PFAS = 7,000 mg d^{-1}) and influent C (∑PFAS = 4,200 mg d^{-1}).

PFOS and PFHxS had high mass flows of digested sludge RK2, where PFOS had the highest of all PFASs (5,000 mg d^{-1}). An increasing mass flow after the secondary clarifier in wastewater and sludge was found for PFBS, PFHxS and PFOS. PFHxS had the highest influent mass flow of PFSAs (Influent AB: 380 mg d^{-1}, Influent C: 690 mg d^{-1}) (Figure 14).

Neither of the C_3 – C_8 PFCAs was removed completely from the wastewater. All of them, except PFPeA, had high mass flows of digested sludge RK2, where PFBA had the highest (850 mg d^{-1}). PFHpA wasn't detected in any sludge besides digested sludge RK2, also at a higher mass flow (200 mg d^{-1}) than at previous steps. PFPeA was not detected until after the secondary clarifier and the highest influent mass flow of C_3 – C_8 PFCAs was obtained by PFBA (Influent AB: 720 mg d^{-1}, Influent C: 1,500 mg d^{-1}). The highest mass flow of sludge for C_3 – C_8 PFCAs was found in final clarifier sludge for PFHxA (740 mg d^{-1}) and PFOA (460 mg d^{-1}). The mass flow increased after the secondary clarifier in wastewater for all C_3 – C_8 PFCAs, except after secondary clarifier B where it decreased for PFPeA, while the levels in sludge increased. An increase in sludge mass flow after the secondary clarifier was also found for PFHxA, PFOA and PFNA (Figure 15).

For C_9 – C_{17} PFCAs, the mass flow is only evident in the sludge phase. For PFTeDA, however, a small mass flow is detected after the primary clarifier A (3.0 mg d^{-1}). High values in digested sludge RK2 are obtained for PFDA (730 mg d^{-1}), PFUnDA (230 mg d^{-1}) and PFDoDA (390 mg d^{-1}). PFDA had the highest mass flows overall for C_9 – C_{17} PFCAs, where the highest was found in secondary clarifier sludge C (1,500 mg d^{-1}). The mass flow increased after the secondary clarifier in sludge for all C_9 – C_{17} PFCAs (Figure 16).

Of the PFAS precursors, FOSA, *N*-EtFOSAA and 6:2 FTSA were the only ones detected in wastewater mass flow. The other precursors only had detected mass flows in the sludge phase. *N*-EtFOSA was only detected in high mass flows of primary clarifier sludge A (2,500 mg d^{-1}). Highest influent and effluent mass flow of precursors, and of all PFASs, was obtained by 6:2 FTSA (Influent AB: 2,200 mg d^{-1}, Influent C: 1,100 mg d^{-1}, Effluent: 5,000 mg d^{-1}). The mass flow in the effluent for 6:2 FTSA was more than double compared to the influent. An increase in mass flow was found for 6:2 FTSA after secondary clarifier B and C, both in wastewater and sludge. After secondary clarifier A the levels increased in sludge, but decreased in wastewater. For *N*-EtFOSAA, the mass flows increased in sludge and decreased in wastewater after the secondary clarifier, at all lines (Figure 17).

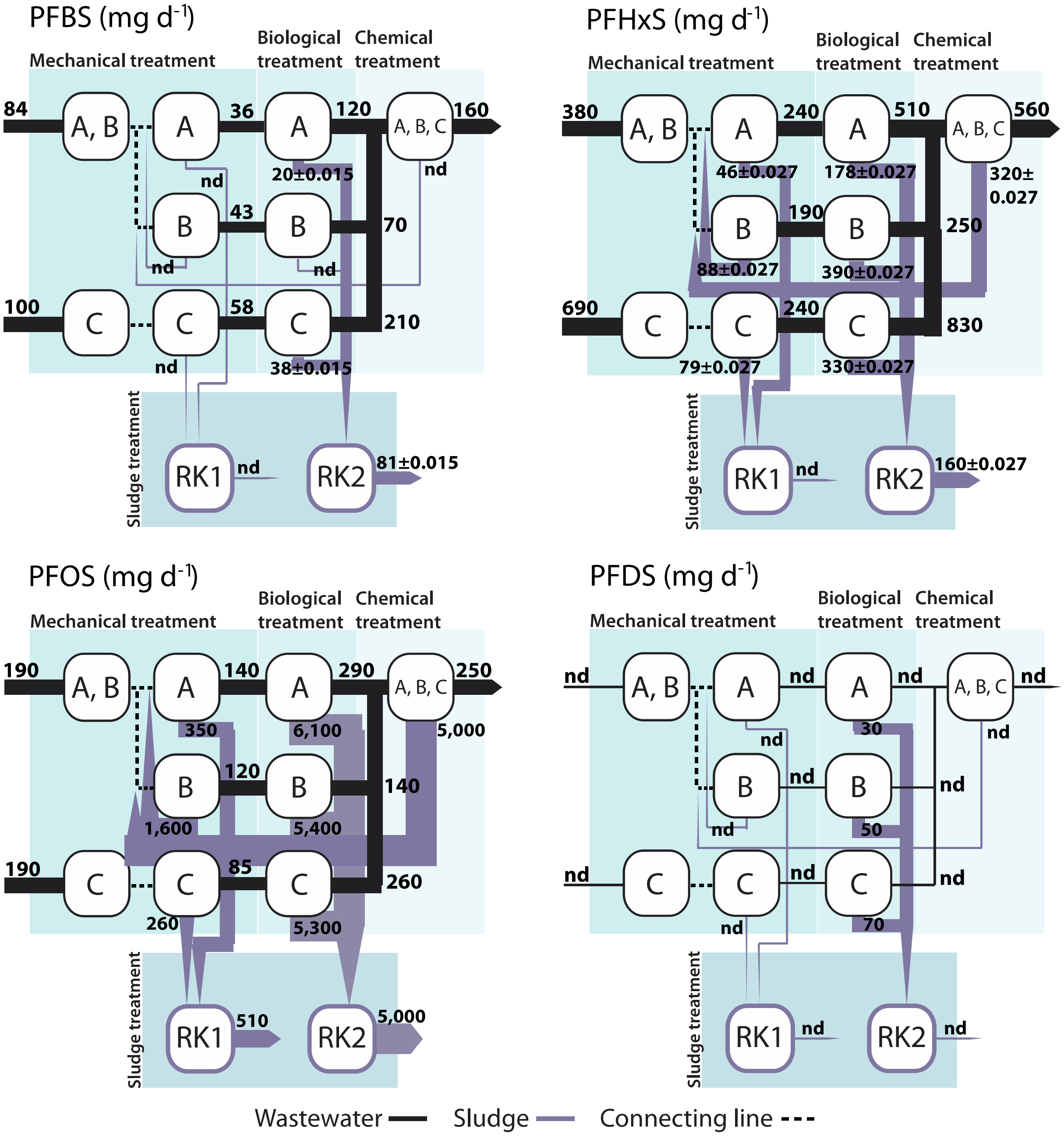

***Figure 14** Mass flows with standard deviations (mg d $^{-1}$) of PFBS, PFHxS, PFOS and PFDS (PFSAs) at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket, A, B and C, with mechanical, biological and chemical treatments. Each treatment step creates sludge, which is sent to the digestion chambers RK1 and RK2 or to another treatment step.*

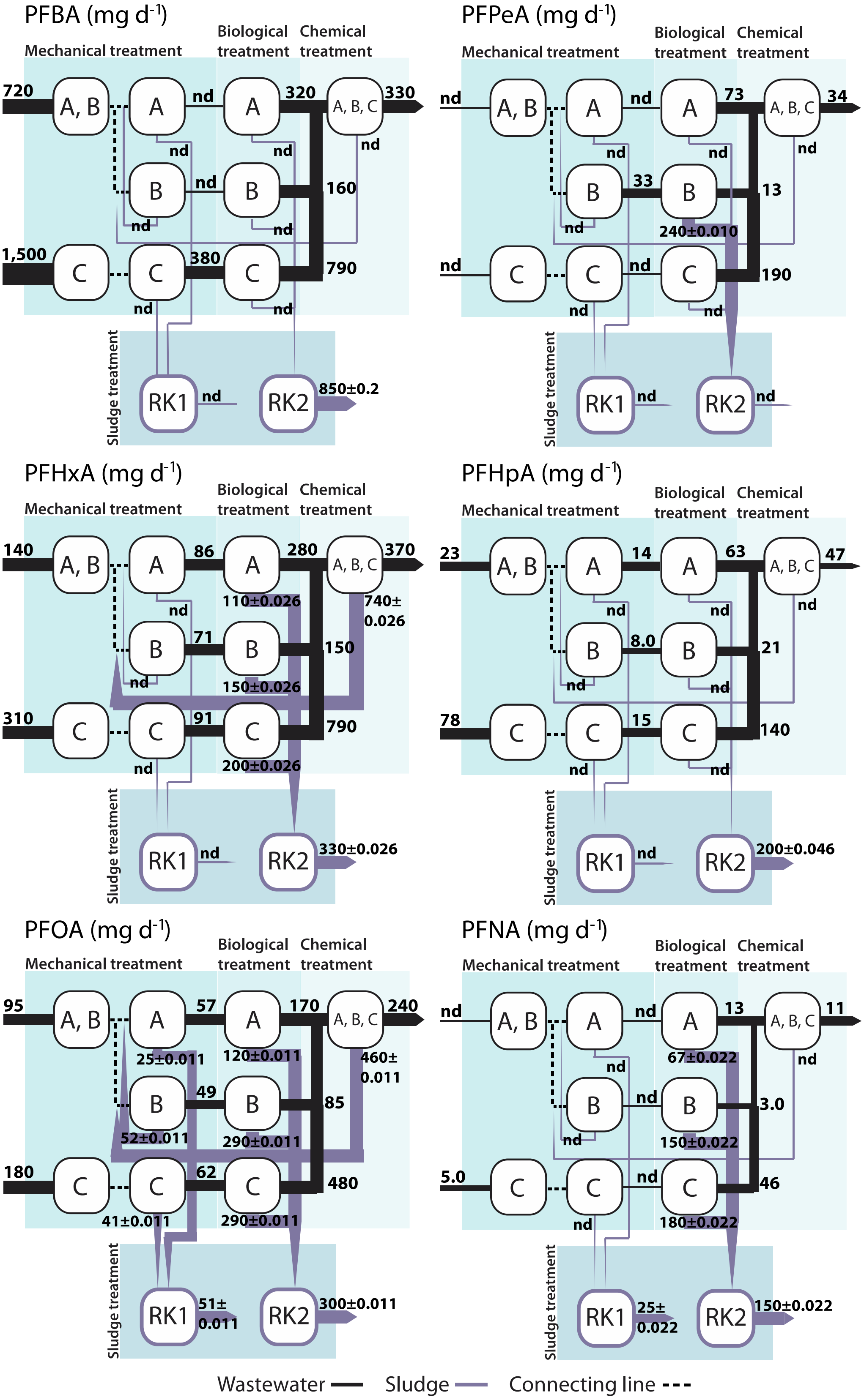

***Figure 15** Mass flows with standard deviations (mg d $^{-1}$) of PFBA, PFPeA, PFHxA, PFHpA, PFOA and PFNA at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket, A, B and C, with mechanical, biological and chemical treatments. Each treatment step creates sludge, which is sent to the digestion chambers RK1 and RK2 or to another treatment step.*

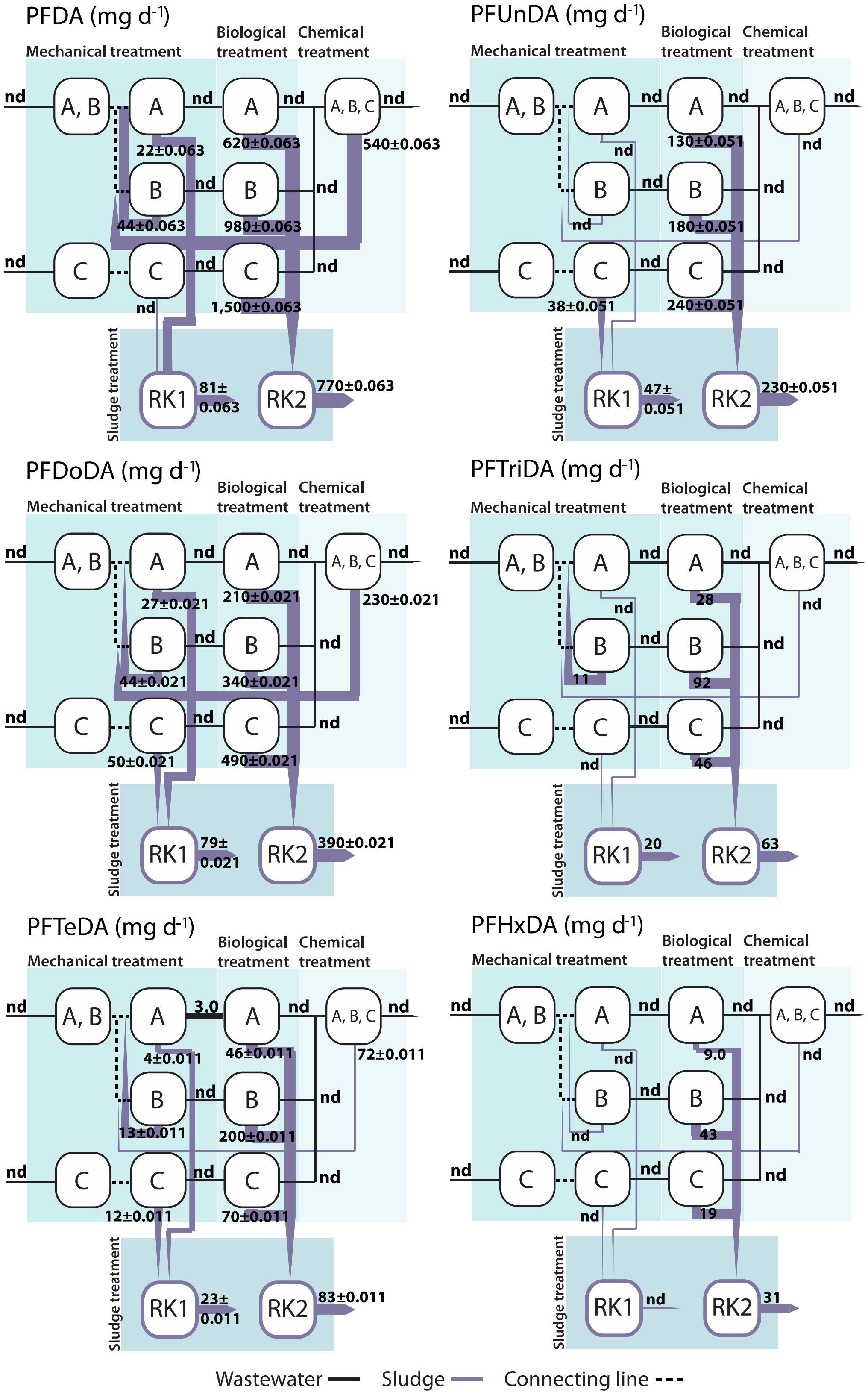

Figure 16 *Mass flows with standard deviations (mg d $^{-1}$) of PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA and PFHxDA at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket, A, B and C, with mechanical, biological and chemical treatments. Each treatment step creates sludge, which is sent to the digestion chambers RK1 and RK2 or to another treatment step.*

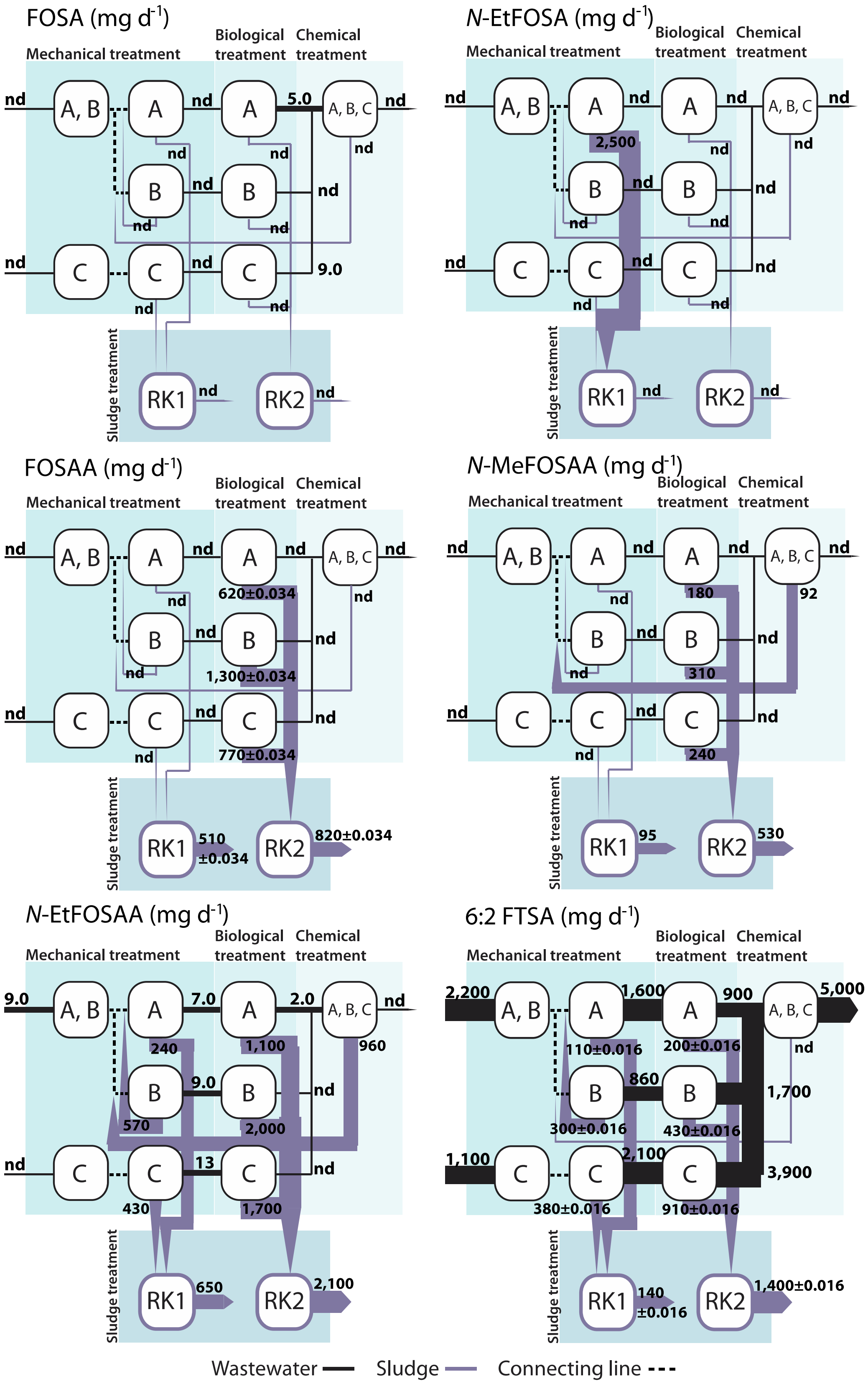

***Figure 17** Mass flows with standard deviations (mg d $^{-1}$) of the PFAS precursors FOSA, N-EtFOSA, FOSAA, N-MeFOSAA, N-EtFOSAA and 6:2 FTSA at the different treatment steps in Kungsängsverket. There are three treatment lines at Kungsängsverket, A, B and C, with mechanical, biological and chemical treatments. Each treatment step creates sludge, which is sent to the digestion chambers RK1 and RK2 or to another treatment step.*

4.3.4 Removal efficiency

The removal efficiency (%) was calculated for each PFAS analyte between the influent and effluent at KV (Equation 8). The removal efficiency was calculated with respect to mass flow (mg d^{-1}) (Table A7 in the Appendix).

$$Removal\ efficiency\ between\ influent\ and\ effluent\ (\%) = \frac{Influent\ AB + Influent\ C - Effluent}{Influent\ AB + Influent\ C} \times 100 \quad (8)$$

The removal efficiencies varied greatly in the WWTP. The overall average removal efficiency between influent and effluent wastewater were -9.4 %. Between influent and effluent wastewater, the smallest removal efficiency was -100 % (PFPeA and PFNA) and the largest 100 % (*N*-EtFOSAA) (Table 9).

In order to investigate whether the wastewater samples were underestimated, ratios between influent, effluent and sludge was calculated (Equation 9 and 10). These ratios were calculated with respect to mass flow (mg d^{-1}) (Table A7 in the Appendix).

$$Influent\ vs\ Effluent\ = \frac{Effluent}{Influent\ AB + Influent\ C} \quad (9)$$

$$Influent\ vs\ Effluent + Sludge = \frac{\text{Effluent+Sludge}}{Influent\ \ AB + Influent\ C} \quad (10)$$

The average ratios between influent, effluent and sludge varied greatly. Overall, there are larger mass flows of PFASs in the influent than in the effluent; the average ratio between influent and effluent was 0.79. Between influent and effluent the smallest ratio was not detected and the largest 2.0. The average ratio between influent, effluent and sludge was 29, meaning that there were generally much larger mass flows of PFASs in sludge than in the influent. The smallest ratio between influent, effluent and sludge was not detected and the largest was 240 (Table 10).

***Table 9** PFAS removal efficiency (%) in Kungsängsverket between influent and effluent wastewater*

Analyte	**Removal efficiency between Influent and Effluent (%)**
PFBS	12
PFHxS	48
PFOS	33
PFDS	nd
PFBA	85
PFPeA	-100
PFHxA	17
PFHpA	54
PFOA	13
PFNA	-100 (-104)
PFDA	nd
PFUnDA	nd
PFDoDA	nd
PFTriDA	nd
PFTeDA	nd
PFHxDA	nd
PFOcDA	nd
FOSA	nd
N-MeFOSA	nd
N-EtFOSA	nd
N-MeFOSE	nd
N-EtFOSE	nd
FOSAA	nd
N-MeFOSAA	nd
N-EtFOSAA	100
6:2 FTSA	-47
Average	-9.4

nd = not detected in influent.

Table 10 *Ratios between Effluent and Influent and (Effluent + Sludge) and Influent*

Analyte	**Effluent / Influent**	**(Effluent + Sludge) / Influent**
PFBS	0.88	1.3
PFHxS	0.52	0.67
PFOS	0.67	14
PFDS	nd	nd
PFBA	0.15	0.52
PFPeA	nd	nd
PFHxA	0.83	1.6
PFHpA	0.46	2.4
PFOA	0.87	1.9
PFNA	2.0	31
PFDA	nd	nd
PFUnDA	nd	nd
PFDoDA	nd	nd
PFTriDA	nd	nd
PFTeDA	nd	nd
PFHxDA	nd	nd
PFOcDA	nd	nd
FOSA	nd	nd
N-MeFOSA	nd	nd
N-EtFOSA	nd	nd
FOSAA	nd	nd
N-MeFOSAA	nd	nd
N-EtFOSAA	0.00	240
N-MeFOSE	nd	nd
N-EtFOSE	nd	nd
6:2 FTSA	1.5	1.9
Average	0.79	29

nd = not detected in influent.

5 DISCUSSION

This study was mostly based on grab samples. The PFAS concentrations and mass flows should therefore be interpreted with care, since they only provide a snap shot and not the full picture of the situation.

5.1 PFASs in the wastewater network

5.1.1 Comparison with earlier studies

The comparisons made below are between influents at WWTPs and PSTs receiving industrial, domestic or mixed wastewater. These were made in order to pinpoint the contamination source of PFASs in Uppsala. No reports on similar studies where PFASs in wastewater networks have been investigated were found on the open literature. It is therefore difficult to compare and discuss the results and find eventual trends.

5.1.2 Domestic versus industrial wastewater

Several researchers found that industrial or mixed wastewater hold higher PFAS concentrations than those dominated by domestic waste (Sinclair and Kannan, 2006; Bossi et al., 2007; Becker et al., 2008; Kim et al., 2012). However, some PSTs that receive domestic wastewater have higher ΣPFAS concentrations (i.e. Bärby hage and Flogsta PST) than some PSTs receiving industrial or mixed wastewater (i.e. Seminaregatan, Strandbodgatan and Tullgarn PST) (Table 1 and Figure 3). Earlier studies (Sinclair and Kannan, 2006; Bossi et al., 2007; Becker et al., 2008; Kim et al., 2012) did not analyze 6:2 FTSA, which is the major component in the wastewater network of Uppsala (Figure 4). This explains why 6:2 FTSA was dominant (average = 52 % of the ∑PFASs, median = 63 % of the ∑PFASs) in this study, whereas in other studies the major PFASs were PFOS (Bossi et al., 2007; Becker et al., 2008) and PFOA (Sinclair and Kannan, 2006; Bossi et al., 2007; Becker et al., 2008; Kim et al., 2012).

PFOS and PFOA were the most dominant substances in both industrial and domestic wastewaters in earlier studies (Kim et al., 2012), where PFOA was more evident in industrial wastewaters and PFOS in domestic (Chen et al., 2012). PFOA was shown to be more evident in industrial (average = 32 ng L^{-1}, median = 39 ng L^{-1}) or mixed (average = 4,000 ng L^{-1}, median = 4.6 ng L^{-1}) wastewater than in domestic (average = 16 ng L^{-1}, median = 6.0 ng L^{-1}). This was true for PFOS as well. Sågargatan PST was the only PST receiving mixed wastewater that had higher PFOA levels (12,000 ng L^{-1} = 22 % of ΣPFAS) than those receiving domestic wastewater. The only PST receiving domestic wastewater with PFOS concentrations higher than for those receiving industrial or mixed wastewater was Bärby hage PST (220 ng L^{-1} = 20 % of ΣPFAS), which also receives wastewater from a known fire-training site. Bärby hage PST excluded, the PFOS levels were generally higher at those PST receiving industrial (average = 19 ng L^{-1}, median = 7.9 ng L^{-1}) or mixed (average = 53 ng L^{-1}, median = 10 ng L^{-1}) wastewater than those receiving domestic (Bärby hage PST excluded, average = 2.5 ng L^{-1}, median = 2.7 ng L^{-1}). The reason to as why the results differs from the results by Chen et al. (2012) with regard to PFOS, may be due to the phase-out of PFOS, where other PFASs have started to emerge as replacements (Glynn et al., 2013; Naturvårdsverket, 2012). 6:2 FTSA is an example of such a substance, which have been replacing PFOS in products like AFFFs (Kemi, 2015). However, the highest levels of 6:2 FTSA were not detected at the PSTs receiving wastewater from fire-training sites (Table 1, Figure 3 and 5).

Skarholmen and Sävja PST showed similar composition profiles (Figure 4). They both receive domestic wastewater, however, the other domestic PSTs (i.e. Bärby hage, Ekeby bruk, Falebro, Flogsta, Seglarvägen and Sundby PST) did not show similar results, which indicate similar activities being held at these locations. Other PSTs receiving domestic wastewater mostly consisted of 6:2 FTSA, where Flogsta PST received the highest levels (540 ng L^{-1} = 1,100 mg d^{-1}) (Figure 3 and 9). There are no reports of AFFF usage at any other PSTs than Bärby hage and Kumlagatan PST (Table 1). Two possible hypotheses, for as to why 6:2 FTSA is detected at other PSTs, could be leaching from fire-training sites (Stock et al., 2007) or an increased usage of 6:2 FTSA in industrial processes and applications as replacement for PFOS (Kemi, 2015).

In the south of Uppsala, the PFSA (PFBS, PFHxS and PFOS) concentrations in purified drinking water range from 3.7 to 5.0 ng L^{-1} (Table 2). In domestic wastewater, in the same area, the concentrations range from 1.1 to 38 ng L^{-1} (Falebro, Seglarvägen, Skarholmen, Sundby, Sävja and Ultuna PST) (Table 1 and Figure 5). This indicates that the PFSA levels in domestic wastewater in the southern parts of Uppsala are not solely from the usage of commercial products and may also originate from purified drinking water. This was also true for PFHxA and PFOA in the southern parts of Uppsala, where the levels in purified drinking water (1.1 – 5.2 ng L^{-1}) seem to have contributed to the levels in domestic wastewater (2.8 – 14 ng L^{-1}) (Table 2 and Figure 5). It is therefore needed to further study the removal efficiency of these substances at the water purification plants that distribute drinking water to the southern parts of Uppsala.

Sågargatan PST (ΣPFAS = 55,000 ng L^{-1} = 110,000 mg d^{-1}) can be seen as a detected hot spot in the wastewater network due to its high concentration and mass flow values, but also due to its contradicting PFAS profile (Figure 3 and 4). The source is unknown, however, the levels could possibly be explained by applications used and/or produced at the industries connected (Table 1). The source cannot be from drinking water due to low PFAS concentrations in purified drinking water in Uppsala (Table 2) compared to the measured values at Sågargatan PST (Figure 3). This analogy can also be drawn to Norra Librobäck PST (ΣPFAS = 2,100 ng L^{-1}) (Figure 3), which had the second highest levels of PFASs in the wastewater network. Norra Librobäck PST receives wastewater dominated by industrial activities (Table 1) and is the only PST with detected levels of *N*-EtFOSA (160 ng L^{-1}). High levels of 6:2 FTSA could also be observed at PSTs receiving industrial wastewater (i.e. Kumlagatan, Norra Librobäck and Seminariegatan PST). This could either be due to usage of 6:2 FTSA in industrial processes and applications as replacement for PFOS (Kemi, 2015) or due to leaching from fire-training sites (Stock et al., 2007), as mentioned above.

5.1.3 Mass flow

The PFAS concentrations from the wastewater network ($\sum$PST: $\sum$PFASs = 110,000 mg d^{-1}) seem to have been diluted when reaching the WWTP influent ($\sum$Influent: $\sum$PFASs = 35,000 mg d^{-1}) (Figure 3 and 10), which is to be expected. However, there were substances which mass flows in the wastewater network seems to have been enhanced, or reduced, when reaching the WWTP influent. Most PFASs had lower mass flows in the WWTP influent than in the wastewater network (PFPeA, PFHxA, PFHpA, PFOA, PFNA, all C_9 – C_{17} PFCAs, FOSAs, FOSEs, FOSAAs and 6:2 FTSA). C_3 – C_8 PFCAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA) had very high mass flows in the wastewater network, ranging from 620 to 39,000 mg d^{-1} in total (Figure 7), which was reduced to ranging from not detected to 440 mg d^{-1} at the WWTP influent (Figure 15). FOSAs, FOSEs and FOSAAs mass flows weren’t reduced as much (Figure 9 and 17). PFASs that had higher mass flows in the WWTP influent than in the wastewater network were: PFBS (∑PST = 130 mg d^{-1}, ∑Influent = 190 mg d^{-1}), PFHxS (∑PST = 680 mg d^{-1}, ∑Influent = 1,100 mg d^{-1}) and PFBA (∑PST = 620 mg d^{-1}, ∑Influent = 2,300 mg d^{-1}) (Figure 6, 7, 14 and 15). It must be noted that the sampling of wastewater at the wastewater network and at KV did not occur on the same day (Table A2 and A3 in the Appendix). The total mass flow in the wastewater network is therefore not expected to be equal to the total mass flow in the WWTP influent. The sudden reduction of the mass flow of C_3 – C_8 PFCAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA) may consequently indicate that the high mass flows from Sågargatan PST are not regular mass flows. Meaning that the high levels of C_3 – C_8 PFCAs at Sågargatan PST that were detected on the 26th of January 2016 can be treated as a point discharge (Figure 3). Analogously, the enhancement of certain mass flows (PFBS, PFHxS and PFBA) may indicate fluctuating PFAS concentrations between the sampling dates. But they could also indicate the occurrence of transformation of these substances within the wastewater network, probably due to precursor degradation.

The mass flows of 6:2 FTSA comes from many different directions in the wastewater network (Figure 9). As mentioned in the previous section, this may either be due to 6:2 FTSA acting as a replacement for PFOS in industrial processes and applications (Kemi, 2015) or due to leaching from fire-training sites (Stock et al., 2007).

5.1.4 PFAS correlation analysis

Strong correlations could be found amongst C_3 – C_8 PFCAs (PFHxA, PFHpA, PFOA and PFNA) ($p < 0.0001$). Weak correlations between PFPeA and the same PFCAs could be found as well ($p < 0.01$). This confirms that the sources of these compounds are related and could act as an indication to the increased usage of shorter chained PFCAs (Kemi, 2015; Svenskt Vatten, 2015). Correlations between PFOS and C_3 – C_8 PFCAs (PFPeA, PFHxA, PFHpA, PFOA and PFNA) could also be found ($p < 0.05$ between PFOS and PFPeA, $p < 0.001$ between PFOS and PFHpA, PFOA, PFNA and $p < 0.0001$ between PFOS and PFHxA), which confirms that the discharges of these compounds are related. PFOS and PFOA has been shown to be the most dominant PFASs in both industrial and domestic wastewaters (Kim et al., 2012), which can be confirmed by Figure 4, where PFOS and C_3 – C_8 PFCAs are evident at all PSTs. The same analogy can be drawn between 6:2 FTSA and C_3 – C_8 PFCAs (PFHxA, PFHpA, PFOA, PFNA), which showed weak correlations ($p < 0.05$).

Weak correlations could be found between PFHxS and PFPeA ($p < 0.05$) and 6:2 FTSA ($p < 0.01$), which can indicate a relation between these discharges. No correlation was found between PFOS and 6:2 FTSA, which indicates that these two substances are not related and do not come from the same source.

5.2 PFASs in Kungsängsverket

5.2.1 Comparison with earlier studies

KV was found to be ineffective in removing PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and 6:2 FTSA from wastewater. This is consistent with the study by Schultz et al. (2006b). Other studies have also shown the unsuccessfulness in removing PFASs by conventional treatment methods (Boulanger et al., 2005; Sinclair and Kannan, 2006; Bossi et al., 2007).

Bossi et al. (2007) investigated the influents and effluents of six different municipal WWTPs regarding PFHxS (Influent: 0.6 – 17 ng L^{-1}, Effluent: <0.2 – 1.0 ng L^{-1}), PFOS (Influent: 2.3 – 7.1 ng L^{-1}, Effluent: <1.5 – 13 ng L^{-1}), PFOA (Influent: 5.5 – 20 ng L^{-1}, Effluent: <2.0 – 18 ng

L^{-1}), PFNA (Influent: <0.8 – 5.0 ng L^{-1}, Effluent: <0.8 – 2.6 ng L^{-1}), PFDA (Influent: <1.6 ng L^{-1}, Effluent: <1.6 – 2.2 ng L^{-1}) and FOSA (Influent: <0.2 – 1.1 ng L^{-1}, Effluent: <0.2 – 1.1 ng L^{-1}). The influent and effluent concentrations were lower at KV (Table A6 in the Appendix), compared to the WWTPs in the study by Bossi et al. (2007), for PFOA, PFNA, PFDA and FOSA. The effluent concentration of PFOS in KV was also lower, while the influent was higher. The only substance that showed higher values in influent and effluent was PFHxS.

At KV, PFOA increased between influent AB and the effluent, while PFHxS, PFOS, PFNA, PFDA and FOSA decreased. The reason for substances like PFOA to increase in concentration could be the presence of PFOA precursors (Sinclair and Kannan, 2006), such as FTOHs, which was not analyzed in this study. In earlier studies, the concentration of PFOS increased between influent and effluent as well (Boulanger et al., 2005; Sinclair and Kannan, 2006; Bossi et al., 2007). In these studies, the PFAS concentrations were generally lower compared to the situation in KV (Boulanger et al., 2005; Sinclair and Kannan, 2006; Bossi et al., 2007).

In sludge, Bossi et al. (2007) detected PFHxS (average = 4.0 ng g^{-1} dw), PFOS (average = 20 ng g^{-1} dw), PFOA (average = 3.0 ng g^{-1} dw), PFNA (average = 2.0 ng g^{-1} dw), PFDA (average = 7.5 ng g^{-1} dw), PFUnDA (average = 2.0 ng g^{-1} dw) and FOSA (average = 1.0 ng g^{-1} dw) in all six WWTPs. The PFAS concentrations in sludge at KV were generally lower for all these substances (Table A6 in the Appendix) than at the WWTPs in the study by Bossi et al. (2007). However, C_9 – C_{17} PFCAs tend to be in higher concentrations in sludge than C_3 – C_8 PFCAs. C_9 – C_{17} PFCAs have therefore a higher tendency to transfer to sludge, which can be confirmed by the increasing sediment-water partition coefficient with increasing chain-length (Schultz et al., 2006b). Even-chained PFCAs tend to transfer to sludge more frequently than odd-chained (Bossi et al., 2007), which can be confirmed in this study, since the concentration of PFOA and PFDA is larger than PFNA and PFUnDA, respectively, in sludge (Figure 12). PFOS was the most dominant substance in sludge at KV, which can be confirmed by earlier studies (Bossi et al., 2007).

An increase in concentration could be found across the second clarifier, which may be due to degradation of precursors (Schultz et al., 2006b). Known PFAS precursors, such as FOSAs, FOSEs and FOSAAs, were either not detected or detected at low concentrations in wastewater at KV, where FOSEs were not detected at all. These precursors may have been present in the particulate phase, since only the dissolved phase was analyzed. In a study by Boulanger et al. (2005), *N*-EtFOSE was similarly not detected in wastewater, but was still shown to degrade into *N*-EtFOSAA during aerobic treatment in the ASP. *N*-EtFOSE can be generated by hydrolysis during aerated conditions in the ASP (Lange, 2000), which could explain why it was not detected in wastewater. It is important to further study the presence of these substances in wastewater, especially during the biological treatment (Schultz et al., 2006b). However, the concentrations of *N*-EtFOSAA did not seem to increase across the second clarifier in KV (Figure 9). This may be explained by the hydraulic residence time, which earlier studies have shown to have an impact on the degradation of *N*-EtFOSE or *N*-EtFOSAA to PFOS, due to its time dependence. This can be confirmed by the moderately low variety between influent and effluent for PFOS in KV. The presence of PFOS within the WWTP can consequently be concluded to come from the wastewater network and an upstream source and not from within the WWTP (Boulanger et al., 2005). This theory can be further projected onto other analyzed PFASs.

5.2.2 Domestic versus industrial wastewater

It is important to further study how the PFASs in WWTP effluents affect the aquatic environment. WWTP effluents are seen as a major source of PFASs into the environment (Loos et al., 2013; Naturvårdsverket, 2016), however, the effluents contribute to a diffuse influence on water recipients and in soil where sludge is spread. Possible measures to decrease discharges of PFASs into the environment are to further enhance the upstream work or to focus on extended treatment steps (Naturvårdsverket, 2016).

WWTPs treating municipal wastewater, a mixture of industrial and domestic wastewater, tend to have higher PFAS concentration than WWTP treating only domestic or only industrial wastewater. The influence industrial wastewater has on the PFAS levels in such WWTPs are therefore important (Guo et al., 2010), but not fully understood. The reason could possibly be that industries are located near municipal WWTPs (Kim et al., 2012), which is the case in this study (Figure 2). This industrial influence has been found to affect the mass flow in WWTPs as well, making it considerably larger (Sinclair and Kannan, 2006). The influence industrial wastewater has on the PFAS levels and mass flow within the WWTP point on the importance of upstream work. There is a trend to disconnect industrial operations from the wastewater network, which Naturvårdsverket supports. The idea is that these industrial operations will be completely in charge of their own wastewater treatment with a local WWTP (Naturvårdsverket, 2016).

5.2.3 Mass flow

Since PFASs are known to be extremely resistant to any kind of degradation (Buck et al., 2011; Naturvårdsverket, 2012) they are not expected to be degraded by an ASP (Sinclair and Kannan, 2006).The PFAS levels and mass flows generally increase after the second clarifier in both wastewater and sludge, which is consistent with previous studies where the mass flow of PFOS increased after the ASP in the second clarifier effluents and sludge (Schultz et al., 2006b; Becker et al., 2008). The mass flows of PFOS in the WWTP effluents was higher in the study by Becker et al. (2008) (3,000 mg d^{-1}), than in studies by Sinclair and Kannan (2006) (1,500 mg d^{-1}) and Schultz et al. (2006b) (600 mg d^{-1}). Where the last holds similar mass flows to what has been detected at KV (250 mg d^{-1}). However, the sludge mass flows were lower for PFOS in the study by Schultz et al. (2006b) (average = 210 mg d^{-1}) than at KV (average = 3,300 mg d^{-1}) (Figure 14).

Decreases in mass flow across the primary clarifier were in general found for PFSAs, C_3 – C_8 PFCAs and 6:2 FTSA. An increase across the second clarifier was found for PFSAs and C_3 – C_8 PFCAs as well, which may be due to degradation of precursors (Schultz et al., 2006b) (Figure 14 and 15).

At KV, final clarifier sludge goes to primary clarifier B, whose sludge in its turn goes to primary clarifier A. The recycling of sludge may cause mass flows to be rather consistent across the treatment steps (Schultz et al., 2006b), which is the case for several PFASs, such as PFHxS, PFOS, PFHxA, PFOA, *N*-EtFOSAA and 6:2 FTSA. This might explain the high concentrations and mass flows of *N*-EtFOSA in sludge from primary clarifier A (Figure 13 and 17).

The PFAS mass flows are generally high out of digestion chamber RK2, which receives sludge from the second clarifier and fully anaerobically digested sludge from the primary clarifier (See section ‘Mass flow’ in ‘PFASs in Kungsängsverket’). The digestion chamber RK1, which receives sludge from the primary clarifier, shows no such trends. This kind of behavior is consistent with earlier studies, where it could either be due to residence time in the digestion chamber, which causes variations in mass flow, or degradation of precursors that causes these excessive mass flows of anaerobically digested sludge (Schultz et al., 2006b). However, this trend is apparent for the precursors FOSAA and 6:2 FTSA as well, both in digestion chamber RK1 and RK2 (Figure 17), implying that these precursors are not the ones that undergo degradation. Samples were only taken of second clarifier sludge and anaerobically digested sludge. No samples were taken of thickened sludge. Also, primary clarifier sludge isn't thickened in a certain chamber before going into digestion; a sample of thickened primary clarifier sludge was therefore not possible (Figure 1). It is therefore not possible to see if the mass flow increases due to anaerobic digestion or not (Schultz et al., 2006b).

The average removal efficiency, between influent and effluent, for all detected PFASs in the influent was -9.4 % (Table 9). One substance had a removal efficiency lower than -100 % (PFNA), which indicates the presence of precursor degradation into PFNA. Again, it should be noted that only the dissolved phase was analyzed in wastewater, which is why ratios between influent, effluent and sludge was calculated (Table 10). The average ratio between influent and effluent was 0.79 and the average between influent, effluent and sludge was 29. These ratios indicate that the influent mass flows of PFASs are indeed underestimated, since the particle bound concentration and the degradation of precursors are unknown. When comparing the PFAS mass flows in the dissolved phase of wastewater with the mass flows of sludge, the results indicate a heavy increase in mass flow (e.g. Figure 17). But in reality, if the particulate phase in wastewater would have been analyzed, the results could have indicated that PFASs in fact were removed by sludge. Earlier studies have shown that PFOS tend to be removed by sludge (22 %) (Chen et al., 2012). Consequently, the risk of spreading PFAS contaminated sludge in agriculture would also need to be investigated, since this enables remobilization of PFASs due to their extreme persistency (Schröder and Meesters, 2005). Analysis of the particulate phase in wastewater would enable a more detailed removal efficiency data to be achieved. However, since the dissolved phase was not removed to a large extent (Table 9), it is most likely that the same trend would have been shown for the particulate phase. From the available data, the general trend seems to be for PFASs to increase in mass flow (Table 9). However, this is true for PFAS precursors as well. PFAS precursors had a small contribution of the ∑PFASs in the WWTP network (average = 5.9 %) and KV (average = 6.3 %) indicating that PFAS precursors have a low relevance as a source for PFCAs and PFSAs or that the PFAS precursors have been already degraded when they reached the PST or there are other precursors than the ones analyzed in this study (e.g. FTOH). The importance to further study the presence of precursors within the WWTP therefore remains (Boulanger et al., 2005).

One substance that was detected in the WWTP influents, *N*-EtFOSAA (Influent AB: 8.7 mg d^{-1}, Influent C: nd), was completely removed (100 %) and was not detected in the effluent (Table 9). However, it is not clear whether it was removed by degradation or by dilution due to the very low mass flows. Also, *N*-EtFOSAA hasn't been removed in earlier studies, where the average removal efficiency was 29 % (Boulanger et al., 2005).

5.2.4 Moisture, dry and organic matter

In this section, trends in moisture, dry and organic matter data are explained. No reports on moisture, dry and organic matter in sludge from a municipal WWTP have been found on the open literature. These data should therefore be interpreted with care.

The calculated dry weights, moisture and organic matter contents of the different sludge samples in KV can provide further information about the mass flows of PFASs in sludge

(Table A4 in the Appendix). It should be noted that during the determination of sludge density, the density of final clarifier sludge was set equal to the density of secondary clarifier sludge B, due to sample shortage (Table A5 in the Appendix). The mass flows of final clarifier sludge should therefore be interpreted with care.

In comparison between sludge with high and low TS-content, those with high TS-content generally had lower mass flows in KV. The highest TS content was found in primary clarifier sludge A (18 %), followed by primary clarifier sludge C (15 %), second clarifier sludge A (10 %), digested sludge RK1 (12 %) and RK2 (12 %), which suggests that high mass flows should be found for these sludge's. However, the trend seemed to be the opposite. The mass flows were generally higher for primary clarifier sludge B than for primary clarifier sludge A and C, for all PFASs. Except *N*-EtFOSAA, which was only detected at high mass flows in primary clarifier sludge A (2,500 mg d^{-1}), and 6:2 FTSA, where primary clarifier sludge C had higher mass flows (380 mg d^{-1}) (Figure 17). The same trend could be observed for second clarifier sludge, where second clarifier sludge B and C generally had higher mass flows than second clarifier sludge A. With one exception (i.e. PFOS), PFOS had higher mass flows of second clarifier sludge A (6,100 mg d^{-1}) than B (5,400 mg d^{-1}) and C (5,300 mg d^{-1}) (Figure 14). This suggests that the TS-content in sludge influences the mass flows when the mass flows are very high. However, this proposition has not been verified in earlier studies found on the open literature.

5.3 Uncertainties during sampling and laboratory work

The uncertainties during the sampling process and laboratory work are described below in order to understand why the results would deviate from earlier studies or be inconsistent.

Since PFASs are surfactants, they tend to occur in higher concentrations near the water surface. At some sampling locations in the wastewater network, the water level was too low to completely fill the sampling device and the top layer (< 30 cm) was therefore sampled. At other locations, the sampling device was completely filled, but just below the surface, the top layer (< 60 cm) was therefore sampled at these PSTs as well. The sampling locations where the PFAS concentrations might be overestimated were: Seminaregatan, Seglarvägen and Sundby PST.

At the beginning of the sampling, the sampler were not rinsed in-between the sampling locations, due to forgetfulness. However, since the wastewater was already contaminated, any cross-contamination between the samples are not likely. The sampling locations where the sampler was not rinsed were: Sågargatan, Skarholm, Sävja, Seglarvägen, Kumlagatan, Falebro, Ultuna and Sundby PST.

Some of the samples of wastewater in KV, which were flow-proportional samples, were taken between 10.00 and 24.00 o'clock due to technological issues. These samples were: primary clarifier A, B and C and secondary clarifier A, B and C. The other samples were taken between 00.00 and 24.00 o'clock. The wastewater samples in the wastewater network were filled into PP-bottles once, rinsed and then filled again. The wastewater samples in KV did not contain enough sample water to rinse the PP-bottle.

During the SPE analysis of wastewater, the SPE cartridges got dry (Primary clarifier A, Seminariegatan PST, Ekeby bruk PST and Ultuna PST), the FXIS11 was not vortexed (Primary clarifier A, Flogsta PST, Seminariegatan PST, Ekeby bruk PST, Seglarvägen PST, Kumlagatan PST, Falebro PST and Ultuna PST) and one sample stood still over the weekend, due to clogging (Norra Librobäck PST).

During the SLE analysis, the homogenized samples did not contain 3 g as requested, the samples ranged instead from 0.9 to 2 g and the sludge sample triplicates were divided into three before entering the homogenizer (final clarifier sludge, digested sludge RK2 and dewatered sludge). However, the sludge samples were homogenized with a spoon before entering the freeze-dryer. This may explain the varying difference percentages between duplicates and triplicates (Table 7). One of the triplicate samples did not contain any ceramic beads while in the homogenizer, however, the sample looked homogenized afterwards (digested sludge RK2). The SLE analysis was not supposed to be disrupted, but due to time issues the analysis was disrupted and the samples were put in the freezer until further analysis the next day. Some of the supernatants were kept in the PP-tube to keep the sample moist. During the last step of the SLE analysis, one of the triplicate samples broke in the centrifuge, making it a duplicate sample instead (primary clarifier sludge A). Another sample broke as well, but not completely. Some of the sample could be recovered (2 mL) (digested sludge RK2). The sludge sample from the final clarifier got lost on the way. An extra extraction was therefore made for this sample and was divided into three parts in order to make up for the loss of the other sample that broke in the centrifuge.

5.4 Ideas for improvements and future perspectives

There are several points in this study that could be improved. These include evaluation and improvement of the grab sampling method and the analysis of both the dissolved and the particulate phase in wastewater. The accuracy of the grab sampling method could be evaluated by taking grab samples at two different time points at the same location. Taking several samples at suspected hot spots could also eliminate the possibility of receiving extreme values when using grab sampling. This is also necessary in order to evaluate the occurrence of point discharges within the wastewater network. Another possibility could also be to take samples under a longer time interval, e.g. time-integrated sampling (like at Tullgarn and Strandbodgatan PST). Further improvements could be made by analyzing the particulate phase in wastewater. Only analyzing the dissolved phase in wastewater creates certain PFASs, such as C_9 – C_{17} PFCAs, to be underestimated. It also enables a more detailed understanding of the sludge removal of PFASs within the WWTP.

The difficulty in the identifications of which PFASs are used where (Kemi, 2015) creates the need and demand on further research regarding the usage and discharges of PFASs. But also to how these can be regulated (Naturvårdsverket, 2016). More studies on a large number of PFASs before and after several treatment steps in WWTP are needed. It is particularly important to study the fate of PFASs in WWTPs, but also to study precursor degradation and partitioning onto sludge. These studies also need to calculate mass flows and study both the dissolved and particulate phase of PFASs in wastewater, similar to the study by Schultz et al. (2006b). It is not only needed studies on conventional WWTPs, but also on those with unconventional treatment processes, like the studies made by Ochoa-Herrera and Sierra-Alvarez (2008), Tang et al. (2006) and Yu et al. (2014).

Further sampling across the biological treatment is needed both in aerated and anoxic basins, in order to track the occurrence of precursors, such as *N*-EtFOSE, during the ASP. Since it seems like digestion of sludge brings high PFAS mass flows (Schultz et al., 2006b), which couldn’t be concluded to be the case at KV, additional sampling across the digestion chamber is needed. It is also important to further investigate how the WWTP effluents affect the environment, the aquatic environment and the drinking water quality with respect to PFASs. As well as to how the usage of PFAS contaminated sludge in agriculture affect the remobilization of PFASs into the environment.

6 CONCLUSIONS

Prevalent levels of 6:2 FTSA in wastewater and a detected hot spot in the wastewater network, with point discharges of C_3 – C_8 PFCAs (Sågargatan), were found. The prevalent levels of 6:2 FTSA in wastewater indicates the increased usage of 6:2 FTSA in industrial processes and applications as replacement for PFOS and/or leaching from fire-training sites.

The WWTP was ineffective in removing C_4, C_6, C_8 PFSAs, C_3 – C_8 PFCAs and 6:2 FTSA from wastewater. It was shown that C_9 – C_{17} PFCAs tend to partition onto sludge to a larger extent than C_3 – C_8 PFCAs, where even-chained PFCAs tend to transfer to sludge more frequently than odd-chained. The concentrations and mass flows tended to increase across the second clarifier in both wastewater and sludge, probably due to precursor degradation.

Drinking water could be seen as a source to C_4, C_6, C_8 PFSAs, but also to C_6 and C_8 PFCAs, in domestic wastewater in southern parts of Uppsala. The source of PFASs in Uppsala's wastewater comes from both industrial applications and commercial products.

Future research regarding PFASs in wastewater is necessary. The sources of PFASs in wastewater, PFASs fate in wastewater treatment, biodegradation of precursors in both aerobic and anoxic zones, alternatives to the conventional treatment methods, how PFASs in the WWTP effluents affect the recipient and also how they affect the drinking water quality are fields that needs to be researched further.

The hypotheses mentioned in the beginning will be tested below:

"*The sampling locations in the wastewater network that receive wastewater from industries will hold higher concentrations of PFASs compared to wastewater dominated by domestic waste.*"

Some PSTs receiving domestic wastewater, Bärby hage and Flogsta PST, have had higher ΣPFAS concentrations than some PSTs that receive industrial or mixed wastewater. However, it should be noted that the highest ΣPFAS concentration detected in the wastewater network of Uppsala comes from a PST that receives mixed wastewater (Sågargatan PST). It should also be noted that Bärby hage PST does not only receive domestic wastewater but also wastewater from a known fire-training site.

"*The composition profile of PFASs and the mass flow data can be used to pinpoint PFAS contamination sources for wastewater.*"

From PFAS composition profiles and mass flow data, the contamination source in Uppsala of PFASs in wastewater have been shown to come from both wastewater dominated by domestic waste and industrial applications.

However, it is recommended to sample and analyze PSTs with high PFAS levels further. Such PSTs were Flogsta, Bärby hage, Norra Librobäck, Kumlagatan and Sågargatan PST, where Sågargatan PST has the highest priority. Sågargatan PST can be seen as a detected hot spot in the wastewater network with point discharges of C_3 – C_8 PFCAs. Flogsta PST is also important to investigate further, due to high concentrations of 6:2 FTSA compared to other PSTs receiving wastewater dominated by domestic waste.

"*The concentrations of perfluoroalkylated sulfonic acids (PFSAs) and perfluoroalkylated carboxylic acids (PFCAs) will be similar or higher in the effluent compared to the influent due to poor removal efficiency in the wastewater treatment plant and degradation of PFAS precursors.*"

PFSAs and PFCAs tend to be similar or lower in concentration in the effluent compared to the influent due to poor removal efficiency. This is also true with regard to mass flow. Whether PFSAs and PFCAs could be removed by sludge cannot be determined, since the particulate phase of wastewater was not analyzed. However, large mass flows of PFASs in sludge were found.

7 REFERENCES

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7.3 Personal messages

Uppsala Vatten och Avfall, 2016a. Kungsängsverket.

Uppsala Vatten och Avfall, 2016b. Pumpningsstationer.

Uppsala Vatten och Avfall, 2016c. Treatment process.

Uppsala Vatten och Avfall, 2016f. PFAS Background levels in drinking water.

8 APPENDIX

***Table A1** Labeling of the samples in KV from Uppsala Vatten's standards* (*Uppsala Vatten och Avfall, 2016c)*

Sample ID	Swedish translation	Explanation
Influent AB	Inkommande AB	Channel before grid rough Treatment AB
Influent C	Inkommande C	Channel before grid rough Treatment C
Primary clarifier A	Försed A	Effluent water from primary clarifier A
Primary clarifier B	Försed B	Effluent water from primary clarifier B
Primary clarifier C	Försed C	Effluent water from primary clarifier C
Secondary clarifier A	Biosed A	Effluent water from secondary clarifier A
Secondary clarifier B	Biosed B	Effluent water from secondary clarifier B
Secondary clarifier C	Biosed C	Effluent water from secondary clarifier C
Effluent	Utgående	Effluent water from the treatment plant
Primary clarifier sludge A	Primärslam A	Primary clarifier sludge from primary clarifier A
Primary clarifier sludge B	Primärslam B	Primary clarifier sludge from primary clarifier B
Primary clarifier sludge C	Primärslam C	Primary clarifier sludge from primary clarifier C
Secondary clarifier sludge A	Bioslam A	Secondary clarifier sludge from secondary clarifier A
Secondary clarifier sludge B	Bioslam B	Secondary clarifier sludge from secondary clarifier B
Secondary clarifier sludge C	Bioslam C	Secondary clarifier sludge from secondary clarifier C
Final clarifier sludge	Kemslam	Final clarifier sludge from final sedimentation
Digested sludge RK1	Rötslam RK1	Digested sludge from digestion chamber 1 (primary clarifier sludge)
Digested sludge RK2	Rötslam RK2	Digested sludge from digestion chamber 2 (fully digested primary clarifier sludge and thickened secondary clarifier sludge)
Dewatered sludge	Avvattnat slam	Dewatered sludge from centrifuge (Noxon)
Dewatering - Reject water	Rejektvatten	Reject water from sludge dewatering (Noxon)

Table A2 *Sampling of wastewater at the pumping stations (PSTs) in Uppsala's wastewater network, how they were taken, when and where, together with the daily flow ($m^3\ d^{-1}$)*

Pumping station	**Description**	**Date**	**Time (h)**	**Latitude**	**Longitude**	**Flow ($m^3\ d^{-1}$)**
Boländerna	Grab sample	16-01-26	-	59°50'38''N	17°40'27''E	m.m.
Bärby hage	Grab sample	16-01-26	-	59°52'41''N	17°36'39''E	590
Ekeby bruk	Grab sample	16-01-26	-	59°50'49''N	17°36'27''E	10
Falebro	Grab sample	16-01-26	-	59°49'34''N	17°43'40''E	88
Flogsta	Grab sample	16-01-26	-	59°50'47''N	17°35'4''E	2,076
Kumlagatan	Grab sample	16-01-26	-	59°50'21''N	17°43'49''E	10
Norra Librobäck	Grab sample	16-01-26	-	59°52'23''N	17°35'14''E	32
Seglarvägen	Grab sample	16-01-26	-	59°47'15''N	17°38'2''E	43
Seminariegatan	Grab sample	16-01-26	-	59°52'13''N	17°37'39''E	232
Skarholmen	Grab sample	16-01-26	-	59°47'13''N	17°36'54''E	352
Strandbodgatan	Time-integrated sample	16-01-28	24	59°51'22''N	17°39'14''E	10,000[a]
Sundby	Grab sample	16-01-26	-	59°49'54''N	17°41'32''E	145
Sågargatan	Grab sample	16-01-26	-	59°50'53''N	17°39'16''E	1,909
Sävja	Grab sample	16-01-26	-	59°49'47''N	17°41'37''E	1,443
Tullgarn	Time-integrated sample	16-01-28	24	59°50'60''N	17°38'53''E	23,936
Ultuna	Grab sample	16-01-26	-	59°48'47''N	17°39'56''E	608

[a] Estimated value due to flow measurement missing
m.m. = measurement missing

***Table A3** Sampling of wastewater and sludge in Kungsängsverket, how they were taken, when they were taken, together with the daily flow ($m^3\ d^{-1}$)*

Kungsängsverket

Treatment step	Description	Date	Time (h)	Flow ($m^3\ d^{-1}$)
Influent AB	Flow-proportional sample	16-01-25	24	20,594[b]
Influent C	Flow-proportional sample	16-01-25	24	20,476[b]
Into primary clarifier A	Flow-proportional sample	16-01-25	14	10,908[b]
Into primary clarifier B	Flow-proportional sample	16-01-25	14	10,753[b]
Into primary clarifier C	Flow-proportional sample	16-01-25	14	20,476[b]
Out of secondary clarifier A	Flow-proportional sample	16-01-25	14	6,243[b]
Out of secondary clarifier B	Flow-proportional sample	16-01-25	14	14,351
Out of secondary clarifier C	Flow-proportional sample	16-01-25	14	20,476
Effluent	Flow-proportional sample	16-01-25	24	41,070
Reject water	Grab sample	16-01-20	24	m.m.
Sludge				
Primary clarifier sludge A	Grab sample	16-01-20	-	79
Primary clarifier sludge B	Grab sample	16-01-20	-	140[a]
Primary clarifier sludge C	Grab sample	16-01-20	-	143
Secondary clarifier sludge A	Grab sample	16-01-20	-	150[a]
Secondary clarifier sludge B	Grab sample	16-01-20	-	200
Secondary clarifier sludge C	Grab sample	16-01-20	-	218
Final clarifier sludge	Grab sample	16-01-20	-	882
Digested sludge RK1	Grab sample	16-01-20	-	160
Digested sludge RK2	Grab sample	16-01-20	-	301
Dewatered sludge	Grab sample	16-01-20	-	m.m.

[a] Estimated flow due to flow measurement missing
[b] Calculated flows
m.m. = measurement missing

Table A4 *Moisture (%), dry matter (TS) and organic matter (OM) in the solid phase*

Sludge samples	Moisture (%)	TS (%)	OM (%)
Primary clarifier sludge A	82	18	90
Primary clarifier sludge B	91	9.5	83
Primary clarifier sludge C	85	15	86
Secondary clarifier sludge A	90	10	75
Secondary clarifier sludge B	91	8.6	80
Secondary clarifier sludge C	94	5.9	67
Final clarifier sludge	97	3.5	50
Digested sludge RK1	88	12	67
Digested sludge RK2	88	12	67
Dewatered sludge	68	32	67

$$Moisture = \frac{filled\ bottle\ before\ burning\ (g) - weight\ after\ 105°C\ (g)}{filled\ bottle\ before\ burning\ (g) - empty\ bottle\ (g)} \times 100\ (\%)$$

$$TS = \frac{weight\ after\ 105°C\ (g) - empty\ bottle\ (g)}{filled\ bottle\ before\ burning\ (g) - empty\ bottle\ (g)} \times 100\ (\%)$$

$$OM = \frac{weight\ after\ 105°C\ (g) - weight\ after\ 550°C}{weight\ after\ 105°C\ (g) - empty\ bottle\ (g)} \times 100\ (\%)$$

Table A5 *Calculated density (g mL^{-1}) for different sludge*

Sludge name	Density (g mL^{-1})
Primary clarifier sludge A	0.99
Primary clarifier sludge B	1.1
Primary clarifier sludge C	1.1
Secondary clarifier sludge A	0.96
Secondary clarifier sludge B	1.1
Secondary clarifier sludge C	1.1
Final clarifier sludge	0.96[a]
Digested sludge RK1	1.1
Digested sludge RK2	1.1
Dewatered sludge	0.86

[a] No sludge sample left to determine density, estimated to have the same density as Secondary clarifier sludge A

$$Density\ (g\ mL^{-1}) = Sample\ weight\ (g) \div Sample\ volume\ (ml)$$

***Table A6** PFAS concentrations with standard deviations (ng L^{-1}) in wastewater and sludge at Kungsängsverket and in wastewater in the wastewater network of Uppsala*

Analyte (ng L-1) / Treatment step	PFBS	PFHxS	PFOS	PFDS	PFBA	PFPeA	PFHxA	PFHpA	PFOA
Influent AB	4.1 ± 0	19 ± 0	9.0 ± 0	nd	35 ± 0	nd	6.5 ± 0	1.1 ± 0	4.6 ± 0
Influent C	4.9 ± 0	34 ± 0	9.1 ± 0	nd	75 ± 0	nd	15 ± 0	3.8 ± 0	8.9 ± 0
Primary clarifier A	3.3 ± 0	22 ± 0	13 ± 0	nd	nd	nd	7.9 ± 0	1.3 ± 0	5.3 ± 0
Primary clarifier B	4.4 ± 0	20 ± 0	12 ± 0	nd	nd	3.4 ± 0	7.4 ± 0	0.84 ± 0	5.0 ± 0
Primary clarifier C	2.8 ± 0	12 ± 0	4.2 ± 0	nd	19 ± 0	nd	4.4 ± 0	0.72 ± 0	3.0 ± 0
Secondary clarifier A	20 ± 0	82 ± 0	46 ± 0	nd	51 ± 0	12 ± 0	44 ± 0	10 ± 0	28 ± 0
Secondary clarifier B	4.9 ± 0	17 ± 0	9.5 ± 0	nd	11 ± 0	0.93 ± 0	10 ± 0	1.4 ± 0	5.9 ± 0
Secondary clarifier C	10 ± 0	40 ± 0	13 ± 0	nd	39 ± 0	9.1 ± 0	38 ± 0	6.7 ± 0	23 ± 0
Dewatering - reject water	1.9 ± 0	5.7 ± 0	1.9 ± 0	nd	nd	nd	39 ± 0	4.8 ± 0	4.0 ± 0
Effluent	4.0 ± 0	14 ± 0	6.1 ± 0	nd	8.1 ± 0	0.83 ± 0	8.9 ± 0	1.1 ± 0	5.9 ± 0

Analyte (ng L-1) / PST	PFBS	PFHxS	PFOS	PFDS	PFBA	PFPeA	PFHxA	PFHpA	PFOA
Boländerna	6.3 ± 0	39 ± 0	8.6 ± 0	nd	33 ± 0	25 ± 0	22 ± 0	5.4 ± 0	20 ± 0
Bärby hage (a)	11 ± 0	155 ± 0	221 ± 0	nd	35 ± 0	80 ± 0	74 ± 0	37 ± 0	97 ± 0
Ekeby bruk (a)	3.7 ± 0	23 ± 0	2.4 ± 0	nd	nd	nd	6.5 ± 0	1.0 ± 0	2.8 ± 0
Falebro (a)	2.7 ± 0	11 ± 0	1.1 ± 0	nd	14 ± 0	3.4 ± 0	3.7 ± 0	0.66 ± 0	2.8 ± 0
Flogsta (a)	1.6 ± 0	8.1 ± 0	1.2 ± 0	nd	nd	1.2 ± 0	4.0 ± 0	0.73 ± 0	3.2 ± 0
Kumlagatan (b)	16 ± 0	145 ± 0	7.9 ± 0	nd	nd	nd	45 ± 0	32 ± 0	50 ± 0
Norra Libroback (b)	nd	47 ± 0	48 ± 0	nd	264 ± 0	nd	89 ± 0	16 ± 0	39 ± 0
Seglarvägen (a)	3.2 ± 0	16 ± 0	1.3 ± 0	nd	50 ± 0	7.5 ± 0	5.2 ± 0	0.79 ± 0	6.0 ± 0
Seminariegatan (b)	1.4 ± 0	3.7 ± 0	1.5 ± 0	nd	2.6 ± 0	1.4 ± 0	4.0 ± 0	0.65 ± 0	6.5 ± 0
Skarholmen (a)	6.1 ± 0	39 ± 0	4.4 ± 0	nd	30 ± 0	nd	14 ± 0	2.8 ± 0	9.5 ± 0
Strandbodgatan (c)	0.7 ± 0	10 ± 0	1.4 ± 0	nd	nd	nd	3.1 ± 0	1.0 ± 0	3.7 ± 0
Sundby (a)	5.8 ± 0	35 ± 0	2.7 ± 0	nd	nd	nd	13 ± 0	1.5 ± 0	8.1 ± 0
Sågargatan (c)	10 ± 0	nd	147 ± 0	nd	nd	7551 ± 0	11591 ± 0	20180 ± 0	11990 ± 0
Sävja (a)	4.8 ± 0	32 ± 0	3.9 ± 0	nd	21 ± 0	nd	12 ± 0	3.0 ± 0	10 ± 0
Tullgarn (c)	3.2 ± 0	17 ± 0	10 ± 0	nd	23 ± 0	nd	4.8 ± 0	1.3 ± 0	4.6 ± 0
Ultuna (a)	3.1 ± 0	11 ± 0	3.0 ± 0	nd	7.7 ± 0	2.4 ± 0	5.6 ± 0	0.57 ± 0	4.3 ± 0

Analyte (ng g-1 dw) / Sludge	PFBS	PFHxS	PFOS	PFDS	PFBA	PFPeA	PFHxA	PFHpA	PFOA
Primary clarifier sludge A	nd	0.48 ± 0.020	3.6 ± 0	nd	nd	nd	nd	nd	0.26 ± 0.010
Primary clarifier sludge B	nd	0.51 ± 0.020	9.5 ± 0	nd	nd	nd	nd	nd	0.30 ± 0.010
Primary clarifier sludge C	nd	0.41 ± 0.020	1.4 ± 0	nd	nd	nd	0.27 ± 0.018	nd	0.21 ± 0.010
Secondary clarifier sludge A	0.12 ± 0.010	1.1 ± 0.020	38 ± 0	0.20 ± 0	nd	nd	0.71 ± 0.018	nd	0.75 ± 0.010
Secondary clarifier sludge B	0.079 ± 0.010	1.7 ± 0.020	23 ± 0	0.21 ± 0	nd	1.0 ± 0.0071	0.63 ± 0.018	nd	1.2 ± 0.010
Secondary clarifier sludge C	0.15 ± 0.010	1.3 ± 0.020	21 ± 0	0.26 ± 0	nd	nd	0.80 ± 0.018	nd	1.1 ± 0.010
Final clarifier sludge	nd	0.36 ± 0.020	5.7 ± 0	nd	nd	nd	0.85 ± 0.018	nd	0.53 ± 0.010
Digested sludge RK1	nd	nd	2.5 ± 0	nd	nd	nd	0.31 ± 0.018	0.29 ± 0.030	0.25 ± 0.010
Digested sludge RK2	0.22 ± 0.010	0.43 ± 0.020	13 ± 0	nd	2.3 ± 0.14	nd	0.89 ± 0.018	0.53 ± 0.030	0.79 ± 0.010
Dewatered sludge	nd	0.58 ± 0.020	15 ± 0	nd	nd	nd	0.70 ± 0.018	nd	0.62 ± 0.010

Analyte (ng L-1) / Treatment step	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Influent AB	nd	nd	nd	nd	nd	nd	nd	nd	nd
Influent C	0.25 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Primary clarifier A	nd	nd	nd	nd	nd	0.31 ± 0	nd	nd	nd
Primary clarifier B	nd	nd	nd	nd	nd	nd	nd	nd	nd
Primary clarifier C	nd	nd	nd	nd	nd	nd	nd	nd	nd
Secondary clarifier A	2.1 ± 0	nd	nd	nd	nd	nd	nd	nd	0.85 ± 0
Secondary clarifier B	0.22 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Secondary clarifier C	2.2 ± 0	nd	nd	nd	nd	nd	nd	nd	0.44 ± 0
Dewatering - reject water	nd	nd	nd	nd	nd	nd	nd	nd	nd
Effluent	0.26 ± 0	nd	nd	nd	nd	nd	nd	nd	nd

Analyte (ng L-1) / PST	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Boländerna	1.1 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Bärby hage (a)	4.5 ± 0	nd	0.37 ± 0	0.24 ± 0	nd	nd	nd	nd	24 ± 0
Ekeby bruk (a)	nd	nd	nd	0.23 ± 0	nd	nd	nd	nd	nd
Falebro (a)	nd	nd	nd	nd	nd	0.25 ± 0	nd	nd	nd
Flogsta (a)	0.73 ± 0	nd	0.45 ± 0	0.34 ± 0	0.36 ± 0	0.35 ± 0	0.40 ± 0	0.28 ± 0	nd
Kumlagatan (b)	6.1 ± 0	7.7 ± 0.54	1.1 ± 0	1.1 ± 0	0.44 ± 0	1.2 ± 0	nd	nd	nd
Norra Libroback (b)	4.1 ± 0	nd	2.0 ± 0	1.5 ± 0	1.2 ± 0	0.62 ± 0	nd	nd	nd
Seglarvägen (a)	0.29 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Seminariegatan (b)	nd	nd	nd	nd	nd	nd	nd	nd	1.9 ± 0
Skarholmen (a)	0.54 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Strandbodgatan (c)	0.30 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Sundby (a)	0.41 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Sågargatan (c)	3958 ± 0	6.0 ± 0.54	nd	nd	nd	nd	nd	nd	nd
Sävja (a)	0.66 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Tullgarn (c)	0.23 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Ultuna (a)	nd	nd	nd	nd	nd	nd	nd	nd	nd

Analyte (ng g-1 dw) / Sludge	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Primary clarifier sludge A	nd	0.23 ± 0.04	nd	0.29 ± 0.010	nd	0.044 ± 0.010	nd	nd	nd
Primary clarifier sludge B	0.10 ± 0.020	0.25 ± 0.04	nd	0.25 ± 0.010	0.061 ± 0	0.076 ± 0.010	nd	nd	nd
Primary clarifier sludge C	nd	nd	0.20 ± 0.040	0.26 ± 0.010	nd	0.062 ± 0.010	nd	nd	nd
Secondary clarifier sludge A	0.42 ± 0.020	3.9 ± 0.04	0.80 ± 0.040	1.3 ± 0.010	0.17 ± 0	0.29 ± 0.010	0.059 ± 0	nd	nd
Secondary clarifier sludge B	0.65 ± 0.020	4.2 ± 0.04	0.76 ± 0.040	1.4 ± 0.010	0.39 ± 0	0.83 ± 0.010	0.18 ± 0	nd	nd
Secondary clarifier sludge C	0.70 ± 0.020	5.8 ± 0.04	1.0 ± 0.040	1.9 ± 0.010	0.18 ± 0	0.28 ± 0.010	0.074 ± 0	nd	nd
Final clarifier sludge	nd	0.61 ± 0.04	nd	0.26 ± 0.010	nd	0.082 ± 0.010	nd	nd	nd
Digested sludge RK1	0.12 ± 0.020	0.40 ± 0.04	0.23 ± 0.040	0.39 ± 0.010	0.10 ± 0	0.11 ± 0.010	nd	nd	nd
Digested sludge RK2	0.40 ± 0.020	2.1 ± 0.04	0.62 ± 0.040	1.0 ± 0.010	0.17 ± 0	0.22 ± 0.010	0.082 ± 0	nd	nd
Dewatered sludge	0.40 ± 0.020	2.2 ± 0.04	0.59 ± 0.040	1.0 ± 0.010	0.19 ± 0	0.24 ± 0.010	0.077 ± 0	nd	nd

Analyte (ng L-1) / Treatment step	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Influent AB	nd	nd	nd	nd	nd	nd	0.42 ± 0	109 ± 0
Influent C	nd	nd	nd	nd	nd	nd	nd	56 ± 0
Primary clarifier A	nd	nd	nd	nd	nd	nd	0.60 ± 0	144 ± 0
Primary clarifier B	nd	nd	nd	nd	nd	nd	1.0 ± 0	88 ± 0
Primary clarifier C	nd	nd	nd	nd	nd	nd	0.64 ± 0	100 ± 0
Secondary clarifier A	nd	nd	nd	nd	nd	nd	0.39 ± 0	144 ± 0
Secondary clarifier B	nd	nd	nd	nd	nd	nd	nd	120 ± 0
Secondary clarifier C	nd	nd	nd	nd	nd	nd	nd	193 ± 0
Dewatering - reject water	nd	nd	nd	nd	nd	nd	nd	65 ± 0
Effluent	nd	nd	nd	nd	nd	nd	nd	121 ± 0

Analyte (ng L-1) / PST	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Boländerna	nd	nd	nd	nd	nd	nd	0.84 ± 0	109 ± 0
Bärby hage (a)	nd	nd	nd	nd	nd	0.31 ± 0	1.4 ± 0	361 ± 0
Ekeby bruk (a)	nd	nd	nd	nd	nd	nd	nd	107 ± 0
Falebro (a)	nd	nd	nd	nd	nd	nd	nd	134 ± 0
Flogsta (a)	nd	nd	nd	nd	nd	nd	nd	543 ± 0
Kumlagatan (b)	nd	nd	nd	nd	nd	nd	1.2 ± 0	418 ± 0
Norra Librobäck (b)	nd	161	nd	nd	nd	nd	2.4 ± 0	1470 ± 0
Seglarvägen (a)	nd	nd	nd	nd	nd	nd	nd	152 ± 0
Seminariegatan (b)	nd	nd	nd	nd	nd	nd	3.3 ± 0	92 ± 0
Skarholmen (a)	nd	nd	nd	nd	nd	nd	nd	2.4 ± 0
Strandbodgatan (c)	nd	nd	nd	nd	nd	nd	nd	69 ± 0
Sundby (a)	nd	nd	nd	nd	nd	nd	1.1 ± 0	24 ± 0
Sågargatan (c)	nd	nd	nd	nd	nd	nd	nd	nd
Sävja (a)	nd	nd	nd	nd	nd	nd	nd	6.7 ± 0
Tullgarn (c)	nd	nd	nd	nd	nd	nd	1.5 ± 0	116 ± 0
Ultuna (a)	nd	nd	nd	nd	nd	nd	nd	100 ± 0

Analyte (ng g-1 dw) / Sludge	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Primary clarifier sludge A	nd	26 ± 0	nd	nd	nd	nd	2.5 ± 0	1.2 ± 0.011
Primary clarifier sludge B	nd	nd	nd	nd	nd	nd	3.3 ± 0	1.7 ± 0.011
Primary clarifier sludge C	nd	nd	nd	nd	nd	nd	2.3 ± 0	2.0 ± 0.011
Secondary clarifier sludge A	nd	nd	nd	nd	3.9 ± 0.020	1.1 ± 0	6.9 ± 0	1.3 ± 0.011
Secondary clarifier sludge B	nd	nd	nd	nd	5.5 ± 0.020	1.3 ± 0	8.3 ± 0	1.8 ± 0.011
Secondary clarifier sludge C	nd	nd	nd	nd	3.0 ± 0.020	1.0 ± 0	6.7 ± 0	3.6 ± 0.011
Final clarifier sludge	nd	nd	nd	nd	nd	0.10 ± 0	1.1 ± 0	nd
Digested sludge RK1	nd	nd	nd	nd	2.5 ± 0.020	0.47 ± 0	3.2 ± 0	0.68 ± 0.011
Digested sludge RK2	nd	nd	nd	nd	2.2 ± 0.020	1.4 ± 0	5.5 ± 0	3.8 ± 0.011
Dewatered sludge	nd	nd	nd	nd	2.4 ± 0.020	1.6 ± 0	5.9 ± 0	1.7 ± 0.011

Table A7 *Mass flows of PFASs with standard deviations (mg d $^{-1}$) of wastewater and sludge in Kungsängsverket and in wastewater in the wastewater network of Uppsala*

Analyte (mg d-1) / Treatment step	**PFBS**	**PFHxS**	**PFOS**	**PFDS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**
Influent AB	84 ± 0	382 ± 0	186 ± 0	nd	719 ± 0	nd	135 ± 0	23 ± 0	95 ± 0
Influent C	101 ± 0	688 ± 0	186 ± 0	nd	1541 ± 0	nd	307 ± 0	78 ± 0	183 ± 0
Primary clarifier A	36 ± 0	241 ± 0	139 ± 0	nd	nd	nd	86 ± 0	14 ± 0	57 ± 0
Primary clarifier B	43 ± 0	190 ± 0	119 ± 0	nd	nd	33 ± 0	71 ± 0	8 ± 0	49 ± 0
Primary clarifier C	58 ± 0	242 ± 0	85 ± 0	nd	379 ± 0	nd	91 ± 0	15 ± 0	62 ± 0
Secondary clarifier A	123 ± 0	513 ± 0	288 ± 0	nd	319 ± 0	73 ± 0	276 ± 0	63 ± 0	172 ± 0
Secondary clarifier B	70 ± 0	247 ± 0	136 ± 0	nd	162 ± 0	13 ± 0	148 ± 0	21 ± 0	85 ± 0
Secondary clarifier C	209 ± 0	828 ± 0	258 ± 0	nd	788 ± 0	186 ± 0	785 ± 0	138 ± 0	475 ± 0
Effluent	163 ± 0	559 ± 0	249 ± 0	nd	332 ± 0	34 ± 0	365 ± 0	47 ± 0	241 ± 0
Analyte (mg d-1) / PST	**PFBS**	**PFHxS**	**PFOS**	**PFDS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**
Bärby hage (a)	6.4 ± 0	92 ± 0	131 ± 0	nd	21 ± 0	47 ± 0	44 ± 0	22 ± 0	57 ± 0
Ekeby bruk (a)	0.04 ± 0	0.23 ± 0	0.024 ± 0	nd	nd	nd	0.07 ± 0	0.010 ± 0	0.028 ± 0
Falebro (a)	0.23 ± 0	1.0 ± 0	0.10 ± 0	nd	1.2 ± 0	0.30 ± 0	0.33 ± 0	0.058 ± 0	0.25 ± 0
Flogsta (a)	3.4 ± 0	17 ± 0	2.4 ± 0	nd	nd	2.5 ± 0	8.4 ± 0	1.5 ± 0	6.6 ± 0
Kumlagatan (b)	0.16 ± 0	1.5 ± 0	0.079 ± 0	nd	nd	nd	0.45 ± 0	0.32 ± 0	0.50 ± 0
Norra Librobäck (b)	nd	1.5 ± 0	1.5 ± 0	nd	8.4 ± 0	nd	2.9 ± 0	0.53 ± 0	1.2 ± 0
Seglarvägen (a)	0.14 ± 0	0.68 ± 0	0.055 ± 0	nd	2.1 ± 0	0.32 ± 0	0.22 ± 0	0.034 ± 0	0.26 ± 0
Seminariegatan (b)	0.33 ± 0	0.85 ± 0	0.35 ± 0	nd	0.60 ± 0	0.33 ± 0	0.93 ± 0	0.15 ± 0	1.5 ± 0
Skarholmen (a)	2.1 ± 0	14 ± 0	1.5 ± 0	nd	11 ± 0	nd	4.8 ± 0	1.0 ± 0	3.3 ± 0
Strandbodgatan (c)	7.0 ± 0	98 ± 0	14 ± 0	nd	nd	nd	31 ± 0	10 ± 0	37 ± 0
Sundby (a)	0.84 ± 0	5.1 ± 0	0.39 ± 0	nd	nd	nd	1.8 ± 0	0.21 ± 0	1.2 ± 0
Sågargatan (c)	20 ± 0	nd	280 ± 0	nd	nd	14415 ± 0	22128 ± 0	38523 ± 0	22890 ± 0
Sävja (a)	6.9 ± 0	46 ± 0	5.6 ± 0	nd	30 ± 0	nd	17 ± 0	4.3 ± 0	15 ± 0
Tullgarn (c)	77 ± 0	397 ± 0	251 ± 0	nd	540 ± 0	nd	116 ± 0	30 ± 0	109 ± 0
Ultuna (a)	1.9 ± 0	6.9 ± 0	1.8 ± 0	nd	4.7 ± 0	1.5 ± 0	3.4 ± 0	0.35 ± 0	2.6 ± 0
Analyte (mg d-1 ww) / Sludge	**PFBS**	**PFHxS**	**PFOS**	**PFDS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**
Primary clarifier sludge A	nd	46 ± 0	345 ± 0	nd	nd	nd	nd	nd	25 ± 0
Primary clarifier sludge B	nd	88 ± 0	1645 ± 0	nd	nd	nd	nd	nd	52 ± 0
Primary clarifier sludge C	nd	79 ± 0	259 ± 0	nd	nd	nd	nd	nd	41 ± 0
Secondary clarifier sludge A	20 ± 0	178 ± 0	6096 ± 0	32 ± 0	nd	nd	114 ± 0	nd	120 ± 0
Secondary clarifier sludge B	nd	390 ± 0	5386 ± 0	50 ± 0	nd	242 ± 0	148 ± 0	nd	291 ± 0
Secondary clarifier sludge C	38 ± 0	325 ± 0	5292 ± 0	67 ± 0	nd	nd	202 ± 0	nd	287 ± 0
Final clarifier sludge	nd	315 ± 0	4970 ± 0	nd	nd	nd	743 ± 0	nd	461 ± 0
Digested sludge RK1	nd	nd	508 ± 0	nd	nd	nd	nd	nd	51 ± 0
Digested sludge RK2	81 ± 0	160 ± 0	5009 ± 0	nd	850 ± 0	nd	332 ± 0	199 ± 0	296 ± 0

Analyte (mg d-1) / Treatment step	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Influent AB	nd	nd	nd	nd	nd	nd	nd	nd	nd
Influent C	5.2 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Primary clarifier A	nd	nd	nd	nd	nd	3.4 ± 0	nd	nd	nd
Primary clarifier B	nd	nd	nd	nd	nd	nd	nd	nd	nd
Primary clarifier C	nd	nd	nd	nd	nd	nd	nd	nd	nd
Secondary clarifier A	13 ± 0	nd	nd	nd	nd	nd	nd	nd	5.3 ± 0
Secondary clarifier B	3.2 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Secondary clarifier C	46 ± 0	nd	nd	nd	nd	nd	nd	nd	9.1 ± 0
Effluent	11 ± 0	nd	nd	nd	nd	nd	nd	nd	nd

Analyte (mg d-1) / PST	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Bärby hage (a)	2.6 ± 0	nd	0.22 ± 0	0.14 ± 0	nd	nd	nd	nd	14 ± 0
Ekeby bruk (a)	nd	nd	nd	0.0023 ± 0	nd	nd	nd	nd	nd
Falebro (a)	nd	nd	nd	nd	nd	0.022 ± 0	nd	nd	nd
Flogsta (a)	1.5 ± 0	nd	0.93 ± 0	0.70 ± 0	0.74 ± 0	0.72 ± 0	0.84 ± 0	0.57 ± 0	nd
Kumlagatan (b)	0.06 ± 0	0.077 ± 1	0.011 ± 0	0.011 ± 0	0.004 ± 0	0.012 ± 0	nd	nd	nd
Norra Librobäck (b)	0.13 ± 0	nd	0.063 ± 0	0.049 ± 0	0.040 ± 0	0.020 ± 0	nd	nd	nd
Seglarvägen (a)	0.013 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Seminariegatan (b)	nd	nd	nd	nd	nd	nd	nd	nd	0.44 ± 0
Skarholmen (a)	0.19 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Strandbodgatan (c)	3.0 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Sundby (a)	0.059 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Sågargatan (c)	7556 ± 0	11 ± 1	nd	nd	nd	nd	nd	nd	nd
Sävja (a)	0.95 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Tullgarn (c)	5.4 ± 0	nd	nd	nd	nd	nd	nd	nd	nd
Ultuna (a)	nd	nd	nd	nd	nd	nd	nd	nd	nd

Analyte (mg d-1 ww) / Sludge	PFNA	PFDA	PFUnDA	PFDoDA	PFTriDA	PFTeDA	PFHxDA	PFOcDA	FOSA
Primary clarifier sludge A	nd	22 ± 0	nd	28 ± 0	nd	4 ± 0	nd	nd	nd
Primary clarifier sludge B	nd	44 ± 0	nd	44 ± 0	11 ± 0	13 ± 0	nd	nd	nd
Primary clarifier sludge C	nd	nd	38 ± 0	50 ± 0	nd	12 ± 0	nd	nd	nd
Secondary clarifier sludge A	67 ± 0	620 ± 0	128 ± 0	214 ± 0	28 ± 0	46 ± 0	9.4 ± 0	nd	nd
Secondary clarifier sludge B	154 ± 0	983 ± 0	179 ± 0	343 ± 0	92 ± 0	195 ± 0	43 ± 0	nd	nd
Secondary clarifier sludge C	178 ± 0	1457 ± 0	242 ± 0	491 ± 0	46 ± 0	70 ± 0	19 ± 0	nd	nd
Final clarifier sludge	nd	538 ± 0	nd	231 ± 0	nd	72 ± 0	nd	nd	nd
Digested sludge RK1	25 ± 0	81 ± 0	47 ± 0	79 ± 0	20 ± 0	23 ± 0	nd	nd	nd
Digested sludge RK2	150 ± 0	773 ± 0	232 ± 0	393 ± 0	63 ± 0	83 ± 0	31 ± 0	nd	nd

Analyte (mg d-1) / Treatment step	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Influent AB	nd	nd	nd	nd	nd	nd	8.7 ± 0	2248 ± 0
Influent C	nd	nd	nd	nd	nd	nd	nd	1140 ± 0
Primary clarifier A	nd	nd	nd	nd	nd	nd	6.6 ± 0	1575 ± 0
Primary clarifier B	nd	nd	nd	nd	nd	nd	9.4 ± 0	856 ± 0
Primary clarifier C	nd	nd	nd	nd	nd	nd	13 ± 0	2056 ± 0
Secondary clarifier A	nd	nd	nd	nd	nd	nd	2.5 ± 0	902 ± 0
Secondary clarifier B	nd	nd	nd	nd	nd	nd	nd	1725 ± 0
Secondary clarifier C	nd	nd	nd	nd	nd	nd	nd	3943 ± 0
Effluent	nd	nd	nd	nd	nd	nd	nd	4985 ± 0

Analyte (mg d-1) / PST	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Bärby hage (a)	nd	nd	nd	nd	nd	0.18 ± 0	0.83 ± 0	213 ± 0
Ekeby bruk (a)	nd	nd	nd	nd	nd	nd	nd	1 ± 0
Falebro (a)	nd	nd	nd	nd	nd	nd	nd	12 ± 0
Flogsta (a)	nd	nd	nd	nd	nd	nd	nd	1128 ± 0
Kumlagatan (b)	nd	nd	nd	nd	nd	nd	0.012 ± 0	4 ± 0
Norra Librobäck (b)	nd	5 ± 0	nd	nd	nd	nd	0.078 ± 0	47 ± 0
Seglarvägen (a)	nd	nd	nd	nd	nd	nd	nd	7 ± 0
Seminariegatan (b)	nd	nd	nd	nd	nd	nd	0.76 ± 0	21 ± 0
Skarholmen (a)	nd	nd	nd	nd	nd	nd	nd	1 ± 0
Strandbodgatan (c)	nd	nd	nd	nd	nd	nd	nd	689 ± 0
Sundby (a)	nd	nd	nd	nd	nd	nd	0.16 ± 0	3 ± 0
Sågargatan (c)	nd	nd	nd	nd	nd	nd	nd	nd
Sävja (a)	nd	nd	nd	nd	nd	nd	nd	10 ± 0
Tullgarn (c)	nd	nd	nd	nd	nd	nd	36 ± 0	2782 ± 0
Ultuna (a)	nd	nd	nd	nd	nd	nd	nd	61 ± 0

Analyte (mg d-1 ww) / Sludge	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-EtFOSE	FOSAA	N-MeFOSAA	N-EtFOSAA	6:2 FTSA
Primary clarifier sludge A	nd	2464 ± 0	nd	nd	nd	nd	235 ± 0	110 ± 0
Primary clarifier sludge B	nd	nd	nd	nd	nd	nd	572 ± 0	297 ± 0
Primary clarifier sludge C	nd	nd	nd	nd	nd	nd	430 ± 0	378 ± 0
Secondary clarifier sludge A	nd	nd	nd	nd	621 ± 0	175 ± 0	1101 ± 0	202 ± 0
Secondary clarifier sludge B	nd	nd	nd	nd	1295 ± 0	308 ± 0	1959 ± 0	427 ± 0
Secondary clarifier sludge C	nd	nd	nd	nd	772 ± 0	243 ± 0	1700 ± 0	907 ± 0
Final clarifier sludge	nd	nd	nd	nd	nd	92 ± 0	955 ± 0	nd
Digested sludge RK1	nd	nd	nd	nd	514 ± 0	95 ± 0	646 ± 0	139 ± 0
Digested sludge RK2	nd	nd	nd	nd	823 ± 0	534 ± 0	2061 ± 0	1425 ± 0