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Contribution of precursor compounds to the release of per- and polyfluoroalkyl substances (PFASs) from waste water treatment plants (WWTPs)

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) are ubiquitous in sludge and water from waste water treatment plants, as a result of their incorporation in everyday products and industrial processes. In this study, we measured several classes of persistent PFASs, precursors, transformation intermediates, and newly identified PFASs in influent and effluent sewage water and sludge from three municipal waste water treatment plants in Sweden, sampled in 2015. For sludge, samples from 2012 and 2014 were analyzed as well. Levels of precursors in sludge exceeded those of perfluoroalkyl acids and sulfonic acids (PFCAs and PFSAs), in 2015 the sum of polyfluoroalkyl phosphoric acid esters (PAPs) were 15–20 ng/g dry weight, the sum of fluorotelomer sulfonic acids (FTSAs) was 0.8–1.3 ng/g, and the sum of perfluorooctane sulfonamides and ethanols ranged from non-detected to 3.2 ng/g. Persistent PFSAs and PFCAs were detected at 1.9–3.9 ng/g and 2.4–7.3 ng/g dry weight, respectively. The influence of precursor compounds was further demonstrated by an observed substantial increase for a majority of the persistent PFCAs and PFSAs in water after waste water treatment. Perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), and perfluorooctane sulfonic acid (PFOS) had a net mass increase in all WWTPs, with mean values of 83%, 28%, 37% and 58%, respectively. The load of precursors and intermediates in influent water and sludge combined with net mass increase support the hypothesis that degradation of precursor compounds is a significant contributor to PFAS contamination in the environment.

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Introduction

Per- and polyfluoroalkyl substances (PFASs) is a group of anthropogenic compounds, that have been released into the environment since the 1950s. These oil- and water-repellent surfactants are used in paper, carpets, clothes, cosmetics,

food packaging, kitchen wares, chrome plating, and aqueous film forming foams (AFFFs) for firefighting (Buck et al., 2011). Of these PFASs, many have been found to be persistent, bioaccumulative, and toxic to humans and the environment. Adverse effects of PFAS include developmental toxicity, neurotoxicity, immunotoxicity, and possibly carcinogenicity

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(DeWitt, 2015). It has been estimated that more than 3000 commercial PFASs are present on the global market of which only a few are being monitored (KEMI, 2015) and it can be assumed that a large proportion is chemicals that are used in our daily life. Release to the environment may occur directly and indirectly through multiple pathways. An important link between the community and the environment is waste water treatment plants (WWTPs). Water and sludge from WWTPs reflects to a large extent what kind of chemicals are being used in and released from articles in the society. This also means that WWTPs via water and sludge should be considered as major point sources and an important transport route for PFASs, both from domestic use and industrial activities (Ahrens and Bundschuh, 2014). Other major point sources are PFAS production sites and firefighting training sites.

Waste water treatment can change the levels and composition of PFAS groups in sewage, and affects the distribution to different environmental compartments. Among factors that affect the composition change in sewage water during WWTP treatment are the partition of PFASs to sludge, and degradation of semi-persistent compounds that act as precursors to persistent PFASs. Higher concentrations in effluents compared to influents are commonly observed for some PFASs, which have been attributed to degradation of precursor compounds during the waste water treatment process (Kunacheva et al., 2011; Campo et al., 2014). Moreover, the preferential enrichment of foremost long-chain PFASs in the WWTP sludge, due to the hydrophobic properties of the fluorinated carbon chain and electrostatic interactions between the head group and the sludge, leads to an altered profile in the effluent water compared to influent (Zhang et al., 2013). The fate of the PFASs sorbed to sludge is generally to be further spread in the environment through application of sludge or sludge-containing products. In 2014, about one quarter of sludge was applied on agricultural soil (24%), one quarter was used to cover mines and dump sites (24%), and almost a third was used to manufacture soil intended for less sensitive land use (29%) (SCB, 2016). Volatile PFASs have been shown to volatilize at open waste water treatment plants and hence WWTPs are significant point sources of PFAS emissions to the atmosphere as well as terrestrial and aquatic environments (Ahrens, 2011).

Analysis of total extractable organic fluorine (EOF) in human serum and wild life has revealed that a large proportion of PFASs is unknown and not covered by analysis of common monitored classes such as PFSAs and PFCAs (Yeung et al., 2008; Loi et al., 2011). Further, it has been debated whether PFASs in WWTPs stem from newly released contaminants through industrial production and consumer usage, or if part of the PFAS burden comes from recirculating levels in drinking water and atmospheric depositions (Filipovic and Berger, 2015).

Measuring both precursors, intermediates, and persistent PFASs in municipal waste water and sludge gives a more comprehensive picture of PFAS loads from both ongoing and historical sources. In recent years, there has been a growing attention towards several classes of PFASs with the ability to biodegrade into persistent PFCAs and PFSAs.

The polyfluoroalkyl phosphoric acid esters (PAPs) comprise a class of commercial compounds that have been produced since the 1970s and used in paper, packaging material

including food packaging, cosmetics and cleaning agents (Pilot Chemical, 2016). The PAPs have been detected globally in sludge, waste water, and indoor dust, at levels similar to PFSAs and PFCAs (Loi et al., 2013; Eriksson and Karrman, 2015). Observations of PAPs in serum and breast milk have revealed exposure of PAPs to humans (D'eon et al., 2009a; Kubwabo et al., 2013; Yeung et al., 2013). Additionally, PAPs have been found in the aquatic environment, such as in fish, mussels, and raptors (Guo et al., 2012; Zabaleta et al., 2015). The relatively low levels of PAPs measured in humans and biota compared to persistent PFASs have been explained by their ability to biodegrade and transform into PFCAs (Lee et al., 2010).

Another precursor class is the fluorotelomer sulfonic acids (FTSAs), which can degrade into PFCAs. FTSAs are a common transformation intermediate from several other PFASs, for example ingredients in firefighting foams and has been detected in AFFFs (D'Agostino and Mabury, 2014), but other applications have been described as well, for instance in ink (Ma et al., 2002). It has been shown that fluorotelomer mercaptoalkylamid sulfonates (FTSASs) that are used in for example AFFFs degrade into FTSAs and further to PFCAs in WWTP sludge (Weiner et al., 2013). FTSAs have been detected in sludge (Loi et al., 2013) and human serum (Lee and Mabury, 2011; Loi et al., 2013; Yeung and Mabury, 2016).

Other PFAS classes that recently gained attention are perfluoroalkyl phosphonic acids (PFPA) and perfluoroalkyl phosphinic acids (PFPIAs), which have been produced and used since the 70s in pesticides, wetting- and leveling agents (Wang et al., 2016). PFPIAs have been shown to biodegrade into corresponding PFPA of the same chain length in rainbow trout (Lee et al., 2012). It has been suggested that PFPA and PFPIAs could be potential precursors of PFCAs. However, further degradation of PFPA to PFCAs was not clear in rainbow trout. PFPA have been detected in effluent waste water (D'eon et al., 2009b; Llorca et al., 2012), and PFPIAs in human serum (Lee and Mabury, 2011).

The number of PFASs in the society is far higher than the target analysis can manage to cover. Numerous PFAS classes have a common degradation pathway where intermediates are fluorotelomer carboxylic acids, both saturated (FTCA) and unsaturated (FTUCA). FTCA/FTUCA have no known usage in consumer products or industrial applications and are therefore indicative of the presence and degradation of fluorotelomer-based precursors.

Only a few studies on sludge and waste water have included newly identified PFASs. The aim of this study was to assess the importance of precursor compounds to the overall release of persistent PFASs into the environment by measuring several PFAS classes including precursors, intermediates and persistent substances in influent, effluent, and sludge from Swedish WWTPs.

1. Materials and methods

1.1. Samples

Samples were taken from three WWTPs in Sweden under the long term national monitoring program by the Swedish EPA;

Henriksdal, Gässlösa, and Umeå. The Henriksdal WWTP serves 737,000 people (656,000 person equivalents, p.e.) and receives water from industries and hospitals. The Umeå WWTP serves 92,000 people (129,000 p.e.) and a hospital. The Gässlösa WWTP serves 82,000 people (73,000 p.e.) and has textile and chemical industries as well as a connected hospital. All three WWTPs have mechanical, chemical, biologic, and anaerobic digestion treatment. Sludge samples were collected as composite samples during one day in October in the years 2012, 2014, and 2015 from all three WWTPs. The residence time of sludge is 19, 25 and 18 days in Henriksdal, Gässlösa, and Umeå, respectively. The annual amount of sludge produced is 14,400, 2400, and 2300 tons (dry weight), respectively. Influent and effluent water samples were collected in October year 2015 and were collected as composites of seven consecutive days. The annual amount of influent water to the WWTPs is reported to be 89, 13, and 13 million m³, respectively. Sludge samples were freeze-dried and stored at –18°C until analysis.

1.2. Chemicals

Standards used for the targeted analytes were native PFCAs (C4–C14, C16, C18), mass-labeled PFCAs (C4, C6, C8–C12, C14, C16) native PFSAs (C4–C10, C12), mass-labeled PFSAs (C4, C6, C8), native and mass-labeled FTUCAs (6:2, 8:2, 10:2), native and mass-labeled FTCAs (5:3, 7:3), native monoPAPs (6:2, 8:2, 10:2), mass-labeled monoPAPs (6:2, 8:2), native diPAPs (6:2, 6:2/8:2, 8:2, 10:2), mass-labeled diPAPs (6:2, 8:2), native and mass-labeled FTSAs (6:2, 8:2), native and mass-labeled FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE, native PFPAs (C6, C8, C10), and native PFPiAs (6/6, 8/8, 10/10). All the standards were obtained from Wellington Laboratories (Guelph, Ontario, Canada) except for 10:2 monoPAP and 10:2 diPAP which were obtained from Chiron (Trondheim, Norway). HPLC-grade acetonitrile and methanol were purchased from Fisher Scientific (Ottawa, Canada). Water was laboratory-produced milli-Q water.

1.3. Extraction

In the sludge extraction and clean-up, 0.25 g freeze-dried sample was used. An amount of 1–8 ng of labeled internal standards was added to the samples followed by the addition of 2 mL 1 mol/L sodium hydroxide in methanol. The samples were ultrasonicated for 15 min, shaken for 15 min, and centrifuged; the supernatant was removed, and the extraction was repeated twice with aliquots of 2 mL methanol. All extraction aliquots were combined and purification was performed with solid phase extraction (SPE) using Oasis Weak Anion Exchange (WAX) sorbents (Waters Corporation, Milford, USA). The sorbents were conditioned with 4 mL methanol followed by 4 mL Milli-Q water. Samples were loaded on the sorbents, which was later washed with 4 mL sodium acetate (NaAc) buffer solution (pH 4), followed by 4 mL of 20% methanol. Cartridges were dried and eluted with 4 mL methanol, which was collected for the analysis of neutral PFASs. After that, 4 mL 2% ammonium hydroxide in methanol was added to the cartridge and the eluate was used for analysis of anionic PFASs. The extracts were evaporated under nitrogen to a final volume of 200 µL.

The water samples were filtered with GF/B glass fiber filters before extraction (Whatman). An amount of 0.5 L was

used. Labeled internal standards (2–4 ng) were added to the samples. SPE was performed using WAX sorbents according to ISO/DIS 25101 with some modifications. Before loading the samples, the WAX sorbents were conditioned with 4 mL methanol and 4 mL Milli-Q water. The sorbents were washed with 4 mL of ammonium acetate buffer solution (pH 4), followed by 4 mL methanol, and finally the analytes were eluted with 4 mL of 0.1% ammonium solution in methanol. The extracts were evaporated to a final volume of 200 µL.

1.4. Instrumental analysis

The sample extracts were split into two fractions and analyzed on an Ultra Performance Liquid Chromatography (UPLC) system coupled to a triple quadrupole mass spectrometer XEVO TQ-S (Waters Corporation, Milford, USA), in negative electrospray ionization mode. A 100 mm C18 BEH column (1.7 µm, 2.1 mm) was used for separation. Mobile phases with 2 mmol/L ammonium acetate in water, and 2 mmol/L ammonium acetate in methanol were used with gradient elution for all analytes except for PAPs, for which water and methanol with addition of 2 mmol/L ammonium acetate and 5 mmol/L 1-methylpiperidine was used. Both quantification and qualification product ions were measured in the multiple reaction monitoring mode, except for a few shorter PFCAs for which only one stable product ion was formed. Information on the mass spectrometric settings is given in the SI.

1.5. Quality control and quality assurance

Calibration curves consisting of at least five points were prepared for the targeted compounds. Procedure blanks treated in the same way as the samples were included in each batch of 8–10 samples. The method limit of detection (LOD) was determined as three times the signal in the procedural blanks, and in absence of the analyte in the blank, the lowest point in the calibration curve. Triplicates of three sludge samples from the WWTPs were used to assess the accuracy, precision, matrix effects, and recoveries of the method. The accuracy of the method was generally satisfactory (46%–138%), with exception of poor accuracy for 10:2 diPAP (4.1%) and PFOSA (189%). Recoveries of native compounds spiked to samples were 23%–91% for PFSAs, PFCAs, FTSAs, FTCAs, FTUCAs, FOSAs, FOSEs, diPAPs, and PFPiAs. Lower recoveries were observed for monoPAPs (3.6%–6.8%), and higher recoveries for PFPAs (68%–164%). Recoveries of labeled internal standards were 24%–91% for all quantified analytes. Detailed description of method validation can be found in the Appendix A.

Quantification of PFCAs, PFSAs, FTCA/FTUCAs, FTSAs, monoPAPs, diPAPs, and FOSA/FOSEs was performed by isotope dilution with mass-labeled internal standards. Spiking experiments showed unsatisfactory recoveries for PFFA/PFPiAs using Cl-PFPHxA as internal standard. Therefore, the calculations for PFFA/PFPiAs were performed using three-point standard addition curves for each sample. The concentrations of PFFA/PFPiAs were therefore not recovery corrected. For quantification, a recovery range of 20%–150% was set as acceptable for most of the analytes. For the diPAPs, where the recoveries were lower, a

lower bound of acceptable recoveries was set to 10%, since it was validated in spiking experiments that the accuracy was satisfactory in this range.

The range of recoveries of reported concentration for the sludge samples were 83%–92% for PFCAs, 86%–87% for PFASs, 66%–77% for FTCA/FTUCAs, 91%–132% for FTSA, 53%–69% for monoPAPs, 25% for diPAPs, 64%–86% for FOSA/FOSEs. For water sample the recoveries were 52%–90% for PFCAs, 74%–83% for PFASs, 49%–78% for FTCA/FTUCAs, 74%–81% for FTSA, 32%–40% for monoPAPs, and 22%–32% for diPAPs.

2. Results and discussion

2.1. PFASs in effluent water and sludge

A broad range of compound classes were detected in the filtered effluent water, including PFCAs, PFASs, FTCA/FTUCAs, FTSA and PFPA/PFPiA (Table 1). The Σ PFAS concentrations were in the range 29.8–77.0 ng/L. Among the precursor compound classes only FTSA was detected; 6:2 FTSA was found in all three WWTPs (mean 3.1 ng/L), while 8:2 FTSA was only detected in Umeå (0.3 ng/L, Appendix A, Table S3). The FTSA concentrations in this study are similar to previously observed in effluent waste water from Germany (Frömel et al., 2016) and the US, where median levels were 2.1 ng/L for 6:2 FTSA and 0.9 ng/L for 8:2 FTSA (Houtz et al., 2016). Analysis of diPAPs in water was hampered by unknown interferences; however a complete analysis could be reported for Henriksdal and Gässlösa effluent water, showing no detectable levels of diPAPs (Appendix A, Table S3). Low concentrations (0.1–0.2 ng/L) of FTCA/FTUCAs were detected in effluent; however the same problem as for diPAPs with interferences occurred for Gässlösa effluent.

Persistent PFCAs predominated the PFAS profile, with Σ PFCA levels of 22–66 ng/L. PFBA was the predominant PFCA with a mean level of 17 ng/L, followed by PFHxA, with a mean level of 9.7 ng/L. Other PFCAs detected were PFPeA, PFOA, PFHpA, PFNA, and PFDA (Appendix A, Table S3). The levels of PFCAs were much higher in Gässlösa compared to Umeå and Henriksdal, mainly attributed to the levels of PFBA and PFHxA, which indicates considerable contribution from industrial activities (textile and

chemical) to the amount of short-chained PFCAs in Gässlösa effluent water.

PFBS, PFOS, and PFHxS were the predominant PFASs in effluent water and had approximately equal contribution to Σ PFSA, with mean values of 1.9 ng/L, 1.9 ng/L, and 1.5 ng/L, respectively. Other PFASs found were PFPeS (mean 0.4 ng/L) and PFHpS (mean 0.1 ng/L) (Appendix A, Table S3). The highest PFSA concentration found was for PFBS in Henriksdal (3.7 ng/L). Branched PFOS isomers accounted for 21%–36% of total PFOS. The PFSA concentrations were similar between the WWTPs, suggesting non-significant contribution from industrial activities to the release of PFASs. The profile observed, with similar concentrations of short-chained PFASs and PFOS, differs from previous studies, where typically PFOS predominates the PFASs in municipal waste water effluent (Sindikü et al., 2013; Campo et al., 2014; Filipovic and Berger, 2015; Houtz et al., 2016). This could be attributed to an increasing production of PFBS after year 2002 in connection with the phase-out of PFOS by the main producer 3 M.

PFPAs and PFPiAs were detected in all three WWTPs, with PFPAs more abundant than PFPiA. PFDPA was the only PFPA detected (mean 1.6 ng/g). C6 PFPiA was detected in all WWTPs, and C6/C8 was detected in Gässlösa only. The concentrations of PFPAs in the effluent water were similar to previous studies from Canada and Germany (D'eon et al., 2009b; Llorca et al., 2012).

In the sludge samples, several classes of precursors, intermediates, and persistent PFASs were frequently detected, including monoPAPs, diPAPs, FTSA, FOSA/FOSEs, FTCA/FTUCAs, PFASs, and PFCAs (Table 2). The PFAS profile in the sludge differed from the profile in effluent water, in both compound class composition and homologue chain length. A vast majority of the PFASs found was precursor compounds and intermediates, contributing to 75%–86% of the Σ PFAS concentration in sludge sampled in 2015.

The monoPAPs and the diPAPs were the predominating precursor classes, with mean concentrations of 9.3 and 8.5 ng/g in 2015, respectively. Up to nine diPAP homologues were detected in the sludge samples (Appendix A Table S4). Previously, varying concentrations and compositions of PAPs in sludge were observed. The mean 6:2 diPAP (2.0 ng/g) and 8:2 diPAP (1.5 ng/g) concentrations in this study were slightly lower than previously reported concentrations in Canada and China,

Table 1 – Concentrations of detected per- and polyfluoroalkyl substances (PFASs) classes in waste water samples collected from wastewater treatment plants (WWTPs) in 2015 (ng/L).

	Umeå		Henriksdal		Gässlösa	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Σ PFCA	19	22	23	33	18	66
Σ PFSA	4.6	4.8	7.2	7.7	3.9	4.8
Σ FTSA	2.9	2.5	6.0	5.1	2.6	2.0
Σ FTCA/FTUCA	0.5	0.4	1.4	<LOD	3.5	n.q.
Σ monoPAP	<LOD	n.q.	<LOD	<LOD	n.q.	n.q.
Σ diPAP	58	n.q.	n.q.	<LOD	n.q.	<LOD
Σ PFPA	11	1.3	1.8	0.6	20	3.0
Σ PFPiA	0.6	0.1	1.6	0.1	0.3	2.1

n.q. not quantified due to low recoveries. LOD: limit of detection; PFCA: perfluoroalkyl acid; PFSA: sulfonic acid; FTSA: fluorotelomer sulfonic acid; FTCA: fluorotelomer carboxylic acid (saturated); FTUCA: fluorotelomer carboxylic acid (unsaturated); PAP: polyfluoroalkyl phosphoric acid ester; PFPA: perfluoroalkyl phosphonic acid; PFPiA: perfluoroalkyl phosphinic acid.

Table 2 – Concentrations of detected per- and polyfluoroalkyl substances (PFASs) classes in sludge samples collected from wastewater treatment plants (WWTPs) (ng/g).

	Henriksdal			Gässlösa			Umeå		
	2012	2014	2015	2012	2014	2015	2012	2014	2015
∑PFCA	6.2	6.2	4.7	13	12	7.3	2.4	1.7	2.5
∑PFSA	10	5.7	3.9	3.5	3.3	3.6	6.3	3.1	1.9
∑FTSA	1.8	1.3	0.9	0.9	1.6	1.2	1.0	1.0	0.8
∑FTCA/FTUCA	15	13	8.9	65	78	51	4.0	5.5	4.1
∑monoPAP	17	12	11	11	6.2	5.8	18	9.9	11
∑diPAP	9.9	8.5	7.5	7.7	7.2	8.8	17	3.3 ^a	9.1
∑PFPIA	<LOD	<LOD	<LOD	0.03	<LOD	<LOD	<LOD	<LOD	<LOD
∑FOSA/FOSE	3.8	2.9	<LOD	3.3	3.5	3.3	<LOD	<LOD	1.3

^a 8:2 diPAP not quantified.

where mean levels were 5.7 ng/g and 11.6 ng/g for 6:2 diPAP, and 23.9 ng/g and 28.1 ng/g for 8:2 diPAP, respectively (D'eon et al., 2009a; Loi et al., 2013). MonoPAPs was the only PAPs class found in sludge in a study from China, where mono-, di-, and triPAPs were analyzed (Liu et al., 2013). The levels in the Chinese sludge samples were in the range < LOD to 4.7 ng/g for 8:2 monoPAP and <LOD to 10.7 ng/g for 10:2 diPAP.

6:2 FTSA was detected in Henriksdal and Gässlösa, and 8:2 FTSA was detected in all three WWTPs, at concentrations ranging from 0.23 to 0.67 ng/g, and 0.55 to 0.75 ng/g, respectively, in 2015 (Appendix A, Table S4). Interestingly, 8:2 FTSA predominated over 6:2 FTSA in two of the WWTPs, Henriksdal and Umeå, while the concentration of 6:2 FTSA and 8:2 FTSA were similar in Gässlösa. Production of PFAS in general has shifted the last years from C8-based chemistry to C6- or C4-based products (OECD, 2007; Ritter, 2010). The presence of higher or similar 8:2 FTSA levels compared to 6:2 FTSA does not follow the predicted pattern, which could indicate a lagging, continued use of C8 products or be a result of preferential sorption of longer chain compounds to sludge. Higher levels of 8:2 FTSA compared to 6:2 FTSA have also been observed in Chinese WWTP sludge (Ruan et al., 2015).

The intermediates 5:3 FTCA, 7:3 FTCA, 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA were found in sludge from all three WWTPs. Their presence indicates the contribution from precursor compounds to persistent PFASs, since they are not intentionally produced and only formed during degradation of precursors. Remarkably higher levels of 5:3 FTCA were found in Gässlösa (43–68 ng/g) compared to Henriksdal (4.8–5.2 ng/g) and Umeå (0.7–2.1 ng/g) (Appendix A, Table S4). 5:3 FTCA will yield PFPeA upon degradation, and PFPeA was also found at notably higher levels in effluent water in Gässlösa (10 ng/L) compared to Henriksdal (4.9 ng/L) and Umeå (2.2 ng/L) (Wang et al., 2012). The second most abundant intermediate was 7:3 FTCA, and other intermediates found were 6:2 FTUCA, 8:2 FTUCA, and 10:2 FTUCA. It is likely that the elevated level in sludge from Gässlösa reflects the usage of unknown PFASs in textile and/or chemical industries present in the area.

Even-numbered homologues predominated the PFCA/PFSA profiles in sludge, however levels were lower than those of the precursor classes. Four PFSA; PFBS, PFHxS, PFOS, and PFDS were found in the sludge samples, while the

odd-numbered PFPeS, PFHpS, and PFNS were not detectable. The abundance followed the order PFOS > PFDS > PFBS > PFHxS (Appendix A, Table S4). The concentrations of L-PFOS were between 1.1 and 3.1 ng/g in 2015. The proportion of branched isomers to total PFOS concentration in the sludge was 12%–16%, which is lower than in the waste water, which may be a result of different hydrophilic properties among the PFOS isomers.

PFHxA, PFOA, PFDA, PFDoDA, and PFUnDA predominated the PFCA profile in sludge. The highest PFCA concentration in 2015 were found for PFHxA in Umeå (0.77 ng/g) and Gässlösa (3.3 ng/g), and PFDA in Henriksdal (1.3 ng/g). Other detected PFCAs were PFHpA, PFNA, PFTrDA, and PFTDA (Appendix A, Table S4).

Most compound classes showed lower sludge concentrations in 2012 compared to 2015 (Fig. 1). The ∑PFAS decreased 23%–43%. The decrease was mainly attributed to the longer-chained PFASs: C8 and longer homologues. The shorter-chained PFASs on the other hand: C6 and shorter homologues, showed an increase in several cases. In Gässlösa, 5:3 FTCA, 6:2 diPAP, 6:2 FTSA, and PFHxA increased. In Henriksdal, 5:3 FTCA and 6:2 diPAP increased while PFHxA remained at the same level, and in Umeå, PFHxA increased while 6:2 diPAP decreased. This might reflect the shift from C8 technology towards shorter-chained homologues, which also includes precursor compounds with shorter perfluorinated chain. Of the persistent PFASs, PFSA decreased more rapidly than PFCAs. A clear decrease of PFOS from 2012 to 2015 was observed in Henriksdal (–62%) and Umeå (–44%), while in Gässlösa the concentration remained at the same level. Gässlösa was also the only WWTP where MeFOSE and EtFOSE were detected in 2015. The presence of PFOS precursors in the sludge in 2015 suggests that although PFOS was phased out 15 years ago, there are still new additions from the technosphere to the environment which adds to already circulating levels.

The daily discharge (D_d) and the daily discharge per person connected to the WWTP (D_{dp}) of persistent PFASs were calculated for the 24 hr composite samples by taking the sum of effluent and sludge concentrations and dividing it by the number of people in households connected to the three WWTPs (Fig. 2). Major contributions to the daily discharge were from PFBA, PFPeA, PFHxA, PFHpA, PFOA, and 6:2 FTSA. Assuming that consumption patterns are similar in different

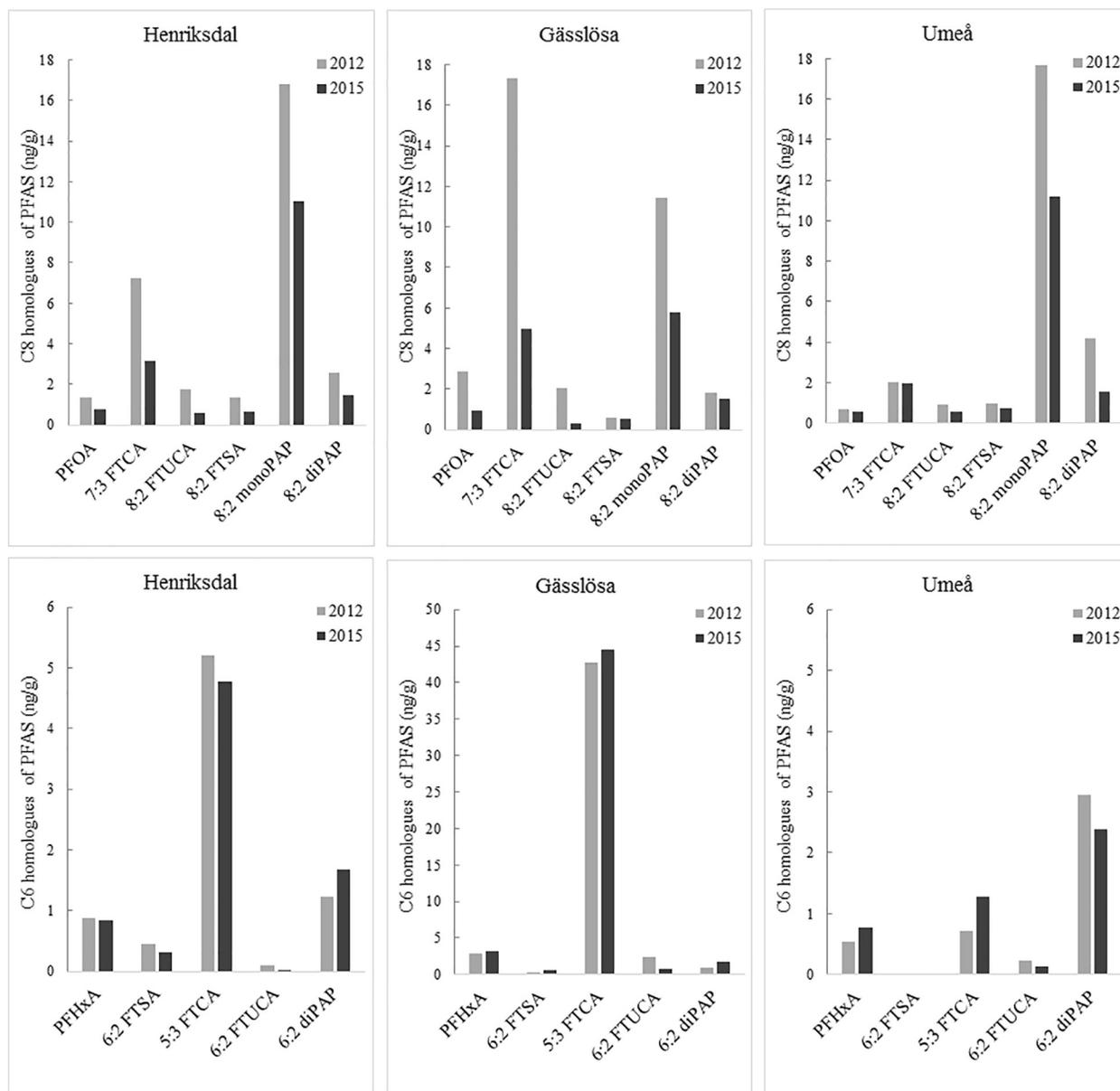


Fig. 1 – Concentrations of C8 and C6 PFAS homologues in sludge collected from WWTPs in 2012 and 2015.

regions in Sweden, the discharge from Umeå should mainly reflect contribution from households and the hospital, while Henriksdal and particularly Gässlösa also could be affected by contribution from industries connected to these WWTPs. The D_{dp} showed 3–7 times higher levels of PFBA, PFPeA, and PFHxA, and 4–31 higher levels of C6/C8 PFPIA and PFDPA in Gässlösa compared to Henriksdal and Umeå, suggesting that industrial activities in this area strongly contributes to release of short-chain PFCAs and PFDPA to the environment. Higher levels were observed for other PFCAs as well in WWTPs with industrial activities. For PFOA, the D_{dp} was higher in Gässlösa (2.5 $\mu\text{g}/\text{day}/\text{person}$) compared to Umeå (1.1 $\text{ng}/\text{day}/\text{person}$), and slightly higher than Henriksdal (1.9 $\mu\text{g}/\text{day}/\text{person}$). The differences in D_{dp} between industrial influence (Gässlösa) and WWTPs dominated by domestic waste water (Henriksdal and Umeå) were

smaller for PFSA than for PFCAs. It was however clear that levels of PFSA homologues were the lowest in Umeå, which is the WWTP supposedly least affected by industrial activities. Only small differences in D_{dp} were observed for monoPAPs and diPAPs for the three WWTPs. These results are similar to a previous study, where industrial WWTPs showed higher concentrations of PFASs in sludge compared to domestic WWTPs, especially for PFCAs (Sindikü et al., 2013) although this is probably connected to the type of industrial activity. Additionally, the proportion between PFCAs and PFSA has been observed to differ between domestic and industrial WWTPs, where the proportion of PFCAs was found to be higher in industrial WWTPs (Alder and van der Voet, 2015). The same pattern was observed in this study, with the highest proportion of PFCAs in Gässlösa, which is connected to textile and chemical industries.

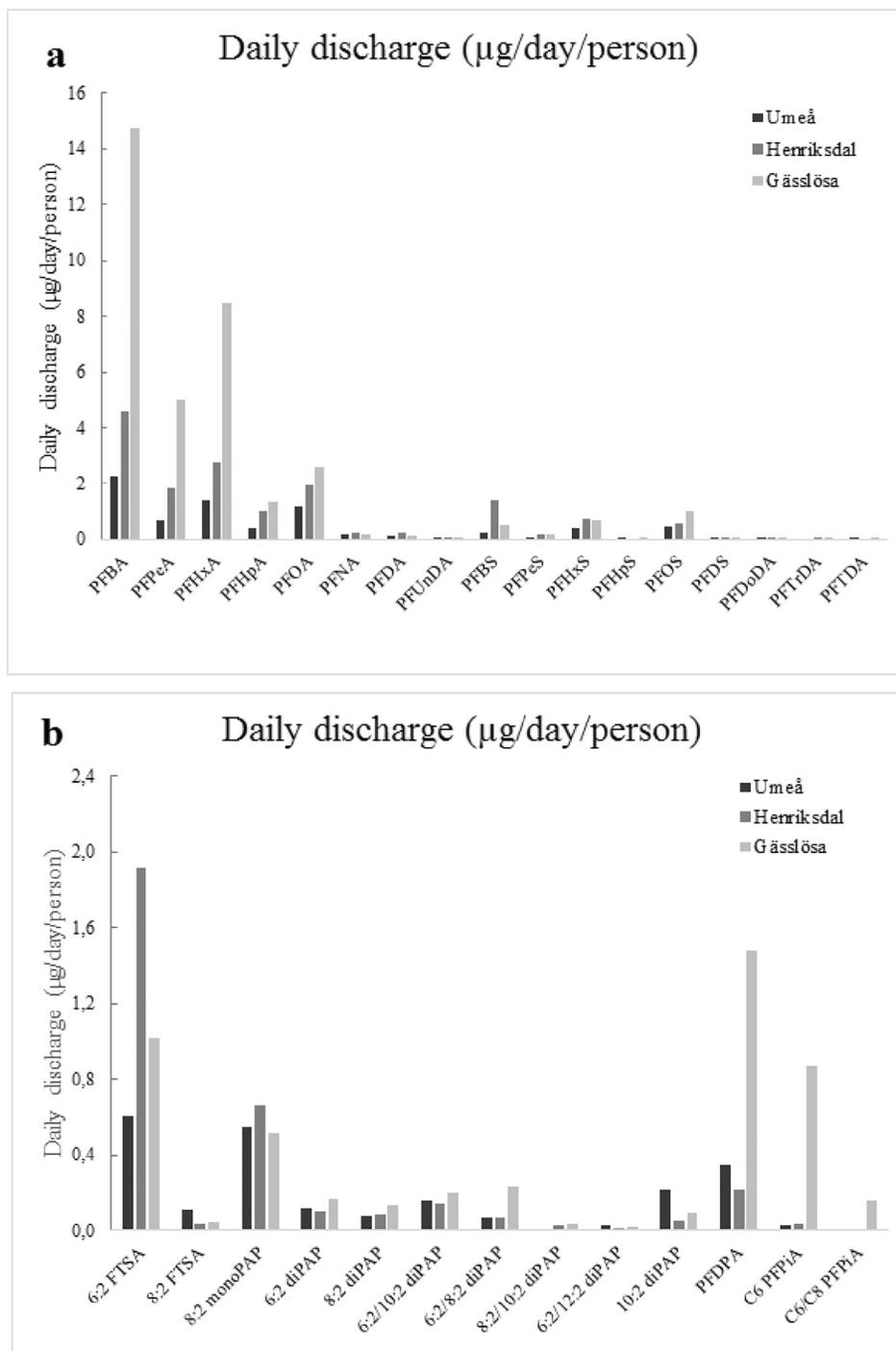


Fig. 2 – Daily discharge ($\mu\text{g/day/person}$) of PFCA and PFSA (a), and FTSA, monoPAP, diPAP, PFPAs, and PFPiAs (b) calculated from sludge and effluent concentrations during one day in the three WWTPs.

2.2. Comparison between influent and effluent water

Similar to the effluent water, a large number of the compound classes analyzed were detected in the influent water; PFCA, PFSA, FTCA/FTUCA, FTSA and PFPA/PFPiA. In addition, diPAP were also detected (Table 1). The Σ diPAP dominated the PFAS influent profile in Umeå with a concentration of 58 ng/g. Due to low recoveries it was not possible to report diPAP concentrations

in influent from the other two WWTPs. The concentration of 6:2 diPAP (7.6 ng/L) and 8:2 diPAP (2.9 ng/L) in the influent water in this study is similar to a previous study from Hong Kong, where concentrations were in the range 0.9–2.4 ng/L for 6:2 diPAP, and 1.2 to 4.0 ng/L for 8:2 diPAP (Loi et al., 2013).

The Σ PFCA in influent were higher in Henriksdal (23.0 ng/L) and Gässlösa (17.6 ng/L), compared to the domestic-dominated WWTP in Umeå (11.8 ng/L) (Table 1). Short-chained PFCA

predominated the PFCA profile; PFHxA predominated in Henriksdal and Gässlösa, while PFPeA predominated in Umeå. The highest PFSA concentration was found for PFBS in Henriksdal (3.2 ng/L), PFOS in Gässlösa (1.5 ng/L) and PFOS in Umeå (2.9 ng/L) (Appendix A Table S3). The contribution of branched PFOS isomers to the total PFOS concentration in influent was in the range 38%–45% compared to 21%–36% in effluent water. The proportion of branched isomers in technical mixtures of PFOS is approximately 30%, and the influent water is therefore slightly enriched in branched PFOS.

PFPA and PFPiA were detected in all influent waters, and the levels of PFPA were higher than the levels of PFPiA. The Σ PFPA was 20 ng/L in Gässlösa, 11 ng/L in Umeå, and 1.8 ng/L in Henriksdal (Table 1).

5:3 FTCA and 7:3 FTCA were detected in all samples of influent water, and 6:2 FTUCA was found in the influent from Gässlösa.

In general, precursor compounds were more frequently detected and at higher levels in the influent water compared to the effluent water, whilst higher levels of persistent PFASs were found in the effluent compared to the influent.

The PAPs could not be detected above LOD in any effluent water, while diPAPs were found in influent water from Umeå, with 6:2 diPAP and 8:2 diPAP concentrations of 7.6 ng/L and 2.9 ng/L, respectively. While the levels of 6:2 FTSA were similar in influent compared to effluent water in all three WWTPs, 8:2 FTSA had higher levels in the influent (0.1–0.9 ng/L) compared to the effluent (<0.1–0.3 ng/L). The Σ PFCA was in the range 12–23 ng/L in the influent, considerably lower than the Σ PFCA (22–65 ng/L) in the influent. This indicates degradation of precursor compounds (e.g., FTSA and diPAPs) to persistent PFAS in the WWTPs. Another possible reason that PFAS concentrations were shown to increase during waste water treatment might be through release from feces particles, though this elimination route is considered to be of minor importance compared to urine elimination and decrease with decreasing chain length, as has been observed in animal studies (Kudo et al., 2001; Cui et al., 2010). The PFPA/PFPiA profile was quite different in the effluent compared to influent. PFPA were higher in the influent (1.8–19.7 ng/L) compared to the effluent <LOD–3.0 ng/L (Appendix A Table S3), and not detected in the sludge. This is similar to a study from China, where PFOPA was found in influent water (1.1 ng/L) but absent in effluent water (Jin et al., 2015).

The daily discharges in effluent water and sludge were compared to the daily incoming amount of PFCAs and PFASs in the influent water, thus reflecting the change in concentration of PFASs in the WWTPs (Appendix A, Fig. S3). There was an apparent increase for most of the persistent PFASs. The highest increase was observed for PFHxA, with a net increase of 35%–156%. PFBA was only possible to quantify in Henriksdal, where it showed a distinct increase of 124%. PFPeA and PFHpA increased in Henriksdal and Gässlösa, the two WWTPs connected to industrial activities. Though the increase was most pronounced for the short-chained PFASs, there was also an increase for PFDA in all WWTPs, for PFNA in Gässlösa, and PFOA in Umeå and Gässlösa. This indicates contribution from precursors also for the release of long-chained PFCAs. The net mass changes of the longer-chain PFASs (C > 10) were not calculated, due to their low levels and

frequency of detection in the water samples. In addition, it is possible that a proportion of the PFASs was distributed to the suspended particulate matters that were separated from the water before analysis. This has been observed in previous studies and could hamper the assessment in this study (Ahrens et al., 2010; Zhao et al., 2016). While short-chained PFASs were mainly distributed to the dissolved phase (>95%), up to 54% of PFOS and 17% of PFOA were found in the particulate phase (Ahrens et al., 2010; Zhao et al., 2016). For assessment of discharge from longer-chained PFAS, the particulate phase should be analyzed as well. PFOS increased by 125% in Gässlösa and with 44% in Henriksdal. Gässlösa was the only WWTP where PFOS precursors were found in 2015, and it's possible that the increased PFOS level is related to degradation from these precursor compounds. The concentrations of N-MeFOSE and N-EtFOSE in the sludge from Gässlösa were 2.4 ng/g and 0.9 ng/g, respectively. PFBS and PFHxS increased in all WWTPs except for PFBS in Gässlösa, where no change was observed.

2.3. Contribution from precursors

The contribution of PFCAs in the effluent originating from precursor degradation could be calculated for the WWTP in Umeå. The other WWTPs did not have a complete report on precursor compounds in the influent water. One WWTP only cannot provide representative data for precursor transformation in WWTPs, but can rather be stated as an example of possible scenarios, and the estimation should be interpreted with caution. Microbial degradation of 6:2 diPAP in sludge has been demonstrated, with a yield of 5% for 6:2 FTOH from 6:2 diPAP of 5% (Lee et al., 2010). Using a 6% yield of PFHxA from 6:2 FTOH (Wang et al., 2005), gives a yield of 0.3% PFHxA from 6:2 diPAP. However, the experiments performed by Lee et al. were designed for mechanistic and not quantitatively purpose, thus the microbial activity was probably much lower than in a WWTP. Hence the yield of 0.3% could be considered as a conservative value. The biotransformation yield of 6:2 diPAP to PFHxA in aerobic soil has been reported to be 6.0% (Liu and Liu, 2016). Using these values as a lower bound and upper bound scenario, the degradation of PAPs accounted for 2.1%–41% of the net increase of PFHxA during the waste water treatment in the Umeå WWTP. Of the total amount PFHxA released in the effluent water, 0.7%–13% could be related to degradation of diPAPs during waste water treatment. The biodegradation yield of 6:2 FTSA to PFHxA has been reported to be 1.1% in activated sludge (Wang et al., 2011). This would correspond to a contribution of 1.1% of the net increase of PFHxA in Umeå effluent, and a contribution of 0.3% from 6:2 FTSA to the total amount of PFHxA emission through effluent waste water. Adding up the contribution of precursor compound degradation to PFHxA during waste water treatment in this study, gives a proportion of 3.1%–42% of the net increase. The remaining 58%–96.9% are likely to originate from unknown precursor compounds, not covered in this study. An earlier study has shown that the presence of unknown organofluorine compounds in human sera samples (14%–69% in Chinese serum samples, and 0–48% in German serum samples), and the amount and proportion of these unidentified organofluorine were shown to increase after the year 2000 (Yeung and Mabury, 2016). It is possible that these

unidentified organofluorine may consist of unknown precursor compounds of PFCAs.

Of the total amount PFHxA released from WWTP, 1.0%–14% can be related to degradation from diPAPs and 6:2 FTSA during waste water treatment.

Using a biotransformation yield of 2.1% for 8:2 diPAP to PFOA from the study by Liu et al., the contribution from diPAPs degradation to the net increase of PFOA in this study can be calculated as 18% (Liu and Liu, 2016). Of the total amount of PFOA released from the WWTP, 5.4% could be assigned to diPAPs degradation. There is no data available about degradation yield for 8:2 FTSA. Assuming a similar yield of PFOA for 8:2 FTSA as for 6:2 FTSA (1.1%), the degradation of 8:2 FTSA to PFOA could account for 0.5% of the net increase. The contribution of 8:2 FTSA to the total amount PFOA released would be 0.15%. This adds up to an estimated contribution of 5.5% from diPAPs and 8:2 FTSA to the total amount of PFOA released through waste water.

During biodegradation of PFCAs, the stable metabolites FTCAs are formed. Assessing the ratio between PFCAs and corresponding metabolites may indicate whether the source is direct or indirect through precursor degradation (Wang et al., 2009). The PFOA/FTCA ratios were calculated in the Umeå WWTP, and were 0.66 for PFHxA/5:3 FTCA, and 0.31 for PFOA/7:3 FTCA. As degradation of fluorotelomer compounds yields approximately similar proportion of PFCAs and FTCAs, these low ratios indicate that the PFCAs originate from precursor degradation.

2.4. Distribution of PFAS between water and sludge

The distribution between sludge and influent water was assessed by calculating the distribution coefficient, $\log K_d$, between PFASs in sludge and water (Appendix A, Table S5). Generally, the $\log K_d$ increased with chain length, as true for PFCAs, PFSAs, and FTSAs for homologues with more than six fluorinated carbons in the alkyl chain (Appendix A, Fig. S5). For shorter-chained PFAS ($C \leq 5$), electrostatic interactions have been hypothesized to be of more importance than hydrophobic interactions for sorption to sludge, and hence the partition to sludge increases with decreasing chain length for homologues (Zhang et al., 2013). The $\log K_d$ of PFCAs and PFSAs were in good agreement with previously reported values (Sun et al., 2012).

The $\log K_d$ value was higher for 8:2 FTSA (3.43) than for 6:2 FTSA (2.08), which indicates a much higher capacity for 8:2 FTSA to partition to the sludge compared to 6:2 FTSA. This could explain the comparatively high proportion of 8:2 FTSA to Σ FTSA in the sludge samples, in relation to known compositions of FTSAs and their precursors in production and manufacturing. For the diPAPs on the other hand, the estimated $\log K_d$ values did not seem to be related to chain length. The monoPAPs were not detected in the influent water and their $\log K_d$ could not be calculated. It is possible that electrostatic interactions are the driving mechanism for the monoalkylated PAPs, and make them sorb strongly to the sludge.

2.5. Environmental implications

The increases of several persistent PFAS during WWTP treatment, especially short-chained homologues, are presumably a

result of degradation of PFCAs precursor compounds during the WWTP process. Detection of FTSAs in the effluent, and FTSAs and PAPs in the sludge, implies that the PFOA load from the WWTPs might continue to increase during their further degradation. For PFCAs longer than C8 and PFSAs longer than C7, the amount distributed to the sludge has a significant impact on the total amount of PFAS released from the WWTPs. The application of sludge in agriculture practice cause continuous exposure of PFASs to humans and the environment through the food chain (Lindstrom et al., 2011; Bizkarguenaga et al., 2016). Though short-chained PFASs are considered to be less bioaccumulative than longer-chain PFASs, they are as persistent and their toxic effects are not fully understood. It has recently been stated that their release into the environment is troublesome because it is a poorly reversible act (Cousins et al., 2016). Continuous release of these short-chain PFCAs from the WWTPs will result in significant impact on the water recipient. Additionally, the environmental fate of PFPAs and PFPiAs, also detected in the effluent, is not well understood. Even PFASs prohibited by regulations, such as PFOS and PFOA, are still circulating and observed at substantial levels in WWTPs. Further studies are needed with the focus on contribution from recently identified and unknown PFASs since a considerable proportion of persistent PFCAs in effluent originate from unknown precursors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2017.05.004>.

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