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Screening of PFASs in sludge and water from waste water treatment plants

Screening av PFASs i slam och vatten från reningsverk

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<p>Period in which underlying data were collected 2012-2015</p>	
<p>Summary</p> <p>The purpose of this study was to assess the contribution from precursor compounds to the total amount of selected PFASs in water and sludge from Swedish waste water treatment plants, as a supplemental to previous studies of two persistent PFAS-classes; perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs). Compound classes added in this study were fluorotelomer sulfonic acids (FTSAs), polyfluoroalkyl phosphoric acid esters (PAPs), perfluoroalkyl phosphonic and phosphinic acids (PFPA, PFPIAs), perfluoroalkane sulfonamides (FOSAs), and sulfonamido ethanols (FOSEs), and also the intermediates fluorotelomer unsaturated carboxylic acids (FTUCAs) and the stable transformation products fluorotelomer carboxylic acids (FTCAs).</p> <p>Three waste water treatment plants were included; Gäsö (Borås), Henriksdal (Stockholm) and Umeå. PFAS levels in sludge from 2012, 2014, and 2015, and in filtered effluent and influent water from 2015 are reported. Precursor compounds were detected in sludge and influent water from all three WWTPs. Levels of precursor compounds in sludge samples exceeded those of persistent PFASs. Increasing PFCA levels in the effluent water compared to the influent water was observed, especially for the short-chained PFCAs. Occurrence of precursor compounds in influent water and sludge indicate degradation of precursor compounds to persistent PFASs.</p>	

Sammanfattning

Syftet med denna studie var att studera bidraget från föregångarämnen till den totala halten av PFAS i slam och vatten från svenska reningsverk, som komplettering till tidigare studier av persistenta PFAS-grupper bestående av perfluorkarboxylsyror (PFCAs) och perfluorsulfonsyror (PFSAs). De föregångarämnen som ingick i denna studie var fluortelomersulfonsyror (FTSAs), polyfluorerade fosfatestrar (PAPs), perfluorfosfonater och perfluorfosfinater (PFPA, PFPiA), sulfonamider (FOSAs), sulfonamidetanoler (FOSEs) samt intermediärer (omättade fluorotelomersyror, FTUCAs) och stabila transformationsämnen (fluorotelomersyror, FTCAs).

De reningsverk som ingått i studien är Gässlösa (Borås), Henriksdal (Stockholm) och Umeå. I denna rapport redovisas PFAS-halterna i slam från 2012, 2014 och 2015, och i filtrerat ingående och utgående vatten från 2015. Samtliga reningsverk påvisade förekomst av föregångarämnen i såväl slam som ingående vatten. I slamproverna var halterna av föregångarämnen och intermediärer högre än halterna av persistenta PFASs. Flera PFCAs, i synnerhet kortkedjade, visade högre halter i utgående vatten i förhållande till ingående vatten. Förekomst av föregångarämnen i ingående vatten och slam visar att nedbrytning i reningsverken kan vara en förklaring till de ökade halter av PFCAs som observerats i utgående vatten, i förhållande till ingående vatten.

Background

Per- and polyfluorinated alkyl substances (PFASs) are anthropogenic compounds that are produced and used in a wide range of products due to their oil- and water repellence properties. It has been estimated that more than 3000 PFASs are currently in use on the global market in commercial products (KEMI 2015). A number of PFASs have been recognized to be bioaccumulating, persistent and toxic (DeWitt 2015). Regulations and voluntary phase-out have led to decreased production of some of the most emergent PFAS compounds; perfluorooctane sulfonic acid (PFOS) and perfluorooctane carboxylic acid (PFOA). In replacement, the production of fluorotelomer compounds, short-chained homologues of PFCAs and PFSA, and polyfluoroether compounds have increased.

PFASs are released to the biosphere through wastewater treatment plants (WWTPs), as a result of industrial activities and domestic usage of PFAS products within the technosphere. The observations of higher levels of PFCAs in effluent water compared to influent water have suggested that this increase may be attributed to degradation of precursor compounds in the waste water treatment process (Kunacheva et al. 2011, Campo et al. 2014). Fluorotelomer compounds have the ability to degrade into persistent PFCAs and PFSA, as has been shown for PAPs and for FTSA in activated sludge (Lee et al. 2010, Wang et al. 2011). PAPs are mainly used in paper and packaging material, including food packaging material, but also in cosmetics, personal care products, paints, and cleaning products (Pilot Chemicals 2017). FTSA-based products have mainly been used as an active ingredient in aqueous film forming foams (AFFF) (Harding-Marjanovic et al. 2015).

Aim

The objectives of this study were to analyse polyfluorinated precursor compounds and intermediates of persistent PFASs, assess their levels and relatively contribution to the total amount of selected PFASs, in addition to previous analysis of PFCAs and PFSA in sludge and water from Swedish wastewater treatment plants.

Project administration and coordination

This project has been led by Umeå University (UmU). The project leader has been responsible for the coordination between participants and contacts with the Swedish Environmental Protection Agency. Analysis and data interpretation have been performed by Örebro University (Oru)

Following persons have participated in the project:

UmU Peter Haglund, Professor, project leader

Oru Anna Kärman, Associate professor

Oru Ulrika Eriksson, PhD

Materials and methods

Samples

Samples from three WWTPs were analyzed; Henriksdal, Gässlösa, and Umeå (table 1). The Henriksdal plant receives municipal wastewater 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 hospital connected. All three WWTPs have mechanical, chemical, biologic, and anaerobic digestion treatment. Sludge samples were collected as composite samples during one day in October the years 2012, 2014, and 2015 from all three WWTPs. Influent and effluent water samples were

collected in October year 2015 and was collected as composites of seven consecutive days. Sludge was freeze dried and all samples were stored in freezer at -18 °C until analysis.

Table 1. Description of three WWTPs included in the study

	Henriksdal	Gässlösa	Umeå
Number of people served	737 000	82 000	92 000
Person equivalents	656 000	73 000	73 000
Amount sludge produced (t/year)	14 400	2 400	2 300
Residence time of sludge (days)	19	25	18
Amount influent water (million m ³)	89	13	13

Extraction and chemical analysis

Forty one (41) PFAS compounds were analyzed (Table S1) representing the different classes PFCAs, PFSAs, FTSAAs, PAPs, PFPAs, PFPiAs, FOSAs, FOSEs, FTUCAs and FTCAs. For the sludge extraction and clean-up, 0.25 g freeze-dried sample was used. Isotopic labeled internal standards were added to the samples, followed by addition of 2 mL 1 M sodium hydroxide in methanol. The samples were ultrasonicated for 15 min, shaken for 15 min, centrifuged, the supernatant was removed, and the extraction was repeated twice with aliquots of 2 mL methanol. Further 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 eluted with 4 mL methanol, followed by elution with 4 mL 2% ammonium hydroxide in methanol, and the fractions were collected for analysis of neutral and anionic PFASs, respectively. The extracts were evaporated and transferred to LC-vials.

For the water extraction and clean-up, 0.5 L was used. The water samples were filtered with GF/B glass fiber filters before extraction (Whatman Isotopic labeled internal standards were added to the samples before extraction with SPE using WAX sorbents, according to ISO/DIS 25101 with some modifications. The WAX sorbents were conditioned with 4 mL methanol and 4 mL Milli-Q water. The water samples were passed through the sorbents, followed by washing with 4 mL of ammonium acetate buffer solution (pH 4) and 4 mL methanol. Finally, the analytes were eluted with 4 mL of 0.1% ammonium solution in methanol, evaporated and transferred to LC-vials.

The sample extracts were analyzed on an UPLC system coupled to a triple quadruple 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 mM ammonium acetate in water, and 2 mM ammonium acetate in methanol were used with gradient elution for all analytes except for PAPs, for which water and methanol with addition of 2 mM ammonium acetate and 5 mM 1-methylpiperidine was used. Both quantification and qualification product ions were measured in the multiple reaction monitoring, except for a few shorter PFCAs for which only one stable product ion was formed in the mass spectrometric analysis.

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 accuracy, precision, matrix effects, and recoveries of the method.

Quantification of PFCAs, PFSAs, FTCA/FTUCAs, FTSA, monoPAPs, diPAPs, and FOSA/FOSEs was performed by isotope dilution with mass labeled internal standards. Spiking experiments showed unsatisfactory recoveries for PFPA/PFPiAs using Cl-PFPH_xA as internal standard. Therefore, the calculations for PFPA/PFPiAs were performed using three-point standard addition curves for each sample. The concentrations of PFPA/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 PFSAs, 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 PFSAs, 49 – 78% for FTCA/FTUCAs, 74 – 81% for FTSA, 32 – 40% for monoPAPs, and 22- 32% for diPAPs.

Results

PFASs in sludge

A majority of the compound classes analyzed were detected in sludge samples 2012-2015; PFCAs, PFSAs, FTSA, FTCA, FTUCA, monoPAPs, diPAPs, FOSA, and FOSEs (table 2). Concentrations of all compounds are given in table S2.

Table 2. Concentrations of PFAS classes (sum of targeted compounds, table S1) in ng/g dry weight and water content (%) in sludge from wastewater treatment plants.

	Henriksdal			Gässlösa			Umeå		
	2012	2014	2015	2012	2014	2015	2012	2014	2015
Water content %	71.7	71.8	74.6	78.3	75.1	76.8	63.3	64.1	67.1
∑PFCa ^a	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 ^b	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 ^c	3.8	2.9	<LOD	3.3	3.5	3.3	<LOD	<LOD	1.3

^a excluding PFBA, PFPeA. ^b excluding 6:2 monoPAP. ^c excluding PFOSA

The composition profiles of PFAS in sludge were dominated by intermediates, transformation products, and precursor compounds, which contributed with 75 – 86% of the ∑PFAS amount (figure 1). PAPs were the predominating precursor class in sludge and up to nine diPAP homologues were detected of which six are quantified and reported (table S2). The PFAS profile differed between wastewater treatment plants. In Gässlösa, the relative contribution from FTCA/FTUCAs was higher than the other wastewater treatment plants, mainly attributed to the comparable high level of the transformation marker 5:3 FTCA. This indicates contribution from precursor compounds to persistent PFASs, since it is not intentionally

produced, and will ultimately yield PFPeA upon further degradation. The variation in concentrations and homologue profile between sampling year was smaller than variations between WWTPs. PFPAs and PFPIAs could not be detected above detection limit and a few compounds (PFBA, PFPeA, 6:2 monoPAP, PFOSA) could not be quantified with acceptable quality.

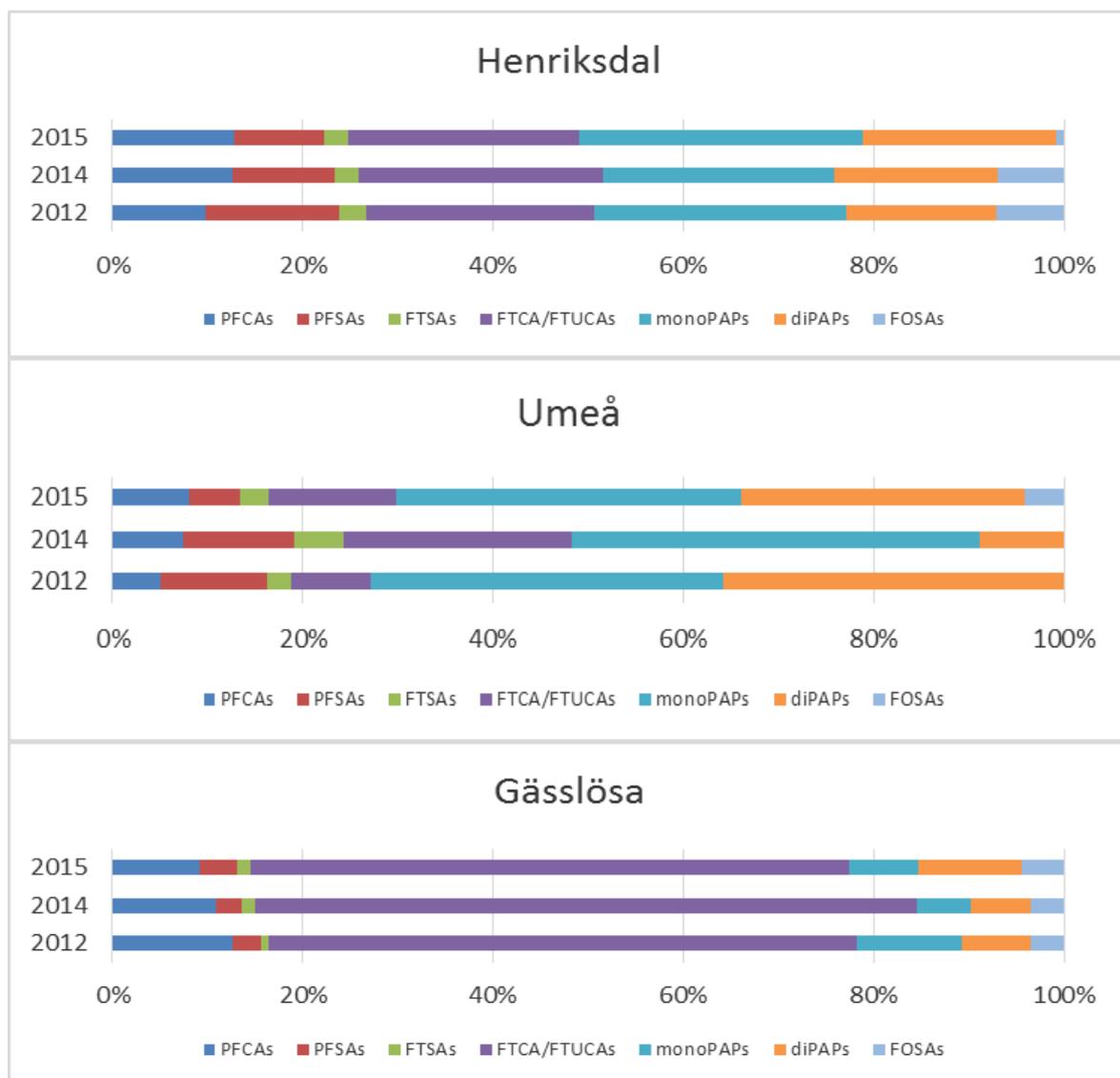


Figure 1. Profile of PFAS classes in sludge sampled 2012, 2014, 2015 at three WWTPs.

PFAS in filtered influent and effluent waste water

In both influent and effluent water, a majority of the compound classes analysed were detected; PFCAs, PFSA, FTSA, FTCA, FTUCA, diPAPs, PFPA, and PFPiA (table 3). Concentrations of individual PFASs are given in table S3.

Table 3. Concentrations (ng/L) of detected PFAS classes in waste water collected 2015.

	Umeå		Henriksdal		Gässlösa	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Σ PFCA ^a	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 ^a	<LOD	n.q.	<LOD	<LOD	n.q.	n.q.
Σ diPAP ^a	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. ^aOne or more homologues are excluded from the sum

In the effluent water, FTSA was the only precursor compound that could be detected and quantified with acceptable quality. 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). Low concentrations of the intermediates FTUCAs (0.07 – 0.08 ng/L) were detected in the effluent.

Persistent PFCAs predominated the PFAS profile in the effluent water, with Σ PFCA levels of 22 - 66 ng/L. PFBA was the predominating PFCA (8.2 – 30 ng/L), followed by PFHxA (5.0 – 17 ng/L). 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.

In the influent water, the diPAPs was the dominating PFAS class in Umeå, with a concentration of 58 ng/g. The diPAP concentrations from the other two WWTPs were not possible to report, due to low recoveries. The FTSA concentrations were similar in the influent water compared to the effluent water. Since the precursor compounds FTSA also are degradation products from other PFASs, it is possible that detection of FTSA in the effluent could be a result of degradation of those FTSA-based compounds in the waste water treatment process.

Mass flow

The daily discharge ($\mu\text{g}/\text{day}/\text{person}$) in the effluent water was compared to the influent water in the WWTPs (figure 2). An increase in mass flow was observed for most of the PFCAs and PFSA in all WWTPs, especially PFBA, PFPeA, and PFHxA. Highest increase was observed for PFHxA with a net increase of 35%, 58%, and 156% in Henriksdal, Umeå, and Gässlösa, respectively.

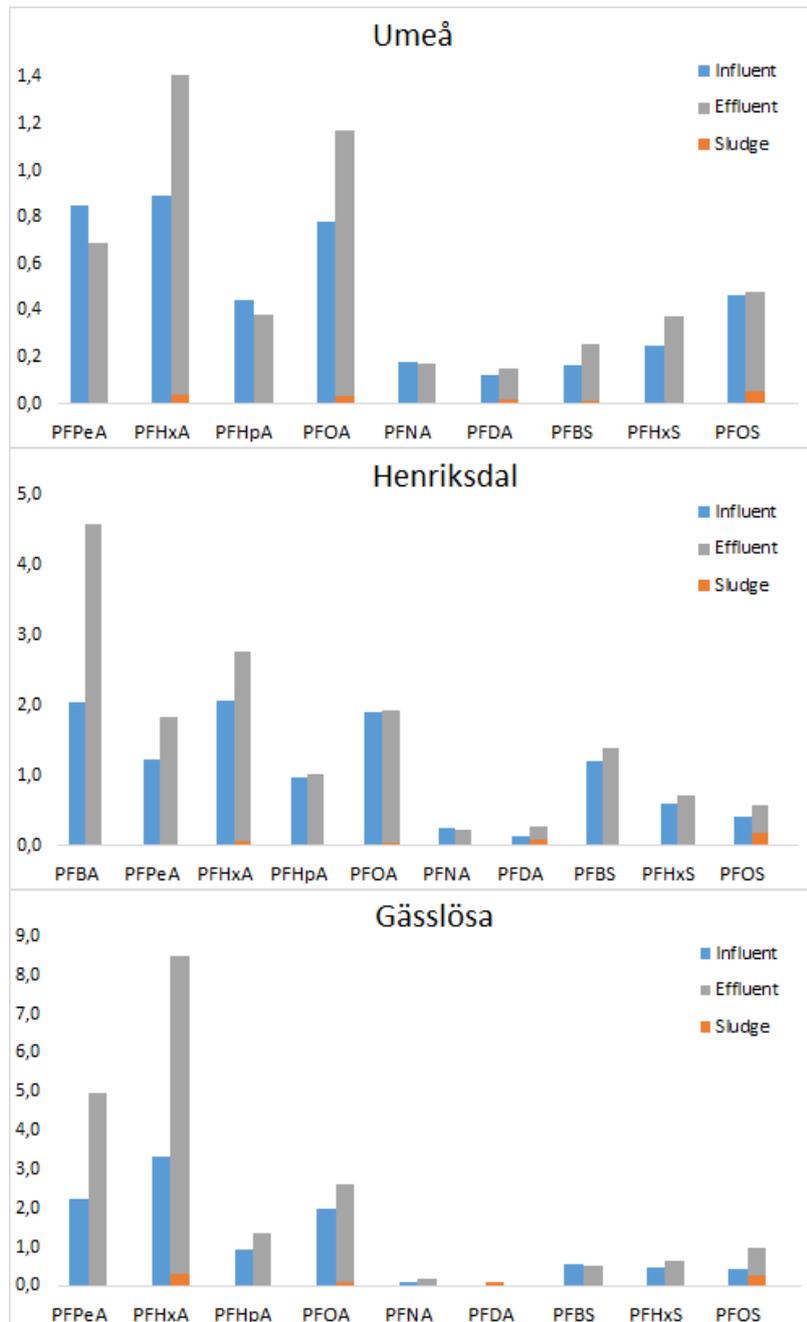


Figure 2. Concentrations of PFCAs and PFSA in influent water, effluent water, and sludge in the three WWTPs ($\mu\text{g}/\text{day}/\text{person}$).

Summary

- Precursor compounds, intermediates, and stable transformation products dominated the PFAS profile in sludge, with a contribution of 75 – 86%.
- PFCA precursor homologues detected in sludge were 6:2 FTSA, 8:2 FTSA, 8:2 monoPAP, 6:2 diPAP, 8:2 diPAP, 6:2/10:2 diPAP, 6:2/8:2 diPAP, 8:2/10:2 diPAP, and 6:2/12:2 diPAP.
- In-between year's differences were smaller than differences between WWTPs for the PFAS profile in sludge samples.
- Precursor compounds of monoPAPs, diPAPs, and FTSA were detected in the influent water.
- The Σ PFAS concentrations were in the range 29.8 – 77.0 ng/L in the effluent water.
- Short-chained homologues dominated the PFCA profile in the effluent water.
- Levels in effluent water were 8.2 – 30 ng/L for PFBA, and 5.0 – 17 ng/L for PFHxA.
- Several PFCAs increased during the wastewater treatment process, with highest increase for short-chained PFCAs; 35%, 58%, and 156% for PFHxA in Henriksdal, Umeå, and Gässlösa, respectively.

Conclusion and recommendations

Precursor compounds made a significant contribution to the total amount of PFAS in the Swedish WWTPs. A longer time series is needed in order to draw conclusions regarding time trends.

Levels of PFASs increased during the WWTP process, especially the short-chained PFCAs. Though short-chained PFASs are considered to be less bioaccumulative than longer-chained PFASs, they are persistent and their toxic effects are not yet fully understood.

Detection of FTSA in the effluent, and FTSA and PAPs in the sludge, implicates that the PFCA load from the WWTPs might continue to increase during their further degradation.

It is possible that a proportion of the PFASs in the WWTPs are unknown, not yet identified compounds. An analysis of the total organofluorine content in sludge and water from WWTPs could provide additional information about the relatively contribution from newly identified and unknown PFAS compounds.

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Supplemental Information

Table S1. Compound classes and compounds analyzed in the study

Class	Abbreviation	Name
PFSA	PFBS	Perfluorobutane sulfonic acid
	PFPeS	Perfluoropentane sulfonic acid
	PFHxS	Perfluorohexane sulfonic acid
	PFHpS	Perfluoroheptane sulfonic acid
	PFOS	Perfluorooctane sulfonic acid
	PFNS	Perfluorononane sulfonic acid
	PFDS	Perfluorodecane sulfonic acid
	PFDoS	Perfluorododecane sulfonic acid
PFCA	PFBA	Perfluorobutanoic acid
	PFPeA	Perfluoropentanoic acid
	PFHxA	Perfluorohexanoic acid
	PFHpA	Perfluoroheptanoic acid
	PFOA	Perfluorooctanoic acid
	PFNA	Perfluorononanoic acid
	PFDA	Perfluorodecanoic acid
	PFUnDA	Perfluoroundecanoic acid
	PFDoDA	Perfluorododecanoic acid
	PFTTrDA	Perfluorotridecanoic acid
PFTDA	Perfluorotetradecanoic acid	
FTCA	5:3 FTCA	5:3 Fluorotelomer carboxylic acid
	7:3 FTCA	7:3 Fluorotelomer carboxylic acid
FTUCA	6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylic acids
	8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acids
	10:2 FTUCA	10:2 Fluorotelomer unsaturated carboxylic acids
FTSA	4:2 FTSA	4:2 Fluorotelomer sulfonic acid
	6:2 FTSA	6:2 Fluorotelomer sulfonic acid
	8:2 FTSA	8:2 Fluorotelomer sulfonic acid
monoPAP	6:2 monoPAP	6:2 Fluorotelomer phosphate monoester
	8:2 monoPAP	8:2 Fluorotelomer phosphate monoester
diPAP	6:2 diPAP	6:2 Fluorotelomer phosphate diester
	8:2 diPAP	8:2 Fluorotelomer phosphate diester
	6:2/10:2 diPAP	6:2/10:2 Fluorotelomer phosphate diester
	6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester
	8:2/10:2 diPAP	8:2/10:2 Fluorotelomer phosphate diester
	6:2/12:2 diPAP	6:2/12:2 Fluorotelomer phosphate diester
PFPA	PFHxPA	Perfluorohexyl phosphonic acid
	PFOPA	Perfluorooctyl phosphonic acid
	PFDPA	Perfluorodecyl phosphonic acid
PFPIA	C6 PFPIA	Bis (perfluorohexyl) phosphinic acid
	C6/C8 PFPIA	Perfluoro (hexyloctyl) phosphinic acid
	C8 PFPIA	Bis (perfluorooctyl) phosphinic acid
FOSA/FOSE	PFOSA	Perfluorooctane sulfonamide
	N-MeFOSA	Methyl perfluorooctane sulfonamide
	N-EtFOSA	Ethyl perfluorooctane sulfonamide
	N-MeFOSE	Methyl perfluorooctane sulfonamide ethanol
	N-EtFOSE	Ethyl perfluorooctane sulfonamide ethanol

Table S2. Concentrations in sludge from wastewater treatment plants in Gässlösa, Umeå, and Henriksdal, 2012 - 2015 (ng/g).

	LOD	Henriksdal			Gässlösa			Umeå		
		2012	2014	2015	2012	2014	2015	2012	2014	2015
PFBA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
PFPeA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
PFBS	0.08	<0.08	0.17	0.11	<0.08	0.09	0.09	0.13	0.14	0.28
PFHxA	0.14	0.87	0.91	0.85	2.91	6.37	3.29	0.54	0.58	0.77
PFHpA	0.07	0.07	0.07	0.18	0.18	0.12	0.07	0.07	0.07	0.07
PFPeS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFHxS	0.09	0.07	<0.09	0.05	<0.09	0.04	0.03	<0.09	<0.09	<0.09
PFHpS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFOA	0.41	1.36	1.13	0.76	2.88	1.17	0.93	0.70	<0.41	0.58
PFNA	0.02	0.33	0.29	0.19	0.40	0.37	0.29	<0.02	<0.02	<0.02
PFOS	0.02	8.10	4.57	3.05	2.97	2.70	3.00	4.65	2.19	1.06
PFDA	0.02	1.43	1.63	1.27	3.12	2.08	1.24	0.44	0.39	0.34
PFUnDA	0.02	0.69	0.72	0.59	1.59	1.08	0.88	0.26	0.38	0.26
PFNS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFDS	0.02	0.56	0.55	0.26	0.16	0.08	0.08	0.59	0.36	0.33
PFDoDA	0.02	1.07	1.09	0.78	0.99	0.61	0.47	0.47	0.34	0.37
PFTrDA	0.02	0.14	0.14	0.12	0.92	0.40	0.13	<0.02	<0.02	0.17
PFDoDS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFTDA	0.02	0.28	0.30	<0.02	0.16	<0.02	0.10	<0.02	<0.02	0.14
4:2 FTSA	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
6:2 FTSA	0.23	0.44	<0.23	0.31	0.31	0.94	0.67	<0.23	<0.23	<0.23
8:2 FTSA	0.02	1.36	1.03	0.64	0.58	0.62	0.55	0.95	1.00	0.75
5:3 FTCA	0.02	5.19	4.48	4.78	42.7	68.0	44.6	0.72	2.16	1.06
6:2 FTUCA	0.02	0.09	0.08	0.03	2.33	4.28	0.78	0.23	0.21	0.13
7:3 FTCA	0.02	7.25	6.64	3.16	17.32	4.70	4.97	2.02	1.87	1.99
8:2 FTUCA	0.02	1.77	0.92	0.58	2.02	0.46	0.28	0.93	1.14	0.55
10:2 FTUCA	0.02	0.71	0.62	0.40	0.34	0.11	0.11	0.15	0.10	0.12
6:2 monoPAP	0.23	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
8:2 monoPAP	1.98	16.8	11.9	11.0	11.4	6.2	5.8	17.7	9.9	11.2
6:2 diPAP	0.05	1.2	1.8	1.7	0.9	1.1	1.8	2.9	2.0	2.4
8:2 diPAP	0.28	2.57*	1.50*	1.49*	1.81*	1.40*	1.54*	4.16*	n.q.	1.55*
6:2/10:2 diPAP	0.28	2.95*	2.70*	2.41*	2.11*	2.14*	2.26*	5.10*	n.q.	3.22*
6:2/8:2 diPAP	0.06	1.61*	1.04*	1.15*	2.22*	1.94*	2.55*	2.87*	n.q.	1.38*
8:2/10:2 diPAP	0.02	1.04*	0.89*	0.47*	0.44*	0.40*	0.42*	1.35*	n.q.	1.00*
6:2/12:2 diPAP	0.02	0.51*	0.58*	0.31*	0.25*	0.23*	0.21*	0.72*	n.q.	0.61*
PFHxPA**	1.66	<1.66	<1.66	<1.66	<1.66	<1.66	<1.66	<1.66	<1.66	<1.66
PFOPA**	2.89	<2.89	<2.89	<2.89	<2.89	<2.89	<2.89	<2.89	<2.89	<2.89
PFDPA**	1.63	<1.63	<1.63	<1.63	<1.63	<1.63	<1.63	<1.63	<1.63	<1.63
C6 PFPiA**	0.02	<0.02	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02
C6/C8 PFPiA**	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
C8 PFPiA**	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFOSA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
N-MeFOSA	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	1.26
N-EtFOSA	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
N-MeFOSE	0.05	2.57	2.87	<0.05	2.31	2.40	2.39	<0.05	<0.05	<0.05
N-EtFOSE	0.05	1.23	<0.05	<0.05	0.97	1.11	0.88	<0.05	<0.05	<0.05

n.q. = not quantified.

* Recovery 10-20%

** Concentrations not corrected for recovery.

Acceptable recovery for labeled internal standard is 20-150%. For some analytes, samples with a recovery of 10-20% have been included in the report, since precision was maintained at recoveries as low as 10%. These concentrations are labeled with * in the table.

Table S3. Concentrations in effluent and influent water from wastewater treatment plants in Gässlösa, Umeå, and Henriksdal 2015 (ng/L).

	LOD	Gässlösa 2015 effl.	Umeå 2015 effl.	Henriksdal 2015 effl.	Gässlösa 2015 infl.	Umeå 2015 infl.	Henriksdal 2015 infl.
PFBA	3.38	30.13	8.17	12.29	<3.38	n.q.	5.50
PFPeA	0.06	10.22	2.51	4.90	4.96	3.09	4.20
PFBuS	0.06	1.08	0.87	3.74	1.12	0.66	3.31
PFHxA	0.46	16.81	4.96	7.32	7.13	3.08	5.86
PFHpA	0.14	2.75	1.39	2.67	1.79	1.22	2.45
PFPeS	0.02	0.37	0.30	0.51	0.33	0.30	0.42
PFHxS	0.10	1.35	1.37	1.90	1.13	0.75	1.78
PFHpS	0.02	0.16	0.13	<0.02	0.07	0.11	0.12
PFOA	0.48	5.19	4.13	5.05	4.18	3.01	5.20
PFNA	0.11	0.36	0.63	0.58	0.30	0.71	0.66
PFOS	0.70	1.49	1.54	<0.70	1.13	1.66	1.01
PFDA	0.22	<0.22	0.47	0.50	0.23	0.47	0.35
PFUnDA	0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
PFNS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFDS	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFDoDA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
PFTrDA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
PFDoDS		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
PFTDA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
4:2 FTSA	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
6:2 FTSA	0.74	1.96	2.57	5.10	2.91	2.54	6.34
8:2 FTSA	0.08	0.13	0.42	0.15	0.20	1.04	0.13
5:3 FTCA	0.02	n.q.	0.24	n.q.	2.80	0.30	1.30
6:2 FTUCA	0.02	n.q.	0.07	n.q.	0.54	<0.02	<0.02
7:3 FTCA	0.02	n.q.	<0.02	n.q.	0.16	0.24	0.13
8:2 FTUCA	0.02	n.q.	0.08	n.q.	<0.02	<0.02	<0.02
10:2 FTUCA	0.97	n.q.	<0.97	n.q.	<0.97	<0.97	<0.97
6:2 monoPAP	0.05	n.q.	n.q.	n.q.	n.q.	<0.05	<0.05
8:2 monoPAP	2.6	n.q.	n.q.	n.q.	n.q.	<2.6	<2.6
6:2 diPAP	0.96	<0.96	n.q.	n.q.	n.q.	7.63	n.q.
8:2 diPAP	0.76	<0.76	n.q.	<0.76	n.q.	2.89*	n.q.
6:2/10:2 diPAP	0.76	<0.76	n.q.	<0.76	n.q.	7.10*	n.q.
6:2/8:2 diPAP	1.24	<1.24	n.q.	n.q.	n.q.	7.18*	n.q.
8:2/10:2 diPAP	0.79	<0.79	n.q.	<0.79	n.q.	2.98*	n.q.
6:2/12:2 diPAP	0.79	<0.79	n.q.	<0.79	n.q.	2.63*	n.q.
PFHxPA**	2.56	<2.56	<2.56	<2.56	10.3	5.12	<2.56
PFOPA**	0.84	<0.84	<0.84	<0.84	4.99	2.77	1.79
PFDPa**	0.02	3.02	1.26	0.59	4.38	2.61	<0.02
C6 PFPiA**	0.02	1.78	0.10	0.10	0.34	0.49	<0.11
C6/C8 PFPiA**	0.02	0.32	<0.02	<0.02	<0.02	0.14	<0.08
C8 PFPiA**	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PFOSA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
N-MeFOSA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
N-EtFOSA		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
N-MeFOSE		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
N-EtFOSE		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.

n.q. = not quantified.

* Recovery 10-20%

** Concentrations not corrected for recovery.

Acceptable recovery for labeled internal standard is 20-150%. For some analytes, samples with a recovery of 10-20% have been included in the report, since precision was maintained at recoveries as low as 10%. These concentrations are labeled with ** in the table.