



Tidstrend av oidentifierade poly- och perfluorerade alkylämnen i slam från reningsverk i Sverige

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Time trend of unidentified poly- and perfluoroalkyl substances in sludge from wastewater treatment plants in Sweden

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<p>Period in which underlying data were collected 2004 - 2005, 2007 - 2015</p>	
<p>Summary The aims of this investigation are 1) to study spatial variation in PFAS discharge by measuring PFAS in sludge samples collected from four wastewater treatment plants (WWTPs: Öhn - Umeå, Bergkvara - Torsås, Henriksdal – Stockholm, and Gässlösa - Borås); 2) to evaluate the amount of unidentified PFAS, if any, in the sludge samples by measuring total organofluorine (TOF) in the samples; 3) to study the temporal discharge and pattern of PFASs by measuring different PFASs in archived sludge samples from two WWTPs (Henriksdal and Gässlösa); and 4) to evaluate temporal changes of the amount of unidentified PFAS, if any, by measuring the amount of TOF in the archived samples from these two WWTPs. Levels of TOF and PFAS are reported for sludge samples from the four WWTPs collected in 2015; temporal analyses of TOF and PFASs were conducted on sludge samples from two WWTPs collected between 2004 and 2015.</p> <p>Different classes of PFASs including PFCAs, PFASs, FTSAAs, FTCAs, diPAPs, FOSAs/FOSEs, diSAmPAP, FOSAAs, PFPAs and PFPiAs were detected in the sludge samples. The levels of TOF and unidentified PFAS were shown to more related to types of industries connected to the WWTPs, not necessarily related to number of people served in that area and the scale of WWTP. Quantifiable PFAS only accounted for 5 to 11% of the TOF in samples collected in 2015 indicating that 89-95% of the measured organofluorine in the samples was unidentified. TOF levels from Gässlösa were approximately 1.6 – 17.7 times higher than those of Henriksdal in corresponding year. The proportion of quantifiable PFAS to TOF decreased from 21% in 2004 to 11% in 2015 in samples from Henriksdal; at the same time increasing levels of unidentified PFAS was also observed between 2012 and 2015.</p>	

Sammanfattning

Syftet med denna studie var 1) att studera geografiska variationer i utsläpp av PFASs genom att mäta PFAS i slamprover från fyra olika reningsverk (Öhn - Umeå, Bergkvara - Torsås, Henriksdal – Stockholm och Gässlösa - Borås); 2) att utvärdera om slammet innehåller oidentifierade PFASs och i sådana fall kvantifiera mängden av dessa; 3) att studera hur profilen av PFAS-ämnen förändras över tid genom att mäta olika PFAS-ämnen i arkiverade slamprover från två reningsverk (Henriksdal och Gässlösa); och 4) att bestämma andelen oidentifierade PFAS genom att mäta totalhalten organiskt fluor (TOF) i de arkiverade proverna från Henriksdal och Gässlösa.

I denna studie rapporteras halterna av TOF och PFAS i slamprover från de fyra ovan nämnda reningsverken insamlade under 2015; vidare rapporteras en tidstrendsstudie utförd för TOF och PFAS i slamprover från Henriksdal mellan 2004 och 2015. Ett flertal PFAS-klasser detekterades i proverna; PFCAs, PFSAAs, FTSAAs, FTCAs, diPAPs, FOSAAs/FOSEs, diSAmPAP, FOSAAs, PFPAs och PFPiAs. Halterna av oidentifierade PFASs visade sig vara relaterade främst till typ av industriell verksamhet i anslutning till reningsverket, snarare än antalet personer anslutna till och storlek på reningsverken. Identifierade PFAS-halter utgjorde endast 5 - 11% av TOF i proverna insamlade under 2015, vilket indikerade att 89 - 95% av TOF var oidentifierade ämnen. Halten TOF i slamproverna från Gässlösa var uppskattningsvis 1.6 – 17.7 gånger högre än TOF i slamprover från Henriksdal motsvarande år. Andelen identifierade PFAS-halter i förhållande till TOF minskade från 21% under 2004 till 11% under 2015 i slamprover från Henriksdal, ökade halter av oidentifierade PFASs observerades också mellan 2012 och 2015.

Background

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are groups of anthropogenic chemicals having the perfluoroalkyl moiety ($C_nF_{2n+1}-$) with different polar heads (e.g., carboxylate, sulfonate, phosphonate). Much attention has been given to two perfluoroalkyl acids (PFAAs) - perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) because of their potential toxic and bioaccumulative effects, as well as their ubiquitous occurrence in the environment including remote areas.¹⁻⁴ Two widely studied fluorosurfactants, PFOS and PFOA, have shown to decline after year 2000 in human blood.^{5,6} The phase-out of perfluorooctanesulfonyl fluoride (POSF)-based products,⁷ industry participation in PFOA Stewardship Program,⁸ and/or regulation under the Stockholm Convention⁹ are some of the reasons for the decline. According to a recent survey conducted by the Swedish Chemical Agency, more than 3000 commercial fluorinated replacement products with the same desirable properties as PFOS and PFOA are used in global market.¹⁰ Although existing analytical methods may measure more than 50 different PFASs in a sample,⁶ it is still technically challenging to determine the whole suite of thousands of individual PFASs in a sample, especially the new products that are of unknown identities and where no authentic analytical standards are available for quantification. The concept using mass balance was developed to evaluate how much of the quantifiable PFAS accounting for the total organofluorine (OF) in a sample in order to estimate how much unidentified PFAS present in a sample. In brief, total fluorine (TF) in any sample consists of inorganic fluorine (IF) and OF. Levels of quantifiable PFAS representing a fraction of known ionizable OF that are readily measured by LC-MS/MS, whereas total OF (TOF: all non/and ionizable OF) are measured by combustion ion chromatography. Our earlier investigation using this concept demonstrated unidentified PFAS in different environmental matrices.¹¹⁻¹⁴ Increasing amounts of unidentified PFAS in sediment cores collected from Lake Ontario between 2001 and 2006¹¹ and in human plasma samples from Germany between 2005 and 2009⁶ were observed.

Wastewater treatment plants (WWTPs) have been suggested to be one of the major secondary sources of PFAS to the aquatic environment.¹⁵ Our recent investigation demonstrated significant proportion up to 95% of unidentified PFAS were found in sewage samples (influent and effluent and sludge) collected in 2016 from three Swedish wastewater treatment plants.¹⁶ Sludge samples may represent the usage of PFAS in daily life. By measuring the TOF and quantifiable PFAS in archived sludge samples may allow time trend analyses of

different PFASs as well as evaluation of any introduction of new fluorinated alternatives and unidentified PFAS over time.

Aim

The aims of this investigation are 1) to study spatial variation in PFAS discharge by measuring PFAS in sludge samples collected from four wastewater treatment plants (WWTPs: Öhn - Umeå, Bergkvara - Torsås, Henriksdal – Stockholm, and Gässlösa - Borås); 2) to evaluate the amount of unidentified PFAS, if any, in the sludge samples by measuring total organofluorine (TOF) in the samples; 3) to study the temporal discharge and pattern of PFASs by measuring different PFASs in archived sludge samples from two WWTPs (Henriksdal and Gässlösa); and 4) to evaluate temporal changes of the amount of unidentified PFAS, if any, by measuring the amount of TOF in the archived samples from these two WWTPs.

Project administration and coordination

This project has been led by Örebro University (Oru). The project leader has been responsible for the coordination with the Swedish Environmental Protection Agency and Dr. Ylva Lind from the Swedish Museum of Natural History for archiving sludge samples from the Environmental Specimen bank (ESB). Analysis and data interpretation were performed by Örebro University (Oru).

Following persons have participated in the project:

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Materials and methods

Sample

Sewage sludge samples from four WWTPs (Öhn - Umeå; Henriksdal - Stockholm; Gässlösa - Borås; and Bergkvara - Torsås) were archived from the Environmental Specimen Bank at the Swedish Museum of Natural History. Samples from Öhn and Bergkvara were collected in 2015; whereas samples from Henriksdal and Gässlösa were collected in 2004 - 2005, 2007-2015. All sludge samples were collected under a national environmental monitoring of outgoing water and sludge from Swedish sewage treatment plants. In brief, the sludge samples

were collected as composite samples during one day in October. After collection, sludge was freeze dried and stored in a freezer at -18°C until analysis.

The information of different WWTPs shown below is based on a published report¹⁷ (Table 1). The Henriksdal plant receives municipal wastewater from industries and hospitals; it serves 737 000 people (656 000 p.e.). The Öhn 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. The Bergkvara WWTP serves 5 900 people (2 500 p.e.). All four WWTPs have mechanical, chemical, and biologic treatment. Henriksdal, Öhn and Gässlösa also have an anaerobic digestion treatment; while Bergkvara has an aerobic digestion treatment.

Table 1. Description of three WWTPs included in the study

	Henriksdal	Gässlösa	Öhn	Bergkvara
Number of people served	737 000	82 000	92 000	5 900
Person equivalents	656 000	73 000	129 000	2 500
Amount sludge produced (t/year)	14 400	2 400	2 300	110
Residence time of sludge (days)	19	25	18	Not available
Year of collection	2004-2005, 2007-2015	2004-2005, 2007-2015	2015	2015
Number of sample	11	11	1	1

Extraction

Sewage sludge samples were analyzed for total organofluorine and a suite of 83 PFASs (Supplementary information (SI) Table S1), which include PFCAs, PFSAAs, FTSAAs, PAPs, PFPAs, PFPiAs, FOSAs, FOSEs, FTUCAs and FTCAs. Samples were analyzed in duplicate; one of the duplicate samples, the spike sample, was spiked with mass-labelled standards (SI Table S1) before extraction to determine the PFAS concentrations in the samples using LC-MS/MS. Another duplicate sample without spiking with any mass-labelled standards, the non-spike sample, was used for total organofluorine (TOF) analysis using combustion ion chromatography (CIC); mass-labelled standards were spiked to the non-spike sample for the determination of the PFAS concentrations in the sample extract using LC-MS/MS; the non-spike sample was used for mass balance analysis of fluorine between quantifiable PFAS and

TOF. Both spike and non-spike samples were subject to same extraction procedure but with different cleanup steps.

For the sludge extraction, 0.25 g freeze-dried sample was used. Mass labelled standards were added to the spike 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) following ISO method.¹⁸ The sorbents were conditioned with a passage of 4 mL 0.1% NH₄OH in methanol, 4 mL methanol and 4 mL Milli-Q water in series. Samples were loaded on the sorbents. After that, the sorbent was washed with 4 mL ammonium acetate buffer solution (pH 4). Cartridges were dried under vacuum. Analytes were eluted with 4 mL methanol (fraction containing neutral compounds), followed by elution with 4 mL 0.1% NH₄OH in methanol (fraction containing anionic compounds). The extracts were evaporated and transferred to LC-vials for instrumental analyses to determine PFAS concentrations in the original samples.

As for non-spike samples, similar to the spike samples, 2 mL of 1 M sodium hydroxide in methanol was added to 0.25 g freeze-dried sample. 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. The methanol extract was first evaporated to 0.5 mL before an ion pair extraction cleanup following published method.¹⁹ In brief, 2 mL of 0.5M tetrabutylammonium sulfate (TBAS) was added to the 0.5 mL methanol extract; the mixture was vortex mixed and then 3 mL of methyl-*tert*-butyl ether (MTBE) was added to the mixture. The mixture was set on a horizontal shaker for 15 min at 250 r.p.m. After that the organic and aqueous phases were separated by using a centrifuge at 8000 g for 10 min. The supernatant was transferred to a new 15 mL tube. Another 3 mL of MTBE was added to the original extract, and the extraction procedure was repeated twice. The combined MTBE was evaporated to dryness and reconstituted in 0.5 mL methanol. An aliquot of the sample was spiked with mass-labelled standards for LC-MS/MS analysis to determine PFAS levels in the sample extract; whereas another aliquot of the sample was used for CIC analysis to determine TOF in the sample extract.

Instrumental analyses

Different classes of PFASs in the samples were analyzed using an Acquity 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 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 were used. Both quantification and qualification product ions were measured in the multiple reaction monitoring, except for PFPA/PFPiAs and a few short-chain PFCAs for which only one stable product ion was formed in the mass spectrometric analysis (SI Table S2).

Total organofluorine in the samples were analyzed using a combustion ion chromatography (CIC). The CIC consists of a combustion module (Analytikjena, Germany), a 920 absorbent module and a 930 Compact IC flex (Metrohm, Switzerland). Separation of anions was performed on an ion exchange column (Metrosep A Supp5 – 150/4) using carbonate buffer (64 mM sodium carbonate and 20 mM sodium bicarbonate) as eluent in isocratic elution. In brief, the sample extract (0.1mL) was set on a quartz boat and placed into the furnace at 1000-1050°C for combustion, during which, all organofluorine was converted into hydrogen fluoride (HF); the HF is then absorbed into Milli-Q water. The concentration of F⁻ in the solution was analyzed using ion chromatography.

Quality control and quality assurance

PFAS. Target analytes were quantified using isotopic dilution with mass-labelled internal standards. For those analytes where no isotopic labelled standards were available, the homologue closest in retention time was used for quantification (SI Table S2). For PFPAs and PFPiAs, where no mass-labelled internal standards were available, quantifications were performed using a matrix-matched calibration curve. Seven-point calibration curves were prepared together with the targeted compounds. Procedure blanks were included in each batch and treated the same way as the 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 (SI Table S2). A standard reference sample (SRM) 2781 domestic sludge was used for quality control. The measured concentrations of PFCAs and PFSAs were well in agreement with previous measured data reported by NIST

(https://nemo.nist.gov/srmors/view_detail.cfm?srm=2781) except for PFHxS; the mean normalized differences (MND) were 2.2% for PFHxA, 21% for PFHpA, 77% for PFHxS, 12% for PFOA, and 7.1% for PFOS. The diPAPs in the SRM sludge sample have previously been reported.¹⁹ The MND of diPAPs in this study compared to the earlier study were 4.6% for 6:2 diPAP, 32% for 8:2 diPAP, and 27% for 6:2/8:2 diPAP. Recoveries of reported concentrations in the sludge samples were in the range 20-150%, except for diPAPs. The range of recoveries were 20 – 140% for PFCAs, 23- 120% for PFSAs, 21-79% for FTSA, 20-147% for FOSA/FOSEs, 22-93% for FOSAs, 11-115% for diPAPs, and 20-140% for PFPA/PFPiAs. Due to the poor recoveries (<10%) of FTUCAs, 8:2 and 10:2 monoPAPs, these compounds were not reported.

TOF. Fluoride signal was observed in combustion blank even when no sample was analyzed. Prior to sample analysis, multiple combustion blanks were performed until stable fluoride signals were reached. Certified Multielement ion chromatography anion standard solution was used as standard solution (Sigma-Aldrich). Anion standard solution of different concentrations was injected onto CIC. The peak area of the standard solution was first subtracted with the peak area of a previous combustion blank before plotted against concentration for the external calibration curve. A five-point calibration curve at 50, 100, 200, 500 and 1000 µg/L standards was constructed, and exhibited good linearity with $R^2 > 0.9999$. Combustion of 100 ng and 500 ng of SRM 2143 – p-Fluorobenzoic (NIST) resulted in recoveries of between 90 - 98%. Combustion of 500 ng of PFOS resulted in recoveries ranging from 89 to 92% and combustion 500 ng of PFOA resulted in 85 to 90% recoveries. Combustion blank was conducted between sample injections to evaluate the presence of carryover between samples. Detectable organofluorine contamination was found in extraction blank (75 ± 2 ng). Quantification of sample was based on the external calibration curve after the peak area of the sample had been subtracted from the previous combustion blank and extraction blank.

Mass balance analysis of organofluorine

The measured PFAS concentrations (ng/g) in the samples were converted into corresponding fluoride concentration (ng F/g) using the following equation:

$$C_F = n_F \times \frac{MW_F}{MW_{PFAS}} \times C_{PFAS}$$

C_F : corresponding fluoride concentration (ng F/mL); **n_F** : number of fluorine in PFAS; **MW_F** : molecular weight of fluorine; **MW_{PFAS}** : molecular weight of PFAS; **C_{PFAS}** : measured PFAS concentration using LC-MS/MS

Levels of unidentified organofluorine were calculated by subtracting all quantifiable PFAS from TOF.

Results

A total of 24 sludge samples were analyzed for TOF and a suite of 83 PFASs of different classes, which included persistent PFCAs, PFSAAs and PFPAs, PFCA precursors (FTSAs, FTCAs, FTUCAs, diPAPs, monoPAPs), PFSA precursors (FOSAs, FOSEs, FOSAAs, diSAmPAP, SAmPAP), and PFPiAs. Concentrations of individual compounds in the sample are provided in SI Table S3 for sludge samples from Öhn, Bergkvara, Henriksdal, Gässlösa collected in 2015, SI Table S4 for sludge samples from Henriksdal collected during 2004, 2005, 2007-2015, and SI Table S5 for sludge samples from Gässlösa collected during 2004, 2005, 2007-2015.

Comparison of PFAS in sludge samples collected in 2015 among the 4 WWTPs

The total PFAS concentrations in sludge samples in descending order were 171 ng/g – Henriksdal, 149 – Öhn, 119 ng/g – Bergkvara, and 96.7 ng/g – Gässlösa (Table 1, Figure 1). Samples from Öhn and Henriksdal had relatively higher concentrations of PFCA precursor compounds; whereas samples from Henriksdal and Gässlösa had relatively higher concentrations of PFSA precursors and persistent PFAAs.

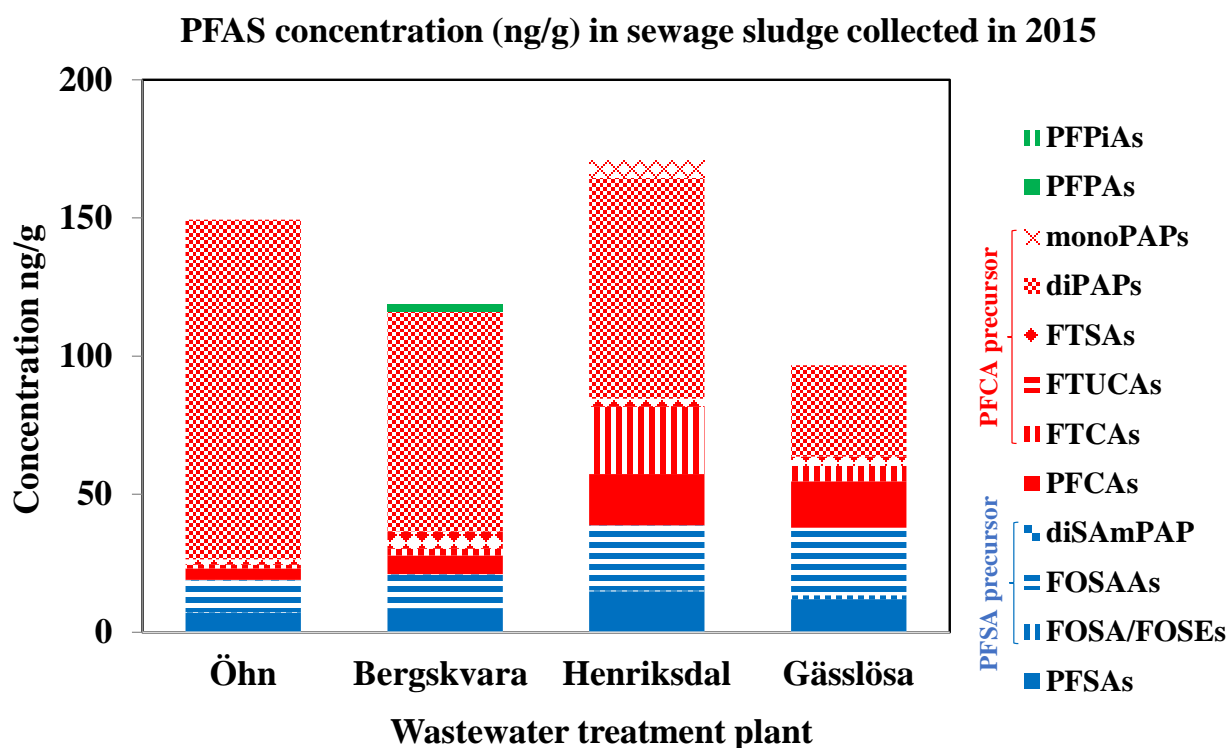


Figure 1. Concentrations (ng/g) of different classes of PFAS in sewage sludge samples from four wastewater treatment plants collected in 2015

Table 1. Summary of different classes of PFASs in sewage sludge samples collected in 2015 from 4 WWTPs.

		Öhn	Bergkvara	Henriksdal	Gässlösa	Öhn	Bergkvara	Henriksdal	Gässlösa
		Concentration ng/g				Composition %			
PFCAs		4.13	6.77	18.5	16.8	2.8	5.7	10.8	17.4
PFCA precursor	FTSAs	2.01	6.38	2.88	3.41	1.3	5.4	1.7	3.5
	FTCAs	1.29	2.39	24.4	5.56	0.9	2.0	14.3	5.7
	FTUCAs								
	diPAPs	123	79.6	80.1	33.0	82.3	66.9	46.9	34.2
	monoPAPs			6.05				3.5	
PFSAs		7.15	8.79	14.8	12.0	4.8	7.4	8.7	12.5
PFSA precursor	FOSA/FOSEs	0.145		0.332	1.4	0.1		0.2	1.4
	FOSAAs	11.6	12.1	23.4	24.4	7.7	10.2	13.7	25.3
	diSAmPAP	0.162	0.161	0.204		0.1	0.1	0.1	
PFPAs			2.75				2.3		
PFPIAs									
Total		149	119	171	96.7				
		Concentration ng/g				Composition %			
Sum of Persistent PFAA		11.3	18.3	33.3	28.9	7.6	15.4	19.5	29.9
Sum of PFCA Precursors		126	88.4	113	42.0	84.5	74.3	66.4	43.4
Sum of PFSA Precursors		11.9	12.3	24.0	25.8	7.9	10.3	14.0	26.7
Total		149	119	171	96.7				

Blank cell indicates sample below respective limit of detection. See SI Table S3 for individual compound concentration. Sum of Persistent PFAA: PFCAs+PFSAs+PFPAs; sum of PFCA precursors: FTSAs+FTCAs+FTUCAs+diPAPs+monoPAPs; sum of PFSA: FOSA/FOSEs+FOSAAs+diSAmPAP.

In general, the sludge samples were dominated by PFCA precursors (average: 67.2%, range: 43.4 - 84.5%), followed by persistent PFAAs (18.1%, 7.6 - 29.9%), and then PFSA precursors (14.8%, 7.9 - 26.7%). One of the PFCA precursors, diPAPs, contributed to 34.2 - 82.3% of total PFAS; different wastewater treatment plants showed different patterns of diPAP congeners (SI Table S3). Öhn showed the greatest diPAP concentrations (123 ng/g), whereas Gässlösa had the lowest concentration (33.0 ng/g, Table 1). For the samples from Öhn and Bergkvara, diPAPs accounted for approximately 82 and 67% of total PFAS, respectively; the samples showed 14 and 13 out of 21 detectable diPAPs; the predominant congeners was 8:2/12:2 (24% for Öhn and 31% for Bergkvara of total diPAPs; SI Table S3). For the samples from Henriksdal and Gässlösa, diPAPs made up of over 34% of the total PFAS. Henriksdal showed 9 detectable diPAP congeners with 6:2/10:2 (24%) as the dominant congener; whereas Gässlösa showed 8 detectable diPAP congeners and was dominated by 6:2/10:2

(27%) congeners (SI Table S3). Another class of related compounds, the monoPAPs, was only quantified in sample from Henriksdal, because of either the presence of interfering substances or poor recoveries (<10%) in other samples. Another group of PFCA precursor, the FTSAAs contributed to approximately 3% (1.3 - 5.4%) of the total PFAS (Table 1). All four samples showed detectable 8:2 FTSA concentrations; 6:2 FTSA was only detected in Bergkvara and Gässlösa (SI Table S3). As for PFCA intermediates, only FTCAs were quantified; because of the poor recoveries (<10%) of FTUCAs, they were not detected or quantified. The FTCAs made up of 5.7% of the total PFAS, of which 7:3 was dominant in samples from Öhn (100%) and Bergkvara (65%), whereas 5:3 was dominant in Henriksdal (65%) and Gässlösa (91%) (SI Table S3). The detection of 7:3 and 5:3 FTCAs suggest the transformation of 8:2 and 6:2 fluorotelomer-based products, respectively.

It was interesting and important to note the detection and significant contribution (mean: 14.8%, range: 7.9-26.7%, Table 1) of PFSA precursors to total PFAS in the samples. Among PFSA precursors, the contribution of FOSAAAs to total PFAS in samples ranged from 7.7% in Öhn up to 25.3% in Gässlösa. Among FOSAA congeners, EtFOSAA was the dominant compound (over 60%), except for sample from Gässlösa (52%). Another PFSA precursor mainly used for paper and packaging, diSAmPAP was also detected (<0.1 – 0.204 ng/g, SI Table S3). EtFOSAA is an oxidation product of EtFOSE, which was primarily used as the building block of the phosphate ester (i.e., diSAmPAP) in paper and packaging protectant applications).²⁰ MeFOSAA is an oxidation product of MeFOSE, which was primarily incorporated into polymeric materials as a surface treatment for products like carpets and textiles and FOSAA (a metabolite of either EtFOSAA or MeFOSAA).²⁰ Like PFOS, these compounds should have phased-out since 2000. However, the concentrations of EtFOSAA were as high as those of PFOS in the same sample.

The persistent PFCA and PFSA contributed to approximately 9.2% (2.8-17.4%) and 8.3% (4.8-12.5%) of the total PFAS, respectively. Long-chain PFCA predominated total PFCA 94.6% (82-100%); PFDA 31.5% (22.3-45.2%), PFUnDA 17.1% (9-29.6%), PFOA 15.6% (12.1-19.7%), and PFDoDA 13.3% (4.9-24.7%) were dominant congeners; whereas other long-chain PFCAs contributed to at most 5% of the total PFCA. As for PFSA, only PFHxS, PFOS and PFDS were detected (SI Table S3); PFOS contributed to over 70% of total PFSA, except for sample from Öhn that PFOS was approximately 45% of total PFSA, and PFHxS made up of the remaining of the PFSA. Another class of PFAS, the PFPAs and PFPiAs, only

the sample from Bergkvara showed detectable concentrations of PFDPA; other congeners were found below limits of detection (SI Table S3).

Time trends of PFAS in sewage sludge

i. Henriksdal

A peak of total PFAS concentration was observed in 2007 (815 ng/g); after that the total PFAS concentration decreased (Table 2, Figure 2). Similar to the results discussed above, diPAP was the predominant class of PFAS (mean: 50.1%, range: 35.6 - 77.5%) in samples between 2004 and 2015. The greatest concentration was observed in 2007 (632 ng/g) and then decreased to 105 ng/g until 2009, and then increased to 328 ng/g in 2010; after that decreasing concentrations were observed (80.1 ng/g in 2015). The major diPAP congener was 8:2/12:2 (24.0%, 15.4 - 30.9%), followed by 6:2/10:2 (14.3%, 5.0 - 31.0%) and 10:2 (14.2%, 8.6 - 15.5%) diPAPs. The trends of 8:2/12:2 and 10:2 diPAPs were similar that both compounds peaked in 2007, and decreasing trends were observed until 2011; after that the levels remained relatively stable (SI Table S4). As for 6:2/10:2 diPAP, one year delay of peak concentration was observed when compared to the 8:2/12:2 and 10:2 diPAPs (SI Table S4).

Table 2. Summary of different classes of PFASs in sewage sludge samples collected at Henriksdal

	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Concentration (ng/g)										
PFCAs	19.8	21.9	20.7	26.5	21.4	22.4	21.0	18.2	15.1	18.9	18.5
FTSAs	8.57	6.93	5.16	7.18	8.16	4.90	5.20	5.16	5.56	3.30	2.88
FTCAs	11.5	2.57	37.1	45.2	15.6	29.3	20.5	22.2	19.5	22.5	24.4
FTUCAs											
diPAPs	104	88.7	632	247	105	328	119	84.5	69.1	97.4	80.1
monoPAPs	3.98			4.11			5.71	4.76	0.567	4.66	6.05
PFSA precursor											
PFSAs	42.9	47.5	48.1	35.4	39.6	27.2	21.9	31.2	14.0	17.0	14.8
FOSA/FOSEs	0.739	4.40	0.704	90.1	0.699	0.900	2.5	36.6	15.1	2.00	0.332
FOSAAs	46.2	39.8	69.5	59.7	17.2	48.4	41.6	33.4	29.4	27.2	23.4
diSAmPAP		1.4	0.502	0.461		0.329	0.542	0.787	0.191	0.218	0.204
PFPAs	3.53	10.3		0.605				0.832			
PFPIAs		17.3	1.88	1.32							
Total	241	241	815	517	208	462	238	238	168	193	171

Blank cell indicates sample below respective limit of detection. See SI Table S3 for individual compound concentration.

FOSAAs was the second dominant class (13.8%, 8.3 - 19.2.6%). The trend of FOSAAs was similar to that of diPAPs with a peak concentration in 2007 (69.5 ng/g), after that the level decreased until 2009 (17.2 ng/g), and then increased up to 48.4 ng/g in 2010, and then the level decreased steadily (23.4 ng/g in 2015; Table 2). The decreasing trend was driven by the decreasing concentrations of EtFOSAA, but not for MeFOSAA or FOSAA (SI Table S4). Another PFSA precursor, the volatile FOSAs/FOSEs, only FOSA, MeFOSE and EtFOSE were occasionally detected in the sludge samples (SI Table S4).

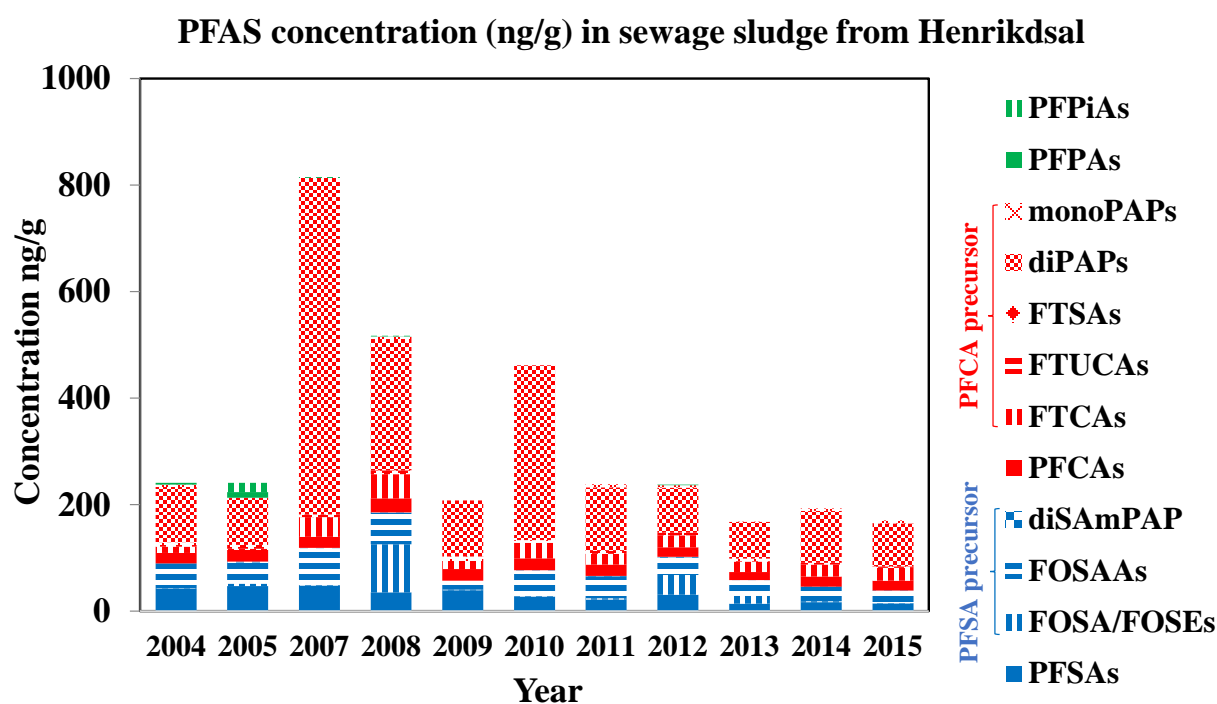


Figure 2. Concentrations (ng/g) of different classes of PFAS in sewage sludge samples collected from Henriksdal.

For PFSA, PFOS was the main contributor (88.9%, 82.8 - 97.9%) and the PFSA made up of approximately 11.2% (5.9 - 19.7%) of the total PFAS during the study period. Decreasing PFSA concentrations were observed from 2004 (42.9 ng/g) to 2015 (14.8 ng/g) (Table 2). Both PFCA (2.5 - 10.8%) and FTCA (0.8 - 14.3%) contributed to approximately on average 8% each to total PFAS in the study period. The levels of PFCA were relatively stable (20 ng/g, 15.1 – 26.5 ng/g) between 2004 and 2015 (Table 2); PFCA was dominated by PFDA (27.5%), followed by PFDoDA (16.7%) and PFOA (16.6%) (SI Table S4). Among the three dominant PFCA congeners, only PFOA showed a decreasing trend between 2004 and 2015 (SI Table S4). As for FTCAs, the composition between 5:3 and 7:3 FTCAs was approximately 55:45. Due to the yearly variation of these FTCAs, no observable trend was noted between 2004 and 2015 (SI Table S4). PFPiAs and PFPAs were occasionally detected

in some samples; the detection frequencies for PFPiAs and PFPAs were 27 and 36% respectively. Relatively high PFPiA and PFPA concentrations were observed in samples from 2005.

ii. Gässlösa

A peak in PFAS concentration was observed in 2005 (1280 ng/g); after that the total PFAS concentration decreased (Table 3, Figure 3). It is interesting to note that the predominating PFAS class varied from year to year, for example PFPiA was the dominant class for years 2004 and 2005 (30.6 - 45.2%); PFCA dominated for years 2007-2009 (36.2 - 62.9%); diPAP was the dominant class for years 2010, 2014-2015 (31.7 - 37.3%); FTCA was the dominant class for years 2011-2013 (40.5 - 53.1%).

Generally speaking, PFCA accounted for an average of 30% (range: 11.7 - 62.9%; SI Table S5) of the total PFAS during the study period. The greatest concentration of PFCA was observed in 2005 (334 ng/g) and the levels decreased to 16.8 ng/g in 2015 (Table 3). The three most dominant PFCA congeners were PUnDA (25.7%), PFDA (25.4%) and PFOA (19.3%) (SI Table S5); different compositions of PFCA were observed between Gässlösa and Henriksdal (PFDA - 27.5%, PFDoDA - 16.7% and PFOA - 16.6%). Decreasing trends were observed for the three PFCAs between 2004 and 2015; other PFCAs (PFNA, PFDoDA, and PFTrDA) also showed similar decreasing trends (SI Table S5).

Table 3. Summary of different classes of PFASs in sewage sludge samples collected in Gässlösa

		2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
		Concentration (ng/g)										
PFCAs		193	334	130	172	165	119	57.1	36.2	42.6	22.7	16.8
PFCA precursor	FTSAs	11.2	9.14	4.65	4.88	6.16	4.89	3.17	3.56	4.31	4.60	3.41
	FTCAs	107	74.0	71.8	6.94	8.73	15.7	159	164	96.9	4.27	5.56
	FTUCAs											
	diPAPs	36.6	72.4	45.6	35.0	118	150	101	44.7	44.7	22.8	33.0
	monoPAPs	17.5		8.02				0.521	3.06	0.831		
PFSA		19.0	22.8	11.4	26.6	18.7	18.2	11.2	9.95	6.44	10.5	12.0
PFSA precursor	FOSA/FOSEs	2.29	34.1	33.7	0.536	1.50	1.80	31.9	22.0	17.9	1.26	1.40
	FOSAAs	114	150	50.9	27.6	86.6	89.3	24.6	25.5	25.2	5.72	24.4
	diSAmPAP		0.879				0.95					
PFPAs		137	218	1.79		1.97	2.48					
PFPiAs		526	367				0.493					
Total		1160	1280	357	274	408	403	389	309	239	72	97

Blank cell indicates sample below respective limit of detection. See SI Table S3 for individual compound concentration.

DiPAP accounted for an average of 20.5% (3.1 - 37.3%) of the total PFAS. The greatest diPAP concentration was observed in the sample collected in 2010 (150 ng/g). Different trend was observed for diPAP when compared to those of PFCA; the levels of diPAP increased from 36.6 ng/g in 2004 up to 150 ng/g in 2010; after that the levels decreased rapidly to 44.7 ng/g in 2012, and remained stable (22.8 - 44.7 ng/g) until 2015 (Table 3). Different diPAP compositions were observed when compared to the patterns of Henriksdal that the major congener of Gässlösa were 8:2 (24.4%, 12.7 - 42.4%), followed by 6:2/10:2 (19.6%, 12.1 - 29.9%) and 6:2/8:2 (17.2%, 10 - 24.7%) (SI Table S5). Decreasing trends of these congeners were observed for 8:2 after 2009 and 6:2/10:2 and 6:2/8:2 after 2010.

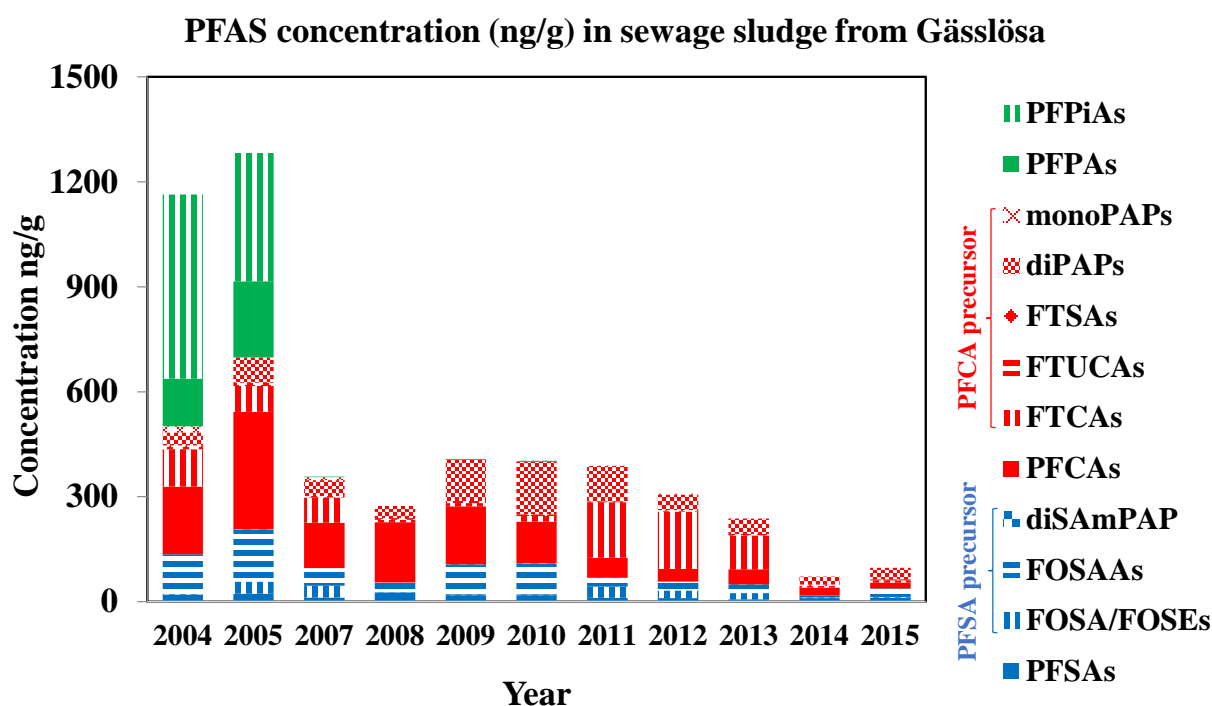


Figure 3. Concentrations (ng/g) of different classes of PFAS in sewage sludge samples collected from Gässlösa.

FTCA contributed to approximately an average of 17.3% (2.1 - 53.1%) to total PFAS. The composition between 5:3 and 7:3 FTCAAs was approximately 11:89 between 2004 and 2010; however, the composition changed to 80:20 between 2011 and 2015 (SI Table S5) indicating a shift from 8:2 fluorotelomer-based compounds to 6:2 fluorotelomer-based compounds.

FOSAAs accounted for approximately an average of 13.4% (6.3 - 25.3%) to the total PFAS. The peak concentration was in 2005 (150 ng/g), after that the level decreased to 27.6 ng/g in 2008, and then increased up to 89.3 ng/g in 2010, and then the level decreased rapidly to 24.6 ng/g in 2011; the levels remained relatively stable until 2015 (24.4 ng/g) (Table 3). EtFOSAA and MeFOSAA contributed to 44% and 51% of FOSAAs (SI Table S5). Both EtFOSAA and MeFOSAA shared similar trends of FOSAAs. Similar to the results of Henriksdal, the volatile FOSAs/FOSEs, FOSA, MeFOSE and EtFOSE were occasionally detected in the sludge samples.

In contrast to PFCA, PFSA only made up of approximately 5.6% (1.6 - 14.6%) of the total PFAS. PFOS contributed to over 90% to the total PFSA. The peak concentrations of PFSA (PFOS) of 27 (25.9) ng/g was observed in 2008; after that the concentrations decreased to 12 (11.5) ng/g in 2015 (Table 3 and SI Table S5). One interesting observation should be noted that detectable concentrations of PFDS were found between 2004 and 2010; after that this compound was found below limit of detection (SI Table S5). In contrast, this compound was still detectable in recent samples from Henriksdal (SI Table S4). Another PFCA precursor, the FTSA, contributed to approximately 2% of the total PFAS. Similar to the observation of FTCA, there was a shift of composition from 8:2 to 6:2 fluorotelomer-based products in recent years. The composition of FTSA between 6:2 and 8:2 were 17:83 between 2004 and 2011; the composition changed to 42:58 between 2012 and 2015 (SI Table S5) indicating a shift from 8:2 fluorotelomer-based product to 6:2 fluorotelomer-based product in recent years. Significant high levels of PFPiAs and PFPAs were detected in 2004 and 2005, which made up of 56.9 and 44.7% of total PFAS, respectively (Table, 3; SI Table S5). After 2005, similar to the results of Henriksdal, they were occasionally detected in samples; the detection frequencies of PFPAs and PFPiAs were 45 and 27%, respectively.

Mass balance analysis of organofluorine

i. Comparison among the four WWTPs

All samples showed detectable TOF concentrations ranging from 606 to 2610 ng F/g; the sample from Gässlösa was the highest, whereas the sample from Öhn was the lowest (Table 4, Figure 4). In order to evaluate how much of the quantifiable PFAS (identified organofluorine) accounting for the TOF in the sample, the levels of PFASs in non-spike samples measured by LC-MS/MS were compared to TOF using CIC after conversion. The quantifiable PFAS only accounted for 5 to 11% of the total organofluorine indicating that 89 - 95% of the measured organofluorine in the samples remained unidentified.

Table 4. Mass balance analysis of organofluorine in sewage sludge samples from 4 wastewater treatment plant collected in 2015.

	Öhn	Bergkvara	Henriksdal	Gässlösa
	Concentration ng F/g			
Sum of quantifiable	55.4	40.6	89.4	286
TOF	606	894	830	2610
Unidentified PFAS	551	853	741	2320
	Composition %			
Quantifiable PFAS	9	5	11	11
Unidentified PFAS	91	95	89	89

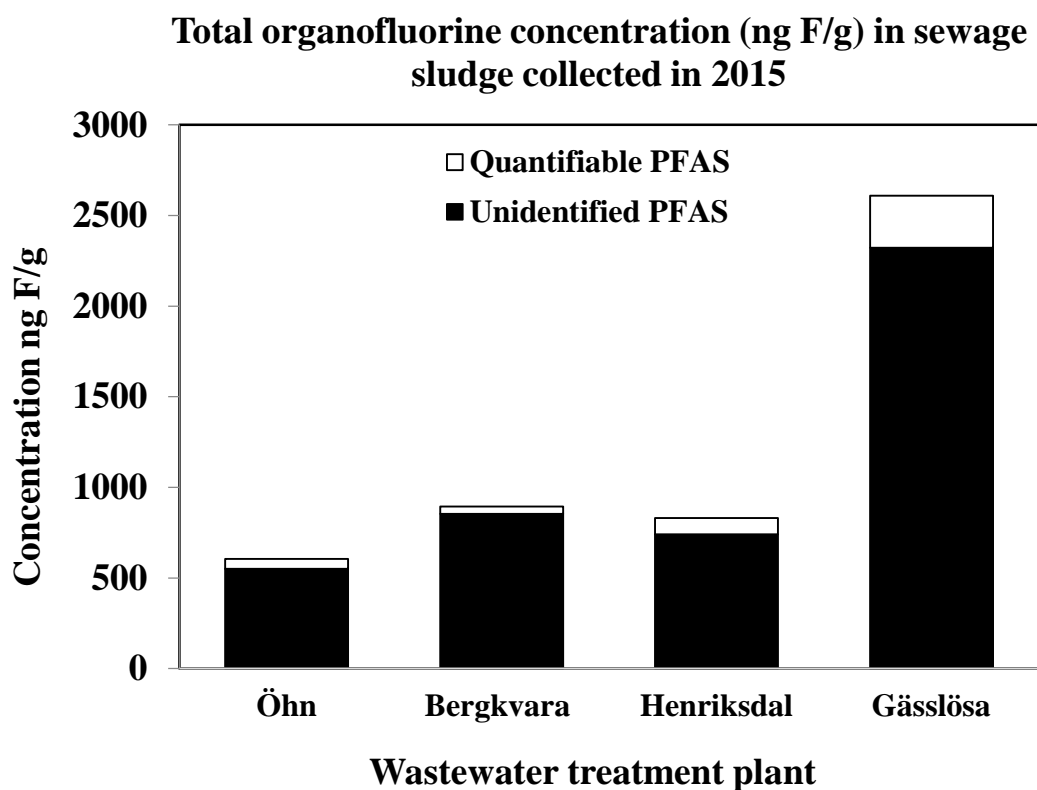


Figure 4. Total organofluorine concentration (ng F/g) in sewage sludge samples from 4 wastewater treatment plant collected in 2015.

ii. Comparison on temporal trends from two WWTPs

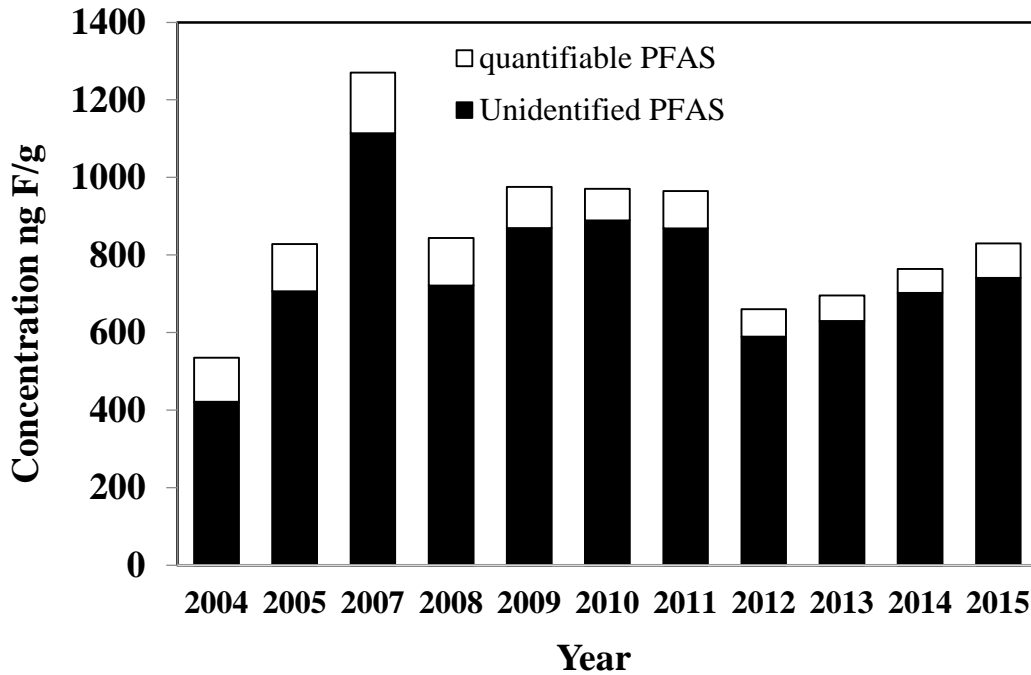
All samples showed detectable organofluorine levels in Henriksdal (535 - 1270 ng F/g) and Gässlösa (1080 - 14600 ng F/g) between 2004 and 2015 (Table 5, Figure 5). Samples from Gässlösa were approximately 1.6 – 17.7 times higher than those of Henriksdal in corresponding year. The greatest TOF levels were observed in samples collected in 2007 for Henriksdal and in 2005 for Gässlösa, which were the same periods for the greatest PFAS levels measured in these two WWTPs (Tables 3-5). The lowest TOF levels were observed in samples collected in 2004 from Henriksdal and 2013 from Gässlösa, which were different from the period in which the lowest total PFAS were observed (Tables 3-5). There was no observable trend of TOF for Henriksdal (Figure 5a), but a decreasing trend was noted for Gässlösa (Figure 5b) between 2004 and 2015.

Table 5. Mass balance analysis of organofluorine in sewage sludge samples from a) Henriksdal and b) Gässlösa

a)	2004	2005	2007	2008	Henriksdal						
					2009	2010	2011	2012	2013	2014	2015
	Concentration ng F/g										
Sum of quantifiable PFAS	113	121	156	123	106	81.7	96.1	70.8	65.9	61.8	89.4
TOF	535	828	1270	844	976	971	965	660	696	764	830
Unidentified PFAS	422	707	1110	721	870	889	869	589	630	702	741
	Composition %										
Quantifiable PFAS	21	15	12	15	11	8	10	11	9	8	11
Unidentified PFAS	79	85	88	85	89	92	90	89	91	92	89
b)	2004	2005	2007	2008	Gässlösa						
					2009	2010	2011	2012	2013	2014	2015
	Concentration ng F/g										
Sum of quantifiable PFAS	496	525	222	219	356	372	225	114	137	196	286
TOF	6840	14600	3360	8770	11600	8250	1900	1820	1080	3610	2610
Unidentified PFAS	6350	14100	3140	8550	11300	7880	1680	1710	946	3420	2320
	Composition %										
Quantifiable PFAS	7.3	3.6	6.6	2.5	3.1	4.5	11.8	6.3	12.7	5.4	11.0
Unidentified PFAS	92.7	96.4	93.4	97.5	96.9	95.5	88.2	93.7	87.3	94.6	89.0

a)

Total organofluorine concentration (ng F/g) in sewage sludge from Henriksdal



b)

Total organofluorine concentration (ng F/g) in sewage sludge from Gässlösa

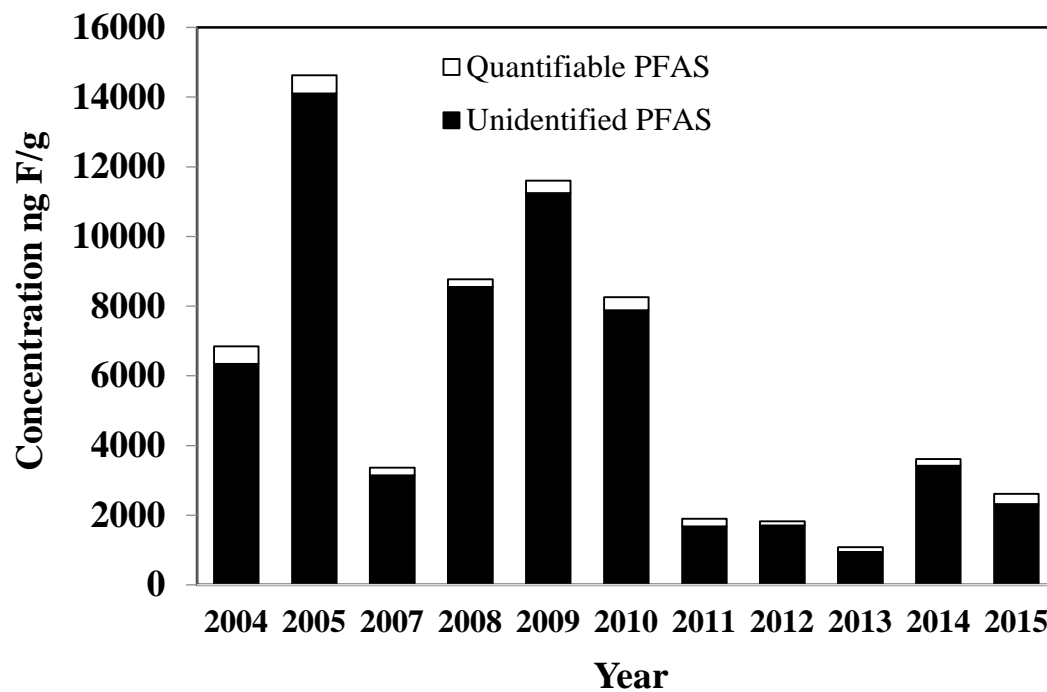


Figure 5. Total organofluorine concentrations (ng F/g) in sewage sludge samples from a) Henriksdal and b) Gässlösa

The levels of PFASs in non-spike samples measured by LC-MS/MS were compared to TOF using CIC after conversion. The quantifiable PFASs in samples from Gässlösa were approximately 1.6 - 17.7 times higher than those of Henriksdal in corresponding year (Table 5). Samples from Henriksdal, the quantifiable PFAS accounted for 8 - 21% of the TOF, whereas quantifiable PFAS accounted for 2-13% of TOF in samples from Gässlösa (Table 5). The samples from Gässlösa had greater proportion and amounts of unidentified organofluorine compared to those of Henriksdal (Table 5). The proportion of quantifiable PFAS to TOF decreased from 21% in 2004 to 11% in 2015 in samples from Henriksdal. Increasing levels of unidentified PFAS was also observed between 2012 and 2015 (Table 5 and Figure 5a), which may suggest an increasing usage of new fluorinated alternatives in recent years. In contrast, it is difficult to conclude if there was any increasing use of new unidentified alternatives in Gässlösa in recent years due to large variation of TOF levels between years (Table 5 and Figure 5b).

Summary

Comparison of sludge samples collected from 2015 among the 4 WWTPs

- Samples from Henriksdal (171 ng/g) had the greatest total quantifiable PFAS concentrations whereas Gässlösa (96.7 ng/g) had the lowest total PFAS concentrations.
- Samples from Öhn and Henriksdal had relatively higher concentrations of PFCA precursor compounds compared to the other two WWTPs, of which diPAP contributed over 73% to the PFCA precursors. Samples from Henriksdal and Gässlösa had relatively higher concentrations of PFSA precursors and persistent PFAAs.
- DiPAP was the main contributor (average of 58%, range 34 - 82%) of the total PFAS among the 4 WWTPs.
- FOSAAs, one group of PFSA precursor made up of 14% (range 7.7 - 10.2%) of the total PFAS after diPAP.
- All samples showed detectable TOF concentrations ranging from 606 (Öhn) to 2610 (Gässlösa) ng F/g.
- The quantifiable PFAS only accounted for 5 to 13% of the total organofluorine indicating that 87-95% of the measured organofluorine in the samples remained unidentified.

Time trends of PFAS and TOF in sewage sludge

- Decreasing trends of total quantifiable PFAS were observed in both Henriksdal and Gässlösa wastewater treatment plants between 2004 and 2015.
- At Henriksdal diPAP (mean: 50.1%, range: 35.6 - 77.5%) was the dominated PFAS class between 2004 and 2015; whereas at Gässlösa the dominating PFAS class varied from year to year: PFPiA for years 2004 and 2005 (30.6-45.2%); PFCA for years 2007-2009 (36.2-62.9%); diPAP for years 2010, 2014-2015 (31.7-37.3%); and FTCA for years 2011-2013 (40.5-53.1%).
- Decreasing trends of PFOS, PFOA, EtFOSAA, 6:2/10:2, 8:2/12:2 and 10:2 diPAPs were observed in Henriksdal.
- Decreasing trends of PFOA, PFNA; PFDA, PFUnDA, PFDoDA, PFTTrDA, PFOS, EtFOSAA, MeFOSAA, 6:2/8:2, 6:2/10:2 and 8:2 diPAPs were observed in Gässlösa.
- The results of 7:3 and 5:3 FTCAs and 8:2 and 6:2 FTSAAs suggest shifts of 8:2 fluorotelomer-based products to 6:2 fluorotelomer-based products in recent years.
- Significant high levels of PFPiAs and PFPAs were detected in Gässlösa samples collected in 2004 and 2005, which contributed to up to 56.9% of total PFAS in those years.
- All samples showed detectable TOF levels at Henriksdal (535 - 1270 ng F/g) and Gässlösa (1080 - 14600 ng F/g) between 2004 and 2015.
- TOF levels in Gässlösa samples were approximately 1.6 - 17.7 times higher than those from Henriksdal for corresponding years.
- No observable trend of TOF was observed for Henriksdal, but a decreasing trend was noted for Gässlösa between 2004 and 2015.
- The quantifiable PFAS accounted for 8 - 21% of the TOF for Henriksdal's samples, whereas 2-13% for Gässlösa.
- The proportion of quantifiable PFAS to TOF decreased from 21% in 2004 to 11% in 2015 in samples from Henriksdal; increasing levels of unidentified PFAS was also observed between 2012 and 2015.

Recommendation

Quite significant proportions of diPAPs and FOSAAs contributed to the total PFAS in sewage sludge suggest that sewage sludge is an important sink for these precursor compounds. Since these compounds have been shown to undergo microbial biodegradation producing PFCAs of different chain lengths (from diPAPs)²¹ and PFOS (from FOSAAs),²² levels of PFAS/TOF in sewage sludge should be measured before applying to agricultural farmland as fertilizer.

Detection of different intermediates such as FTCAs and FOSAs/FOSEs indicates transformation of fluorotelomer-based compounds and PFOS-based precursor compounds.^{22,23} Volatile breakdown compounds such as fluorotelomer alcohol (FTOH) and FOSAs/FOSEs might be released during the transformation process. Measurements of these volatile compounds around WWTPs may help to understand the transport of these compounds to the environment. Analysis of archived samples showed the change of use of different PFASs (from 8:2 fluorotelomer-based to 6:2 fluorotelomer-based) in recent years. More comprehensive picture of the use of PFASs will be provided when more archived samples are analyzed from different WWTPs receiving different types of waste.

Significant proportion of total organofluorine in sewage sludge samples remained unidentified. The levels of unidentified PFAS were more related to types of industries connected to the WWTPs, not necessarily related to number of people served and scale of the WWTPs. For example, Henriksdal WWTP was the largest scale and served the most population among the other 3 WWTPs; however, its total PFAS and TOF were comparable to those of Bergkvara which is a small scale of WWTP serving the least population. On the other hand, although Gässlösa did not have the greatest total PFAS levels among the 4 WWTPs, the levels of TOF and unidentified PFAS were at least 2.5 times higher than those of the other 3 WWTPs. Further study should also investigate sewage samples from other WWTPs which receive industrial wastewater to understand what types of PFASs and evaluate the TOF levels in those industrial wastes.

Those unidentified PFAS might also consist of unidentified intermediate or PFCA/PFSA precursor compounds. Total oxidizable precursor (TOP) assay is an oxidative conversion method that can convert all PFCA and PFSA precursors as well as intermediates to persistent PFCA.²⁴ The combination of the use of TOF and TOP assay analyses may help understand how much of the unidentified PFAS in the sample accounted by the precursor compounds.

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Supplementary Information (SI)

Table S1. Compound classes and compounds analyzed in current investigation

a) Persistent PFASs

Class	Acronym	Name	Quantified with analytical standard	Quantified with surrogate compound
Perfluoroalkyl sulfonates (PFASs)				
	PFBS	Perfluorobutane sulfonic acid	X	
	PFPeS	Perfluoropentane sulfonic acid	X	
	PFHxS	Perfluorohexane sulfonic acid	X	
	PFHpS	Perfluoroheptane sulfonic acid	X	
	L-PFOS	Perfluorooctane sulfonic acid	X	
	PFNS	Perfluorononane sulfonic acid	X	
	PFDS	Perfluorodecane sulfonic acid	X	
	PFDoDS	Perfluorododecane sulfonic acid	X	
Perfluorinated carboxylates (PFCAs)				
	PFBA	Perfluorobutanoic acid	X	
	PFPeA	Perfluoropentanoic acid	X	
	PFHxA	Perfluorohexanoic acid	X	
	PFHpA	Perfluoroheptanoic acid	X	
	PFOA	Perfluorooctanoic acid	X	
	PFNA	Perfluorononanoic acid	X	
	PFDA	Perfluorodecanoic acid	X	
	PFUnDA	Perfluoroundecanoic acid	X	
	PFDoDA	Perfluorododecanoic acid	X	
	PFTrDA	Perfluorotridecanoic acid	X	
	PFTDA	Perfluorotetradecanoic acid	X	
	PFHxDA	Perfluorohexadecanoic acid	X	
	PFOcDA	Perfluorooctadecanoic acid	X	
Perfluorinated phosphonates (PFPA)s				
	PFHxPA	Perfluorohexyl phosphonic acid	X	
	PFOPA	Perfluorooctyl phosphonic acid	X	
	PFDPA	Perfluorodecyl phosphonic acid	X	
	PFDoPA	Perfluorododecyl phosphonic acid		PFDoPA
	PFTePA	Perfluorotetradecyl phosphonic acid		PFTePA
	PFHxDPA	Perfluorohexadecyl phosphonic acid		PFHxDPA

b) PFAS precursor compounds

Class	Acronym	Name	Quantified with analytical standard	Quantified with surrogate compound
Perfluoroalkyl sulfonate (PFSA) precursors				
	FOSA	Perfluorooctane sulfonamide	x	
	MeFOSA	Methyl perfluorooctane sulfonamide	x	
	EtFOSA	Ethyl perfluorooctane sulfonamide	x	
	MeFOSE	Methyl perfluorooctane sulfonamide ethanol	x	
	EtFOSE	Ethyl perfluorooctane sulfonamide ethanol	x	
	FOSAA	Perfluorooctane sulfonamidoacetate	x	
	MeFOSAA	Methyl perfluorooctane sulfonamidoacetate	x	
	EtFOSAA	Ethyl perfluorooctane sulfonamidoacetate	x	
	SAmPAP	Ethylperfluorooctanesulfonamidoethyl phosphate	x	
	diSAmPAP	bis-(ethylperfluorooctanesulfonamidoethyl) phosphate	x	

Table S1b (Cont'd)

Class	Acronymn	Name	Quantified with analytical standard	Quantified with surrogate compound
Perfluorinated carboxylate (PFCA) precursors				
	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	x	
	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	x	
	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	x	
	5:3 FTCA	5:3 Fluorotelomer carboxylic acid	x	
	7:3 FTCA	7:3 Fluorotelomer carboxylic acid	x	
	6:2 FTUCA	6:2 Fluorotelomer unsaturated carboxylic acids	x	
	8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acids	x	
	10:2 FTUCA	10:2 Fluorotelomer unsaturated carboxylic acids	x	
	6:2 monoPAP	6:2 Fluorotelomer phosphate monoester	x	
	8:2 monoPAP	8:2 Fluorotelomer phosphate monoester	x	
	10:2 monoPAP	10:2 Fluorotelomer phosphate monoester	x	
	4:2 diPAP	4:2 Fluorotelomer phosphate monoester		6:2 diPAP
	4:2/6:2 diPAP	4:2/6:2 Fluorotelomer phosphate diester		6:2 diPAP
	2:2/8:2 diPAP	2:2/8:2 Fluorotelomer phosphate diester		6:2 diPAP
	6:2 diPAP	6:2 Fluorotelomer phosphate diester	x	
	4:2/8:2 diPAP	4:2/8:2 Fluorotelomer phosphate diester		6:2 diPAP
	2:2/10:2 diPAP	2:2/10:2 Fluorotelomer phosphate diester		6:2 diPAP
	8:2 diPAP	8:2 Fluorotelomer phosphate diester	x	
	6:2/10:2 diPAP	6:2/10:2 Fluorotelomer phosphate diester		8:2 diPAP
	4:2/12:2 diPAP	4:2/12:2 Fluorotelomer phosphate diester		8:2 diPAP
	6:2/8:2 diPAP	6:2/8:2 Fluorotelomer phosphate diester		8:2 diPAP
	4:2/10:2 diPAP	4:2/10:2 Fluorotelomer phosphate diester		8:2 diPAP
	8:2/10:2 diPAP	8:2/10:2 Fluorotelomer phosphate diester		8:2 diPAP
	6:2/12:2 diPAP	6:2/12:2 Fluorotelomer phosphate diester		8:2 diPAP
	10:2 diPAP	10:2 Fluorotelomer phosphate diester	x	
	8:2/12:2 diPAP	8:2/12:2 Fluorotelomer phosphate diester		10:2 diPAP
	6:2/14:2 diPAP	6:2/14:2 Fluorotelomer phosphate diester		10:2 diPAP
	10:2/12:2 diPAP	10:2/12:2 Fluorotelomer phosphate diester		10:2 diPAP
	8:2/14:2 diPAP	8:2/14:2 Fluorotelomer phosphate diester		10:2 diPAP
	12:2 diPAP	12:2 Fluorotelomer phosphate diester		10:2 diPAP
	10:2/14:2 diPAP	10:2/14:2 Fluorotelomer phosphate diester		10:2 diPAP
	8:2/16:2 diPAP	8:2/16:2 Fluorotelomer phosphate diester		10:2 diPAP

Table S1b (Cont'd)

Class	Acronym	Name	Quantified with analytical standard	Quantified with surrogate compound
Perfluorinated phosphinates (PFPIAs)				
	6:6 PFPIA	Bis (perfluorohexyl) phosphinic acid	x	
	6:8 PFPIA	Perfluoro (hexyloctyl) phosphinic acid	x	
	8:8 PFPIA	Bis (perfluorooctyl) phosphinic acid	x	
	6:10 PFPIA	Perfluoro (hexyldecyl) phosphinic acid		C8/C8 PFPIA
	8:10 PFPIA	Perfluoro (octyldecyl) phosphinic acid		C8/C8 PFPIA
	6:12 PFPIA	Perfluoro (hexyldodecyl) phosphinic acid		C8/C8 PFPIA
	10:10 PFPIA	Bis (perfluorodecyl) phosphinic acid		C8/C8 PFPIA
	8:12 PFPIA	Perfluoro (octyldodecyl) phosphinic acid		C8/C8 PFPIA
	6:14 PFPIA	Perfluoro (hexyltetradecyl) phosphinic acid		C8/C8 PFPIA
	10:12 PFPIA	Perfluoro (decyldodecyl) phosphinic acid		C8/C8 PFPIA
	8:14 PFPIA	Perfluoro (octyltetradecyl) phosphinic acid		C8/C8 PFPIA
	12:12 PFPIA	Bis (perfluorododecyl) phosphinic acid		C8/C8 PFPIA
	10:14 PFPIA	Perfluoro (decyltetradecyl) phosphinic acid		C8/C8 PFPIA
	14:14 PFPIA	Bis (perfluorotetradecyl) phosphinic acid		C8/C8 PFPIA

Table S2. List of analytes, MRM transitions, cone voltage, and collision energy used for quantification and qualification of PFAS.

a) Persistent PFASs

Analyte	Precursor/ product ions quantification (m/z)	Cone (V)	Col (eV)	Precursor/ product ions qualification (m/z)	Cone (V)	Col (eV)	Internal standard
Perfluoroalkyl sulfonates (PFASs)							
PFBS	298.9/98.9	20	26	298.9/79.96	20	26	¹³ C-PFH _x A
PFPeS	348.90/98.96	20	26	348.90/79.96	20	30	¹³ C-PFH _x A
PFH _x S	398.9/98.9	20	30	398.9/79.96	20	34	¹⁸ O-PFH _x S
PFHpS	448.97/98.90	20	30	448.97/79.96	20	35	¹³ C-PFOS
L-PFOS	498.97/98.96	20	38	498.97/79.96, 498.97/169.03	20	44, 34	¹³ C-PFOS
PFNS	548.90/98.96	20	38	548.90/79.96	20	44	¹³ C-PFOS
PFDS	598.97/98.9	20	42	598.97/79.96	20	58	¹³ C-PFOS
PFDoDS	698.90/98.90	20	40	698.90/79.96	20	45	¹³ C-PFOS
Perfluorinated carboxylates (PFCAs)							
PFBA	212.97/169	20	11				¹³ C-PFBA
PFPeA	262.97/219	20	8				¹³ C-PFH _x A
PFH _x A	312.97/269	20	9	312.97/118.95	20	26	¹³ C-PFH _x A
PFHpA	362.97/319	20	10	362.97/168.97	20	16	¹³ C-PFH _x A
PFOA	412.97/369	20	10	412.97/168.97	20	18	¹³ C-PFOA
PFNA	462.99/419	20	12	462.99/219	20	18	¹³ C-PFNA
PFDA	512.97/469	20	11	512.97/219	20	18	¹³ C-PFDA
PFUnDA	562.97/519	20	12	562.97/268.99	20	18	¹³ C-PFUnDA
PFDoDA	612.97/569	34	14	612.97/168.96	40	22	¹³ C-PFDoDA
PFTTrDA	662.9/619	20	14	662.9/168.96	20	26	¹³ C-PFDoDA
PFTDA	712.9/669	20	14	712.9/168.97	20	28	¹³ C-PFDoDA
PFH _x DA	812.9/769	30	15	812.9/168.96	42	32	¹³ C-PFDoDA
PFOcDA	912.9/869	36	15	912.9/168.96	36	36	¹³ C-PFDoDA
Perfluorinated phosphonates (PFPA)s							
PFH _x PA	398.97/79	62	26				¹³ C-PFOA
PFOPA	499/79	62	30				¹³ C-PFOA
PFDPa	599.03/79	62	30				¹³ C-PFOA
PFDoPA	699/79	62	30				¹³ C-PFOA
PFTePA	799/79	62	30				¹³ C-PFOA
PFH _x DPA	899/79	62	30				¹³ C-PFOA

Table S2b PFAS precursors

Analyte	Precursor/ product ions quantification (m/z)	Cone (V)	Col (eV)	Precursor/ product ions qualification (m/z)	Cone (V)	Col (eV)	Internal standard
Perfluoroalkyl sulfonate (PFSA) precursors							
FOSA	497.9/168.96	82	28	497.9/78	82	30	¹³ C-FOSA
MeFOSA	512/169	27	45				² H-Me-FOSA
EtFOSA	526/169	27	45				² H-Me-FOSA
MeFOSE	616/59	27	45	556.03/121.99	42	34	² H-Me-FOSE
EtFOSE	630/59	27	45	570.1/135.98	48	32	² H-Me-FOSE
FOSAA				555.8/418.85			² H -Et-FOSAA
MeFOSAA				569.78/482.76			² H -Et-FOSAA
EtFOSAA				583.84/482.8			² H -Et-FOSAA
SAmPAP	649.8 > 96.9	2	26	649.8 > 168.9	2	36	¹³ C-8:2 diPAP
diSAmPAP	1202.6 > 525.9	92	46	1202.6 > 168.9	92	64	¹³ C-8:2 diPAP

Table S2b PFAS precursors

Class	Analyte	Precursor/ product ions quantification (m/z)	Cone (V)	Col (eV)	Precursor/ product ions qualification (m/z)	Cone (V)	Col (eV)	Internal standard
Perfluorinated carboxylate (PFCA) precursors								
	4:2 FTSA	327/307	20	20	327/81	20	28	¹³ C-6:2 FTSA
	6:2 FTSA	427/407	20	20	427/81	20	28	¹³ C-6:2 FTSA
	8:2 FTSA	527/507	20	20	527/80	20	28	¹³ C-8:2 FTSA
	5:3 FTCA	340.9/236.97	10	16	340.92/16.93	10	22	¹³ C-6:2 FTUCA
	7:3 FTCA	356.9/292.91	10	18	356.9/242.95	10	36	¹³ C-6:2 FTUCA
	6:2 FTUCA	440.9/336.89	12	14	440.9/316.93	12	20	¹³ C-8:2 FTUCA
	8:2 FTUCA	456.9/392.84	10	18	456.9/392.84	10	38	¹³ C-8:2 FTUCA
	10:2 FTUCA	556.84/492.82	8	16	556.84/242.94	8	38	¹³ C-8:2 FTUCA
	6:2 monoPAP	442.9 > 96.95	10	18	442.90 > 422.89	10	12	¹³ C-6:2 monoPAP
	8:2 monoPAP	542.9 > 97	22	14	542.90 > 522.90	22	14	¹³ C-8:2 monoPAP
	10:2 monoPAP	642.97 > 97.00	24	28	649.78 > 525.83	24	22	¹³ C-8:2 monoPAP
	4:2 diPAP	588.9 > 97	64	28	588.9/342.91	64	18	¹³ C-6:2 diPAP
	4:2/6:2 diPAP	688.9/97	64	28	688.9/342.91, 688.9/442.91	64	18	¹³ C-6:2 diPAP
	2:2/8:2 diPAP	688.9/97	64	28	688.9/242.91, 688.9/542.91	64	18	¹³ C-6:2 diPAP
	6:2 diPAP	788.9/97	64	28	788.9/442.91	64	18	¹³ C-6:2 diPAP
	4:2/8:2 diPAP	788.9/97	64	28	788.9/342.91, 788.9/542.91	64	18	¹³ C-6:2 diPAP
	2:2/10:2 diPAP	788.9/97	64	28	788.9/242.91, 788.9/642.91	64	18	¹³ C-6:2 diPAP
	8:2 diPAP	988.78/96.94	68	34	988.78/542.81	68	26	¹³ C-8:2 diPAP
	6:2/10:2 diPAP	988.78/96.94	68	34	988.78/442.81, 988.78/ 642.81	68	26	¹³ C-8:2 diPAP
	4:2/12:2 diPAP	988.78/96.94	68	34	988.78/342.81, 988.78/742.81	68	26	¹³ C-8:2 diPAP
	6:2/8:2 diPAP	888.78/96.94	66	34	888.78/442.81, 888.78/542.81	66	26	¹³ C-6:2 diPAP
	4:2/10:2 diPAP	888.78/96.94	66	34	888.78/342.81, 888.78/642.81	66	26	¹³ C-6:2 diPAP
	8:2/10:2 diPAP	1088.78/96.94	68	34	1088.78/542.81, 1088.78/642.81	68	26	¹³ C-8:2 diPAP
	6:2/12:2 diPAP	1088.78 > 96.94	68	34	1088.78 > 442.81, 1088.78 > 742.81	68	34	¹³ C-8:2 diPAP

10:2 diPAP	1188.78/96.94	68	34	1188.78/642.81	68	26	¹³ C-8:2 diPAP
8:2/12:2 diPAP	1188.78/96.94	68	34	1188.78/742.81, 1188.78/542.81	68	26	¹³ C-8:2 diPAP
6:2/14:2 diPAP	1188.78/96.94	68	34	1188.78/842.81, 1188.78/442.81	68	26	¹³ C-8:2 diPAP
10:2/12:2 diPAP	1288.78 > 96.94	68	34	1288.78 > 642.81, 1288.78 > 742.81	68	26	¹³ C-8:2 diPAP
8:2/14:2 diPAP	1288.78 > 542.81, 1288.78 > 842.81	68	26	1288.78 > 96.94	68	34	¹³ C-8:2 diPAP
12:2 diPAP	1388.78 > 96.94	68	34	1388.78 > 742.81	68	26	¹³ C-8:2 diPAP
10:2/14:2 diPAP	1388.78 > 96.94	68	34	1388.78 > 642.81, 1388.78 > 842.81	68	26	¹³ C-8:2 diPAP
8:2/16:2 diPAP	1388.78 > 96.94	68	34	1388.78 > 542.81, 1388.78 > 942.81	68	26	¹³ C-8:2 diPAP

Class	Analyte	Precursor/ product ions quantification (m/z)	Cone (V)	Col (eV)	Precursor/ product ions qualification (m/z)	Cone (V)	Col (eV)	Internal standard
Perfluorinated phosphinates (PFPIAs)								
	6:6 PFPIA	701/401	62	28				¹³ C-PFDoDA
	6:8 PFPIA	801/401	24	28	801/501	24	28	¹³ C-PFDoDA
	8:8 PFPIA	901/501	24	28				¹³ C-PFDoDA
	6:10 PFPIA	1001/401	24	28	1001/601	24	28	¹³ C-PFDoDA
	8:10 PFPIA	1101/501	24	28	1101/601	24	28	¹³ C-PFDoDA
	6:12 PFPIA	1101/401	24	28	1101/701	24	28	¹³ C-PFDoDA
	10:10 PFPIA	1201/601	24	28				¹³ C-PFDoDA
	8:12 PFPIA	1201/601	24	28	1201/701	24	28	¹³ C-PFDoDA
	6:14 PFPIA	1201/401	24	28	1201/801	24	28	¹³ C-PFDoDA
	10:12 PFPIA	1301/601	24	28	1301/701	24	28	¹³ C-PFDoDA
	8:14 PFPIA	1301/501	24	28	1301/801	24	28	¹³ C-PFDoDA
	12:12 PFPIA	1401/701	24	28				¹³ C-PFDoDA
	10:14 PFPIA	1401/601	24	28	1001/801	24	28	¹³ C-PFDoDA
	14:14 PFPIA	1501/701	24	28				¹³ C-PFDoDA

Table S3. Individual PFAS concentrations (ng/g) in the four WWTPs collected in 2015**a) Persistent PFASs**

	Öhn	Bergkvara	Henriksdal	Gässlösa
	Conc (ng/g)			
Perfluoroalkyl sulfonates (PFASs)				
PFBS	<0.1	<0.1	<0.1	<0.1
PFPeS	<0.1	<0.1	<0.1	<0.1
PFHxS	3.49	2.04	0.728	0.501
PFHpS	<0.1	<0.1	<0.1	<0.1
L-PFOS	2.99	6.76	13.4	11.5
PFNS	<0.1	<0.1	<0.1	<0.1
PFDS	0.667	<0.1	0.698	<0.1
PFDoDS	<0.1	<0.1	<0.1	<0.1
Perfluorinated carboxylates (PFCAs)				
PFBA	<4.1	<4.1	<0.1	<0.1
PFPeA	<0.2	<0.1	<0.1	<0.1
PFHxA	<0.9	<0.9	3.07	3.03
PFHpA	<0.4	<0.4	<0.4	<0.3
PFOA	0.812	0.977	2.28	2.70
PFNA	0.193	0.397	0.756	0.897
PFDA	0.922	3.06	6.04	4.47
PFUnDA	0.540	2.00	1.70	2.85
PFDoDA	1.02	0.331	2.65	1.63
PFTTrDA	0.174	<0.2	1.06	0.732
PFTDA	0.471	<0.1	0.936	0.530
PFHxDA	n.q.	n.q.	0.384	n.q.
PFOcDA	n.q.	n.q.	<0.1	n.q.
Perfluorinated phosphonates (PFPAAs)				
PFHxPA	<0.1	<0.1	<0.1	<0.1
PFOPA	<0.1	<0.1	<0.1	<0.1
PFDPA	<0.1	2.75	<0.1	<0.1
PFDoPA	<0.1	<0.1	<0.1	<0.1
PFTePA	<0.1	<0.1	<0.1	<0.1
PFHxDPA	<0.1	<0.1	<0.1	<0.1

n.q.:not quantified because of poor recoveries (<10%)

Table S3b PFAS precursors

	Öhn	Bergkvara	Henriksdal	Gässlösa
	Conc (ng/g)			
Perfluoroalkyl sulfonate (PFSA) precursors				
FOSA	0.145	<1.0	0.332	1.40
MeFOSA	n.q.	n.q.	n.q.	<0.1
EtFOSA	n.q.	n.q.	n.q.	<0.1
MeFOSE	<0.1	<0.1	n.q.	n.q.
EtFOSE	n.q.	<0.1	n.q.	n.q.
FOSAA	2.11	n.q.	2.05	n.q.
MeFOSAA	1.61	1.59	6.50	11.7
EtFOSAA	7.84	10.5	14.9	12.7
SAmPAP	n.q.	n.q.	n.q.	n.q.
diSAmPAP	0.162	0.161	0.204	<0.1

n.q.:not quantified because of poor recoveries (<10%)

Table S3b (Cont'd)

	Öhn	Bergkvara	Henriksdal	Gässlösa
	Conc (ng/g)			
Perfluorinated carboxylate (PFCA) precursors				
4:2 FTSA	<0.1	<0.1	<0.1	<0.1
6:2 FTSA	<6.2	3.75	<1.3	1.52
8:2 FTSA	2.01	2.62	2.88	1.88
5:3 FTCA	<0.1	0.830	15.8	5.04
7:3 FTCA	1.29	1.56	8.61	0.517
6:2 FTUCA	n.q.	n.q.	n.q.	n.q.
8:2 FTUCA	n.q.	n.q.	n.q.	n.q.
10:2 FTUCA	n.q.	n.q.	n.q.	n.q.
6:2 monoPAP	n.q.	n.q.	6.05	n.q.
8:2 monoPAP	n.q.	n.q.	n.q.	n.q.
10:2 monoPAP	n.q.	n.q.	n.q.	n.q.
4:2 diPAP	<0.1	<0.1	<0.1	<0.1
4:2/6:2 diPAP	<0.1	<0.1	<0.1	<0.1
2:2/8:2 diPAP	<0.1	<0.1	<0.1	<0.1
6:2 diPAP	7.87	2.66	7.80	7.68
4:2/8:2 diPAP	<0.1	<0.1	<4.9	<0.1
2:2/10:2 diPAP	<0.1	<0.1	<4.9	<0.1
8:2 diPAP	5.51	3.44	7.24	7.06
6:2/10:2 diPAP	6.16	5.64	19.01	8.96
4:2/12:2 diPAP	<0.1	<0.1	<0.1	<0.1
6:2/8:2 diPAP	3.41	4.31	7.32	5.52
4:2/10:2 diPAP	<0.1	<0.1	<0.1	<0.1
8:2/10:2 diPAP	<0.1	<0.1	<0.1	<0.1
6:2/12:2 diPAP	3.30	2.45	1.80	<0.1
10:2 diPAP	19.0	12.0	9.53	<0.1
8:2/12:2 diPAP	29.3	24.6	14.8	1.28
6:2/14:2 diPAP	18.4	10.2	7.28	0.961
10:2/12:2 diPAP	9.65	6.03	<0.1	<0.1
8:2/14:2 diPAP	10.7	5.14	<0.1	<0.1
12:2 diPAP	1.46	0.301	<0.1	<0.1
10:2/14:2 diPAP	2.69	0.211	<0.1	<0.1
8:2/16:2 diPAP	1.62	<0.1	<0.1	<0.1

Table S3b (Cont'd)

	Öhn	Bergkvara	Henriksdal	Gässlösa
	Conc (ng/g)			
Perfluorinated phosphinates (PFPIAs)				
6:6 PFPIA	<0.1	<0.1	<0.1	<0.1
6:8 PFPIA	<0.1	<0.1	<0.1	<0.1
8:8 PFPIA	<0.1	<0.1	<0.1	<0.1
6:10 PFPIA	<0.1	<0.1	<0.1	<0.1
8:10 PFPIA	<0.1	<0.1	<0.1	<0.1
6:12 PFPIA	<0.1	<0.1	<0.1	<0.1
10:10 PFPIA	<0.1	<0.1	<0.1	<0.1
8:12 PFPIA	<0.1	<0.1	<0.1	<0.1
6:14 PFPIA	<0.1	<0.1	<0.1	<0.1
10:12 PFPIA	<0.1	<0.1	<0.1	<0.1
8:14 PFPIA	<0.1	<0.1	<0.1	<0.1
12:12 PFPIA	<0.1	<0.1	<0.1	<0.1
10:14 PFPIA	<0.1	<0.1	<0.1	<0.1
14:14 PFPIA	<0.1	<0.1	<0.1	<0.1

Table S4. Individual PFAS concentrations (ng/g) in sewage sludge samples collected from Henriksdal

a) Persistent PFAS

	Henriksdal										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluoroalkyl sulfonates (PFASs)											
PFBS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFPeS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxS	0.438	0.770	1.91	0.880	0.588	1.849	0.776	0.698	0.294	0.491	0.728
PFHpS	0.190	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-PFOS	36.6	39.3	41.0	29.2	38.0	22.5	19.3	29.6	13.7	15.7	13.4
PFNS	n.q.	<0.1	<0.1	<0.1	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFDS	5.73	7.43	5.18	5.34	1.05	2.89	1.81	0.921	<0.1	0.78	0.698
PFDoDS	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Perfluorinated carboxylates (PFCAs)											
PFBA	<0.6	<0.1	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.6	<0.1	<0.1
PFPeA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxA	3.34	3.25	2.54	3.52	2.93	2.48	2.31	1.89	1.84	2.20	3.07
PFHpA	<2.6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	n.q.	<0.4	<0.4
PFOA	4.34	3.60	3.53	6.40	4.57	3.89	2.85	2.40	2.42	2.06	2.28
PFNA	0.569	0.581	1.17	1.02	1.85	1.08	1.01	0.916	0.689	0.840	0.756
PFDA	4.57	6.17	4.93	6.28	5.58	6.66	6.51	5.25	3.72	6.58	6.04
PFUnDA	1.74	1.61	2.48	2.33	1.92	2.41	2.15	1.93	1.42	1.99	1.70

PFD_oDA	2.82	4.61	3.94	3.97	2.61	4.14	3.64	3.41	2.88	2.95	2.65
PFT_rDA	0.980	0.929	0.888	1.66	0.965	0.566	1.28	1.35	1.01	1.25	1.06
PFTDA	1.09	1.13	1.22	1.31	0.992	1.20	1.24	1.08	1.08	1.05	0.936
PFH_xDA	n.q.	n.q.	n.q.	0.509	<0.1	n.q.	0.495	0.463	n.q.	0.529	0.384
PFO_cDA	n.q.	n.q.	n.q.	<0.1	<0.1	n.q.	<0.1	<0.1	n.q.	<0.1	<0.1
Perfluorinated phosphonates (PFPA_s)											
PFH_xPA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFOPA	2.46	4.16	<0.1	<0.1	<0.1	<0.1	<0.1	0.832	<0.1	<0.1	<0.1
PF_DPA	1.07	4.91	<0.1	0.605	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFD_oPA	<0.1	1.22	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFT_ePA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFH_xDPA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

n.q.: not quantified because of poor recoveries (<10%)

Table S4b PFAS precursors

	Henriksdal										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluoroalkyl sulfonate (PFSA) precursors											
FOSA	0.739	4.4	0.704	2.4	0.699	0.9	2.5	2.4	0.7	2	0.332
MeFOSA	n.q.	<0.1	n.q.	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	n.q.
EtFOSA	n.q.	<0.1	n.q.	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	n.q.
MeFOSE	n.q.	n.q.	n.q.	86.35	n.q.	n.q.	n.q.	33.0	8.24	n.q.	n.q.
EtFOSE	n.q.	n.q.	n.q.	1.33	n.q.	n.q.	n.q.	1.22	6.13	n.q.	n.q.
FOSAA	9.04	7.88	5.73	4.23	4.84	7.48	3.36	2.73	2.77	2.16	2.05
MeFOSAA	11.6	8.36	14.8	15.3	3.57	9.83	9.88	9.85	8.19	7.98	6.50
EtFOSAA	25.6	23.6	49.0	40.2	8.82	31.14	28.4	20.8	18.4	17.1	14.9
SAmPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
diSAmPAP	n.q.	1.41	0.502	0.461	<0.1	0.329	0.542	0.787	0.191	0.218	0.204

n.q.: not quantified because of poor recoveries (<10%)

Table S4b (Cont'd)

	Henriksdal										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluorinated carboxylate (PFCA) precursors											
4:2 FTSA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2 FTSA	1.28	0.93	<1.3	1.61	1.90	<1.3	<1.3	<1.3	2.46	<1.3	<1.3
8:2 FTSA	7.28	6.01	5.16	5.56	6.25	4.90	5.20	5.16	3.10	3.30	2.88
5:3 FTCA	8.70	1.36	17.2	22.0	2.99	16.67	11.5	13.3	11.6	14.1	15.8
7:3 FTCA	2.85	1.21	19.9	23.2	12.6	12.67	8.95	8.83	7.91	8.43	8.61
6:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
8:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
10:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
6:2 monoPAP	3.98	n.q.	n.q.	4.11	n.q.	n.q.	5.71	4.76	0.57	4.66	6.05
8:2 monoPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
10:2 monoPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
4:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
4:2/6:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2:2/8:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2 diPAP	7.31	4.46	11.4	6.15	5.61	4.07	7.72	5.37	6.96	7.50	7.80
4:2/8:2 diPAP	<4.9	<0.1	0.20	<4.9	<4.9	<4.9	<4.9	<4.9	<0.1	<4.9	<4.9
2:2/10:2 diPAP	<4.9	<0.1	<4.9	<4.9	<4.9	<4.9	<4.9	<4.9	<0.1	<4.9	<4.9

8:2 diPAP	15.5	13.5	36.8	25.7	21.1	19.2	13.9	9.84	8.56	6.00	7.24
6:2/10:2 diPAP	12.8	12.4	33.3	60.8	10.4	13.6	37.0	22.1	8.8	19.7	19.0
4:2/12:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2/8:2 diPAP	8.88	7.45	28.3	14.9	8.79	11.2	15.8	9.87	8.62	6.54	7.32
4:2/10:2 diPAP	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:2/10:2 diPAP	6.64	7.00	24.6	15.5	9.13	12.8	8.88	6.92	4.24	5.90	5.32
6:2/12:2 diPAP	4.25	2.52	12.5	4.74	1.86	6.86	2.11	1.63	1.82	2.41	1.80
10:2 diPAP	16.0	14.4	91.5	38.2	18.4	45.8	10.3	7.85	9.28	14.8	9.53
8:2/12:2 diPAP	32.4	18.2	180	56.5	27.6	92.1	18.4	13.7	14.7	22.7	14.8
6:2/14:2 diPAP	<0.1	8.87	74.8	10.5	2.34	34.4	5.22	7.27	5.69	9.21	7.28
10:2/12:2 diPAP	n.q.	<0.1	47.7	6.19	<0.1	35.0	<0.1	<0.1	<0.1	1.30	<0.1
8:2/14:2 diPAP	n.q.	<0.1	63.8	7.63	<0.1	33.6	<0.1	<0.1	0.366	1.32	<0.1
12:2 diPAP	n.q.	<0.1	4.64	<0.1	<0.1	3.76	<0.1	<0.1	<0.1	<0.1	<0.1
10:2/14:2 diPAP	n.q.	<0.1	9.44	<0.1	<0.1	8.01	<0.1	<0.1	<0.1	<0.1	<0.1
8:2/16:2 diPAP	n.q.	<0.1	12.5	<0.1	<0.1	7.82	<0.1	<0.1	<0.1	<0.1	<0.1

n.q.: not quantified because of poor recoveries (<10%)

Table S4b (Cont'd)

	Henriksda										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluorinated phosphinates (PFPIAs)											
6:6 PFPIA	<0.1	4.55	0.922	0.640	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:8 PFPIA	<0.1	6.89	0.961	0.678	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:8 PFPIA	<0.1	2.17	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:10 PFPIA	<0.1	2.37	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:10 PFPIA	<0.1	0.957	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:12 PFPIA	<0.1	0.366	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:10 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
12:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
14:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table S5. Individual PFAS concentrations (ng/g) in sewage sludge samples collected from Gässlösa
a) Persistent PFASs

	Gässlösa										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluoroalkyl sulfonates (PFASs)											
PFBS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFPeS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxS	0.397	0.777	0.300	0.280	0.783	0.631	0.341	0.394	0.230	0.346	0.501
PFHpS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
L-PFOS	18.4	21.2	11.1	25.9	16.7	16.8	10.9	9.55	6.21	10.2	11.5
PFNS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFDS	0.274	0.761	<0.1	0.397	1.15	0.657	<0.1	<0.1	<0.1	<0.1	<0.1
PFDoDS	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Perfluorinated carboxylates (PFCAs)											
PFBA	<0.6	<0.1	<0.6	<0.1	<0.1	<0.1	<0.6	n.q.	<0.6	<0.1	<0.1
PFPeA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxA	4.23	4.59	2.88	2.18	6.18	8.20	7.17	3.29	3.89	4.27	3.03
PFHpA	1.64	<0.3	1.34	<0.3	<0.3	<0.3	0.769	0.577	0.499	<0.3	<0.3
PFOA	44.0	35.9	18.4	11.9	34.9	23.7	18.7	12.5	7.01	3.75	2.70
PFNA	14.6	38.8	7.55	8.95	7.12	5.00	1.86	1.32	4.61	1.01	0.897
PFDA	43.7	69.1	33.5	26.7	40.6	40.1	14.0	11.2	11.7	6.21	4.47
PFUnDA	54.7	120	47.6	68.9	53.9	30.9	7.30	4.23	12.2	2.95	2.85

PFDoDA	14.4	21.6	8.07	10.7	5.56	4.78	3.70	3.12	2.70	1.76	1.63
PFTrDA	16.0	40.0	8.62	41.1	15.9	5.14	3.611	<0.3	<0.3	2.16	0.732
PFTDA	n.q.	4.05	1.64	1.59	1.37	1.057	<0.7	<0.7	<0.7	0.598	0.530
PFHxDA	<0.1	n.q.	<0.1	n.q.	n.q.	n.q.	n.q.	<0.1	<0.1	n.q.	n.q.
PFOcDA	<0.1	n.q.	<0.1	n.q.	n.q.	n.q.	n.q.	<0.1	<0.1	n.q.	n.q.
Perfluorinated phosphonates (PFPA)s											
PFHxPA	28.4	83.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFOPA	67.2	86.0	1.3292	<0.1	1.19	2.48	<0.1	<0.1	<0.1	<0.1	<0.1
PFDPa	39.8	43.0	0.4572	<0.1	0.778	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFDoPA	1.16	5.29	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFTePA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFHxDPA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

n.q.: not quantified because of poor recoveries (<10%)

Table S5b PFAS precursors

	2004	2005	2007	2008	2009	Gässlösa					
						2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluoroalkyl sulfonate (PFSA) precursors											
FOSA	2.29	4.10	1.00	0.54	1.50	1.80	0.36	0.00	0.51	1.00	1.40
MeFOSA	n.q.	<0.1	<0.1	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
EtFOSA	n.q.	<0.1	<0.1	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MeFOSE	n.q.	<0.1	23.8	n.q.	n.q.	n.q.	21.7	15.6	12.1	0.259	n.q.
EtFOSE	n.q.	30.0	8.97	n.q.	n.q.	n.q.	9.85	6.46	5.33	<0.1	n.q.
FOSAA	n.q.	8.45	3.55	n.q.	9.84	9.96	2.16	1.92	1.02	n.q.	n.q.
MeFOSAA	59.0	66.6	20.6	13.7	32.0	32.1	10.7	9.85	9.97	2.90	11.7
EtFOSAA	55.0	75.4	26.7	13.9	44.7	47.2	11.7	13.7	14.2	2.82	12.7
SAmPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
diSAmPAP	<0.1	0.879	<0.1	<0.1	0.489	0.948	0.419	<0.1	0.154	<0.1	<0.1

n.q.: not quantified because of poor recoveries (<10%)

Table S5b (cont'd)

	Gässlösa										
	2004	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluorinated carboxylate (PFCA) precursors											
4:2 FTSA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2 FTSA	1.54	0.643	0.754	0.769	1.24	0.974	0.745	1.53	1.11	2.51	1.52
8:2 FTSA	9.63	8.50	3.89	4.11	4.92	3.92	2.43	2.03	3.20	2.10	1.88
5:3 FTCA	7.33	1.88	5.66	0.888	1.39	3.32	109	123	77.6	3.54	5.04
7:3 FTCA	99.8	72.2	66.2	6.05	7.35	12.3	49.5	40.8	19.3	0.723	0.517
6:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
8:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
10:2 FTUCA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
6:2 monoPAP	17.5	n.q.	8.016	n.q.	n.q.	n.q.	0.521	3.06	0.831	n.q.	n.q.
8:2 monoPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
10:2 monoPAP	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
4:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
4:2/6:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2:2/8:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2 diPAP	5.51	9.59	7.08	6.09	8.92	10.4	7.85	3.91	7.24	4.10	7.68
4:2/8:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
2:2/10:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

8:2 diPAP	11.2	16.7	18.8	14.8	24.0	19.2	13.4	8.75	7.65	6.09	7.06
6:2/10:2 diPAP	9.50	14.2	11.7	6.61	14.6	18.7	12.2	6.77	7.56	6.82	8.96
4:2/12:2 diPAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:2/8:2 diPAP	8.57	14.3	7.99	4.31	14.4	15.0	15.8	7.75	11.0	4.59	5.52
4:2/10:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:2/10:2 diPAP	1.25	4.12	n.q.	0.930	10.6	8.10	4.21	2.33	2.12	1.22	1.59
6:2/12:2 diPAP	0.569	1.60	n.q.	n.q.	2.44	3.25	1.68	0.845	1.09	<0.1	<0.1
10:2 diPAP	<0.1	4.53	n.q.	n.q.	14.1	28.7	15.8	5.47	2.97	<0.1	<0.1
8:2/12:2 diPAP	<0.1	5.05	n.q.	2.15	23.5	35.3	21.1	7.00	4.03	<0.1	1.28
6:2/14:2 diPAP	<0.1	2.35	n.q.	0.111	5.39	11.7	6.36	1.84	1.05	<0.1	0.961
10:2/12:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	1.40	<0.1	<0.1	<0.1	<0.1
8:2/14:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	1.06	<0.1	<0.1	<0.1	<0.1
12:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:2/14:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:2/16:2 diPAP	<0.1	<0.1	n.q.	n.q.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

n.q.: not quantified because of poor recoveries (<10%)

Table S5b (cont'd)

	2004	2005	2007	2008	2009	Gässlösa					
						2010	2011	2012	2013	2014	2015
	Conc (ng/g)										
Perfluorinated phosphinates (PFPIAs)											
6:6 PFPIA	164	87.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:8 PFPIA	174	129	<0.1	<0.1	<0.1	0.493	<0.1	<0.1	<0.1	<0.1	<0.1
8:8 PFPIA	100	58.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:10 PFPIA	44.1	49.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:10 PFPIA	31.9	31.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:12 PFPIA	12.7	12.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:10 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
6:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
8:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
12:12 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
14:14 PFPIA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1