



Pilotstudie avseende oidentifierade poly- och perfluorerade alkylämnen i slam och avloppsvatten från reningsverk i Sverige



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| <p>Period in which underlying data were collected 2015-2016</p> | |
| <p>Summary The aim of this investigation are 1) to measure the amount and proportion of unidentified PFASs had been used in daily life by analyzing total organofluorine (TOF) and quantifiable PFASs in influent samples; and 2) to measure the amount and proportion of unidentified PFASs released into the environment by analyzing TOF and quantifiable PFASs in effluent samples and sludge samples from municipal waste water treatment plants. Sewage (influent and effluent) and sludge were collected in 2015 and 2016 from three wastewater treatment plants (Gässlösa (Borås), Henriksdal (Stockholm) and Öhn (Umeå)). Levels of TOF and PFAS in sludge from 2016 and filtered effluent and influent samples from 2015 and 2016 are reported. Different classes of PFASs including PFCAs, PFASs, FTASs, FTCAs, diPAPs, FTUCAs, FOSAs, FOSAAs, PFPAs and PFPiAs were detected in sewage and sludge samples. For influent and effluent samples, all detectable neutral and/or cationic PFASs remained unidentified; for the anionic fraction, 79-94% of the TOF were unidentified. For sludge samples, a significant proportion (42-82%) of total anionic organofluorine remained unidentified.</p> | |

Sammanfattning

Syftet med denna studie var att studera totalhalten av PFASs samt andelen okända, hittills ännu ej identifierade PFAS-ämnen i vatten och slam från svenska reningsverk genom att analysera totalt organiskt fluor (TOF) och kvantifierbara PFAS-ämnen. Studien syftar till att kartlägga omfattningen av kända och okända PFAS-ämnen, både dem som är i omlopp och används i produkter i samhället, och dem som släpps ut i miljön. Avloppsvatten (ingående och utgående) och slam provtogs under 2015 och 2016 vid tre olika reningsverk; Gässlösa (Borås), Henriksdal (Stockholm) och Öhn (Umeå). I denna rapport redovisas halter av TOF och PFAS-ämnen i slam från 2016 och ingående och utgående avloppsvatten från 2015 och 2016. Flera olika PFAS-klasser detekterades i slam och avloppsvatten; PFCAs, PFSAs, FTSAAs, FTCAs, FTUCAs, FOSAs, FOSAAs, diPAPs, PFPAs och PFPiAs. De neutrala och/eller katjoniska PFAS-ämnena i ingående och utgående vatten var ej identifierbara, medan 79-95% av de anjoniska PFAS-ämnena var okända, ej identifierbara ämnen. I slamproverna var en betydande del (42-82%) okända ämnen.

Background

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic compounds that are produced and used in a wide range of products due to their oil- and water repellence properties. A number of PFASs have been recognized to be bioaccumulative, persistent and toxic (DeWitt 2015). Regulations and voluntary phase-out have led to decreased production of some of the most emergent PFAS compounds; perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA).

Declining trends in two widely used fluorosurfactants, PFOS and PFOA, have been reported in human blood. These declining trends might be related to the phase-out of perfluorooctanesulfonyl fluoride (POSF)-based products (3M, 2000), industry participation in PFOA Stewardship Program (USEPA, 2006), and/or regulation under the Stockholm Convention (COP-4, 2009). Up to date, more than 3000 commercial fluorinated replacement products with the same desirable properties are present on the global market (KEMI, 2015). Even though existing analytical methods can measure more than 50 different PFASs (Yeung & Mabury, 2016), it is technically challenging to determine the whole range of thousands of individual PFASs in a sample especially since new products are constantly introduced on the market. In order to understand how much of the known fraction accounts for the total organofluorine (OF), the concept of mass balance is used. Total fluorine (TF) in any sample is equal to the sum of inorganic fluorine (IF) and OF. Levels of quantifiable PFASs representing a fraction of known ionizable OF are measured by LC-MS/MS, whereas total OF (TOF: all non/and ionizable OF) are measured by CIC. Our earlier investigations using this concept demonstrated unidentified PFAS in different matrices (Yeung & Mabury, 2016; Yeung et al., 2008, 2009a,b) and increasing amounts of unidentified PFAS in sediment cores collected from Lake Ontario (Yeung et al., 2013) and in human plasma samples from Germany (Yeung & Mabury, 2016), which suggest that more unidentified PFAS were being used yearly.

Wastewater treatment plants (WWTPs) have been suggested to be one of the major sources of PFAS to the aquatic environment (Filipovic & Berger 2015). Recent studies have shown more unidentified PFAS were being used and released yearly (Yeung et al., 2013; Yeung and Mabury 2016). The information regarding the release of these unidentified PFAS and the mass balance of unidentified PFAS before and after receiving different wastewater treatment processes is lacking.

Aim

The objectives of this investigation are 1) to measure the amount of unidentified PFASs had been used in daily life by analyzing TOF and quantifiable PFASs in influent samples; and 2) to measure the amount of unidentified PFASs released into the environment by analyzing TOF and quantifiable PFASs in effluent samples and sludge samples, as sludge sample may be applied to agricultural field as fertilizer.

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 Prof. Peter Haglund from Umeå University for sample collection. Analysis and data interpretation were performed by Örebro University (Oru)

Following persons have participated in the project:

Oru Anna Kärrman, Associate professor

Oru Leo Yeung, Senior lecturer

Oru Ulrika Eriksson, PhD

Materials and methods

Samples

Sewage (influent and effluent) and sludge samples from three WWTPs (Henriksdal in Stockholm, Gässlösa in Borås, and Öhn in Umeå) were analyzed (Table 1). Sludge samples were collected as composite samples during one day in October 2016 from all three WWTPs. Influent and effluent samples were collected in October 2016; and they were collected as composites of seven consecutive days. Remaining samples (influent and effluent) collected in 2015 from an earlier project were also analyzed in the current investigation. Sludge was freeze dried and all samples were stored in freezer at -18°C until analysis, whereas influent and effluent samples were filtered and stored at 4°C before extraction.

The Henriksdal plant receives municipal wastewater from industries and hospitals. 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. All three WWTPs have mechanical, chemical, biologic, and anaerobic digestion treatment.

Table 1. Description of three WWTPs included in the study

| | Öhn | Gässlösa | Henriksdal |
|--|---------|----------|------------|
| Number of people served | 92 000 | 82 000 | 737 000 |
| Person equivalents | 129 000 | 73 000 | 656 000 |
| Amount sludge produced (t/year) | 2 300 | 2 400 | 14 400 |
| Residence time of sludge (days) | 18 | 25 | 19 |
| Amount influent water (million m ³ /year) | 13 | 13 | 89 |
| Influent – 2016 | √ | √ | √ |
| Effluent – 2016 | √ | √ | √ |
| Sludge – 2016 | √ | √ | √ |
| Influent – 2015 | √ | √ | |
| Effluent – 2015 | √ | √ | |

√ denotes samples were available for analysis.

Extraction and instrumental analyses

Sewage and sludge samples were analyzed for total organofluorine and a suite of 78 and 71 PFASs, respectively (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**, were spiked with mass-labelled standards before extraction to determine the PFAS concentrations in the samples using LC-MS/MS. Another duplicate sample without any spiking mass-labelled standards, the **non-spike sample**, were used for total organofluorine (TOF) analysis using combustion ion chromatography (CIC); mass-labelled standards were spiked to the non-spike sample when determining the PFAS concentrations in the extract using LC-MS/MS. Both spike and non-spike samples were subject to the same extraction procedure.

For the sludge extraction and clean-up, 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). 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; 20 mL 0.01% NH₄OH in water and 30 mL of water were also applied onto the sorbent to remove inorganic fluorine. 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.

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); mass labelled standards were added to the spike samples before extraction with SPE using WAX sorbents, according to ISO/DIS 25101 (ISO, 2009) with some modifications. 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; 20 mL 0.01% NH₄OH in water and 30 mL of water were also applied onto the sorbent to remove inorganic fluorine. 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.

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 was used. Both quantification and qualification product ions were measured in the multiple reaction monitoring, except for 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. The CIC consists of a combustion module (Analytikjena, Germany), an 920 absorbent module and an 930 Compact IC flex (Metrohm, Switzerland). Separation of anions were 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 (0.1 mL) 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 standard were available, the

homologue closest in retention time was used for quantification (SI Table S2). 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. Acceptable recoveries were set to 20-150%. The range of internal standard recoveries of reported concentrations for the water samples were 25-85% for PFCAs, 47-87% for PFSAAs, 30-87% for FTCA/FTUCAs, 46-78% for FTSAs, 21-115% for FOSAAs, 22% for diPAPs, 27-73% for FOSA/FOSEs. For the sludge samples, the recoveries were in the range 20-81% for PFCAs, 31-81% for PFSAAs, 52-79% for FTSAs, 41-93% for FOSAAs, and 36-115% for diPAPs. Duplicate sample analysis was used to assess the precision the method.

TOF. Fluoride signal was observed in combustion blank even when no sample was analyzed. This fluoride contamination was believed to be coming from Teflon tubing in the combustion module. Five times lower fluoride signal was observed after replacement of the Teflon tubings with PEEK tubings. Prior to samples 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 $\mu\text{g/L}$ 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 injection to evaluate the presence of carryover between samples. Detectable organofluorine contamination was found in extraction blank (258 ± 17 and 418 ± 13 pg in neutral and anionic fractions, respectively). 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.

Attempt to measure inorganic fluoride using capillary electrophoresis was also made to ensure no inorganic fluoride present in the sample extract for TOF analysis. Due to the presence of significant amounts of other ions that interfered with the fluoride signal during capillary electrophoresis analysis, identification and quantification of fluoride ion in sample extracts could not be made. Prior to actual sample analysis, removal of inorganic fluoride experiment on SPE was performed. The washing step using 20 mL 0.01% NH_4OH in MilliQ followed by 30 mL of Milli-Q water showed 100% removal of 1000 ng F during SPE.

Mass balance analysis of organofluorine

The measured PFAS concentrations (ng/L or ng/g) in the samples were converted into corresponding fluoride concentration (ng F/L or 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 TOF from all quantifiable PFAS.

Results

PFAS in sludge

Different classes of PFASs including PFCAs, PFSAAs, FTSAAs, FTCAAs, FOSAAs/FOSEs, FOSAAs, diPAPs, PFPAs and PFPiAs were detected in sludge samples; due to poor recoveries of monoPAPs and FTUCAs, they were not quantified in the sludge samples (Table 2) Concentrations of individual compounds are provided in SI Table S3.

Table 2. Concentrations (ng/g d.w.) and composition (%) of PFAS classes (sum of targeted compounds, SI Table S3) in ng/g dry weight (d.w.) in sludge samples.

| WWTP | Öhn | Gässlösa | Henriksdal | Öhn | Gässlösa | Henriksdal |
|---------------------|------------|------------|------------|------|----------|------------|
| | ng/g d.w. | | | % | | |
| ∑PFCA | 5.01 | 10.5 | 10.2 | 3.3 | 5.7 | 3.5 |
| ∑PFSA | 6.76 | 9.40 | 8.90 | 4.4 | 5.1 | 3.0 |
| ∑FTSA | 1.86 | 1.75 | 1.47 | 1.2 | 0.9 | 0.5 |
| ∑FTCA | 5.49 | 17.6 | 130 | 3.6 | 9.5 | 44.5 |
| ∑FTUCA | n.q. | n.q. | n.q. | - | - | - |
| ∑FOSA/FOSE | | 0.881 | | | 0.5 | |
| ∑FOSAA | 11.3 | 18.4 | 17.3 | 7.4 | 9.9 | 5.9 |
| ∑diPAP | 120 | 125 | 121 | 78.9 | 67.2 | 41.5 |
| ∑PFPA | 0.439 | 0.553 | 0.781 | 0.3 | 0.3 | 0.3 |
| ∑PFPiA | 1.34 | 1.71 | 2.09 | 0.9 | 0.9 | 0.7 |
| ∑ ₇ PFAS | 152 | 186 | 292 | | | |

n.q.: not quantified due to poor recoveries (<10%); Blank cell indicates sample below respective LOQ of individual compound; Zero was assigned when sample below LOQ.

PFAS composition in sludge samples collected in 2016

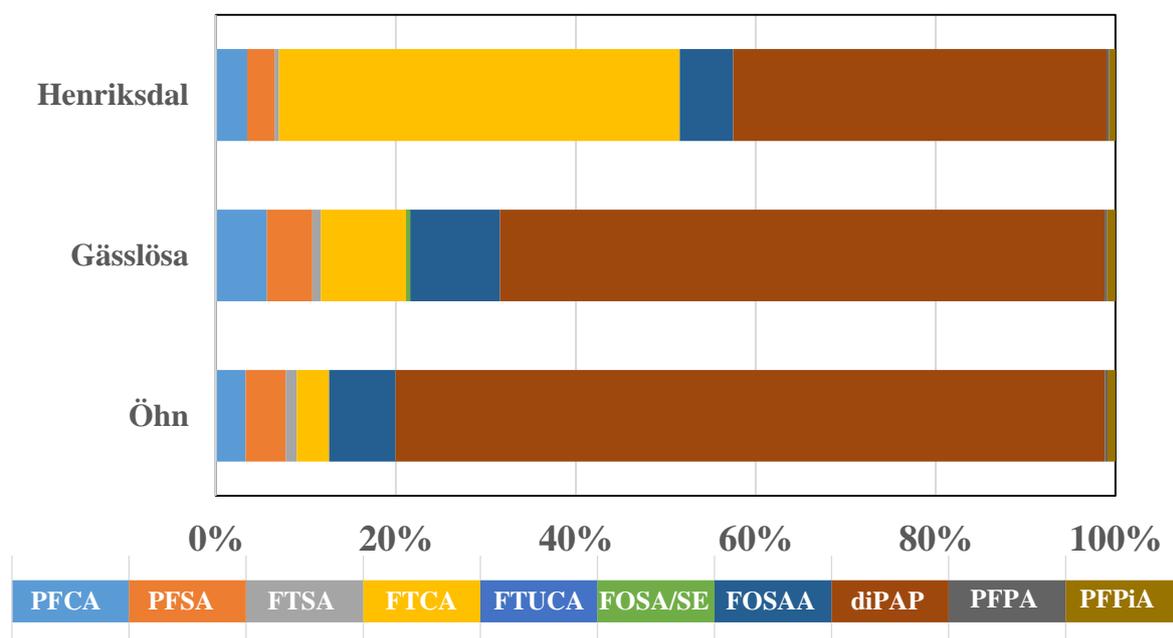


Figure 1. Profiles of PFAS classes in sludge samples from WWTPs.

The total PFAS concentrations in sludge ranged from 152 – 292 ng/g d.w (Table 2, Figure 1). The average composition profiles of PFASs in descending order were diPAPs (approximately 62.5%), FTCAs (19.2%), FOSAAs (7.8%), PFSA (4.2%) and PFCAs (4.1%), FTSA (0.9%), PFPiAs (0.8%) and PFPAs (0.3), and FOSA/FOSE (0.2%). There is no observable differences in PFAS composition among the three WWTPs that PFCA precursor compounds (FTCAs and diPAPs), contributed a major proportion (over 80%) to the total PFASs in the sample. There were some differences in the composition of PFCA precursors between Henriksdal and Öhn and Gässlösa. For samples collected from Öhn and Gässlösa, diPAPs contributed to most of the proportion of PFCA precursors; whereas for samples collected from Henriksdal, FTCAs and diPAPs contributed approximately equal proportion to the PFCA precursor. Up to 14 congeners of diPAPs were detected (SI Table S3bii); 10:2-, 8:2/12:2- and 6:2/14:2-diPAPs were dominant congeners contributing to approximately to 16, 25 and 12% of detectable diPAP congeners. As for FTCA, 5:3 was the dominant congener contributed from 57 to 91% of total FTCA (SI Table S3bii). Another class of PFOS precursor compounds, FOSAA, contributed to approximately 10% to the total PFAS (Table 2). EtFOSAA was the major congener (approximately 55%) in this group, followed by MeFOSAA (24%) and FOSAA (21%)(SI Table S3bi). EtFOSAA is an oxidation product of *N*-ethyl perfluorooctanesulfonamidoethanol (EtFOSE) primarily used as the building block of the phosphate ester (diSAmPAP, also detected in sludge samples) in paper and packaging protectant applications. MeFOSAA is an oxidation product of *N*-methyl perfluorooctanesulfonamidoethanol (MeFOSE) primarily incorporated into polymeric materials as a surface treatment for products like carpets and textiles. FOSAA is a metabolite of either EtFOSAA or MeFOSAA. It is interesting to note the detection of these compounds, because these chemicals had been phase-out since 2000. However, their levels were higher than those of PFOS in the samples collected in 2016. Among PFCAs, long-chain (C8 and higher congeners) accounted for over 80%; PFHxA was the only detectable short-chain compound. PFOS was the dominant PFSA (approximately 62%) followed by PFHxS

(31%)(SI Table S3a). Another class of commercially available PFASs (PFPA and PFPiAs), only C8 PFPA was detected in the samples (SI Table S3a), whereas 6:6-, 6:8- and 8:8 PFPiAs were also detected (SI Table S3biii).

PFAS in filtered influent and effluent samples

For both influent and effluent samples, PFASs were only reported for dissolved phase. Among the PFASs, PFCAs, PFSAs, FTSAs, FTCAs, FTUCAs, FOSA/FOSE, FOSAAs and PFPAs were detected; diPAPs and PFPiAs were only detected in influent samples (Table 3). Concentrations of individual PFASs are provided in SI Table S4.

Levels of total PFASs varied among WWTPs; samples from Gässlösa showed the highest concentrations in both influent and effluent samples, which were 1.6- and 3-fold higher than those of the influent samples collected from Henriksdal and Öhn, respectively; and were 2.5-fold higher than those of effluent samples collected from Öhn and Hendriksdal.

Approximately 65% of the total PFASs were contributed by/consisted of PFCAs, followed by PFSAs (14%); FTSAs accounted for 8.4%, whereas FTCAs and PFPAs contributed to 3.7% and 4.2% to the total, respectively (Figure 2). Precursors of PFOS (FOSAs and FOSAAs) accounted for 2.4% and 1.9%, respectively. FTUCAs were found approximately less than 0.3% to the total in effluent and influent samples. In influent samples, diPAPs and PFPiAs accounted for less than 0.5% of the total.

Persistent PFCAs predominated the PFAS profile in the effluent water (Figure 2); PFCAs ranged from 22.9 – 101 ng/L (Table 3). Short-chain PFCAs accounted for 74% of the total PFCAs, where PFBA and PFHxA were the major components (SI Table S4a). PFOA was the major component of the long-chain PFCA. Relatively high levels of MeFOSAA (1.03 ng/L) and EtFOSAA (1.46 ng/L) were found in sample collected from Öhn when compared to Gässlösa (MeFOSAA: 0.555 ng/L, EtFOSAA: 0.485 ng/L) and Henriksdal (MeFOSAA: 0.107 ng/L, EtFOSAA: 0.318 ng/L). The levels of PFCAs were much higher in Gässlösa compared to those of Öhn and Henriksdal, which suggested considerable contribution from industrial activities (textile and chemical).

The total PFAS levels in influent samples were, in general, lower than those of respective effluent water (Table 3). Both 6:2 and 8:2 FTSAs were detected in all three WWTPs, where 6:2 FTSA (mean: 3.55 ng/L) had higher concentrations than 8:2 FTSA (0.704 ng/L, SI Table S4bii). Different intermediates FTCAs/FTUCAs were detected; 5:3 FTCA (measured up to 5.05 ng/L) showed relatively higher concentrations than other FTCAs/FTUCAs (e.g., 0.160 ng/L for 6:2 FTUCA). Detection of these intermediates and the increased levels of PFCAs suggest that degradation of fluorotelomer-based compounds (e.g., diPAPs and FTSAs) took place during wastewater treatment.

It is interesting to note that levels of FTSAs increased after wastewater treatment in Öhn suggesting degradation of FTSA precursor compounds during the wastewater treatment process; one of the potential sources of FTSA precursors is FTSA-based fire fighting foam (Weiner et al., 2013).

Table 3. Concentrations (ng/L) and composition (%) of detected PFAS in wastewater.

| WWTP | Öhn | Öhn | Henriksdal | Öhn | Gässlösa | Henriksdal | Öhn | Gässlösa | Henriksdal |
|----------------------|---------------|-------------|-------------|-------------|-------------|-------------|-------------|------------|-------------|
| | Effluent | Influent | Influent | Influent | Influent | Influent | Effluent | Effluent | Effluent |
| | 2015 | 2015 | 2015 | 2016 | 2016 | 2016 | 2016 | 2016 | 2016 |
| | Conc. ng/L | | | | | | | | |
| ∑PFCA | 22.9 | 25.4 | 35.2 | 16.1 | 57.1 | 26.0 | 29.2 | 101 | 32.6 |
| ∑PFSA | 4.37 | 2.14 | 7.38 | 3.47 | 10.9 | 7.45 | 9.25 | 17.4 | 11.1 |
| ∑FTSA | 2.44 | 2.16 | 7.29 | 0.969 | 3.29 | 9.91 | 4.29 | 2.92 | 6.18 |
| ∑FTCA | 0.808 | | 6.76 | 1.07 | 5.73 | 1.18 | 2.64 | 1.91 | |
| ∑FTUCA | | | | | 0.160 | | | 0.090 | |
| ∑FOSA/FOSE | 1.31 | | 3.19 | 3.52 | | | | | |
| ∑FOSAA | | 0.512 | | 0.972 | 0.466 | 2.59 | 2.49 | 1.04 | 0.425 |
| ∑diPAP | | | | | 1.35 | | | | |
| ∑PFPA | | 2.44 | 4.16 | 1.27 | 3.01 | 3.97 | 1.42 | 3.01 | 1.20 |
| ∑PFPIA | | 0.455 | | | | | | | |
| ∑ ₇₈ PFAS | 31.8 | 33.1 | 63.9 | 27.4 | 82.0 | 51.1 | 49.3 | 127 | 51.5 |
| | Composition % | | | | | | | | |
| ∑PFCA | 72.0 | 76.7 | 55.0 | 58.8 | 69.6 | 50.9 | 59.2 | 79.2 | 63.3 |
| ∑PFSA | 13.7 | 6.5 | 11.5 | 12.7 | 13.3 | 14.6 | 18.8 | 13.7 | 21.6 |
| ∑FTSA | 7.7 | 6.5 | 11.4 | 3.5 | 4.0 | 19.4 | 8.7 | 2.3 | 12.0 |
| ∑FTCA | 2.5 | | 10.6 | 3.9 | 7.0 | 2.3 | 5.4 | 1.5 | |
| ∑FTUCA | | | | | 0.2 | | | 0.1 | |
| ∑FOSA/FOSE | 4.1 | | 5.0 | 12.9 | | | | | |
| ∑FOSAA | | 1.5 | | 3.6 | 0.6 | 5.1 | 5.1 | 0.8 | 0.8 |
| ∑diPAP | | | | | 1.6 | 0.0 | | | |
| ∑PFPA | | 7.4 | 6.5 | 4.6 | 3.7 | 7.8 | 2.9 | 2.4 | 2.3 |
| ∑PFPIA | | 1.4 | | | | | | | |

Blank cell indicates sample below respective LOQ of individual compound; Zero assigned when samples below LOD.

PFAS composition in influent and effluent samples collected in 2015 and 2016

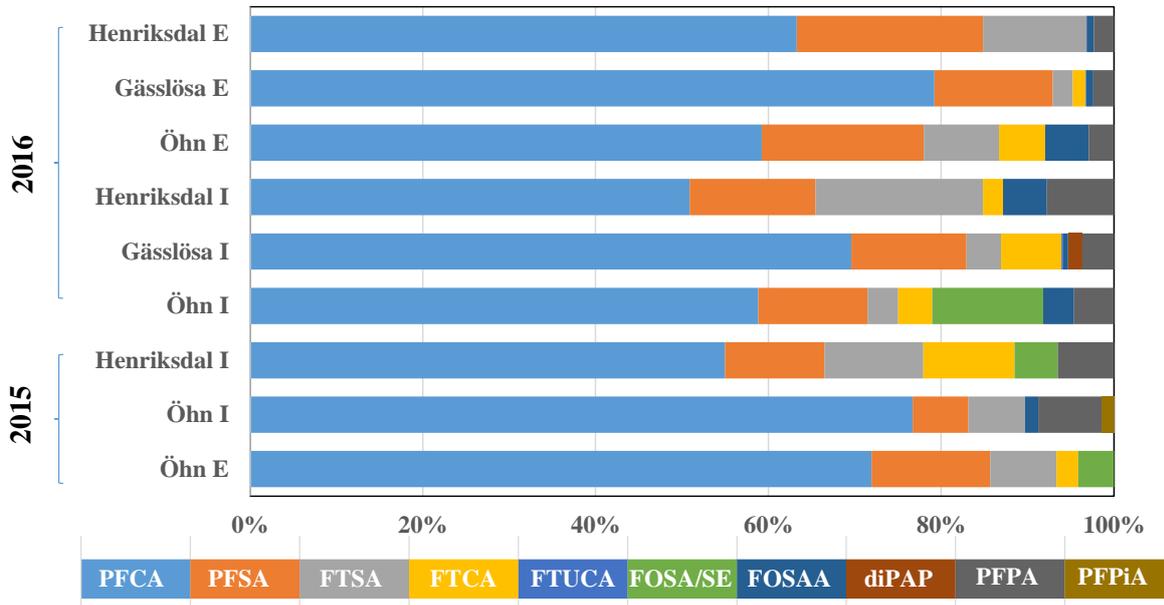


Figure 2. Profiles of PFAS classes in dissolved phase of influent (I) and effluent (E) samples from WWTPs.

Total organofluorine (TOF) in sewage (influent and effluent) and sludge samples

For sewage samples, TOF were measured for both neutral and anionic fractions. However, for sludge samples, TOF were only reported for anionic fraction due to an interfering peak co-eluted with fluorine that confounded the results. Levels of TOF of sewage and sludge samples are provided in Table 4.

Table 4. Concentrations of total organofluorine (ng F/L), identified organofluorine (ng F/L), ratio of unidentified organofluorine (%) a) in influent (I) and effluent (E) samples collected in 2015-2016 and b) in sludge samples collected in 2016.

| a) | Öhn | | Henriksdal | Öhn | | Gässlösa | | Henriksdal | |
|-------------------------------------|------------|-----------------|-------------------|------------|------------|------------|-------------------|------------|------------|
| | I | E | I | I | E | I | E | I | E |
| | 2015 | 2015 | 2015 | 2016 | 2016 | 2016 | 2016 | 2016 | 2016 |
| Neutral | | | | | | | | | |
| Extractable organofluorine (ng F/L) | 175 | 129 | <50 | 107 | 348 | 220 | 345 | 118 | 526 |
| Identified organofluorine (ng F/L) | <2 | <2 ^a | <2 | <2 | <2 | <2 | <2 | <2 | <2 |
| Unidentified organic fluorine (%) | 100 | 100 | N.A. ^b | 100 | 100 | 100 | 100 | 100 | 100 |
| Anionic | | | | | | | | | |
| Extractable organofluorine (ng F/L) | 81.5 | 169 | <50 | 161 | 136 | 253 | <50 | 98.2 | 293 |
| Identified organofluorine (ng F/L) | 16.5 | 21.1 | 17.2 | 11.1 | 19.9 | 35.6 | 45.7 | 20.6 | 17.4 |
| Unidentified organic fluorine (%) | 80 | 88 | N.A. ^c | 93 | 85 | 86 | N.A. ^c | 79 | 94 |
| Total | | | | | | | | | |
| Total organofluorine (ng F/L) | 257 | 299 | <50 | 268 | 484 | 473 | 345 | 217 | 819 |
| Identified organofluorine (ng F/L) | 16.5 | 21.1 | 17.2 | 11.1 | 19.9 | 35.6 | 45.7 | 20.6 | 17.4 |
| Unidentified organofluorine (%) | 94 | 93 | N.A. ^b | 96 | 96 | 93 | 87 | 91 | 98 |

^aSum of LOD of 5 neutral compounds (FOSA, MeFOSA, EtFOSA, MeSE, EtFOSE); ^bN.A.: not applicable due to both extractable organofluorine and identified organofluorine were both below respective detection limit; ^cN.A.: not applicable due to extractable organofluorine was below detection limit

| b) | Öhn | Gässlösa | Henriksdal |
|------------------------------------|-------------------|----------|------------|
| | 2016 | 2016 | 2016 |
| Total organofluorine (ng F/g) | <50 | 55.7 | 154 |
| Identified organofluorine (ng F/g) | 21.2 | 32.2 | 28.4 |
| Unidentified organofluorine (%) | N.A. ^a | 42 | 82 |

^aN.A.: not applicable due to extractable organofluorine was below detection limit

For sewage samples, 4 out of 5 influent samples showed detectable TOF levels (217 – 819 ng F/L); influent sample from Henriksdal collected from 2015 showed TOF level below 50 ng F/L (limit of detection of CIC). All effluent samples showed detectable TOF levels (299 – 819 ng F/L) (Table 4a, Figure 3).

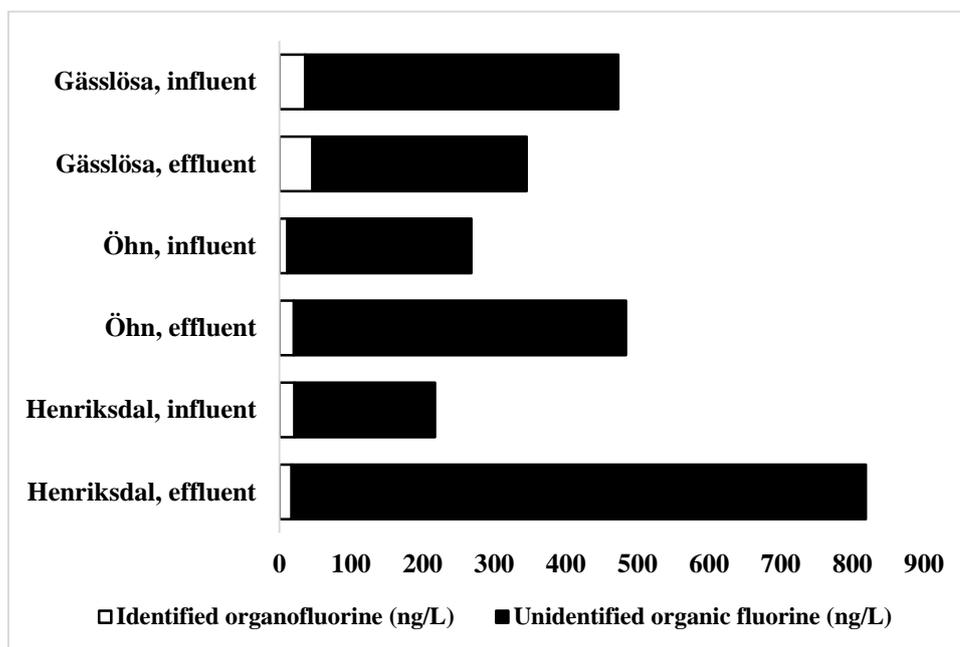


Figure 3. Identified organofluorine and unidentified organofluorine in effluent and influent water from wastewater treatment plants in Gässlösa, Öhn, and Henriksdal sampled in 2016.

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. It is interesting and important to note that regardless effluent or influent samples all detectable TOF in the neutral fraction remained unidentified. As for the anionic fraction, the known PFAS only accounted for approximately 5 – 21% of the total (Table 4a); no observable difference in percentage of identified vs unidentified was noted between influent and effluent samples. These results suggest the presence of a large proportion of PFAS that remain unknown. The neutral fraction may contain neutral compounds (e.g., FOSA, EtFOSA); however, they were not detected in the samples. Different classes of precursor compounds of PFSA and PFCAs proposed in other studies (Lee et al., 2010; Rhoads et al., 2008) were detected in the present investigation and known intermediates (FTCAs and FTUCAs) were also monitored in the current investigation. However, there were/might also be some other intermediates or unidentified intermediates that were not measured, which contributed to the unidentified fraction. Other newly identified neutral compound that were not monitored in the current study, for example 6:2 fluorotelomer sulfonamide alkylamide, perfluorohexane sulfonamide or 6:2 fluorotelomer sulfonamide may account for the unknown proportion (D'Agostino and Mabury, 2017). Some cationic fluorinated analytes may be present in this neutral fraction as well (D'Agostino and Mabury, 2014). Results from influent and effluent indicated that large proportions of unidentified PFASs are in use and released into the environment.

As for sludge samples, Gässlösa and Henriksdal showed detectable TOF levels of 55.7 and 154 ng F/g d.w., respectively in the anionic fraction; sample from Öhn showed below 50 ng F/g d.w (limit of detection of CIC) (Table 4b). The known PFAS in sludge samples accounted for approximately 18% and 58% of the total for Henriksdal and Gässlösa, respectively (Table 4b). These results showed a contrast in percentage of anionic unidentified PFASs between sewage (79-94%) and sludge (42-82%) samples (Table 4, Figure 4). Since interfering peak co-elute with fluoride ion in the neutral fraction that no TOF were reported at this stage, further cleanup step is needed before CIC analysis to confirm how much organofluorine present in the neutral fraction of sludge samples.

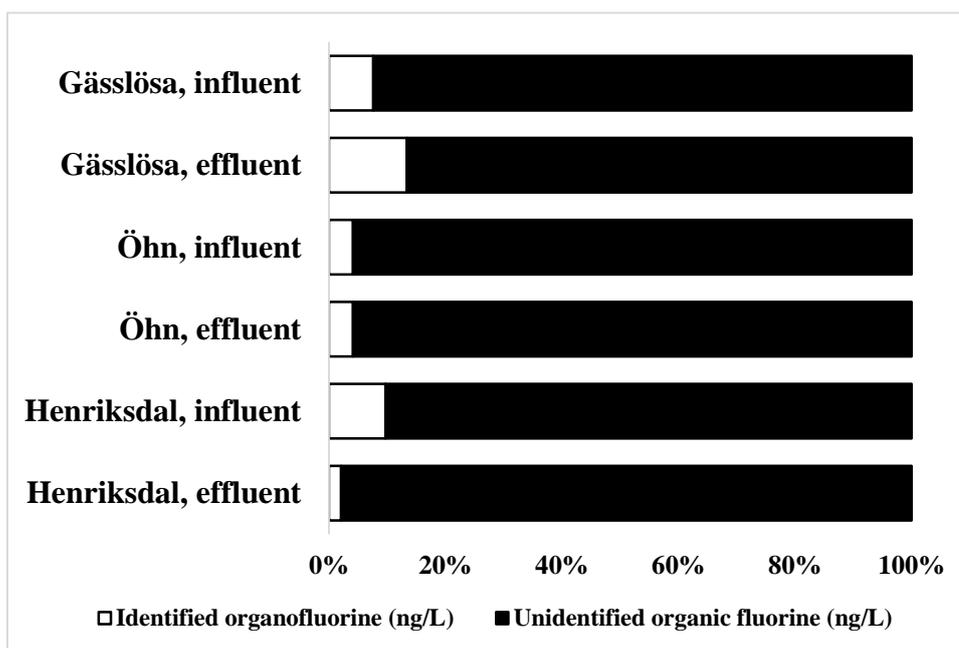


Figure 4. Identified organofluorine (%) and unidentified organofluorine (%) in effluent and influent water from wastewater treatment plants in Gässlösa, Öhn, and Henriksdal sampled in 2016.

Summary

Sludge

- DiPAPs, one group of the PFCA precursor compounds, contributed a major proportion (63%) to the total targeted/analyzed PFASs in the sludge samples.
- Sludge seemed to be a sink of diPAPs during the waste water treatment process.
- PFOS precursor compounds, EtFOSAA, MeFOSAA and FOSAA, contributed to approximately 10% to the total targeted/analyzed PFAS, and their levels were higher than those of PFOS.
- A significant proportion (42-82%) of total anionic organofluorine remained unidentified.

Influent and effluent

- PFCAs, PFSAs, FTSAAs, FTCAAs, FTUCAs, FOSA/FOSE, FOSAAs and PFPAs were detected; diPAPs and PFPiAs were only detected in influent samples.
- Approximately 65% of the total targeted PFASs consisted of PFCAs; the remaining composition were from PFSAs (14%), FTSAAs (8.4%), FTCAAs (3.7%), FOSA/FOSE (2.4%), PFPAs (2.3%), FOSAAs (0.8%), diPAPs (0.2%) and PFPiAs (0.2%).

- Short-chain PFCAs accounted for 74% of the total targeted PFCAs; PFBA and PFHxA were the major components. PFOA was the major component of the long-chain PFCA.
- All detectable neutral and/or cationic PFASs in the analysis of total organofluorine remained unidentified.
- For the anionic fraction, the known targeted PFAS only accounted for approximately 5 – 21% of the total organofluorine.
- A significant large proportion (79-94%) of unidentified PFASs were being/are used and released into the environment.

Recommendations

Sludge was shown to be an important sink for diPAPs and FOSAAs. Since diPAPs and FOSAAs have been shown to undergo microbial biodegradation producing PFCAs of different chain lengths and PFOS, respectively, it is not recommended to apply sludge to agricultural farmland as fertilizer. 6:2 FTSA has been shown to be one of the degradation products of 6:2 fluorotelomer sulfonamide-based product associated with fire fighting foam. Detection of 6:2 FTSA may suggest the presence of other 6:2 fluorotelomer sulfonamide-based chemicals that were not measured, and they might be part of the unidentified PFAS in the sample. Analysis on archived sludge samples may give temporal trends on diPAP and organofluorine contamination in Sweden.

Significant proportion of total organofluorine in sewage samples remained unidentified. Further study should also investigate the TOF in the recipient water from wastewater treatment plants to assess how much unidentified organofluorine in the environment. Detection of precursors of PFCAs and PFSAAs suggested the presence of a number of some other intermediates or unidentified intermediates, which might also contributed to the unidentified proportion. Further study on mass balance of transformation/degradation of PFSA/PFCA precursors may give an insight on how much unidentified organofluorine produced during these processes. Besides, identification of these unidentified PFASs and toxicity testing on these unidentified PFASs are warranted. Measurements of some newly identified PFAS alternatives (D'Agostino and Mabury, 2017) such as 6:2 FTAA, 6:2 FTAB, 6:2 FTSam or ultrashort-chain PFASs are needed. Total oxidizable precursor (TOP) assay on PFAS is also recommended to evaluate how much PFCA precursors contributed to the unidentified proportion (Houtz and Sedlak, 2012).

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Supplemental Information

Table S1. Compound classes and compounds analyzed in the study

a) Persistent PFAS

| 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 | | PFDPa |
| | PFTePA | Perfluorotetradecyl phosphonic acid | | PFDPa |
| | PFHxDPA | Perfluorohexadecyl phosphonic acid | | PFDPa |

b) PFAS precursors

i) Perfluoroalkyl sulfonate (PFSA) precursors

| Class | Acronym | Name | Quantified with analytical standard | Quantified with surrogate compound |
|--------------|-----------------|--|--|---|
| | 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 | |

ii) Perfluorinated carboxylate (PFCA) precursors

| Class | Acronym | Name | Quantified with analytical standard | Quantified with surrogate compound |
|-------|------------------------|--|-------------------------------------|------------------------------------|
| | 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 | |
| <hr/> | | | | |
| | 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 acid | x | |
| | 8:2 FTUCA | 8:2 Fluorotelomer unsaturated carboxylic acid | x | |
| | 10:2 FTUCA | 10:2 Fluorotelomer unsaturated carboxylic acid | x | |
| <hr/> | | | | |
| | 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 | |
| <hr/> | | | | |
| | 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 |

iii) Perfluorinated phosphinates (PFPIAs)

| Class | Acronym | Name | Quantified with analytical standard | Quantified with surrogate compound |
|--------------|----------------|---|--|---|
| 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 PFAS

| 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 |
| PFT _r DA | 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 |

b) PFAS precursors

i) Perfluoroalkyl sulfonate (PFSA) precursors

| Analyte | Precursor/ product ions quantification (m/z) | Cone (V) | Col (eV) | Precursor/ product ions qualification (m/z) | Cone (V) | Col (eV) | Internal standard |
|-----------------|---|-------------|-------------|--|-------------|-------------|---------------------------|
| 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 |

ii) Perfluorinated carboxylate (PFCA) 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 |
|-------|-----------------|---|-------------|-------------|--|-------------|-------------|-----------------------------|
| | 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 |

iii) Perfluorinated phosphinates (PFPIAs)

| Class | Analyte | Precursor/ product ions quantification (m/z) | Cone (V) | Col (eV) | Precursor/ product ions qualification (m/z) | Cone (V) | Col (eV) | Internal standard |
|-------|--------------------|---|-------------|-------------|--|-------------|-------------|------------------------|
| | 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. Concentrations in sludge samples from wastewater treatment plants (WWTPs) collected in 2016 (ng/g, d.w.).

a) Persistent PFAS

| WWTPs | Öhn | Gässlösa | Henriksdal |
|--|-------------------|----------|------------|
| Conc (ng/g, d.w.) | | | |
| Perfluoroalkyl sulfonates (PFASs) | | | |
| PFBS | <0.03 | <0.03 | <0.03 |
| PFPeS | <0.02 | <0.02 | <0.02 |
| PFH _x S | 3.32 | 2.45 | 1.63 |
| PFHpS | <0.02 | <0.02 | <0.02 |
| L-PFOS | 2.76 | 6.37 | 6.95 |
| PFNS | <0.02 | <0.02 | <0.02 |
| PFDS | 0.680 | 0.580 | 0.320 |
| PFDoDS | <0.02 | <0.02 | <0.02 |
| Perfluorinated carboxylates (PFCAs) | | | |
| PFBA | <4.09 | <4.09 | <4.09 |
| PFPeA | <0.18 | <0.18 | <0.18 |
| PFH _x A | 0.902 | 1.41 | 2.35 |
| PFHpA | <0.38 | <0.38 | <0.38 |
| PFOA | 0.940 | 1.27 | 1.84 |
| PFNA | 0.190 | 0.490 | 0.520 |
| PFDA | 0.880 | 2.59 | 2.46 |
| PFUnDA | 0.540 | 1.39 | 1.22 |
| PFDoDA | 0.908 | 2.19 | 1.02 |
| PFT _r DA | 0.204 | 0.445 | 0.362 |
| PFTDA | 0.450 | 0.730 | 0.380 |
| PFH _x DA | n.q. ^a | n.q. | n.q. |
| PFOcDA | n.q. | n.q. | n.q. |
| Perfluorinated phosphonates (PFPA)s | | | |
| PFH _x PA | n.q. | n.q. | n.q. |
| PFOPA | 0.439 | 0.53 | 0.781 |
| PFDPA | <0.3 | <0.3 | <0.3 |
| PFDoPA | <0.02 | <0.02 | <0.02 |
| PFTePA | <0.02 | <0.02 | <0.02 |
| PFH _x DPA | <0.02 | <0.02 | <0.02 |

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

b) PFAS precursors**i) Perfluoroalkyl sulfonate (PFSA) precursors**

| | Öhn | Gässlösa | Henriksdal |
|---|-------------------|-----------------|-------------------|
| | Conc (ng/g, d.w.) | | |
| Perfluoroalkyl sulfonate (PFSA) precursors | | | |
| FOSA | n.q. ^a | 0.881 | n.q. |
| MeFOSA | n.q. | n.q. | n.q. |
| EtFOSA | n.q. | n.q. | n.q. |
| MeFOSE | n.q. | <0.4 | n.q. |
| EtFOSE | n.q. | <0.2 | n.q. |
| FOSAA | 2.18 | 4.23 | 3.61 |
| MeFOSAA | 1.70 | 4.18 | 5.82 |
| EtFOSAA | 7.37 | 10.0 | 7.90 |
| SAmPAP | n.q. | n.q. | n.q. |
| diSAmPAP | 0.195 | 0.202 | 0.147 |

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

ii) Perfluorinated carboxylate (PFCA) precursors

| | Öhn | Gässlösa | Henriksdal |
|------------------------|-------------------|----------|------------|
| | Conc (ng/g, d.w.) | | |
| 4:2 FTSA | <0.02 | <0.02 | <0.02 |
| 6:2 FTSA | <0.02 | <0.02 | <0.02 |
| 8:2 FTSA | 1.86 | 1.75 | 1.47 |
| 5:3 FTCA | 3.12 | 11.5 | 119 |
| 7:3 FTCA | 2.37 | 6.13 | 11.2 |
| 6:2 FTUCA | n.q. ^a | n.q. | n.q. |
| 8:2 FTUCA | n.q. | n.q. | n.q. |
| 10:2 FTUCA | n.q. | n.q. | n.q. |
| 6:2 monoPAP | n.q. | n.q. | n.q. |
| 8:2 monoPAP | n.q. | n.q. | n.q. |
| 10:2 monoPAP | n.q. | n.q. | n.q. |
| 4:2 diPAP | <1.91 | <1.91 | <1.91 |
| 4:2/6:2 diPAP | <0.02 | <0.02 | <0.02 |
| 2:2/8:2 diPAP | <0.02 | <0.02 | <0.02 |
| 6:2 diPAP | 6.59 | 8.96 | 8.30 |
| 4:2/8:2 diPAP | <0.02 | <0.02 | <0.02 |
| 2:2/10:2 diPAP | <0.02 | <0.02 | <0.02 |
| 8:2 diPAP | 4.40 | 4.39 | 4.96 |
| 6:2/10:2 diPAP | 7.31 | 6.38 | 8.33 |
| 4:2/12:2 diPAP | <0.02 | <0.02 | <0.02 |
| 6:2/8:2 diPAP | 4.95 | 4.89 | 7.71 |
| 4:2/10:2 diPAP | <0.02 | <0.02 | <0.02 |
| 8:2/10:2 diPAP | 3.64 | 3.58 | 3.76 |
| 6:2/12:2 diPAP | 3.24 | 3.18 | 3.29 |
| 10:2 diPAP | 18.7 | 20.4 | 17.8 |
| 8:2/12:2 diPAP | 29.4 | 30.0 | 31.2 |
| 6:2/14:2 diPAP | 15.3 | 14.4 | 15.2 |
| 10:2/12:2 diPAP | 9.98 | 11.1 | 8.94 |
| 8:2/14:2 diPAP | 10.7 | 12.5 | 8.81 |
| 12:2 diPAP | 1.18 | 1.32 | 0.76 |
| 10:2/14:2 diPAP | 2.71 | 2.26 | 1.36 |
| 8:2/16:2 diPAP | 1.87 | 1.55 | 0.998 |

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

iii) Perfluorinated phosphinates (PFPIAs)

| | Öhn | Gässlösa | Henriksdal |
|---|-------------------|-----------------|-------------------|
| | Conc (ng/g, d.w.) | | |
| Perfluorinated phosphinates (PFPIAs) | | | |
| 6:6 PFPIA | 0.634 | 0.758 | 0.773 |
| 6:8 PFPIA | 0.708 | 0.953 | 1.32 |
| 8:8 PFPIA | <0.02 | <0.02 | <0.02 |
| 6:10 PFPIA | <0.02 | <0.02 | <0.02 |
| 8:10 PFPIA | <0.02 | <0.02 | <0.02 |
| 6:12 PFPIA | <0.02 | <0.02 | <0.02 |
| 10:10 PFPIA | <0.02 | <0.02 | <0.02 |
| 8:12 PFPIA | <0.02 | <0.02 | <0.02 |
| 6:14 PFPIA | <0.02 | <0.02 | <0.02 |
| 10:12 PFPIA | <0.02 | <0.02 | <0.02 |
| 8:14 PFPIA | <0.02 | <0.02 | <0.02 |
| 12:12 PFPIA | <0.02 | <0.02 | <0.02 |
| 10:14 PFPIA | <0.02 | <0.02 | <0.02 |
| 14:14 PFPIA | <0.02 | <0.02 | <0.02 |

Table S4. Concentrations in effluent (E) and influent (I) water from wastewater treatment plants in Öhn, Gässlösa and Henriksdal 2015 - 2016 (ng/L).

a) Persistent PFAS

| | Öhn | | Henriksdal | Öhn | | Gässlösa | | Henriksdal | | |
|--|-------------------|-------|------------|-------|-------|----------|-------|------------|-------|--|
| | E | I | E | I | E | I | E | I | E | |
| | 2015 | 2015 | 2015 | 2016 | 2016 | 2016 | 2016 | 2016 | 2016 | |
| Conc (ng/L) | | | | | | | | | | |
| Perfluoroalkyl sulfonates (PFSAs) | | | | | | | | | | |
| PFBS | 0.803 | 0.668 | 4.22 | 0.498 | 1.12 | 1.82 | 2.76 | 1.91 | 2.77 | |
| PFPeS | 0.217 | 0.209 | 0.517 | 0.171 | 0.209 | 1.34 | 1.65 | 0.320 | 0.324 | |
| PFHxS | 2.54 | 1.16 | 2.41 | 0.927 | 1.63 | 4.66 | 5.10 | 1.65 | 2.18 | |
| PFHpS | 0.811 | 0.098 | 0.23 | 0.083 | 0.260 | 0.178 | 0.337 | <0.01 | 0.204 | |
| L-PFOS | n.r. ^a | n.r. | n.r. | 1.79 | 6.03 | 2.94 | 7.54 | 3.57 | 5.62 | |
| PFNS | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | |
| PFDS | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| PFDoDS | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| Perfluorinated carboxylates (PFCAs) | | | | | | | | | | |
| PFBA | 11.7 | 8.37 | 14.3 | 2.02 | 4.92 | n.q. | n.q. | <0.63 | 7.17 | |
| PFPeA | 1.86 | 2.94 | 4.42 | 1.32 | 2.65 | 11.6 | 21.0 | 5.06 | 5.15 | |
| PFHxA | 5.17 | 7.69 | 7.81 | 5.36 | 8.15 | 16.6 | 33.3 | 9.56 | 7.64 | |
| PFHpA | 1.63 | 1.77 | 3.53 | 1.16 | 1.93 | 10.2 | 16.6 | 2.57 | 3.84 | |
| PFOA | 2.57 | 3.71 | 4.84 | 4.82 | 7.1 | 17.2 | 25.9 | 6.48 | 6.03 | |
| PFNA | <0.1 | 0.578 | 0.261 | 0.610 | 1.81 | 0.970 | 1.94 | 1.18 | 1.45 | |
| PFDA | <0.12 | 0.315 | <0.12 | 0.690 | 2.26 | 0.520 | 1.63 | 1.16 | 1.16 | |
| PFUnDA | <0.06 | <0.06 | <0.06 | 0.12 | 0.36 | <0.06 | 0.27 | <0.06 | 0.14 | |
| PFDoDA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| PFTTrDA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| PFTDA | n.q. ^b | n.q. | n.q. | <0.01 | n.q. | n.q. | n.q. | n.q. | n.q. | |
| PFHxDA | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | |
| PFOcDA | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | |
| Perfluorinated phosphonates (PFPA)s | | | | | | | | | | |
| PFHxPA | <0.1 | 1.85 | 2.69 | 0.905 | 1.14 | 1.37 | 1.57 | n.q. | 0.928 | |
| PFOPA | <0.1 | 0.588 | 1.47 | 0.361 | 0.282 | 1.64 | 1.44 | n.q. | 0.270 | |
| PFDPA | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | n.q. | <0.1 | |
| PFDoPA | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 3.24 | <0.1 | |
| PFTePA | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.731 | <0.1 | |
| PFHxDPA | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | |

^an.r.: not reported due to contamination was found in extraction blanks; these values were not reported from the present investigation; however, these samples have been analyzed and reported to be 1.54ng/L, 1.66ng/L, and <0.70ng/L for effluent and influent from Öhn and effluent, Henriksdal, respectively in another study by Eriksson U., Haglund P., Kärrman A. Screening av PFAS i slam och vatten från avloppsreningsverk

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

b) PFAS precursors

i) Perfluoroalkyl sulfonate (PFSA) precursors

| | Öhn | | Henriksdal | | Öhn | | Gässlösa | | Henriksdal | |
|-----------------|-------------|-------------------|------------|-----------|-----------|-----------|-----------|-----------|------------|-------|
| | E 2015 | I 2015 | E 2015 | I 2016 | E 2016 | I 2016 | E 2016 | I 2016 | E 2016 | |
| | Conc (ng/L) | | | | | | | | | |
| FOSA | 1.31 | <0.38 | 3.19 | 3.52 | <0.38 | <0.38 | <0.38 | <0.38 | <0.38 | <0.38 |
| MeFOSA | <0.01 | n.q. ^a | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | n.q. |
| EtFOSA | <0.01 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | n.q. |
| MeFOSE | <0.01 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| EtFOSE | <0.01 | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| FOSAA | <0.01 | 0.104 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| MeFOSAA | <0.01 | 0.226 | <0.01 | 0.371 | 1.03 | 0.155 | 0.555 | 0.660 | 0.660 | 0.107 |
| EtFOSAA | <0.01 | 0.182 | <0.01 | 0.601 | 1.46 | 0.311 | 0.485 | 1.93 | 1.93 | 0.318 |
| SAmPAP | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. |
| diSAmPAP | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |

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

ii) Perfluorinated carboxylate (PFCA) precursors

| | Öhn | | Henriksdal | | Öhn | | Gässlösa | | Henriksdal | |
|--------------------|-------------|-------------------|------------|-----------|-----------|-----------|-----------|-----------|------------|-----------|
| | E 2015 | I 2015 | E 2015 | I 2016 | E 2016 | I 2016 | E 2016 | I 2016 | E 2016 | I 2016 |
| | Conc (ng/L) | | | | | | | | | |
| 4:2 FTSA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 6:2 FTSA | 2.44 | 2.09 | 7.29 | 0.969 | 3.79 | 1.79 | 2.75 | 9.37 | 5.71 | |
| 8:2 FTSA | <0.02 | 0.070 | <0.02 | <0.02 | 0.491 | 1.50 | 0.168 | 0.540 | 0.472 | |
| 5:3 FTCA | 0.808 | <0.01 | 6.76 | 0.984 | 2.54 | 5.05 | 1.91 | 1.18 | <0.01 | |
| 7:3 FTCA | <0.01 | <0.01 | <0.01 | 0.090 | 0.104 | 0.676 | <0.01 | <0.01 | <0.01 | |
| 6:2 FTUCA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.16 | 0.064 | <0.01 | <0.01 | |
| 8:2 FTUCA | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | |
| 10:2 FTUCA | <0.01 | n.q. ^a | <0.01 | <0.01 | <0.01 | <0.01 | 0.026 | <0.01 | <0.01 | |
| 6:2 monoPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.24 | <0.24 | 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. | |
| 10:2 monoPAP | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | n.q. | |
| 4:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 4:2/6:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 2:2/8:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 6:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | 0.277 | <0.03 | n.q. | n.q. | |
| 4:2/8:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 2:2/10:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 8:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | 0.412 | <0.01 | n.q. | n.q. | |
| 6:2/10:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | 0.501 | <0.01 | n.q. | n.q. | |
| 4:2/12:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 6:2/8:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | 0.156 | <0.02 | n.q. | n.q. | |
| 4:2/10:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 8:2/10:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 6:2/12:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 10:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 8:2/12:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.02 | <0.02 | n.q. | n.q. | |
| 6:2/14:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 10:2/12:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 8:2/14:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 12:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 10:2/14:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |
| 8:2/16:2 diPAP | n.q. | n.q. | n.q. | n.q. | n.q. | <0.01 | <0.01 | n.q. | n.q. | |

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

iii) Perfluorinated phosphinates (PFPiAs)

| | Öhn | | Henriksdal | | Öhn | | Gässlösa | | Henriksdal | |
|--------------------|-------------|-----------|------------|-----------|-----------|-----------|-----------|-----------|------------|-------|
| | E 2015 | I 2015 | E 2015 | I 2016 | E 2016 | I 2016 | E 2016 | I 2016 | E 2016 | |
| | Conc (ng/L) | | | | | | | | | |
| 6:6 PFPiA | <0.08 | 0.455 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 6:8 PFPiA | <0.08 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 8:8 PFPiA | <0.06 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 6:10 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 8:10 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 6:12 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 10:10 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 8:12 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 6:14 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 10:12 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 8:14 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 12:12 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 10:14 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| 14:14 PFPiA | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |