



A Pilot Study of the Fluorinated Ingredient of Scotchgard Products and Their Levels in WWTP Sludge and Landfill Leachate from Sweden

Pilotstudie av Fluorerade Ingredienser i
Scotchgardprodukter och Deras Halter i
Avloppsslam från Reningsverk och Lakvatten från
Deponier i Sverige

A Pilot Study of the Fluorinated Ingredient of Scotchgard Products and Their Levels in WWTP Sludge and Landfill Leachate from Sweden

Pilotstudie av Fluorerade Ingredienser i Scotchgardprodukter och Deras Halter i Avloppsslam från Reningsverk och Lakvatten från Deponier i Sverige

<p>Report authors</p> <p>Felicia Fredriksson, Örebro University Ulrika Eriksson, Örebro University Anna Kärrman, Örebro University Leo Yeung, Örebro University</p>	<p>Responsible publisher</p> <p>Örebro University</p> <p>Postal address</p> <p>School of Science and Technology Örebro University SE-701 82 Örebro, Sweden</p> <p>Telephone</p> <p>019-30 1421</p>
<p>Report title and subtitle</p> <p>A Pilot Study of the Fluorinated Ingredient of Scotchgard Products and Their Levels in WWTP Sludge and Landfill Leachate from Sweden</p>	<p>Purchaser</p> <p>Swedish Environmental Protection Agency, Environmental Monitoring Unit SE-106 48 Stockholm, Sweden</p> <p>Funding</p>
<p>Keywords for location (specify in Swedish)</p> <p>Bergkvara, Gässlösa, Henriksdal, Hässleholm, Vetlanda, Öhn och Örebro</p>	
<p>Keywords for subject (specify in Swedish)</p> <p>Polymerer med fluorerade sidokedjor, lakvatten, slam, PFAS, EOF, avloppsreningsverk, prekursorer</p>	
<p>Period in which underlying data were collected</p> <p>2004-2016 (excluding 2005 and 2006)</p>	
<p>Summary</p> <p>This study performed by Örebro University on behalf of the Swedish Environmental Agency aims at assessing the occurrence and levels of the newly identified side-chain fluorinated polymers from an environmental perspective. The aims of present study are 1) to develop instrumental and extraction methods to measure the active ingredient of two Scotchgard products (two side-chain fluorinated polymers, hereafter referred to as Pre-2002 and Post-2002) in sludge and leachate samples from Swedish wastewater treatment plants and landfills; 2) to evaluate if Pre-2002 and Post-2002 may be responsible for the unidentified organofluorine in the sludge samples from our previous screening study reporting extractable organofluorine (EOF); and 3) to conduct a mass balance analysis on EOF and sum of 93 per- and polyfluoroalkyl substances (PFAS) including Pre-2002 and Post-2002 in the sludge and landfill leachate samples to assess the levels of unidentified EOF that potentially are other polymeric or non-polymeric PFAS.</p> <p>Levels of Pre-2002 and Post-2002 and EOF are reported for sludge samples from four wastewater treatment plants (Bergkvara in Torsås, Gässlösa in Borås, Henriksdal in Stockholm, and Öhn in Umeå) collected in</p>	

2015, and leachate samples from three different landfills (Atleverket in Örebro, Hässleholm Kretsloppscenter in Hässleholm, and Flishult in Vetlanda). Sludge samples from Gässlösa wastewater treatment plant collected between 2004 and 2016 (excluding 2005 and 2006) were analyzed to assess any temporal trends of the two side-chain fluorinated polymers (Pre-2002 and Post-2002). The present investigation reported levels of both Pre-2002 and Post-2002 in all sludge samples (158-2618 ng/g d.w.). Levels of Pre-2002 were always higher than those of Post-2002 in the same samples. A declining trend was observed for Pre-2002 in sludge samples from Gässlösa but no clear trend was noted for Post-2002. The concentrations of the Pre-2002 and Post-2002 in sludge were higher than the sum of 83 PFAS analyzed in the previous screening study. No relationship between number of people that the wastewater treatment plants served and the concentrations of EOF and Pre-2002 and Post-2002 could be observed. The concentrations of both EOF and Pre-2002 and Post-2002 seem to be more related to the types of industry located in that area. Only three of the five leachate samples showed detectable levels of Pre-2002. Post-2002 was not detected in any of the landfill leachates. The low levels could be due to that both compounds are strongly sorbed to particles, which indicates the fate and distribution of these compounds. For both the sludge and leachate samples, the quantified levels of Pre-2002 and Post-2002 only contributed to a minor part of the EOF. A high proportion of unknown EOF still remains and may be related to other polymeric or non-polar PFAS.

Sammanfattning

Denna rapport innefattar en pilotstudie där två nyligen upptäckta polymerer med fluorerade sidokedjor studeras ur ett miljöperspektiv genom att undersöka deras förekomst och nivåer i svenska slam- och lakvattenprover. Syftet med denna studie var 1) att utveckla extraktions- och instrumentella metoder för analys av den aktiva ingrediensen i två Scotchgardprodukter (vilka benämns i denna rapport som Pre-2002 and Post-2002) i slam- och lakvatten från svenska reningsverk och deponier; 2) att utvärdera om Pre-2002 och Post-2002 kan förklara en del av halten oidentifierat organiskt fluor (OF) i slamprover som visats i vår tidigare screeningstudie; och 3) att genomföra en massbalansanalys av extraherbart OF (EOF) och $\Sigma 93$ PFAS inklusive Pre-2002 och Post-2002 i slam- och lakvattenprover för att bedöma delen av okänt EOF som potentiellt kan vara andra PFAS ämnen.

I denna studie rapporteras koncentrationer av Pre-2002 och Post-2002, samt EOF för slamprover från fyra reningsverk (Bergkvara i Torås, Gässlösa i Borås, Henriksdal i Stockholm och Öhn i Umeå) insamlade under 2015, samt lakvattenprover från tre olika avfallsdeponier (Atleverket i Örebro, Hässleholm Kretsloppscenter i Hässleholm och Flishult i Vetlanda). En tidstrend av halterna Pre-2002 and Post-2002 mellan 2004 och 2016 (2005 och 2006 saknades) utfördes i slamprover från Gässlösa reningsverk. Detekterade koncentrationer av både Pre-2002 och Post-2002 hittades i alla slamprover (158-2618 ng/g d.w.). En minskning i koncentration av Pre-2002 kunde ses från 2004 till 2016 i slamprover från Gässlösa reningsverk, medan ingen trend för Post-2002 observerades. Halten av Pre-2002 and Post-2002 var högre än summan av de 83 PFAS-ämnena som analyserats i den tidigare screeningstudien. Inget tydligt samband kunde ses mellan antalet personer anslutna till reningsverket och halterna av oidentifierat EOF samt de detekterade polymererna med fluorerade sidokedjor. Nivåerna av EOF, Pre-2002, och Post-2002 visade sig vara relaterat främst till typ av industriell verksamhet i anslutning till reningsverket. Endast tre av fem lakvattenprover visade detekterbara koncentrationer av Pre-2002. Post-2002 detekterades inte alls i lakvatten. De låga nivåerna i lakvattenproverna kan förklaras av att Pre-2002 och Post-2002 starkt adsorberar till partiklar, vilket visats i andra studier. Detta ger ytterligare en inblick i hur dessa ämnen transporteras i miljön. Andelen av Pre-2002 och Post-2002 i både slam och lakvattenproverna är låg i förhållande till halten EOF, som fortfarande utgörs av en stor andel oidentifierat EOF. Den stora mängden okänt EOF kan därför ha sitt ursprung i andra icke- eller polymeriska PFAS-ämnena.

Background

Per- and polyfluoroalkyl substances (PFAS) are a large group of man-made compounds consisting of several classes. Their unique physicochemical properties such as thermal and chemical stability, water-, oil- and dust repellence, result in wide range of industrial and commercial applications, as surface protector, non-stick cookware and in cosmetics (KEMI 2015). Several PFAS have been found to pose a risk to the environment due to their mobility, persistency, bioaccumulative and toxic potential (Giesy, Kannan and Jones, 2001; DeWitt, 2015). Voluntary phase out and regulations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), two widely used PFAS, may have resulted in a decrease in levels of these compounds (Yeung et al., 2013). However, the production has changed from long-chain PFAS (compounds with more than six fluorinated carbons for sulfonates and compounds with more than seven fluorinated carbons for carboxylates) towards short-chain products, for example perfluorobutanesulfonyl fluoride (PBSF) and more complex structures including branched- and cyclic moieties (KEMI, 2015). Recent report from Organisation for Economic Co-operation and Development (OECD) identified over 4700 PFAS-related compounds based on their Chemical Abstracts Service (CAS) number on the global market; of these 15% belongs to polymers (OECD, 2018). Only a minor part of these several thousand compounds are commonly monitored and the focus are mainly on non-polymer PFAS such as the classes sulfonates, carboxylates and some of their precursors. The knowledge regarding polymeric PFAS is limited. Based on global usage and degradation potential to aliphatic PFAS, better understanding on the source, fate and transport of this compound class is needed.

Side-chain fluorinated polymers are compounds with a structure of a non-fluorinated polymer backbone with per-/polyfluorinated side-chains (Buck et al., 2011). They are commonly applied to materials to give oil- and water repellency and have been used in a series of household products (Chu and Letcher, 2017). Fluorinated compounds have been identified in impregnation sprays from the trademark Scotchgard, and are suspected to be side-chain fluorinated polymers (3M, 2019). Scotchgard is a registered trademark of 3M Company used for a series of surface treatment products such as carpet, upholstery and curtains. Their chemical identities are a trade secret of 3M Company, and therefore their structures are not yet determined. What is known is that the perfluorooctanesulfonyl-based formulation, mainly the *N*-methyl-perfluorooctanesulfonyl chemistry ($C_8F_{17}SO_2N(CH_3)^-$) was manufactured and used in Scotchgard formulation up until year 2002. Due to the phase-out of the C8 chemistry

by the 3M Company (3M, 2002), another formulation using *N*-methyl-perfluorobutanesulfonyl chemistry ($C_4F_9SO_2N(CH_3)^-$) was introduced after 2002. A recent study has identified the major fluorinated components in both before and after 2002 Scotchgard fabric protector products using electrospray ionization mass spectrometry (ESI MS) (Chu and Letcher, 2014). A perfluorooctane sulfonamide based side-chain component was detected in the pre 2002 product named as S1 (hereafter referred as Pre-2002 in this report), and a perfluorobutane sulfonamide based side-chain component was detected in the post 2002 product named as S2 (hereafter referred as Post-2002 in this report). The identified fragments of S1 (Pre-2002) and S2 (Post-2002) agreed with the phase-out plan for POSF-based products by the 3M Company (3M, 2000). However, the detailed structure of the two products are not yet determined. The same research group also determined the levels of S1 (Pre-2002) and S2 (Post-2002) in aquatic sediment and biosolid-augmented agricultural soils from Great Lakes basin of North America (Chu and Letcher, 2017). The reported levels of S1 (Pre-2002) and S2 (Post-2002) in the aquatic sediment and agricultural soil samples (0.24 - 476.25 and 3.18 – 240.48 ng/g d.w., respectively). In a recent study, Letcher et al., 2020 reported levels of S1 (Pre-2002) and S2 (Post-2002) in biosolids from wastewater treatment plants from Canada. The levels of S1 (Pre-2002) ranged from 1.08 to 105 ng/g d.w. and those of S2 (Post-2002) ranged from 37.5 to 2051 ng/g d.w.. Results from both studies showed that the sum of S1 (Pre-2002) and S2 (Post-2002) were much higher than the sum of 22 PFAS in the same samples, which suggested significant proportion of fluorinated chemicals are overlooked in the environment.

Both Pre-2002 and Post-2002 have been widely used in commercial applications as a spray, which suggest that they might possess strong sorption behavior on surfaces in human indoor environments (e.g., curtains, textiles, upholstery) (Renner, 2006). It is reasonable to hypothesize that Pre-2002 and Post-2002 could end up in the environment in sediment, sludge and soil, from direct sources such as wastewater treatment plants (WWTPs) (Arvaniti and Stasinakis, 2015; Buck et al., 2011; Lindstrom et al., 2011).

Our previous screening studies using a mass balance approach on Swedish sewage water and sludge samples indicated significant amount and proportion of unidentified extractable organofluorine (EOF) in the samples, where only 6 - 21% and 2.5-13% of the EOF were accounted by quantifiable PFAS (Yeung et al., 2016; Yeung et al., 2017). One hypothesis is that these side-chain fluorinated polymers (e.g., Pre-2002 and Post-2002) might be present in

the sewage water from wastewater treatment plants (WWTPs) and could therefore explain the unidentified EOF observed in the previous studies. Measuring these two side-chain fluorinated polymers in WWTPs with a mass balance approach may indicate the importance of the polymeric PFAS contribution to the unidentified EOF.

Aim

The objectives of present study are 1) to develop instrumental analysis methods to measure the active ingredient of two Scotchgard products (two suspected side-chain fluorinated polymers: Pre-2002 and Post-2002) using LC-MS/MS; 2) to analyze sludge extracts from the previous screening study (Yeung et al., 2017) to evaluate if Pre-2002 and Post-2002 may account for the unidentified organofluorine in the sludge samples; 3) to develop extraction methods for the sludge and landfill leachate samples to measure the levels of Pre-2002 and Post-2002 using the instrumental methods stated above; and 4) to conduct a mass balance analysis on EOF and $\Sigma 93$ PFAS including Pre-2002 and Post-2002 in the sludge and landfill leachate samples to assess the levels of unidentified EOF that potentially are other polymeric or non-polymeric PFAS.

Project administrator and coordinator

This project has been led by Örebro University (ORU), where all analysis, data interpretation and quantification were performed.

Following persons from ORU have participated in the project:

Felicia Fredriksson, PhD student

Ulrika Eriksson, postdoctoral researcher

Anna Kärrman, associate professor

Leo Yeung, associate professor, project leader

Samples

Sludge samples. A total of 14 sludge samples were analyzed which include 11 samples collected from Gässlösa (Borås) wastewater treatment plant (WWTP) between 2004 and 2016 (excluding 2005 and 2006) and three samples collected in 2015 from the WWTPs Bergkvara (Torås, $n=1$), Henriksdal (Stockholm, $n=1$) and Öhn (Umeå, $n=1$). All samples were collected under a national environmental monitoring of outgoing water and sludge from Swedish sewage treatment plants, and the sludge samples were freeze-dried and stored at the Swedish Museum of Natural History (Haglund, 2019).

Sludge sample extracts. A total of 12 sample extracts from the previous screening study (Yeung et al., 2017) were re-analyzed for the side-chain fluorinated polymers (Pre-2002 and Post-2002) using an optimized instrumental method. These samples were extracted in 2017 with another extraction method for PFAS analysis and stored in $-20\text{ }^{\circ}\text{C}$.

Landfill leachates. A total of five landfill leachate samples from three different landfill sites were provided directly from the waste facilities in Sweden in 2018 (Atleverket in Örebro, Hässleholm Kretsloppscenter in Hässleholm, and Flishult in Vetlanda) and were stored in $+4^{\circ}\text{C}$ until analysis.

Sample information

Wastewater treatment plants (WWTPs). The details of the operating scales of the four WWTPs are provided in Table 1. All information described below is based on a published report of Haglund, 2019. In brief, Henriksdal WWTP is one of the largest WWTP in Sweden serving 824 000 people and is connected to two large hospitals and industries such as food production and laundry. The Öhn WWTP serves a hospital and 99 000 people. Gässlösa WWTP serves 91 000 people and receives wastewater from a hospital, chemical and plastic industries and several large textile industries. Bergkvara is a small WWTP and serves 5 900 people. Biological, chemical and mechanical treatments are used in all four WWTPs. Anaerobic digestion treatment is used for all four WWTPs except Bergkvara where an aerobic digestion treatment is used.

Table 1. Information of the four different WWTPs (Gässlösa, Öhn, Bergkvara, and Henriksdal) included in the project.

	Gässlösa	Öhn	Bergkvara	Henriksdal
Number of people served	91 000	99 000	4 300	824 000
Person equivalents	91 000	92 000	3 000	950 000
Amount sludge produced (t/year)	2 430	2 490	83	18 000
Residence time of sludge (days)	25	18	n.a.	19

n.a.: not available

Landfill sites. Landfill leachates from three different disposal plants were analyzed; they were from Atleverken (Örebro, $n=1$, an active municipality landfill), Flishult (Vetlanda, $n=1$, an active hazardous landfill) and Hässleholm Kretsloppscenter ($n=3$). The three samples from Hässleholm Kretsloppscenter were from different landfill sites; one sample from an old closed non-hazardous landfill, one from an active non-hazardous landfill and one from an active hazardous landfill. The landfill leachates were filtered, and only the filters were extracted and analyzed for the side-chain fluorinated polymers.

Sample extraction and clean-up

Sludge. The sludge samples were analyzed for the two side-chain fluorinated polymers, Pre-2002 and Post-2002, and additional for 91 non-polymeric PFAS and EOF (Supplementary information (SI), Table S 1). Extraction method employed was a liquid-solid extraction modified from Chu and Letcher, 2017. Figure 1 shows the schematics of the extraction and clean-up procedures. Briefly, approximately 0.25 ± 0.005 g freeze dried sludge sample was added in a 15 mL PP tube; then 8 mL of extraction solution acetone:hexane (50:50, v/v) was added to the sample. Followed by vortex mixed for 60 s and ultrasonication for 15 min. The solid and solvent were separated by centrifugation at 6000 g for 15 min. After centrifugation, the supernatant was transferred to a new PP tube. The extraction steps were repeated twice and all the aliquots (approximately 24 mL) were combined. The extract was gently evaporated to dryness under nitrogen gas and reconstituted with 2 mL of dichloromethane (DCM). The extract was vortex mixed for 60 s and ultrasonicated for 20 min before subject to two different solid phase extraction (SPE) clean-ups. First, a disposable silica gel SPE cartridge (500 mg, J.T. Baker®, PA, United States), purchased from GTF/Fisher Scientific was conditioned with 3 mL of DCM. Sample extract was loaded to the cartridge at an approximate rate of 1 to 2 drops per second. The sorbent was washed with 6 mL of DCM, and thereafter the target

analytes were eluted with 2 mL of a mixture of acetonitrile (ACN) and DCM (40:60, v/v). The extract was collected in a new PP tube, evaporated gently to dryness under nitrogen gas and reconstituted with 2 mL of ACN. The extract was vortexed, and ultrasonicated for 10 min before the second clean-up using dispersive-SPE. Approximately 200 mg of Supel QuE Z-Sep (Bellefonte, PA, USA) sorbent purchased Sigma-Aldrich was added to the extract and vortexed for 1 min. The extract including the sorbent was evaporated to around 1 mL and then filtered into LC-vial with a 0.2 μm GHP filter (Waters Corporation, Milford, USA). It was further evaporated to dryness under nitrogen gas and reconstituted with 0.5 mL of methanol (MeOH). The final extract was split for respective instrumental analyses (Figure 1).

Leachate. Of the five leachate samples, only the suspended particles in the leachate were analyzed because the major proportion (99.8%) of both Pre-2002 and Post-2002 has been found to strongly sorb onto particles (Fredriksson et al., 2019). The landfill leachates were filtered using GF/B glass microfiber filters (Whatman, 150mm, 1.0 μm pore size). The suspended particles collected from the GF/B glass microfiber filters were extracted with the same procedure as the sludge samples (described in previous section) with some modifications. In brief, the filter was cut and placed in a 50 mL PP tube; 35 mL of the extraction solution was added; the sample was then vortex mixed, and ultrasonicated. The supernatant was transferred to a new 50 mL PP tube. The extraction procedure was repeated three times using 15, 20 and 15 mL of extraction solution instead of 35 mL. All supernatants were combined and concentrated under nitrogen gas and reconstituted with 2 mL of DCM and subjected to further cleanups as sludge samples (described in previous section).

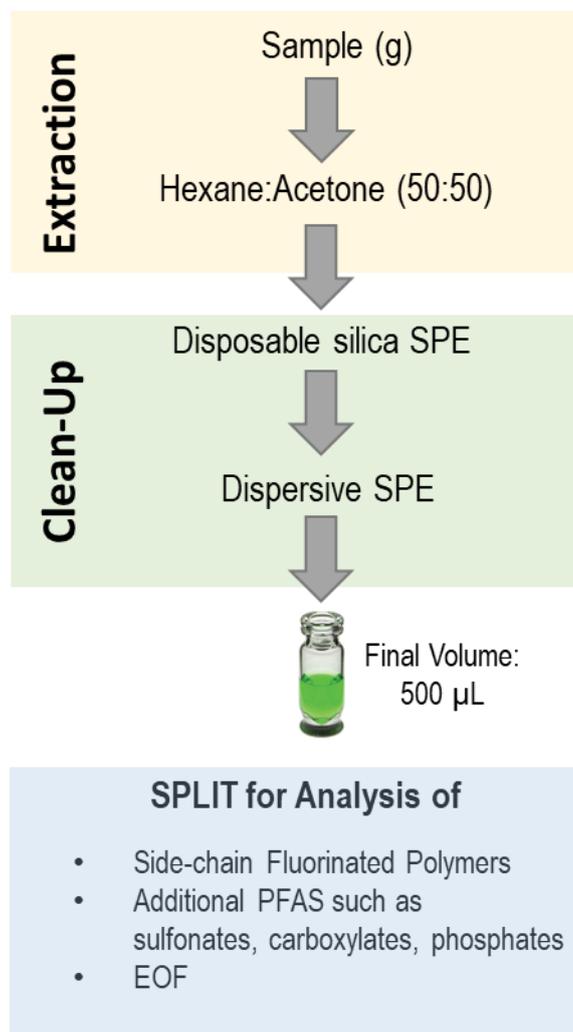


Figure 1. Schematics showing the sample procedure including extraction and the clean-up methods.

Instrumental analysis and quantification

Target compounds. A list of 93 target PFAS is provided in Supplementary information. Different classes of PFAS including the side-chain fluorinated polymers, Pre-2002 and Post-2002, were analyzed in negative electrospray ionization using an Acquity UPLC system coupled to a triple quadrupole mass spectrometer XEVO TQ-S (Waters Corporation, Milford, USA). The column for the separation was a 100 mm C18 BEH column (1.7 µm, 2.1 mm). The mobile phases were 2mM ammonium acetate in water:MeOH (70:30) (A) and MeOH (B). For analysis of PAPs (Polyfluoroalkyl phosphate esters), an additional additive, 5 mM 1-methylpiperidine, were added in the mobile phases. Most of the PFAS were quantified by internal calibration (SI, Table S 1). Most of the analytical standards were purchased from Wellington Labs (Guelph, ON). The standards for Pre-2002 and Post-2002 were technical mixtures of Scotchgard™ pre-2002 formulation (100 µg/mL in methanol) and Scotchgard™

post-2002 formulation (100 µg/mL in methanol) purchased from AccuStandard Inc. (New Haven, CT, USA). These two standard solutions were prepared from commercial products of Scotchgard™ fabric protector produced before 2002 and after 2002 by the 3M Company. Since no suitable internal standards was available for Pre-2002 and Post 2002, the concentrations of Pre-2002 and Post-2002 were quantified by an external calibration curve.

Extractable organofluorine (EOF). The levels of EOF were determined by using a combustion ion chromatograph (CIC, Analytikjena, Germany; Metrohm, Switzerland). An ion-exchange column (Metrosep A Supp5 – 150/4) and isocratic elution with carbonate buffer (64 mM sodium carbonate and 20 mM sodium bicarbonate) was used for the separation of anions. Details of the method are provided elsewhere (Yeung et al., 2016).

Mass balance analysis of organofluorine

The mass balance was calculated by converting the quantifiable PFAS level (ng/g) to corresponding fluoride level (ng F/g) by using the following equation:

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

where C_F is the corresponding fluoride level (ng F/g), n_F stands for the number of fluorine in the PFAS, MW_F is the molecular weight of fluorine, MW_{PFAS} stands for the molecular weight of PFAS and C_{PFAS} is the measured PFAS concentration using LC-MS/MS.

Since the molecular structures of Pre-2002 and Post-2002 are unknown, the fluoride content was estimated from the technical mixture using CIC. Results show that 100 µg/mL of the Pre-2002 standard gave the fluoride content of 0.596 ± 0.130 µg F/mL which indicated that the fluoride content of the Pre-2002 was 0.5-0.7%. Similar results show that the fluoride content of the Post-2002 was 1.9-2.2%. In order to convert the Pre-2002 and Post-2002 into fluoride equivalent, concentration in the samples was multiplied with 0.6% and 2% for Pre-2002 and Post-2002, respectively. The levels of unidentified extractable organofluorine were estimated by subtracting the EOF from the quantifiable PFAS including the Pre-2002 and Post-2002.

Quality control and quality assurance

Target Compounds. Several procedures were made to obtain a low limit of detection (LOD), for examples only PFAS free consumables such as polypropylene (PP) were used, the

glassware were baked at 450°C for 12 hours before use, and an isolator column in the UPLC system was installed to separate system contamination from the injected sample. The LOD was determined as the average level of the individual PFAS plus three times the standard deviation (SD) of the procedure blanks; if no analyte was detected in the procedure blanks the lowest point in the calibration curve was used. In order to check for blank contamination, at least three procedure blanks were included in every extraction batch of 10 samples. No detectable levels of target PFAS were found in the procedure blanks.

Side-chain fluorinated polymers. The performance of the instrumental method was assessed based on precision and linearity. An eleven-point calibration curve consisting of 1 up to 3000 ng/mL was constructed. The linearity of the calibration curves were $R^2 > 0.99$ for both Pre-2002 and Post-2002. The instrumental precision was evaluated based on triplicate injections of standards at different levels (12, 60, 120 ng/mL); the relative standard deviation was found to be 4 to 12%. Several QC standards ($n=7$) were injected during the whole run and resulted in deviation of Pre-2002 and Post-2002 at 9% and 4%, respectively. A low PFAS-contaminated sediment sample (>20 cm depth) was spiked and extracted and the recoveries of Pre-2002 and Post-2002 were found to be $86 \pm 8\%$ and $41 \pm 2\%$, respectively. A spike recovery test with standard reference material NIST2781 of domestic sludge from the U.S. department of commerce national institute of standards and technology (Gaithersburg, MD) was performed, but high levels of Pre-2002 (21081 ng/mL) was found, and therefore the recovery could not be obtained for this compound. The recovery for Post-2002 was found to be similar as for the sediment ($57 \pm 4\%$), and therefore the recovery for Pre-2002 were assumed to be similar as well. Ionization suppression (up to 50%) was observed for Pre-2002 and Post-2002; further confirmation of the results with standard addition is recommended.

Extractable organofluorine. Fluoride signal was detected in the combustion blank, even when no extract were analyzed. Multiple combustion blanks were conducted before analysis until a stable fluoride signal were reached. Certified Multielement ion chromatography anion standard solution (Sigma-Aldrich) was used for the five-point external calibration curve (20, 50, 100, 250, 500 and 1000 ng F/mL) resulting in linearity $R^2 > 0.9999$. When the concentration of the extract exceeded the range of the calibration, the extract was diluted in order to fit in the calibration range. Combustion efficiency was evaluated by combustion of 500 ng of PFOS and PFOA which resulted in recoveries ranging from 89 to 92% for PFOS and 85 to 90% for PFOA. To assess if carryover between samples occur, combustion blanks

between sample injections were conducted. In general, carry-over was negligible except for after high levels of EOF was injected, resulting in 5 to 10 % of carryover. In that case, the sample after a high EOF level sample was re-injected to confirm the results. Since the system background contained fluoride, before quantification using the external calibration curve, the peak area of standard and sample was first subtracted with the average peak area of the combustion blanks before and after. Several standard injections resulted in a variation of 7%.

Results and discussion

Side-chain fluorinated polymers – Pre-2002 and Post-2002

Extraction and instrumental methods were developed for the two newly identified Scotchgard compounds (Pre-2002 and Post-2002). A modified extraction method based on a previous study (Chu and Letcher, 2017) using acetone:hexane (1:1) as extraction solution resulted the best recovery for both Pre-2002 and Post-2002 at $86 \pm 8\%$ and $41 \pm 2\%$, respectively.

A total of 19 samples, including sludge ($n=14$) and leachate ($n=5$) were extracted with the new optimized method and analyzed for the two side-chain fluorinated polymers, Pre-2002 and Post-2002. Only the suspended particles in the leachate were extracted and analyzed due to our results showing that these two compounds are strongly sorbed onto particles (Fredriksson et al., 2019).

Sludge. Using the new optimized extraction method, all sludge samples showed detectable levels of both Pre-2002 (142 – 2514 ng/g d.w.) and Post-2002 (11 – 104 ng/g d.w., Table 2). The levels for Pre-2002 were more than 7-fold higher compared to Post-2002. A recent study showed detection of both Pre-2002 and Post-2002 in biosolids from Canadian WWTPs (Letcher et al., 2020). The levels of Pre-2002 ranged from 1.08 to 105 ng/g d.w., whereas levels of Post-2002 ranged from 37.5 to 2051 ng/g d.w. The levels of Post-2002 was higher than those of Pre-2002, which is in contrast with the present study. This difference might suggest different usages and sources between Sweden and Canada. Very few data on these compounds are available. Further investigation is needed to understand their pollution sources, fate and transport in the environment.

The reported concentrations of the sum of Pre-2002 and Post-2002 in the sludge samples were much higher than the sum of 83 PFAS reported in the previous screening study for the same

sample (Yeung et al., 2017, Table 2). Similar observation was noted in the recent study that the levels of the sum of Pre-2002 and Post-2002 were much higher than the sum of the 22 PFAS in the same sample (Letcher et al., 2020). The high contribution of Scotchgard compounds (Pre-2002 and Post-2002) indicates the importance of monitoring these chemicals, it also suggest that a significant proportion of fluorinated chemicals are neglected in the environment and in most of the monitoring studies. All these results show that sludge contained significant amounts of both polymeric and ionic PFAS.

Table 2. Concentration (ng/g d.w.) of Pre-2002 and Post-2002 in sludge, together with the sum of the 83 PFAS from previous study on the same samples.

Sludge					
Site	Year	Concentration (ng/g d.w.)			
		Present study			Previous study (Yeung et al., 2017)
		Pre-2002	Post-2002	∑Side-chain fluorinated polymers	∑PFAS₈₃
Gässlösa	2016	532	22	554	186
	2015	586	36	622	97
	2014	746	27	773	72
	2013	721	30	750	239
	2012	995	99	1094	309
	2011	1058	63	1121	389
	2010	835	52	887	403
	2009	1061	56	1117	408
	2008	736	41	777	275
	2007	1574	101	1675	357
	2004	2514	104	2618	1160
Gässlösa	2015	586	36	622	97
Öhn	2015	150	18	168	149
Bergkvara	2015	142	21	163	119
Henriksdal	2015	148	11	159	171

Comparison between WWTPs. The levels for both Pre-2002 and Post-2002 were similar among Henriksdal, Bergkvara and Öhn WWTPs (Figure 2), but Pre-2002 was always higher than Post-2002 in the same sample. The concentration of Pre-2002 at Gässlösa WWTP was four times higher than the other WWTPs and Post-2002 shows an observable higher level as well. Pre-2002 and Post-2002 are used as an active ingredient in impregnation for textiles. The Gässlösa WWTP received wastewater from large textile industries, which may be one of reasons for the elevated concentrations of Pre-2002 and Post-2002 when compared to the other three WWTPs. The levels of the side-chain fluorinated polymers in sludge from WWTPs may therefore be related more to the types of industries connected to the area, than the number of people served in the area. Further study is needed to clarify this point due to small number of samples included in this study.

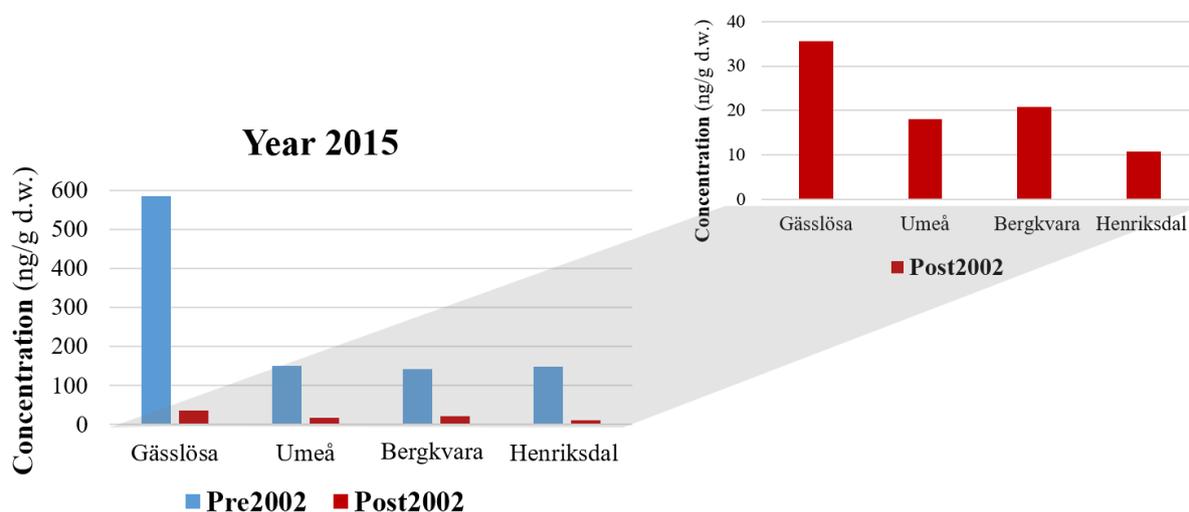


Figure 2. Levels of Pre-2002 and Post-2002 for four WWTPs (Gässlösa, Umeå, Bergkvara and Henriksdal) in sludge samples collected in 2015.

Temporal trend. An investigation on temporal trends for both Pre-2002 and Post-2002 was conducted in samples from Gässlösa WWTP, (Figures 3 and 4). A decline of the concentration of Pre-2002 was observed between 2004 and 2008. The decline of Pre-2002 may be due to the phase-out of POSF-based compounds since 2002 by 3M Company. In contrast, no specific trend was observed for Post-2002.

Concentrations of Pre-2002 in sludge from Gässlösa WWTP

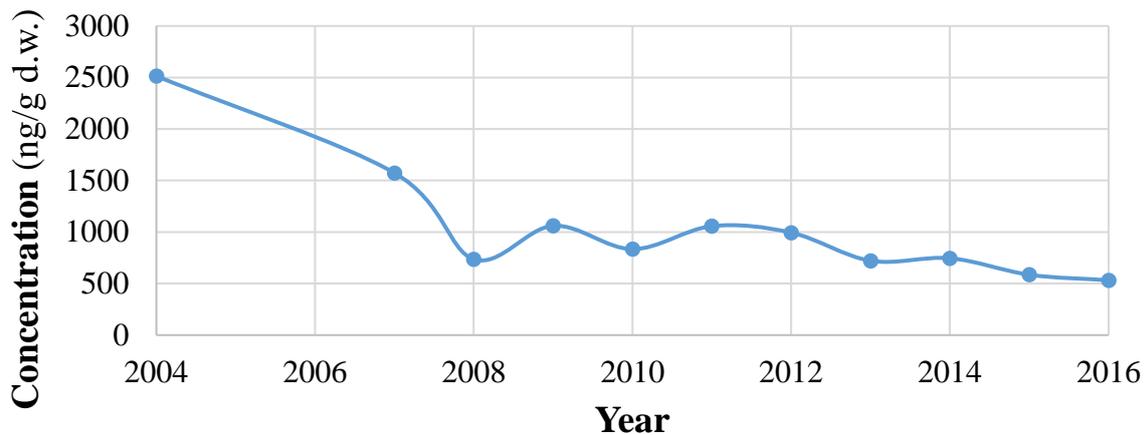


Figure 3. Concentrations (ng/g d.w.) of Pre-2002 in sludge samples collected from Gässlösa WWTP (2004, 2007-2016).

Concentrations of Post-2002 in sludge from Gässlösa WWTP

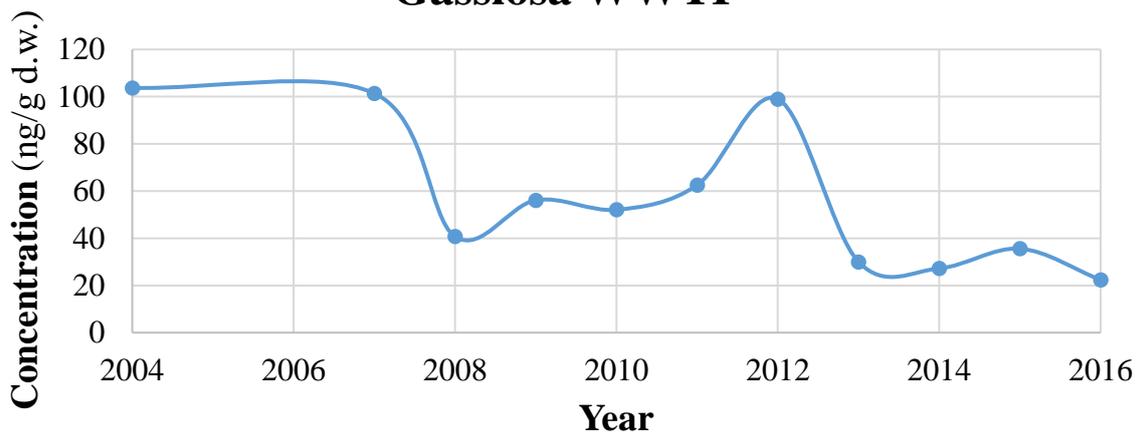


Figure 4. Concentrations (ng/g d.w.) of Post-2002 in sludge samples collected from Gässlösa WWTP (2004, 2007-2016).

Landfill leachate. Of the five leachate samples, only three samples show detectable levels of Pre-2002 in the suspended phase, whereas no sample showed detectable concentrations of Post-2002. As indicated above, the Pre-2002 and Post-2002 were shown to be strongly sorbed to particles, and it is therefore reasonable to believe that these compounds are sorbed to the particles.

Table 3. Concentration (ng/g d.w.) of Pre-2002 and Post-2002 in the leachate particles from different landfill sites.

Leachate			
Site	Year	Concentration (ng/g d.w.)	
		Pre-2002	Post-2002
Atleverket (active non-hazardous landfill)	2017	10.7	<0.5
Hässleholm Kretsloppscenter (not active non-hazardous landfill)	2017	0.822	<0.5
Hässleholm Kretsloppscenter (active non-hazardous landfill)	2017	0.988	<0.5
Hässleholm Kretsloppscenter (active hazardous landfill)	2017	<0.5	<0.5
Flishult (active hazardous landfill)	2017	<0.5	<0.5

Previous screening study. One of the aims in the current study was to investigate if these newly identified side-chain fluorinated polymers (Pre-2002 and Post-2002) could explain a part of the remaining proportion (42-82%) of unidentified EOF found in the previous screening study (Yeung et al., 2017). These sample extracts were re-analyzed using the newly developed instrumental method for the side-chain fluorinated polymers. However, no detectable levels of either Pre-2002 or Post-2002 were found in these 12 sludge sample extracts, meaning that these compounds could therefore not be the unidentified EOF in these extracts. The previous screening study used an ion-pair extraction, which target neutral and ionic PFAS in the samples. Our recent investigation showed low recoveries of Pre-2002 and Post-2002 using the ion-pair extraction (Fredriksson et al., 2019). This is the likely explanation for the absence of Pre-2002 and Post-2002 in the sample extracts from the previous study.

Mass balance analysis

In order to conduct the mass balance analysis, the Pre-2002 and Post-2002 and measurable PFAS need to be converted into fluoride equivalent content before any comparison with EOF levels. In the current analysis mostly non-polar organofluorine is extracted which might include neutral PFAS such as perfluorobutanesulfonamide (FBSA), perfluorohexanesulfonamide (FHxSA), perfluorooctanesulfonamide (FOSA) and some perfluorinated phosphinates (PFPiAs) as well as some polymeric compounds including the side-chain fluorinated compounds. Some of the legacy PFAS were co-extracted, for example perfluoroalkyl sulfonates (PFSA)s such as PFOS. Although current method was not optimized for these compounds, their contribution to EOF was also included since they contributed to the fluoride signal (SI Tables S2-4). The conversion of concentrations from ng/g (obtained from LC-MS/MS) to ng F/g (obtained from CIC) is explained in the Mass balance analysis of organofluorine in the Material and Method section.

A total of 14 sludge and leachate samples showed detectable EOF concentrations (Table 4). EOF in sludge samples ranged from 90 ng F/g in Öhn sludge collected in 2015 up to 81846 ng F/g in Henriksdal sludge collected in 2015. EOF of leachate particle samples ranged from 277 ng/g (Altleverket) to 10133 ng F/g (Flishult).

Table 4. Concentration (ng F/g d.w.) and composition (%) of EOF in sludge and leachate samples, (Measurable PFAS: the sum of detectable PFAS concentrations in the extract; empty cell indicates sample below detectable levels). NH stands for non-hazardous landfill whereas H is an abbreviation for hazardous landfill.

	Sample Location	Year of Sample Collection	EOF	Identified		Unidentified	Identified		Unidentified
				Pre-2002 and Post- 2002	Measurable PFAS		Pre-2002 and Post- 2002	Measurable PFAS	
				ng F/g					
						%			
Sludge	Gässlösa	2004	878	19.67	170	689	2.2	19.3	78.4
	Gässlösa	2007	235	13.04	5.1	217	5.6	2.2	92.3
	Gässlösa	2008	136	5.97	6.4	124	4.4	4.7	90.9
	Gässlösa	2009	751	8.55	3.5	739	1.1	0.5	98.4
	Gässlösa	2010	159	6.88	3.0	150	4.3	1.9	93.8
	Gässlösa	2011	243	8.65	4.1	231	3.6	1.7	94.8
	Gässlösa	2012	397	8.94	1.9	386	2.3	0.5	97.3
	Gässlösa	2013	646	5.65	1.6	639	0.9	0.3	98.9
	Gässlösa	2014	296	5.77	2.2	288	2.0	0.8	97.3
	Gässlösa	2015	188	4.81	2.9	181	2.6	1.5	95.9
	Gässlösa	2016	116	4.17	1.3	110	3.6	1.1	95.3
	Gässlösa	2015	188	4.81	2.9	181	2.6	1.5	95.9
	Öhn	2015	90	1.41	1.0	87	1.6	1.1	97.3
Bergkvara	2015	122	1.41	0.6	120	1.2	0.5	98.3	
Henriksdal	2015	81846	1.25	1.1	81844	0.0	0.0	100	
Leachate	Atleverket NH (active)	2017	277	0.07	71.8	205	0.027	25.9	74.1
	Hässleholm NH (closed)	2017	775	0.01	168	607	0.001	21.6	78.4
	Hässleholm NH (active)	2017	1045	0.01	143	902	0.001	13.7	86.3
	Hässleholm H (active)	2017	4227		1254	2973		29.7	70.3
	Flishult H (active)	2017	10133		2153	7980		21.2	78.8

Comparison between WWTPs. Different levels of EOF were observed from different WWTPs (Table 4 and Figure 5). Sludge from Öhn, Bergkvara and Gässlösa WWTPs showed similar levels while a much higher level of EOF was found in the sludge sample from Henriksdal. In contrast to results from the previous screening study using another extraction method targeted on ionic PFAS (Yeung et al., 2017), Gässlösa was found to contain the highest EOF. It is not clear what is causing the difference in EOF levels between the four locations. The observed levels of EOF did not seem to increase proportionally to the person equivalents for the four sewage treatment plants. The type of industries serving the plants may be one of the main contributor to the EOF in the samples. Types of treatment processes (physical vs biological vs chemical) might also contribute to the difference in EOF. Similar to the results discussed above, the Pre-2002 and Post-2002 and other detectable PFAS only contributed to a minor proportion (up to 4%) to the EOF; significant amount and proportion of the EOF remain unidentified.

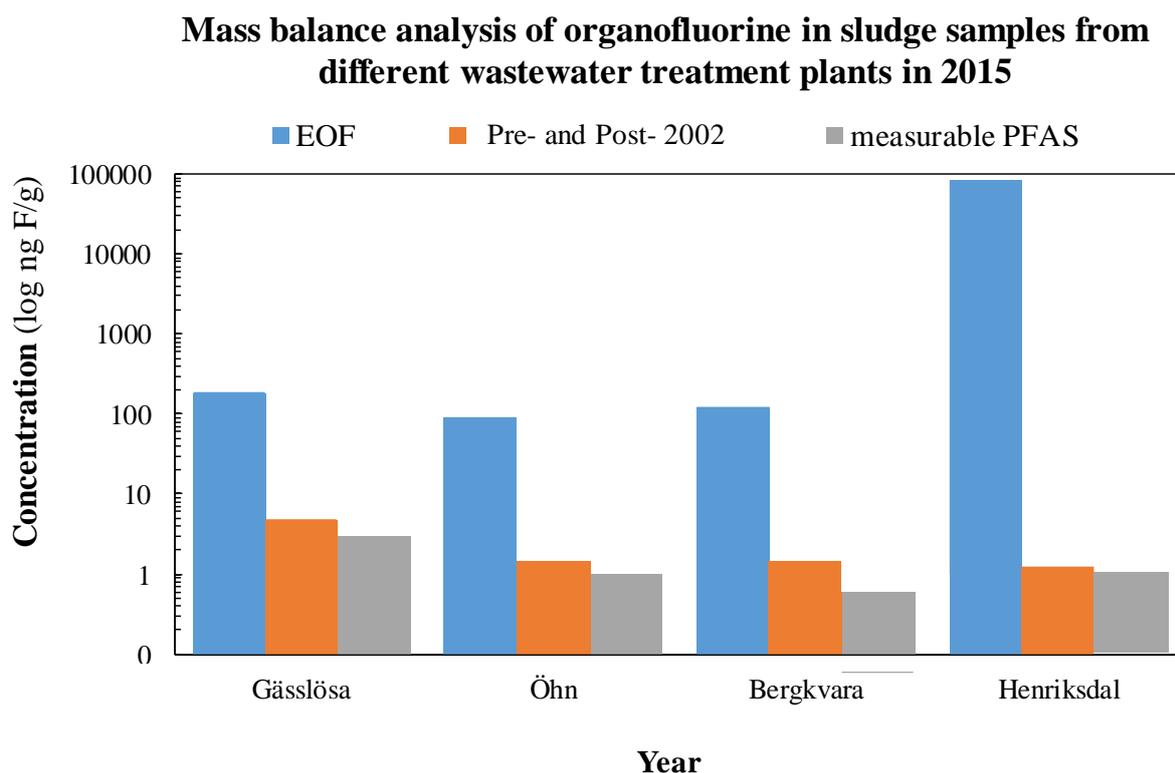


Figure 5. Concentrations (ng F/g d.w.) of EOF, Pre- and Post-2002 and measurable PFAS in the sludge samples collected from different WWTP in 2015, (Measurable PFAS is the sum of detectable PFAS concentrations in the extract). Note the logarithmic scale on the y-axis.

Temporal trends. Temporal changes of EOF in sludge samples from Gässlösa are provided in Table 4 and Figure 6. In general, the EOF in sludge showed a decreasing trend, which is similar to the results of the earlier report (Yeung et al., 2017). However, the EOF composition in the present investigation is different compared to the previous study. In the previous study, neutral and ionic PFAS should be the major components of the EOF given the extraction method used. Whereas, in present study an extraction method targeting non-polar and polymeric PFAS was used. Nonetheless, both results suggest reduced release of fluorinated compounds in recent years. The sum of Pre-2002 and Post-2002 contributed to between 1 to 5.6% of the EOF. Other PFAS measured in the sample extract accounted for between 0.3 to 6.2 % (except for 2004 when it was 19 %). The detectable PFAS in sludge from 2004 stands out from the rest of the years; relatively large proportion (19%) of the detectable PFAS belongs to PFPiAs. These results show that significant amount and proportion of extractable organofluorine remain unidentified.

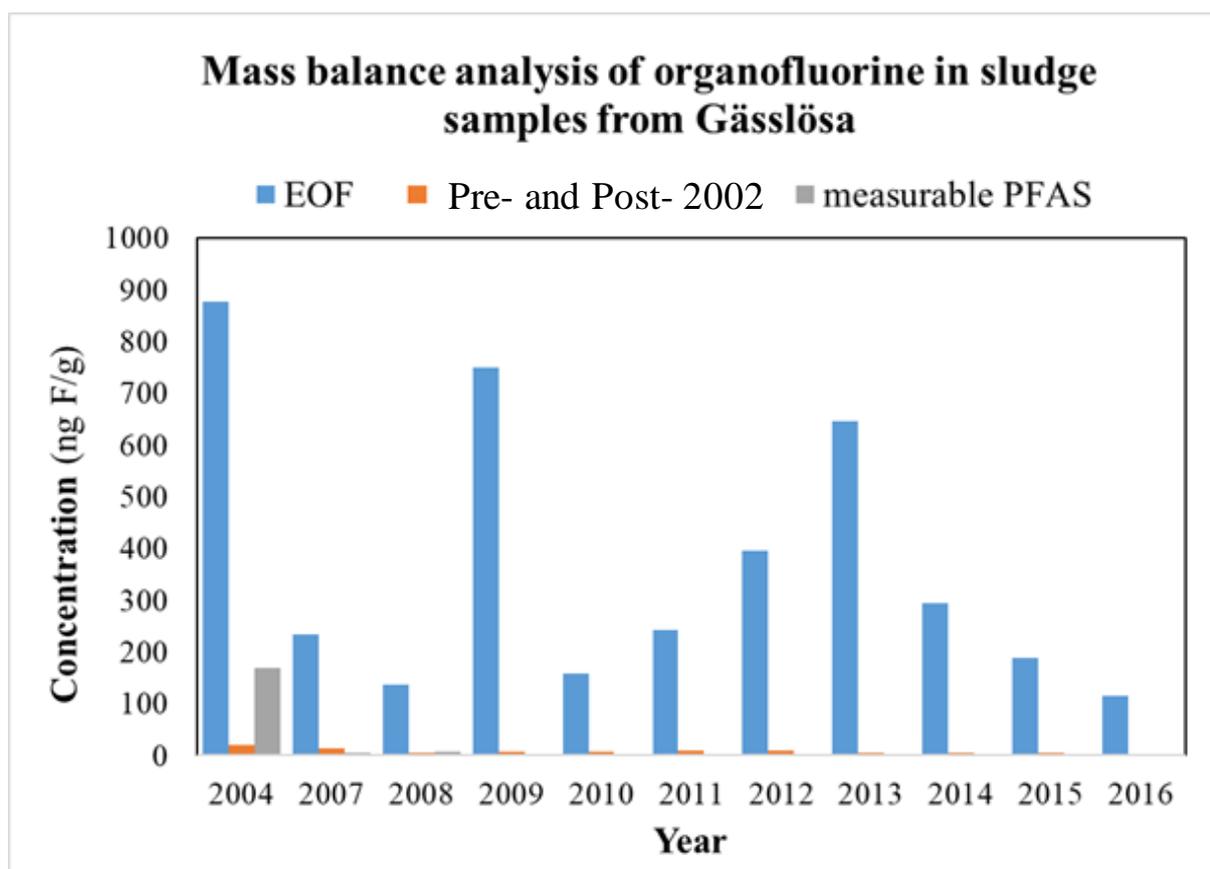


Figure 6. Concentrations (ng F/g d.w.) of EOF, Pre-2002 and Post-2002 and measurable PFAS in the sludge samples collected from Gässlösa WWTP (2004, 2007-2016), (Measurable PFAS is the sum of detectable PFAS concentrations in the EOF).

Landfill leachate. Among the five landfills (Figure 7), three of them received non-hazardous waste; two of them are still active. The remaining two landfills are still active and receiving hazardous waste. Levels of EOF in the landfill leachate particles are in the range of 277 to 1045 ng F/g for the non-hazardous landfills. Landfills receiving hazardous waste showed higher EOF levels (4227-10133 ng F/g). Interestingly, the closed landfill site still leaches out EOF (Table 4). Compared to the sludge samples, a relative higher amount of measurable PFAS were detected in the landfill leachate particles contributing to between 14 to 30% of the EOF. In contrast, Pre-2002 and Post-2002 only contributed up to 0.03% of the EOF. Similar to the results for the sludge samples, significant amounts and proportion of EOF remained unidentified. Several new PFAS were detected on the leachate particles but not in the sludge samples, which include the FBSA, FHxSA and PFECHS. These compounds should be included in regular monitoring programme.

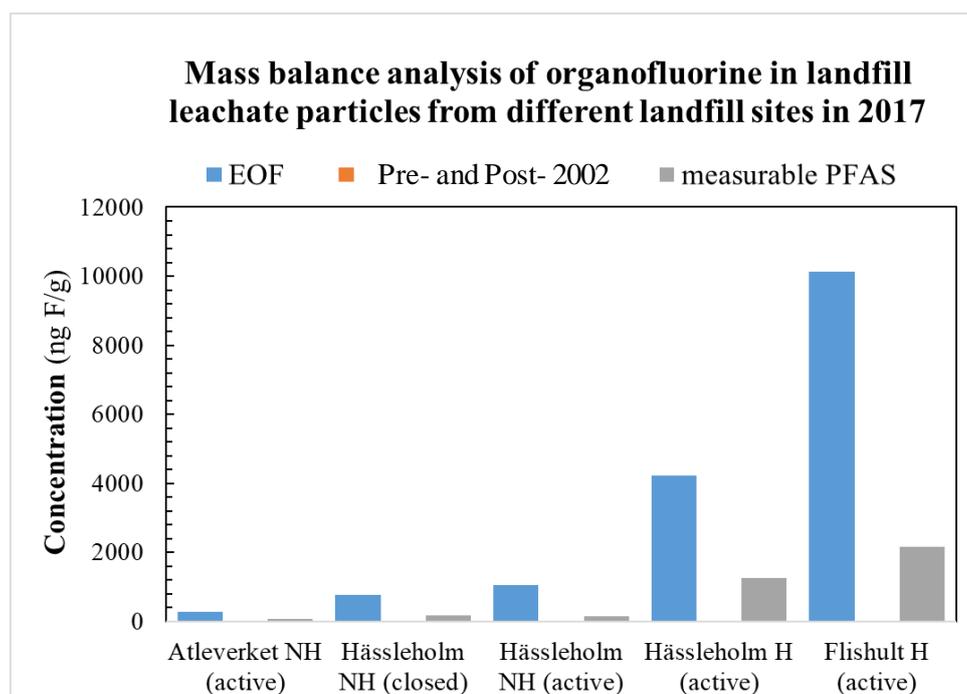


Figure 7. Concentrations (ng F/g d.w.) of EOF, Pre-2002 and Post-2002 and measurable PFAS in landfill leachate particles from different landfill sites in 2017 (Measurable PFAS: the sum of detectable PFAS concentrations in the extract). NH stands for non-hazardous landfill whereas H is an abbreviation for hazardous landfill.

Remarks

- Pre-2002 and Post-2002 were not detected in any of the sludge sample extracts from the previous screening study since a different extraction method was used in that study; these substances could not explain the unidentified EOF in the previous study focused on neutral and ionic PFAS.
- Detectable levels of Pre-2002 and Post-2002 were observed in all sludge samples in the present study using a newly developed extraction method.
- The reported concentrations of Pre-2002 and Post-2002 in the sludge samples were much higher than the sum of 83 PFAS reported in the previous study for the same sample.
- Levels of Pre-2002 were always higher than those of Post-2002 in the same sample, which is different from a recent study (Letcher et al., 2020), where levels of Post-2002 was found to be higher than Pre-2002 in biosolids collected from Canada.
- Declining trend was observed for Pre-2002 in sludge samples from Gässlösa WWTP but no clear trend was noted for Post-2002.
- The levels for both Pre-2002 and Post-2002 were similar among Henriksdal, Bergkvara and Öhn WWTPs.
- Pre-2002 and Post-2002 are used as an active ingredient in impregnation for textiles. The Gässlösa WWTP received wastewater from textile industries, which may be one of the reasons for the elevated concentrations of Pre-2002 and Post-2002 when compared to the other three WWTPs.
- The levels of the Pre-2002 and Post-2002 in sludge from WWTPs may therefore be related more to the types of industries, than the number of people served in the area.
- Only three out of five leachate samples show detectable levels of Pre-2002. No sample showed detectable levels of Post-2002.
- The EOF in sludge from Gässlösa WWTP showed a decreasing trend, which is similar to the results of the earlier report (Yeung et al., 2017).
- Similar levels of EOF were found for sludge from Bergkvara, Gässlösa and Öhn.
- A much higher level of EOF was found in the sludge sample from Henriksdal WWTP, in contrast to our previous screening study (Yeung et al., 2017) where sludge from Gässlösa WWTP was found to contain the highest EOF. The two studies uses different extraction methods; highest EOF for Gässlösa was found using a method optimized

for ionic PFAS while highest EOF for Henriksdal was found using a method optimized for side-chain fluorinated polymers.

- Higher levels of EOF were found in landfill leachate receiving hazardous waste compare to landfill leachate receiving domestic and non-hazardous waste.
- The old landfill site still leached out significant amount of EOF.
- Compared with the sludge samples, a relatively higher amount of measurable PFAS were detected in the landfill leachate particles contributing to between 14 to 30% of the EOF; in contrast, the side-chain fluorinated polymers (Pre-2002 and Post-2002) only contributed up to 0.03% of the EOF.
- The mass balance analysis show significant amounts and proportion of unidentified EOF in both sludge and leachate samples which might be polymeric or non-polar organofluorine.
- Several new PFAS were detected on the leachate particles but not in the sludge samples, which include FBSA, FHxSA and PFECHS.

Recommendations and future aspects

High amounts of Pre-2002 and Post-2002 relative to targeted PFAS were detected in sludge. Together with the results of current and previous screening studies, sludge might be an important sink for some PFAS in wastewater treatment plants. Although a decreasing trend of Pre-2002 was observed in Gässlösa WWTP, the levels of the Pre-2002 were still much higher than the sum of 83 PFAS in recent years (Yeung et al., 2017). An *in vitro* metabolic study (Chu and Letcher, 2014) on the Pre-2002 and Post-2002 using Wistar-Han rat liver microsomes showed the formation of two metabolites, FOSA and FBSA for Pre-2002 and Post-2002, respectively. No information is available on the transformation products and the rate of Pre-2002 and Post-2002 during the wastewater treatment processes. Degradation experiments should be conducted to investigate the rate of degradation as well as formed transformation products during the wastewater treatment processes. It is important to understand the mechanisms of the degradation of Pre-2002 and Post-2002 and the environmental consequences. Some volatile compounds might be formed during the transformation process of Pre-2002 and Post 2002, and they will form subsequent persistent PFASs. Given the concentrations found in present study, it is justified to continue measurements of Pre-2002 and Post-2002 together with the potential metabolites in future monitoring programmes. Side-chain fluorinated polymers have been used in a number of commercial and industrial applications. One of the commonly uses is surface treatment to provide water- and oil repellency. It is important to point out that Pre-2002 has been phased out since 2002. The occurrence and sources of Pre-2002 found in the present study is not clear. Further investigation on influent and sludge samples from various wastewater treatment plants may provide further information on the occurrence and levels of these substances in Sweden.

The low detection rates and levels of Pre-2002 and Post-2002 in landfill leachate do not necessarily indicate that landfills are not a source of these compounds. Given the sorption properties and that landfill leachate might have been recycled within the landfill site that these substances can either be sorbed to landfill particles or undergo transformation into other products. One important observation is that some novel PFAS such as FBSA, FHxSA and PFECHS were detected in the particles. As discussed above FBSA was found to be one of the transformation products of Post-2002, which might suggest that degradation of Post-2002 is taking place in the landfills. These novel PFAS (FBSA, methyl perfluorobutanesulfonamide (MeFBSA), FHxSA, methyl-perfluorohexanesulfonamide (MeFHxSA) and PFECHS) could

therefore be important for environmental assessments and should be included in monitoring programmes.

A significant proportion of EOF in the sludge samples remained unidentified, which is similar to the results of the previous screening study (Yeung et al., 2017). The EOF measured in current investigation represented those non-polar, long-chain or polymeric PFAS or some monomers breakdown from polymers, which is different from that of the previous study that contained neutral, polar, short to medium chain PFAS. OECD published a database with more than 4700 substances with CAS number related to PFAS; 15% of the 4700 substances belongs to polymeric or side-chain co-polymeric products. In the current study, only two of them were measured. It is therefore not surprising that the Scotchgard compounds (Pre-2002 and Post-2002) measured in current investigation only account for at most 6% of the EOF. Several studies have demonstrated the formation of perfluorinated carboxylates (PFCAs) or PFASs through the degradation of side-chain fluorinated co-polymers (Washington et al., 2015, Rankin et al., 2014, Washington et al., 2019). It is still challenging to measure fluorinated polymers or side-chain co-polymers in environmental samples (Keegan et al., 2015). Using the extraction method employed in this study to measure EOF in sludge together with active air sampling of potential degradation products (e.g., FTOH, FBSA, FHxSA, Fluorinated acrylates) in the wastewater treatment plant, may help improve the understanding on the occurrence and sources of fluorinated polymers or side-chain fluorinated polymers in the environment. Total oxidizable precursor (TOP) assay is an oxidative conversion method that can convert all PFCA and PFSA precursors as well as intermediates to persistent PFCAs. It is currently not clear if the method works on polymers, but an optimized method that proved efficient would help in the understanding of how much of the side-chain fluorinated polymers are present in different environmental samples.

References

- 3M. Company. (2000). Phase-Out Plan for POSF-Based Products. US. EPA Administrative Record AR226-0600.
- 3M. Company. USA. Material Safety Data Sheet Scotchgard Fabric Protector (Cat. No. 4101, 4106) 10/16/19: www.3M.com.
- Arvaniti, O.S., Stasinakis, A.S.,(2015). Review on the Occurrence, Fate and Removal of Perfluorinated Compounds During Wastewater Treatment. *Science of the Total Environment*, 524, 81–92.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. and van Leeuwen, S. P. (2011). Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management*, 7: 513-41.
- Chu, S., Letcher, R. J. (2014). In Vitro Metabolic Formation of Perfluoroalkyl Sulfonamides from Copolymer Surfactants of Pre- and Post-2002 Scotchgard Fabric Protector Products. *Environmental Science and Technology*, 48 (11), 6184–6191.
- Chu, S., Letcher, R.J. (2017). Side-chain Fluorinated Polymer Surfactants in Aquatic Sediment and Biosolid-augmented Agricultural Soil from the Great Lakes Basin of North America, *Science of the Total Environment*, 607-608: 262-70.
- DeWitt, J.C. (2015). Toxicological Effects of Perfluoroalkyl and Polyfluoroalkyl Substances, DOI 10.1007/978-3-319-15518-0.
- Fredriksson, F., Kärrman, A., Eriksson, U., Yeung, L.W.Y. (2019). Characterisation of Technical Mixtures Containing Side-chain Fluorinated Polymers. 39th International Symposium on halogenated Persistent Organic Pollutants, Oral Presentation (4A-PM1-05) Kyoto Japan, 20190928
- Giesy, J. P., Kannan, K., Jones, P. D. (2001). Global Biomonitoring of Perfluorinated Organics, *Scientific World Journal*, 1: 627-9.
- Haglund, P. (2019). Miljöövervakning av Utgående Vatten och Slam från Svenska Avloppsreningsverk: Resultat från År 2016-2017 och en Sammanfattning av Slamresultaten för Åren 2004-2017. Report submitted to Naturvårdsverket (219-13-004). <http://naturvardsverket.diva-portal.org/smash/get/diva2:1343079/FULLTEXT01.pdf>
- KEMI, (2015). Förekomst och Användning av Höglfluorerade Ämnen och Alternativ (The Presence and Use of Highly Fluorinated Compounds and Alternatives). Report 6/15. <https://www.kemi.se/global/rapporter/2015/rapport-6-15-forekomst-och-anvandning-avhogfluorerade-amnen-och-alternativ.pdf>.
- Letcher, R. J., Chu, S., and Smyth, S. A. (2020). Side-Chain Fluorinated Polymer Surfactants in Biosolids from Wastewater Treatment Plants. *Journal of Hazardous Materials*, 122044.
- Liu, J., Mejia Avendano, S. (2013). Microbial Degradation of Polyfluoroalkyl Chemicals in the Environment: A Review. *Environmental International*, 61: 98-114.
- Lindstrom, A.B., Strynar, M.J., Libelo, E.L., (2011). Polyfluorinated Compounds: Past, Present, and Future. *Environmental Science and Technology*, 45, 7954–7961
- Organisation for Economic Co-operation and Development., (2018). Environment, Health and Safety Publications Series on Risk Management No.39. ENV/JM/MONO(2018)7.
- Rankin, K., Lee, H., Tseng, P. J., & Mabury, S. A. (2014). Investigating the Biodegradability of a Fluorotelomer-based Acrylate Polymer in a Soil–Plant Microcosm by Indirect and Direct Analysis. *Environmental Science and Technology*, 48(21), 12783-12790.

- Rankin, K., & Mabury, S. A. (2015). Matrix Normalized MALDI-TOF Quantification of a Fluorotelomer-based Acrylate Polymer. *Environmental Science and Technology*, 49(10), 6093-6101.
- Renner, R., (2006). The Long and the Short of Perfluorinated Replacements. *Environmental Science and Technology*, 40, 12–13.
- Washington, J.W., Jenkins, T.M., Rankin, K., & Naile, J.E. (2015). Decades-scale Degradation of Commercial, Side-chain, Fluorotelomer-based Polymers in Soils and Water. *Environmental Science and Technology*, 49(2), 915-923.
- Washington, J.W., Rankin, K., Libelo, E.L., Lynch, D. G., & Cyterski, M. (2019). Determining Global Background Soil PFAS Loads and the Fluorotelomer-based Polymer Degradation Rates That Can Account for These Loads. *Science of the Total Environment*, 651, 2444-2449.
- Yeung, L.W.Y., Robinson, S.J., Koschorreck, J. Mabury, S.A. (2013). Part II. A Temporal Study of PFOS and Its Precursors in Human Plasma from Two German Cities in 1982-2009, *Environmental Science and Technology*, 47: 3875-82.
- Yeung, L.W.Y., Eriksson, U., Kärrman A., (2016). Pilotstudie Avseende Oidentifierade Poly- och Perfluorerade Alkylämnen i Slam och Avloppsvatten från Reningsverk i Sverige. Report submitted to Naturvårdsverket. <http://naturvardsverket.diva-portal.org/smash/get/diva2:1112388/FULLTEXT01.pdf>
- Yeung, L.W.Y., Eriksson, U., and Kärrman, A., (2017). Tidstrend av Oidentifierade Poly- och Perfluorerade Alkylämnen i Slam från Reningsverk i Sverige. Report submitted to Naturvårdsverket. <http://naturvardsverket.diva-portal.org/smash/get/diva2:1138488/FULLTEXT01.pdf>

Supplemental Information

Table S 1. List of analytes in their specific PFAS class, MRM transitions, cone voltage and collision energy used for qualification and quantification of PFAS.

<i>Analyte</i>	<i>Precursor/ product ions quantification (m/z)</i>	<i>Cone (V)</i>	<i>Col (eV)</i>	<i>Precursor/ product ions qualification (m/z)</i>	<i>Cone (V)</i>	<i>Col (eV)</i>	<i>Corresponding Internal Standard</i>
Precursors of perfluoroalkyl sulfonate (PFSA)							
FBSA	297.90/77.92	20	20	297.90/118.94	20	15	¹³ C M ₄ PFBA
Me-FBSA	311.93/111.93	14	20	311.97/218.95	14	16	¹³ C M ₄ PFBA
FHxSA	397.90/77.92	30	26	397.90/168.94	30	28	¹⁸ O ₂ PFHxS
Me-FHxSA	411.97/168.93	24	24	411.97/318.96	24	20	¹⁸ O ₂ PFHxS
FOSA	497.90/78.00	82	30	497.90/168.96	82	28	¹³ C M ₈ FOSA
MeFOSA	512/169	27	45				² H ₅ MeFOSA
EtFOSA	526/169	27	45				² H ₅ MeFOSA
MeFOSE	616/59	27	45	556.03/121.99	42	34	² H ₅ MeFOSE
EtFOSE	630/59	27	45	570.1/135.98	42	34	² H ₅ MeFOSE
FOSAA	555.84/218.90	60	30	55.8/418.85	60	24	² H ₅ EtFOSAA

MeFOSAA	569.78/418.87	16	18	569.78/482.76	16	14	² H ₅ EtFOSAA
EtFOSAA	583.84/418.84	18	20	583.84/482.8	18	16	² H ₅ EtFOSAA
<hr/>							
SAmPAP	649.8/96.9	2	26	649.8/168.9	2	36	¹³ C M ₂ 8:2monoPAP
diSAmPAP	1202.6/525.9	92	46	1202.6/168.9	92	64	¹³ C M ₄ 8:2 diPAP
Perfluoroalkyl sulfonates (PFSAs)							
<hr/>							
PFBS	298.9/98.9	20	26	298.9/79.96	20	26	¹³ C M ₃ PFBS
PFPeS	348.90/98.96	20	26	348.90/79.96	20	30	¹⁸ O ₂ PFH _x S
L-PFH _x S	398.9/98.9	20	30	398.9/79.96	20	34	¹⁸ O ₂ PFH _x S
PFHpS	448.97/98.90	20	30	448.97/79.96	20	35	¹³ C M ₄ PFOS
L-PFOS	498.97/98.96	20	38	498.97/79.96 498.97/169.03	20	44 34	¹³ C M ₄ PFOS
PFNS	548.90/98.96	20	38	548.90.97/79.96	20	44	¹³ C M ₄ PFOS
PFDS	598.97/98.9	20	42	598.97/79.96	20	58	¹³ C M ₄ PFOS
PFD _o DS	698.97/98.90	20	40	698.97/79.96	20	45	¹³ C M ₄ PFOS
Precursors of perfluorinated carboxylate (PFCA)							
<hr/>							
4:2 FTSA	327/307	20	20	327/81	20	28	¹³ C M ₂ 6:2 FTSA

6:2 FTSA	427/407	20	20	427/81	20	28	¹³ C M ₂ 6:2 FTSA
8:2 FTSA	527/507	20	20	527/80	20	28	¹³ C M ₂ 8:2 FTSA
<hr/>							
3:3 FTCA	240.9/116.98	10	30	240.90/176.98 240.90/59.07	10 10	8 14	¹³ C M ₂ 6:2 FTUCA
5:3 FTCA	340.9/236.97	10	16	340.9/216.93	10	22	¹³ C M ₂ 6:2 FTUCA
7:3 FTCA	356.9/292.91	10	18	356.9/242.95	10	36	¹³ C M ₂ 8:2 FTUCA
<hr/>							
6:2 FTUCA	440.9/336.89	12	14	440.9/336.89	12	20	¹³ C M ₂ 6:2 FTUCA
8:2 FTUCA	456.9/392.84	10	18	456.9/342.88	10	38	¹³ C M ₂ 8:2 FTUCA
10:2 FTUCA	556.84/492.82	8	16	556.84/492.82	8	38	¹³ C M ₂ 10:2 FTUCA
<hr/>							
6:2 monoPAP	442.9/96.95	10	18	442.90/422.89	10	12	³ C M ₄ 6:2monoPAP
8:2 monoPAP	542.9/97	22	14	542.90/522.90	22	14	¹³ C M ₄ 8:2monoPAP
10:2 monoPAP	642.97/97.00	24	28	649.78/525.83	24	22	¹³ C M ₄ 8:2monoPAP
<hr/>							
4:2 diPAP	588.9/97	64	28	588.9/342.91	64	18	¹³ C M ₄ 6:2 diPAP
4:2/6:2 diPAPs	688.9/97	64	28	688.9/342.91 688.9/442.91	64	18	¹³ C M ₄ 6:2 diPAP
2:2/8:2 diPAPs	688.9/97	64	28	688.9/242.91 688.9/542.91	64	18	¹³ C M ₄ 6:2 diPAP

6:2 diPAP	788.9/97	64	28	788.9/442.91	64	18	¹³ C M ₄ 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 M ₄ 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 M ₄ 6:2 diPAP
8:2 diPAP	988.78/96.94	68	34	988.78/542.81	68	26	¹³ C M ₄ 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 M ₄ 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 M ₄ 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 M ₄ 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 M ₄ 8:2 diPAP
8:2/10:2 diPAP	1088.78/96.94	68	34	1088.78/542.81 1088.78/642.81	68	26	¹³ C M ₄ 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 M ₄ 8:2 diPAP
10:2 diPAP	1188.78/96.94	68	34	1188.78/642.81	68	26	¹³ C M ₄ 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 M ₄ 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 M ₄ 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 M ₄ 8:2 diPAP
8:2/14:2 diPAP	1288.78/96.94	68	34	1288.78/542.81 1288.78/842.81	68	26	¹³ C M ₄ 8:2 diPAP
12:2 diPAP	1388.78/96.94	68	34	1388.78/742.81	68	26	¹³ C M ₄ 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 M ₄ 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 M ₄ 8:2 diPAP

Perfluorinated carboxylates (PFCAs)

PFBA	212.97/169	20	11	-	-	-	¹³ C M ₄ PFBA
PFPeA	262.97/219	20	8	-	-	-	¹³ C M ₃ PFPeA
PFHxA	312.97/269	20	9	312.97/118.95	20	26	¹³ C M ₂ PFHxA
PFHpA	362.97/319	20	10	362.97/168.97	20	16	¹³ C M ₂ PFHpA
L-PFOA	412.97/369	20	10	412.97/168.97	20	18	¹³ C M ₄ PFOA
PFNA	462.99/419	20	12	462.99/219	20	18	¹³ C M ₅ PFNA
PFDA	512.97/469	20	11	512.97/219	20	18	¹³ C M ₂ PFDA
PFUnDA	562.97/519	20	12	562.97/268.99	20	18	¹³ C M ₂ PFUnDA
PFDoDA	612.97/569	34	14	612.97/168.96	40	22	¹³ C M ₂ PFDoDA

PFTrDA	662.9/619	20	14	662.9/168.96	20	26	¹³ C M ₂ PFD _o DA
PFTDA	712.9/669	20	14	712.9/168.97	20	28	¹³ C M ₂ PFTDA
PFH _x DA	812.9/769	30	15	812.9/168.96	42	32	¹³ C M ₂ PFH _x DA
PFOcDA	912.9/869	36	15	912.9/168.96	36	36	¹³ C M ₂ PFH _x DA

Perfluorinated phosphonates (PFPA)s

PFH _x PA	398.97/79	62	26	-	-	-	¹³ C M ₄ PFOA
PFOPA	499/79	62	30	-	-	-	¹³ C M ₄ PFOA
PFDPa	599.03/79	62	30	-	-	-	¹³ C M ₅ PFNA
PFD _o PA	699/79	62	30	-	-	-	¹³ C M ₄ PFOA
PFTePA	799/79	62	30	-	-	-	¹³ C M ₄ PFOA
PFH _x DA	899/79	62	30	-	-	-	¹³ C M ₄ PFOA

Perfluorinated phosphinates (PFPIAs)

Precursors of PFAS

6:6 PFPIA	701/401	62	28	-	-	-	¹³ C M ₂ PFD _o DA
6:8 PFPIA	781/401	24	28	801/501	24	28	¹³ C M ₂ PFTDA
8:8 PFPIA	901/501	24	28	-	-	-	¹³ C M ₂ PFTDA

6:10 PFPiA	1001/401	24	28	1001/601	24	28	¹³ C M ₂ PFD ₀ DA
8:10 PFPiA	1101/501	24	28	1101/601	24	28	¹³ C M ₂ PFD ₀ DA
6:12 PFPiA	1101/401	24	28	1101/701	24	28	¹³ C M ₂ PFD ₀ DA
10:10 PFPiA	1201/401	24	28	-	-	-	¹³ C M ₂ PFD ₀ DA
8:12 PFPiA	1201/601	24	28	1201/701	24	28	¹³ C M ₂ PFD ₀ DA
6:14 PFPiA	1201/401	24	28	1201/801	24	28	¹³ C M ₂ PFD ₀ DA
10:12 PFPiA	1301/601	24	28	1301/701	24	28	¹³ C M ₂ PFD ₀ DA
8:14 PFPiA	1301/501	24	28	1301/801	24	28	¹³ C M ₂ PFD ₀ DA
12:12 PFPiA	1401/701	24	28	-	-	-	¹³ C M ₂ PFD ₀ DA
10:14 PFPiA	1401/601	24	28	1001/801	24	28	¹³ C M ₂ PFD ₀ DA
14:14 PFPiA	1501/701	24	28	-	-	-	¹³ C M ₂ PFD ₀ DA

Novel PFASs

11CIPF3OUdS	630.90/459.98	58	24	630.90/83.03 639.90/98.95	58 58	24 26	¹³ C M ₄ PFOS
9CIPF3ONS	530.90/350.98	58	24	530.90/83.03 530.90/98.95	58 58	24 26	¹³ C M ₄ PFOS
T-PFECHS	460.84/380.94	2	24	460.84/98.88 460.84/118.96	2 2	26 38	¹³ C M ₄ PFOA

Side-chain fluorinated polymers

Pre-2002	1315.1/525.9	23	31	1315.1/744	8	18	-
Post-2002	1634.2/311.90	10	41	1634.2/219	13	26	

Table S 2. Individual PFAS concentration in (ng/g d.w.) in eleven sludge samples from Gässlösa wastewater treatment plant collected between 2004 and 2016.

Sludge											
	Gässlösa										
	2004	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
PFHxA	0.02		0.01	0.01		0.01			0.02		0.01
L-PFOA	0.03					0.02					
PFUnDA	0.01		0.02			0.01					
PFHxDA	0.02	0.07	0.01	0.01	0.08	0.01	0.05	0.05	0.06	0.06	0.05
PFBS	0.008					0.01		0.01		0.02	0.03
L-PFHxS	0.10	0.04	0.08	0.08	0.06	0.07	0.02	0.05	0.06	0.04	0.03
FOSA	0.09	1.7	0.03	0.03	0.64	0.02	0.53	0.13	0.48	0.56	0.36
L-PFOS	3.6	3.1	5.8	3.0	2.9	5.1	2.2	1.6	1.8	2.3	1.3
PFDS	1.4	0.13	0.52		0.06						
6:2 FTSA	0.67		0.36	0.13					1.1	0.79	0.05
8:2FTSA	0.01										
6:6PFPIA	33	0.60	0.23	0.26	0.21	0.27	0.18	0.24	0.09	0.18	0.11
6:8 PFPIA	158	1.9	1.4	1.1	0.61	0.69		0.38		0.50	
8:8 PFPIA	42		1.2	0.65							
T-PFECHS				0.005		0.007					

Note: Only detectable concentrations are shown in the table. These concentrations were only used for a mass balance analysis. The levels do not represent the actual concentration in the sample, because the method used was not optimized for these PFAS, it only represent the known fluorine in the extractable organofluorine.

Table S 3. Individual PFAS concentration in (ng/g d.w.) in four sludge samples from four different wastewater treatment plants in Sweden (Gässlösa, Öhn, Bergkvara and Henriksdal) collected in 2015.

Sludge				
	2015			
	Gässlösa	Öhn	Bergkvara	Henriksdal
PFHxA		0.007	0.01	0.02
L-PFOA		0.03		
PFHxDA	0.06		0.06	0.10
PFBS	0.02			
L-PFHxS	0.04	0.03	0.05	0.02
FOSA	0.56	0.04	0.09	0.50
L-PFOS	2.3	1.4	0.72	0.85
6:2 FTSA	0.79	0.07		0.15
6:6 PFPiA	0.18			
6:8 PFPiA	0.50			

Note: Only detectable concentrations are shown in the table. These concentrations were only used for a mass balance analysis. The levels do not represent the actual concentration in the sample, because the method used was not optimized for these PFASs, it only represent the known fluorine in the extractable organofluorine.

Table S 4. Individual PFAS concentration in (ng/g d.w.) in five leachate samples from three different landfill sites in Sweden (Atleverket, Hässleholm Kretsloppscenter and Flishult) collected in 2017.

Leachate					
	Atleverket	Hässleholm Kretsloppscenter			Flishult
	<i>Active non-hazardous landfill</i>	<i>Closed non-hazardous landfill</i>	<i>Active non-hazardous landfill</i>	<i>Active hazardous landfill</i>	<i>Active non-hazardous landfill</i>
FBSA		4.6	3.4	10	
FHxSA	0.77	6.9	5.8	80	2.5
PFHxA				0.29	0.17
PFHpA				0.21	0.06
PFOA				0.26	0.19
PFHxDA	0.03	0.18	0.18	1.3	1.1
PFBS	1.4	22	13	43	47
PFPeS	0.53	4.9	4.7	61	0.36
L-PFHxS	8.0	42	55	944	7.5
PFHpS	2.6	7.7	5.7	97	9.3
FOSA	0.82	4.0	4.0	5.0	1.6
L-PFOS	96	170	131	725	3270
PFNS	0.10				
6:6PFPiA	0.10				
T-PFECHS	1.8	3.9	2.4	34	1.3

Note: Only detectable concentrations are shown in the table. These concentrations were only used for a mass balance analysis. The levels do not represent the actual concentration in the sample, because the method used was not optimized for these PFASs, it only represent the known fluorine in the extractable organofluorine.