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Department of Applied Environmental Science

Stockholm University

Waste Incineration as a Possible Source of Perfluoroalkyl Acids to the Environment – Method Development and Screening

Oskar Sandblom

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Stockholm University

106 91 Stockholm

Abstract

Atmospheric deposition has been suggested to be a major input pathway of perfluoroalkyl acids (PFAAs) to the Baltic Sea catchment area and to the Baltic Sea itself. However, the sources of PFAAs to the atmosphere are not well characterized. In this study we investigated if waste incineration plants in Sweden could be a source of PFAAs to the atmosphere and to the environment in general. Samples of the end products from waste incineration were collected at four different incineration plants. The plants differed in size and technical advancement and were considered to be representative for the majority of waste incineration plants in Sweden. The collected samples were slag from the furnaces, fly ash from the flue gases, "bambergkaka" (a mix of fly ash and sludge from wastewater treatment) as well as condensate and wastewater from the cleaning process of the flue gases. Two methods were developed, one for analysis of PFAAs in solid samples and one for water samples. Method validation showed good performance for both methods in terms of precision and accuracy, despite low recoveries obtained for the method for solid samples. The results from sample analysis revealed that PFAAs were present in all solid samples at concentrations in the low to sub ng/g range and in all but one condensate and wastewater samples at concentrations in the low to sub ng/L range. The quantified concentrations were used to estimate the potential annual discharges of PFAAs from waste incineration plants to the environment. Emission scenarios via landfills, via wastewater treatment plants and to the atmosphere were considered. The main conclusion of this study is that waste incineration in Sweden is not a significant source of PFAAs to the atmosphere or to the environment in general.

Table of contents

1. Introduction

1.1. Per- and polyfluoroalkyl substances

Per- and polyfluoroalkyl substances (PFASs) are a diverse group of chemicals that have been produced for over 60 years (Buck et al., 2011). PFASs have a unique set of chemical properties, as they are both hydrophobic and oleophobic. These properties are very useful in industrial applications where they are widely used, e.g., as processing additives in fluoropolymer production, as well as in consumer products such as aqueous film-forming fire-fighting foams or in water- and stain-repellent surface treatments of textiles, carpets or paper products (Kissa 2002).

Perfluoroalkyl acids (PFAAs) are a sub-group of PFASs that include both perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), which are the two most studied PFASs to date. Historically, the production volume of PFOS has been considerably larger than that of PFOA. For example, in 2000 the production of PFOS-based chemicals was estimated to 3500 tons compared to 500 tons for PFOA (Prevdoruos et al., 2006). However, between 2000 and 2002 the major manufacturer of PFOS, the 3M Company, phased out their production of PFOS and related chemicals. This resulted in a global drop in production volume of PFOS in 2003 (3M Company, 2003). PFOS continued to be produced in southeast Asia at unknown quantities (Paul et al., 2009) and from 2003 – 2008 there was large-scale production in China with extensive use of perfluorooctane sulfonyl fluoride (POSF)-based products as surface treatment in the textile industry. The reported production volume in China before 2004 was less than 50 tons per year; this expanded to about 250 tons per year by 2006 and decreased to 100 tons per year in 2008. Recently Chinese manufacturers have made an effort to develop alternative substances to replace PFOS and related chemicals (Wang et al., 2014).

1.2.Bioaccumulation and toxicology of PFAAs

Long-chain perfluoroalkane sulfonic acids (PFSAs, e.g. PFOS) and perfluoroalkyl carboxylic acids (PFCAs, e.g. PFOA) are known to bioaccumulate (Conder et al., 2008). Temporal trend studies of PFAA concentrations in Baltic Sea herring (1980−2010) and sea eagle eggs (1966−2010) showed an increase in concentrations of PFOS and long-chain PFCAs (Bignert et al. 2012). PFAAs may also trigger adverse effects in wildlife and humans (Lau et al., 2007). Studies on non-human primates and rats with repeated dosing experiments of PFOS have shown effects such as reduced bodyweight, reduced cholesterol and an increase in liver size (Goldenthal et al., 1978, Seacat et al., 2002, Seacat et al., 2003). There are also studies that have shown that exposure to PFAAs during prenatal stages can cause developmental toxicity in rats and mice (Lau et al., 2004).

1.3. Regulations and industrial action

The potential impacts on wildlife, environment and human health have led to actions against emissions of PFAAs around the globe. In 2006, the U.S. Environmental Protection Agency (USEPA) initiated the PFOA Stewardship Program. In this initiative, eight major companies committed to reduce the emissions and the product contents of PFOA and other related chemicals globally by 95% no later than year 2010. Furthermore, this program works toward eliminating the emissions and product content of these chemicals completely by 2015 (U.S.

EPA, 2006). In a related effort, the Canadian environmental and health authorities together with five companies agreed to restrict the use of PFCAs in consumer products (Environment Canada 2010). At the same time, the European Parliament issued a Marketing and Use Directive restricting the use of PFOS in the European Union (European Parliament 2006). All these measures together may eventually lead to decreasing levels of long-chain PFAAs in the environment. However, due to continued production and emissions in South-East Asia and due to the extraordinary persistence of PFAAs, it may take a long time for concentrations to decrease significantly, especially in environmental compartments where PFAAs accumulate.

1.4. PFAAs in the atmospheric environment

In recent years, the influx and fate of PFASs in the atmosphere has been recognized as an emerging issue in the field of environmental chemistry of PFAAs (Ahrens et al., 2011). Furthermore, a mass balance study of PFAAs in the Baltic Sea suggested that atmospheric input is the dominant current pathway for PFAAs to the Baltic Sea catchment area and to the Baltic Sea itself (Filipovic et al., 2013). However, there is a lack of understanding of the atmospheric sources of PFAAs measured in deposition samples. One such source are volatile or semi-volatile PFASs that can act as precursors to PFAAs, i.e. that can be transformed to PFAAs through atmospheric oxidation processes. Such precursors are, e.g., fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs) (Ellis et al., 2004; Prevedouros et al., 2006). Another source of atmospheric PFAAs could be their release on airborne particles or aerosols from high-temperature processes. As an example, Ellis and co-workers have shown that PFAAs can be formed by thermolysis of fluoropolymers (Ellis et al., 2001). On the other hand, two studies performed under laboratory conditions have shown that textiles treated with fluorotelomer-based polymers do not form any detectable amount of PFCAs when incinerated under conditions typical for waste incineration plants (Taylor et al., 2014; Yamada et al., 2005). It remains unclear if incineration of consumer products can be a significant source of PFAAs to the (atmospheric) environment.

2. Objective of the study

The main objective of this study was to investigate if waste incineration plants in Sweden are a significant source of PFAAs to the atmosphere and to the environment in general. An important sub-goal was the development, optimization and validation of analytical methods for quantification of PFAAs in the different sample matrixes collected from the incineration plants.

3. Materials and methods

3.1. General description of the cleaning process in the waste incineration plants

The waste incineration plants participating in this study span from basic to very advanced. However, even though there were quite big differences in size, capacity and technical equipment between the plants, they generally operated in the same way to incinerate the waste and clean the flue gases. The flow chart in Figure 1 gives a schematic overview of how the incineration plants are generally built up.

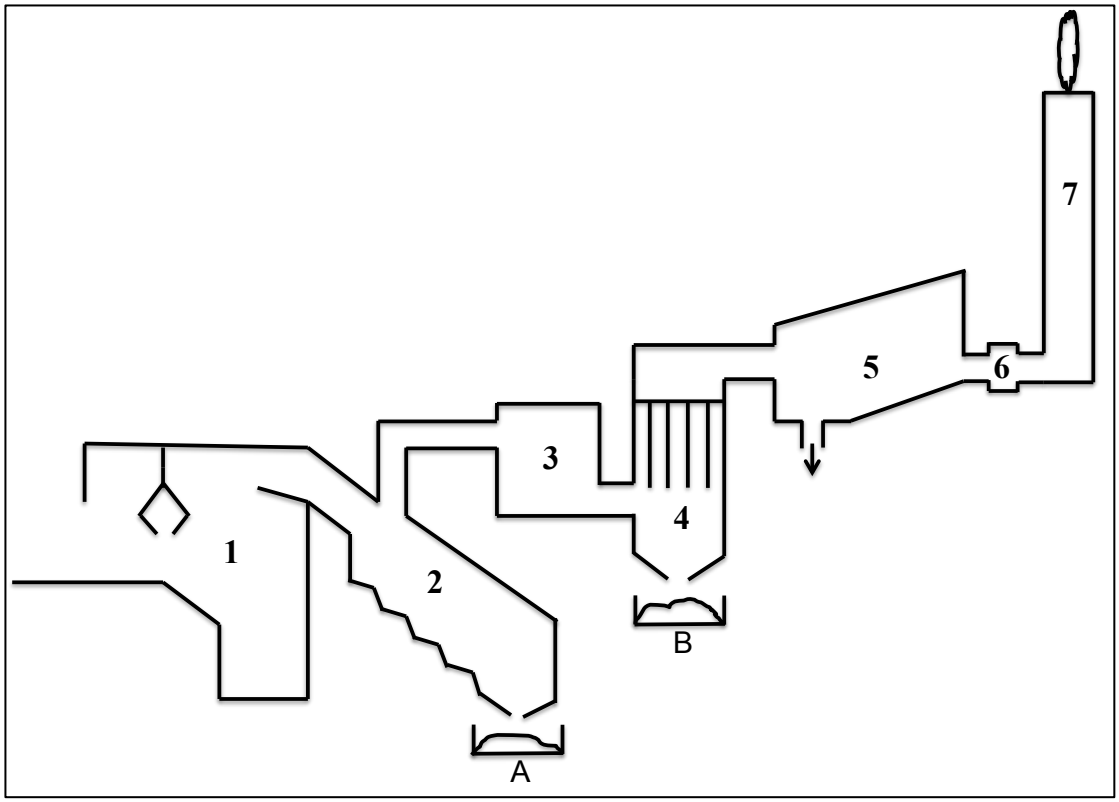

Figure 1 Flowchart representing the general setup of a waste incineration plant in Sweden. 1: Waste input room 2: The tilted traveling grate furnace 3: Mixing chamber where quick lime and active carbon is added to the flue gases 4: Sleeve filter and/or electrochemical filter 5: Wet scrubber with condenser 6: Fan 7: smoke stack A: Bunker for the collection of the slag B: bunker for the collection of the fly ash

The furnace used is usually a tilted traveling grate furnace in which the waste is incinerated at >850°C as it moves down the grate. Ammoniac is added in the furnace to reduce nitrogen oxides in the flu-gases. The burnt waste (slag) is cooled and transported to landfill or it can be used as a supplement to gravel in road construction.

The flu-gas is cleaned in several steps. In the first step quicklime and active carbon is added to react with, e.g., hydrogen chloride and sulfur dioxide. The products formed in this step and the remaining fly ash are separated using a sleeve filter and/or an electrochemical filter. The separated fly ash can either be transported directly to landfill or it can be mixed with sludge from the water treatment (if water treatment is done on site) to a cement-like substance called "bambergkaka", and then transported to landfill.

In the second step the flu-gas is led through a two-step wet scrubber, consisting of an acidic and a neutral step. In the scrubber inlet the temperature of the flu-gas is lowered to the point where saturation occurs with water. The water is then pumped through the acidic step, where, e.g., hydrogen chloride, ammoniac, and mercury are separated, and then through the neutral step, where, e.g., sulfur dioxides are separated through addition of lye. The water is then guided to a condenser to separate water vapor from the flu-gas. The remaining flu-gas is then guided to the smoke stack by fans. The flu-gas exhaust is monitored for emissions of nitrogen oxides, carbon monoxides, hydrogen chloride, sulfur dioxide, methane, water vapor, and particles.

The samples for this study were collected from four waste incineration plants in Sweden. The capacity of the four plants range from 20 000 - 750 000 tons of waste per year. All four plants

are operating in agreement with the laws and regulations set by the EU and the Swedish government (European Parliament, directive 2000/76/EG; Miljöbalken, 1998:808; Avfalsförordning, 2011:927). The waste incineration plants participating in the study wished to remain anonymous. Therefore, the four plants will hereafter be named Plant A, Plant B, Plant C, and Plant D. In Table 1 the plant capacities and cleaning methods are listed.

Table 1. Capacity and cleaning process for the four plants investigated in this study

Plant name	Capacity (t/yr)	Flu-gas cleaning	Wet scrubber	Water treatment
Plant A	20 000	✓	✗	✗
Plant B	130 000	✓	✓	✓
Plant C	550 000	✓	✓	✓
Plant D	750 000	✓	✓	✓

3.2. Sample matrices

The sample collection from Plants A, B, and C was done on site by a worker from the plant and by myself. Plant D had an internal sampling campaign planned that coincided with the present study. The samples were collected in September 2013 (plant A), October 2013 (Plant B and C) and December 2013 (plant D). All samples were collected in one-liter polypropylene containers that were pre-cleaned by rinsing with methanol. The samples collected from the different plants and analyzed in this study are listed in Table 2. The samples collected were grab samples and should therefore only be considered as representative of the day or even the hour that the samples were collected. Gaseous samples from the exhaust fumes were not available for this study.

Table 2. Number and type of samples collected at the different plants. The collected samples were grab samples representing a single point in time.

Plant name	Slag[1]	Fly ash[2]	Bambergkaka[3]	Condensate[4]	Wastewater[5]
Plant A	1	1	-	-	-
Plant B	-	1	1	1	-
Plant C	-	1	1	2[c]	-
Plant D	3[a]	2[b]	-	1	1
Total	4	5	2	4	1

[1] The burnt material from the incinerator
[2] Airborne particles separated from the smoke gases
[3] Cement-like product consisting of sludge from the water treatment and fly ash
[4] Water collected in and after the wet scrubbing step
[5] Water collected from the storm drain system
[a] The samples were collected from three different furnaces
[b] The samples were collected from two different flu-gas channels from different furnaces
[c] Two samples were collected, one from within the wet scrubbing step (condensate (B)) and one from the cleaned condensate (condensate (A)).

3.3. Chemicals and reagents

All native and isotope-labeled standard compounds were purchased from Wellington Laboratories (Guelph, ON, Canada) in 2 µg/mL solution mixtures. The analytes that were

targeted in this study were perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonic acid (PFOS). $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS and $^{13}C_4$-PFOS were used as isotope-labeled surrogate internal standards (IS). The IS used for spiking the samples were in a methanol (MeOH) solution at a concentration of 10 pg/µL. $^{13}C_8$-PFOA and $^{13}C_8$-PFOS were used as volumetric recovery standards (RIS) when calculating the method recovery of the internal standards. The RIS were in a MeOH solution at a concentration of 20 pg/µL. The following reagents and solvents were used: 1-methyl piperidine (Merck Eurolab, Stockholm, Sweden), ammonium hydroxide solution (Fluka, Buchs, Switzerland), formic acid (Fisher Scientific GTF, Gothenburg, Sweden), ammonium acetate (Merck, Darmstadt, Germany), MeOH LiChrosolv grade (Merck), acetonitrile LiChrosolv grade (Merck) and Milli-Q water (produced in-house). All reagents and solvents were purchased with the highest purity available and used as received.

3.4. Analytical methods

3.4.1. Method development for solid samples

In this study three different methods were tested for analysis of PFAAs in slag, fly ash, and bambergkaka. The methods are summarized below.

Method S1. Extraction using sonication in MeOH and filtration through micro centrifuge filters (2 µm) for extract cleanup.

Method S2. Extraction using sonication in MeOH and solid-phase extraction cleanup using an OASIS WAX SPE column (6 cc, 150 mg sorbent, 30 µm particles; Waters, Milford, USA).

Method S3. Soxhlet extraction with MeOH and SPE cleanup using an OASIS WAX SPE column.

Method S2 showed the best overall performance and was chosen for a complete validation and for analysis of the samples. It is described in detail below. For a complete description of the other two tested methods see Appendix A1.

Method S2
The wet sample was dried in an oven at 100 ºC until constant weight was obtained (typically 12 h overnight). The water content was determined gravimetrically. On the day before extraction, 1 g of the homogenized, dried sample was weighed into a 13 mL polypropylene (PP) test tube and spiked with 100 µL of the IS-solution to obtain an IS-concentration of 1 ng/g sample. This was done on the day before extraction to ensure equilibration of the IS with the sample matrix. On the day of extraction, a volume of 5 mL of MeOH was added and the sample was subsequently vortex mixed for 30 s. The sample was ultrasonicated for 15 minutes and then vortex mixed again. Then the sample was centrifuged for 5 min at 3000 rpm. The supernatant was transferred into a new 13 mL PP-tube. The extraction procedure was repeated with 5 mL MeOH and the combined extracts were concentrated to 1 mL using nitrogen gas. The concentrated extract was diluted with 9 mL of Milli-Q water and vortex mixed thoroughly.

The extract cleanup method was based on a weak anion exchange (WAX) solid phase extraction methodology previously developed and described in detail (Chu and Letcher, 2008). An OASIS WAX SPE column was washed and conditioned with 3 mL of MeOH and 3 mL Milli-Q water, respectively. The sample extract was ultrasonicated for 5 min before it was loaded onto the SPE column. The column was then washed with 1 mL 2% formic acid in Milli-Q water and then with 2 mL of Milli-Q water (discarded). The column was dried under vacuum. Two fractions were eluted. Fraction 1 (containing neutral compounds) was eluted with 2 mL MeOH and saved, but not analyzed within the present study. Fraction 2 (containing the PFAA target analytes) was eluted with 2 mL 1% NH_4OH in MeOH. Fraction 2 was evaporated to dryness and reconstituted in 100 µL of MeOH and 150 µL of 4 mM NH_4OAc in water. The final extract was vortex mixed and ultrasonicated for 5 minutes, transferred to a PP auto sampler vial for instrumental analysis and spiked with 50 µL of RIS-solution. A series of procedural blank experiments were performed and analyzed along with each batch of samples.

3.4.2. Method development for water samples

Two different methods were tested for analysis of PFAAs in wastewater and condensate. The methods are summarized below.

Method W1. Extraction and cleanup using a CUQAX 256 SPE column (C8 + quaternary amine – 500 mg sorbent, 6 mL; UCT, Bristol, USA).

Method W2. Extraction and cleanup using an OASIS WAX SPE column.

Method W2 showed the best overall performance and was chosen for a complete validation and for analysis of the samples. It is described in detail below. For a complete description of method W1 see Appendix A2.

Method W2
On the day before extraction 50 mL of the sample were weighed into a 50 mL PP-test tube and spiked with 100 µL of the IS-solution to obtain an IS-concentration of 20 ng/L sample. On the day of extraction, an OASIS WAX SPE column was washed and conditioned with 3 mL of MeOH and 3 mL milli-Q water, respectively. The sample was ultrasonicated for 5 min before it was loaded onto the SPE column at a speed of approximately 1 mL/min. The washing and elution procedure of the SPE column as well as the preparation of the final extract were identical to the procedure described for method S2 above. A series of procedural blank experiments were performed and analyzed along with each batch of samples.

3.4.3. Method validation experiments

Procedural blank experiments were performed in exactly the same way as sample analyses but without any sample matrix, i.e. the IS were spiked directly on the SPE-column. Procedural blanks were extracted alongside all the sample batches during method development, method validation and sample analysis. The procedural blanks were also used to determine the method detection limits (MDLs).

The MDL was defined for each method and compound based on the average blank contamination plus three times the standard deviation of the blanks. PFDA, PFUnDA and

PFDoDA did not display a procedural blank contamination. For these PFAAs the MDL was set at a signal to noise ratio of 3 in the sample chromatogram.

The recoveries of the PFAAs in the analytical methods were determined using spiked IS (see discussion in section 4.1.3.). The spike concentrations of the IS were 1 ng/g in the solid samples and 20 ng/L in the water samples. The recoveries of the IS were calculated relative to the RIS. Recovery experiments were performed both for procedural blanks and for samples from precision testing and from accuracy testing (see paragraphs below).

Method precision was tested by triplicate sample analysis of a sample of fly ash and slag (method S2) and a condensate sample (method W2). Precision is expressed as the relative standard deviation of the quantified PFAA concentrations in the triplicate analysis.

Accuracy was tested using controlled spike and extraction experiments with a fly ash sample and a condensate sample. Nine aliquots of the fly ash sample (1 g each) and of the condensate sample (0.05 L each) were prepared. The aliquots were spiked one day prior to extraction with three different concentrations of PFAA standards, each concentration in triplicate. For the fly ash sample the spike concentrations were 0.1 ng/g, 0.6 ng/g and 3.0 ng/g, respectively, and for the condensate the spike concentrations were 2.0 ng/L, 12 ng/L and 60 ng/L, respectively. The samples were extracted and quantified together with all other samples using the method S2 and W2, respectively. From the concentrations quantified in the spiked samples, the quantified levels in the corresponding unspiked samples (PFAA levels present in the samples plus blank contribution) were subtracted. Accuracy was then expressed as the (corrected) quantified concentration in the fortified sample relative to the target (spike) concentration. Accuracy was only determined in cases where the spike concentration of the PFAA was at least as high as the quantified concentration in the corresponding unspiked sample.

3.4.4. Instrumental method

All extracts were analyzed by ultra performance liquid chromatography coupled to tandem mass spectrometry (UPLC/MS/MS) based on a method published by Vestergren et al. (2012). An Acquity UPLC system equipped with a BEH C18 (1.7 μm particles, 2.1 × 50 mm) analytical separation column (Waters) was employed. The column temperature was held at 40°C. A volume of 5 μL extract was injected in the partial loop injection mode. The mobile phase consisted of solvent A 90% water and 10% acetonitrile with 2 mM ammonium acetate and solvent B 100% acetonitrile with 2 mM ammonium acetate. A gradient elution with a flow rate of 0.4 mL/min was applied. The initial conditions were 90% of solvent A and 10% of solvent B. The percentage of B was linearly increased to 100% from injection to 5 min and held at 100% B until 8 min. Initial conditions were regained at 9 min and held until 10 min for column equilibration.

The detection system used was a Xevo-TQS triple quadrupole mass spectrometer (Waters), which was operated in negative electrospray ionization (ESI-) mode. The following instrumental parameters were used: Capillary voltage 3.0 kV, source temperature 150 °C, desolvation temperature 350 °C, desolvation gas flow 600 L/h and cone gas flow 150 L/h. The mass spectrometer was operated in multiple reaction monitoring mode (MRM). The MRM transition channels, cone voltages and collision energies used are summarized in appendix B.

4. Results and discussion

4.1. Method validation

4.1.1. Procedural blank contamination

A series of procedural blank experiments were performed during method development, method validation and sample analysis (see section 3.4.3.). Procedural blank contamination with several target PFAAs was observed for all tested methods. In general, the highest procedural blank contamination was observed for PFBA, followed by PFNA and PFOA. For the methods tested for solid samples, the procedural blank contamination was higher for method S3 (involving Soxhlet extraction, see Appendix A1.) than for the methods employing sonication in the extraction step. This, together with the fact that Soxhlet extraction is significantly more labor- and time-consuming, was the main reason why method S2 was the method of choice for sample analysis. The procedural blank concentrations of the methods that were finally applied (method S2 and W2) are given in Table 3. Some blank levels were relatively high; however, the blank contamination for all PFAAs was repeatable between sample batches extracted at different days, resulting in low standard deviations of the blank levels. No attempt was made to find the source(s) of the blank contamination.

Table 3 Average procedural blank, standard deviation, method detection limit and blank corrected method detection limit for PFAAs analysed by method S2 for solid samples (ng/g) and method W2 for water samples (ng/L)

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Method S2 (ng/g)									
Average blank	0.663	0.092	0.154	0.227	-	-	-	0.013	0.124
STD[°]	0.057	0.008	0.004	0.007	-	-	-	0.001	0.043
MDL[#]	0.833	0.116	0.167	0.249	0.114[a]	0.085[a]	0.118[a]	0.016	0.251
BC-MDL*	0.170	0.024	0.013	0.022	0.114[a]	0.085[a]	0.118[a]	0.003	0.128
Method W2 (ng/L)									
Average blank	15.4	1.64	3.48	4.26	-	-	-	0.200	1.09
STD[°]	1.25	0.104	0.291	0.311	-	-	-	0.041	0.505
MDL[#]	19.1	1.95	4.35	5.19	0.165[a]	0.244[a]	0,285[a]	0.323	2.60
BC-MDL*	3.74	0.312	0.874	0.932	0.165[a]	0.244[a]	0.285[a]	0.122	1.52

[°] Standard deviation of the blanks

[#] MDL was calculated using average blank + 3 x standard deviation of the blank

* BC-MDL is the blank corrected MDL

[a] PFDA, PFUnDA and PFDoDA did not display a procedural blank contamination. For these PFAAs the MDL was set at a signal to noise ratio of three in the sample chromatogram.

4.1.2. Method detection limits

MDLs were defined based on blank contamination as explained in section 3.4.3. and are listed for method S2 and W2 in Table 3. The blank contamination was consistent between different batches of blank experiments; therefore, quantified concentrations of PFAAs in samples (see section 4.2. later) as well as calculated MDLs were corrected using the average quantified blank level for each PFAA. All blank corrected MDLs for method S2 were in the pg/g range and for method W2 in the single digit to sub ng/L range (Table 3).

4.1.3. Recoveries

Determination of recoveries of native PFAAs from spiked samples would have been highly uncertain, especially at low spiking levels, due to the blank contamination for many PFAAs (see section 4.1.1.) and due to the presence of PFAAs in all investigated sample matrices (see section 4.2. below). Therefore, recoveries were determined based on controlled spike and extraction experiments with IS. This was possible since an authentic mass-labeled standard was available for each of the target analytes.

Method S2 recoveries

In the initial method development and comparison, the IS were spiked to the different sample matrices immediately before extraction. This led to quantitative recoveries (80-122 %) for method S2 as shown in Table 4. Based on these results and based on results from procedural blank testing (see also section 4.1.1.), method S2 was selected as the method of choice for analysis of solid samples. However, during method validation and sample analysis the IS were spiked onto the sample matrix one day before extraction. This was done to ensure that the IS were properly equilibrated with the sample matrix and thus representative for the analytes present in the sample. The recoveries obtained using this procedure are also given in Table 4. They were very low, especially for fly ash samples (0-10 %). This shows the importance of a proper method development and testing and the importance of letting the IS equilibrate with and sorb to the sample matrix before extraction is started. If the procedure used during method development had been used in sample analysis, the levels of the analytes in the samples would have been underestimated considerably. Quantitative recoveries were obtained in the procedural blank experiments using both procedures (Table 4).

Table 4 Recoveries (%) of IS calculated for method S2 (solid samples) during method development and during method validation. The only difference was that the IS were spiked immediately before extraction during method development and one day prior to extraction during method validation.

Method S2	MPFBA	MPFHxA	MPFOA	MPFNA	MPFDA	MPFUnDA	MPFDoDA	MPFHxS	MPFOS
Method development									
Procedural blank	71	101	91	95	93	108	113	109	98
Plant A. Fly ash	80	116	94	89	89	96	103	119	91
Plant D. Fly ash[1]	90	114	103	115	115	118	122	107	107
Method validation									
Procedural blank[2]	94	118	115	119	121	124	122	102	120
Plant A. Fly ash	2	2	5	2	1	1	0	3	5
Plant D. Fly ash[1]	3	5	8	5	5	7	7	7	10

[1] Fly ash sample was taken from furnace 6
[2] The values are averages of several procedural blank experiments

Recoveries of the IS were also calculated for the experiments performed for accuracy testing (Figure 2) and for the triplicate sample analysis performed for precision testing (Figure 3). In accordance with the results presented in Table 4, quantitative recoveries in the range of 90-120 % were obtained in the procedural blank experiments for method S2 (Figure 2A), indicating that the method in principle is stable and reproducible. However, the recoveries from spiked fly ash (Figure 2C and 3B) were again much lower, ranging from 4-10 %. This indicates that the employed extraction method was not efficient in extracting the IS from the sample matrix. Also for the spiked slag sample (Figure 3A) the recoveries were

unsatisfactory, though with 10-30 % consistently higher than for fly ash, which suggests a weaker sorption of PFAAs to slag compared to fly ash. Due to the low recoveries obtained from real samples with method S2, the results for solid samples have to be considered semi-quantitative.

Method W2 recoveries

The recoveries of the IS in the procedural blank experiments of method W2 ranged from 40-150 % (Figure 2B) and for spiked condensate samples (Figure 2D and 3C) from 60-140 %. A consistent pattern of PFAA recoveries was found for method W2, with highest recoveries for PFHxA to PFDA, PFHxS and PFOS, while PFBA, PFUnDA and PFDoDA generally showed slightly lower recoveries. This could be due to the high water solubility of PFBA (breakthrough on the SPE column) and the low water solubility of the long chain PFUnDA and PFDoDA (strong sorption to the SPE column, especially in the case of absence of matrix constituents, i.e. the procedural blank experiments, see Figure 2B). Overall, the recovery results show that the method is stable, reproducible and well suited for analysis of water samples from incineration plants.

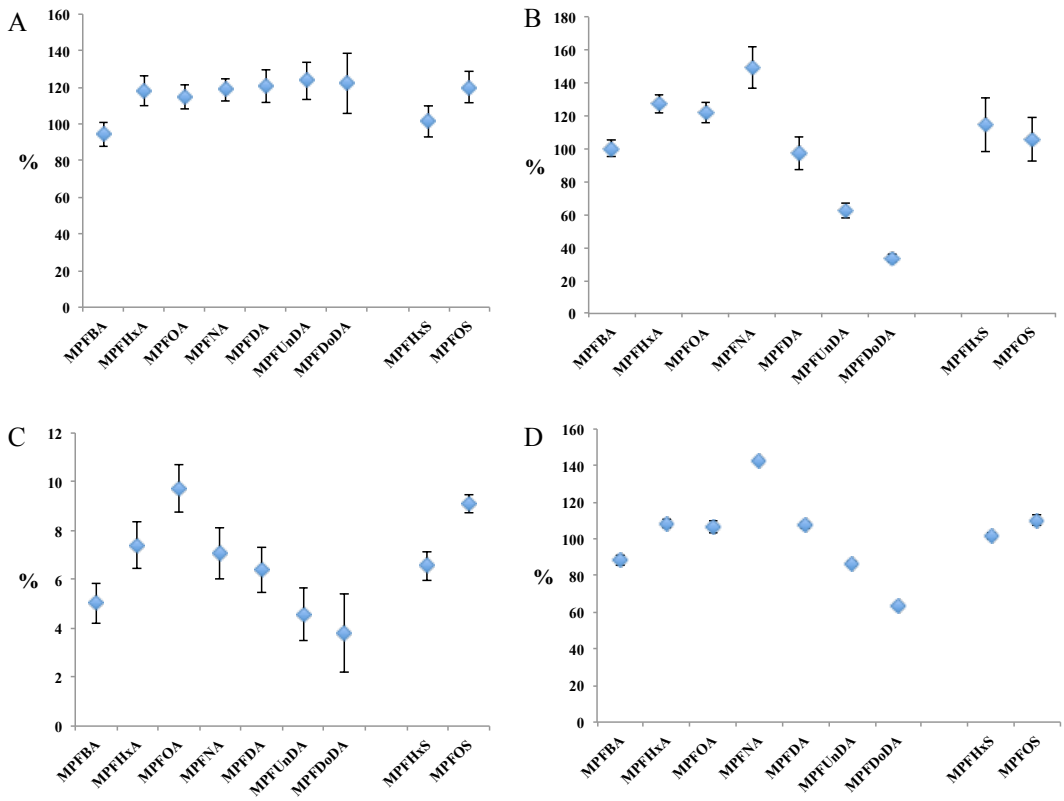

Figure 2 Average recoveries of the IS and standard deviation for the accuracy testing experiments. A: Procedural blanks method S2 (corresponding to slag, fly ash and bambergkaka samples); B: Procedural blanks method W2 (corresponding to condensate and wastewater samples); C: Fly ash sample; D: Condensate.

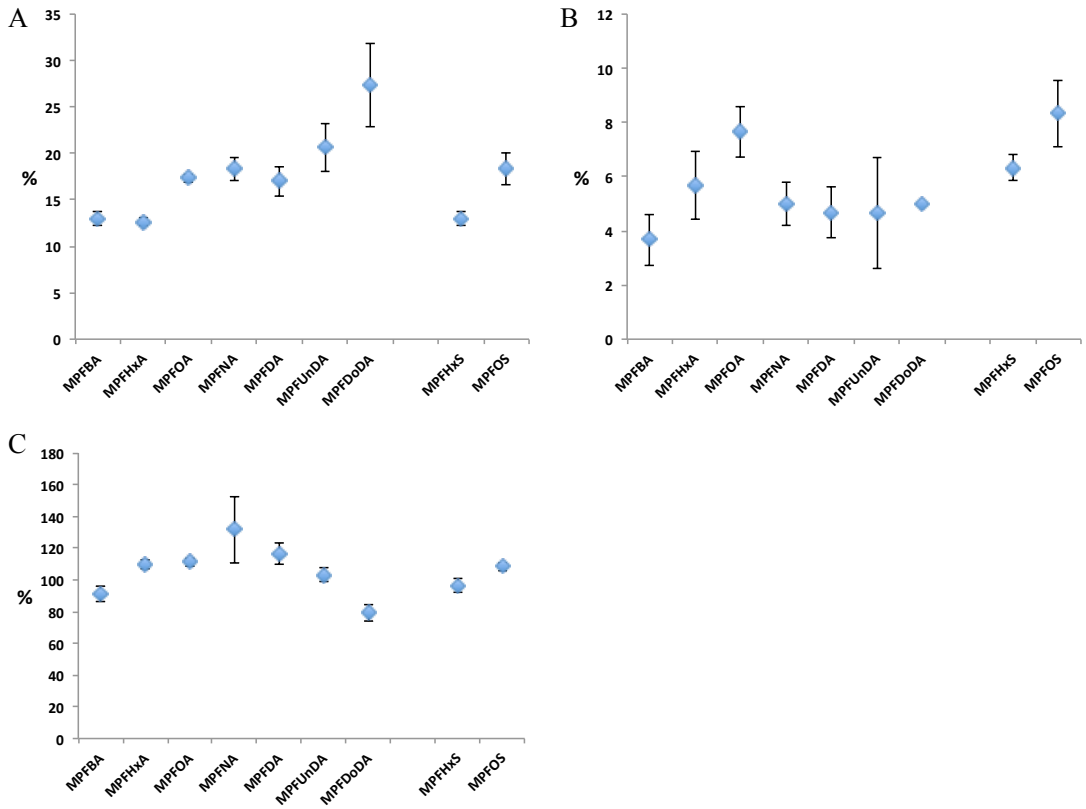

Figure 3 Average recoveries of the IS and stadard deviation for triplicate sample analysis (precision testing). A: Slag sample; B: Fly ash sample; C: Condensate.

4.1.4. Precision

The results from precision testing are summarized in Table 5. The relative standard deviations for all detected PFAAs in all investigated matrices (including slag and fly ash) was <30%. In 9 out of 12 cases it was ≤16%. This shows that the method is precise despite the low recoveries calculated for solid samples (see section 4.1.3.). A further proof of the precision of the methods are the generally low standard deviations obtained for the IS recoveries shown in Figure 2 and 3.

Table 5 Precision testing. Precision is expressed as relative standard deviation (%) of quantified PFAA concentrations in triplicate analysis of real samples.

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Plant A									
Slag	8	11	4	8	12	< MDL	< MDL	< MDL	25
Plant D									
Fly ash	< MDL	16	7	29	< MDL	< MDL	< MDL	< MDL	26
Plant C									
Condensate	< MDL	12	< MDL	< MDL	< MDL	< MDL	< MDL	5	< MDL

4.1.5. Accuracy

The results from accuracy testing are shown in Figure 4. Due to relatively high blank values, accuracy could not be reliably assessed for several PFAAs at the lowest spike levels, especially for the experiments with fly ash (Figure 4A, see section 3.4.3. for the criterion when accuracy was assessed). For all cases where accuracy was evaluated (i.e. all results shown in Figure 4), satisfactory results (typically within ±20% of the target value) were obtained. The only exception was PFDoDA in the condensate (Figure 4B), which may again have to do with the low water solubility of this compound and hence the difficulty to measure PFDoDA representatively in a water sample.

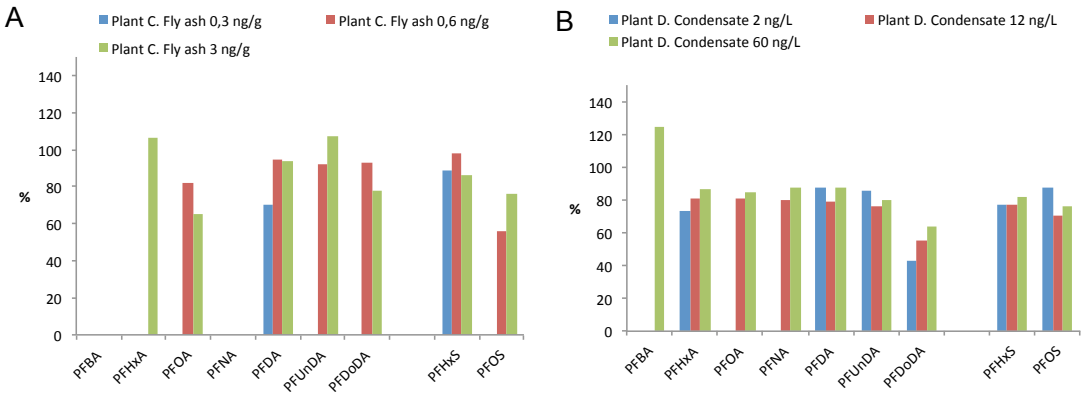

Figure 4 Accuracy testing. Accuracy is expressed as the quantified concentration of an analyte relative to its target concentration (%) in a controlled spike and extraction experiment. A: Results for fly ash; B: Results for condensate. Results are only shown when the spike concentration was at least as high as the concentration (including blank contamination) quantified in the unspiked sample.

4.2. PFAA concentrations in samples from incineration plants

4.2.1. Recoveries of IS in the samples

In order to evaluate the reliability of the quantification of the different PFAAs in the samples from the incineration plants, the recoveries of all IS in all samples were calculated and plotted in Figure 5 (solid samples) and Figure 6 (water samples).

Solid samples (method S2)
The recoveries of the IS in slag and bambergkaka (Figure 5A) were generally between 10-20%. The pattern of PFAA recoveries was consistent for all samples except for the slag sample from Plant A. The consistency of the pattern indicates that the method is reproducible (see also section 4.1.4.). The deviation of the PFAA recovery pattern for the slag from Plant A could not be explained. It could be due to different composition of the slag compared to the other samples. By visual inspection the slag samples from the different plants looked very different. The reason for this could be differences in the incineration process or differences in the composition of waste that was incinerated at the time when the samples were collected.

The recoveries of the IS in the fly ash samples were again generally below 10% (Figure 5B) and showed more variation between plants than for slag and bambergkaka. The variation was most likely due to differences in composition of the samples. The plants sampled in this study have different systems to separate and clean the fly ash. As with the slag samples the fly ash samples visually looked different and may also have different composition depending on the waste that was incinerated at the time of the sample collection. The recoveries of the IS (apart

from MPFOA, MPFHxS and MPFOS) in fly ash from Plant A and B were extremely low (≤2%). Quantification of PFAAs other than PFOA, PFHxS and PFOS in fly ash from Plant A and B was therefore not attempted.

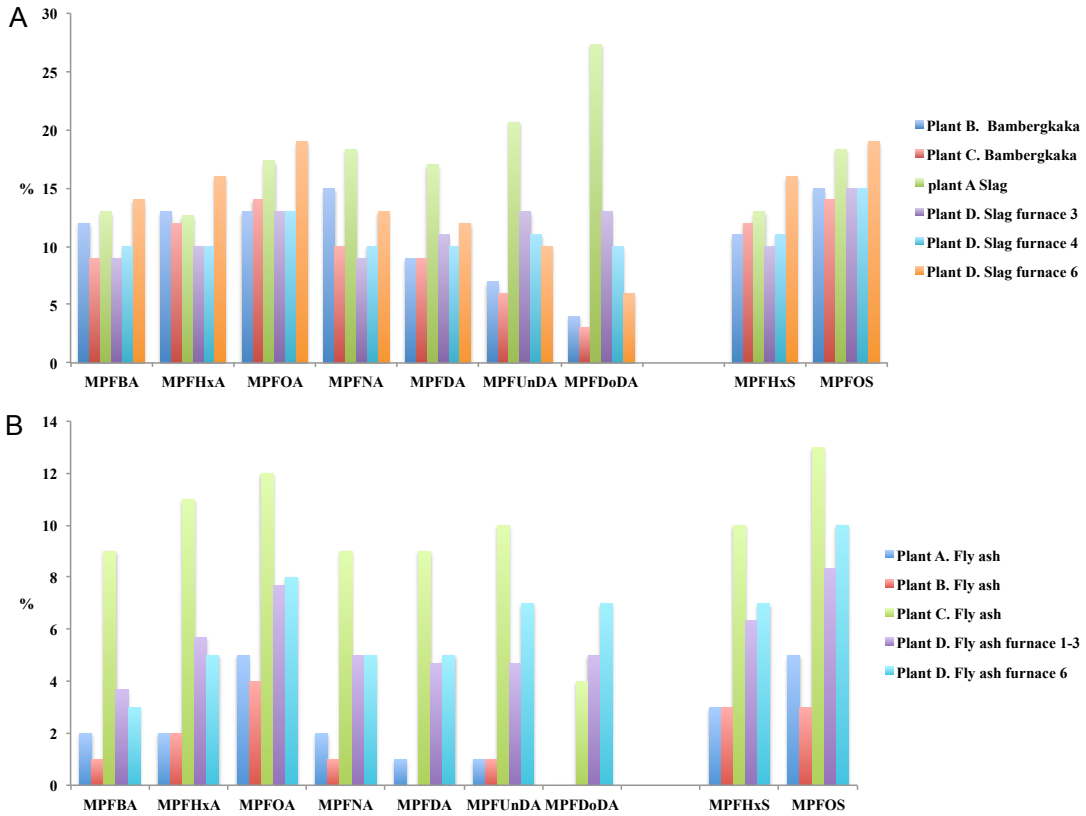

Figure 5 Recoveries of the IS in solid samples. A: Slag and bambergkaka samples; B: Fly ash samples.

Water samples (method W2)

Figure 6 shows the recoveries of the IS in the condensate and wastewater samples. The recoveries for Plant C condensate (B) and Plant B condensate were consistently lower than for the other samples. The reason for this is probably that these two samples were collected within the wet scrubbing steps and had a lower pH value (<4) than the rest of the samples. A low pH in water samples has earlier been reported to lead to analytical difficulties and low recoveries in the quantification of PFAAs (Vierke et al., 2013). Nevertheless, the recoveries of the PFAAs follow the same qualitative pattern in all samples, which was also the pattern observed in recovery testing (see section 4.1.3.).

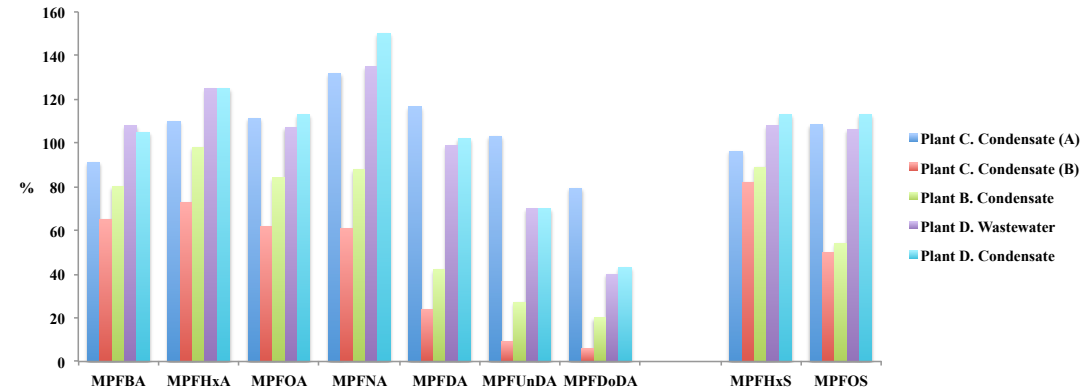

Figure 6 Recoveries of the IS in condensate and wastewater samples.

Apart from the long chain compounds PFDA, PFUnDA and PFDoDA in the two samples with lower pH, all IS recoveries ranged from 50-140%, which indicates that the method was working well and produced quantitative data.

4.2.2. PFAAs in solid samples

The PFAA concentrations measured in the slag, fly ash and bambergkaka are summarized in Table 6. They were all in the single digit to sub ng/g range. Due to the low recoveries leading to elevated uncertainties in quantification (see section 4.1.3. and 4.2.1.) the concentrations shown in Table 6 have to be considered as semi-quantitative. The highest concentrations (in the low ng/g range) were consistently quantified for PFNA. Also PFBA, PFHxA and PFOS showed occasional levels in the ng/g range. The highest levels of PFNA and PFOS were found in fly ash samples. PFOA was detected in all samples at sub ng/g levels, whereas PFDA, PFUnDA, PFDoDA and PFHxS were below their respective MDLs in the majority or in all samples.

Table 6 Blank corrected PFAA concentrations (ng/g) in the slag, fly ash and bambergkaka samples

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Plant A									
Slag[a]	0.719	0.675	0.181	1.61	*<0.114*	0.091	*<0.118*	*<0.003*	0.430
Fly ash	-^	-^	0.622	-^	-^	-^	-^	*<0.003*	2.99
Plant B									
Bambergkaka	1.06	0.747	0.162	2.20	*<0.114*	*<0.085*	*<0.118*	*<0.003*	*<0.128*
Fly ash	-^	-^	0.718	-^	-^	-^	-^	*<0.003*	3.05
Plant C									
Bambergkaka	1.91	0.988	0.136	2.34	*<0.114*	*<0.085*	*<0.118*	*<0.003*	0.195
Fly ash	1.67	0.802	0.177	2.56	*<0.114*	*<0.085*	*<0.118*	*<0.003*	*<0.128*
Plant D									
Slag furnace 3	2.02	1.13	0.137	2.51	*<0.114*	*<0.085*	*<0.118*	*<0.003*	*<0.128*
Slag furnace 4	1.54	0.966	0.142	2.15	*<0.114*	*<0.085*	*<0.118*	*<0.003*	*<0.128*
Slag furnace 6	1.17	0.878	0.352	1.78	0.312	*<0.085*	*<0.118*	0.068	0.732
Fly ash furnace 1-3[a]	*<0.170*	1.94	0329	5.89	0.358	*<0.085*	*<0.118*	*<0.003*	0.459
Fly ash furnace 6	*<0.170*	1.67	0.260	6.63	0.808	*<0.085*	*<0.118*	0.171	4.91

[a] The values for these samples are given as average of triplicate analysis.
< Below the MDL (value of MDL given in italic)
^ Not quantifiable due to the very low recoveries of the IS.

4.2.3. PFAAs in water samples

Table 7 shows the PFAA concentrations found in the condensate and wastewater samples. The concentrations were in the single digit to sub ng/L range. The highest levels were quantified for PFBA, PFHxA, PFNA and PFDA in condensate, whereas in wastewater (one sample from Plant D) only low levels of PFHxA and PFHxS were found. The PFAA concentrations revealed considerable differences between the plants. In the condensate from Plant B all target analytes were detected at ng/L levels with the exception of PFHxS at 0.3 ng/L, whereas in the condensate from Plant D all investigated PFAAs were below their

respective MDL. This could be due to that the condensate from Plant B was collected within the wet scrubbing step and therefore contains a higher concentration of the analytes. The condensate from Plant D was collected after the cleaning of the condensate before it is sent on to the municipal waste water treatment plant. This is supported by the results from Plant C where higher levels of PFHxA and PFNA were found in condensate (B) from within the wet scrubbing compared to condensate (A) representing the cleaned condensate.

Table 7 Blank corrected PFAA concentrations (ng/L) in the condensate and wastewater samples

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Plant B									
Condensate	6.68	1.50	1.88	4.35	9.71	1.82	2.90	0.298	2.04
Plant C									
Condensate (A)[a]	*<3.74*	1.47	*<0.874*	*<0.932*	*<0.165*	*<0.244*	*<0.285*	0.16	*<1.52*
Condensate (B)	*<3.74*	5.91	*<0.874*	8.69	*<0.165*	*<0.244*	*<0.285*	*<0.122*	*<1.52*
Plant D									
Condensate	*<3.74*	*<0.312*	*<0.874*	*<0.932*	*<0.165*	*<0.244*	*<0.285*	*<0.122*	*<1.52*
Wastewater	*<3.74*	0.614	*<0.874*	*<0.932*	*<0.165*	*<0.244*	*<0.285*	0.158	*<1.52*

[a] The values for this sample are given as average of triplicate analysis.
< Below the MDL (value of MDL given in italic)

4.3. Environmental implications

In order to be able to estimate the maximum potential contribution from waste incineration plants to environmental emissions of PFAAs in Sweden, the amount slag and fly ash annually produced by Swedish waste incineration plants was calculated (Table 8). The amounts were calculated to represent the maximum possible amounts as stated in the report "Svensk avfallshantering 2013" (Avfall Sverige 2013).

Table 8 Maximum total amounts of slag and fly ash produced by Swedish waste incineration plants per year, based on the maximum amount of waste incinerated (Avfall Sverige 2013)

	kg/yr
Waste[a]	5 042 020 000
Slag[b]	1 008 404 000
Fly ash[c]	252 101 000

[a] The amount of waste represents the amount from the plants included in the organization Avfall Sverige
[b] The amount of slag is stated to be 15 – 20 % of the total amount of waste. Here, the amount is set at 20 %.
[c] The amount of fly ash is stated to be 3 – 5 % of the total amount of waste. Here, the amount is set at 5 %.

Furthermore, the average concentrations of PFAAs quantified in slag and fly ash were calculated (Table 9) for each compound based on the results given in Table 6. Values below the MDL were substituted with the corresponding MDL for the calculation of averages.

Table 9 Average PFAA concentrations (ng/g) in slag and fly ash based on the measured concentrations from Table 6

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Slag	1.148	0.832	0.196	1.877	0.141	0.088	0.118	0.014	0.380
Fly ash	0.384	1.772	0.395	5.909	0.318	0.085	0.118	0.027	1.778

The calculated averages in Table 9 are to be considered as rough estimates as the concentrations measured were semi-quantitative and showed a large variability between the four plants in this study. Furthermore, the samples taken in this study were grab samples, which are only representative for the day the samples were collected. It is also possible that concentrations would vary depending on the type of waste incinerated at the time the samples were collected. Based on the average PFAA concentrations (Table 9) and the maximum total amounts of slag and fly ash produced annually (Table 8), a rough estimate of the total amounts of PFAAs deposited annually from Swedish waste incineration plants in landfills was calculated (Table 10).

Table 10 Estimates of the total amounts of PFAAs (kg/yr) deposited annually in landfills with slag and fly ash from Swedish waste incineration plants

	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFHxS	PFOS
Slag	1.157	0.839	0.197	1.892	0.142	0.089	0.119	0.014	0.383
Fly ash	0.097	0.447	0.100	1.490	0.080	0.021	0.030	0.007	0.448

The amounts calculated in Table 10 are relatively low compared to the annual inputs of PFAAs to the Baltic Sea reported in a recent mass balance study by Filipovic et al. (2013). This study reported inputs of PFHxA of 150 – 600 kg/yr, PFOA 900 - 1000 kg/yr, PFDA 200 – 500 kg/yr and PFOS 1200 kg/yr from riverine discharges, atmospheric deposition, wastewater treatment plant discharges and inflow from the North Sea to the Baltic Sea. These values represented the inflow from the entire catchment area of the Baltic Sea. Even though Sweden makes up only about 30 % of this catchment area, the potential contribution from slag and fly ash from Swedish waste incineration plants (Table 10) to the PFAA discharges to the Baltic Sea are insignificant. Furthermore, considering that the slag and the fly ash are used and disposed of in different ways (landfill, road construction etc.), only a fraction of the amounts given in Table 10 may actually end up in the environment.

There is no information available on the total volumes of condensate and wastewater from the incineration plants in Sweden. The reason for this is that there are different ways of cleaning and releasing the water in different plants. Some of the plants have an in-house water treatment and release system. Some plants send the condensate and wastewater to municipal wastewater treatment plants. There are also plants that do not have a wet scrubbing cleaning step of the flu gases. It is therefore not possible to give an estimate of the total discharges of PFAAs in condensate and wastewater from waste incineration plants. However, a recent mass balance study of PFAAs in the Baltic Sea and its catchment area (Filipovic et al., 2013) found that wastewater treatment plant discharges only represented $\leq 2\% - 4\%$ of the total input of PFAAs to the Baltic Sea when compared on a basin basis. Given that many waste incineration plants discharge their condensate and wastewater to municipal wastewater treatment plants, and given the fact that this water only makes up a fraction of the total wastewater treatment plant influents, it can be concluded that the PFAAs potentially discharged to the environment from waste incineration plants in this way are not of concern.

As there were no samples from the exhaust fumes of the incineration plants available for this study, PFAAs emitted to the atmosphere could not be directly analyzed. However, three of the four investigated plants had a wet scrubbing cleanup step of the flu-gases. Due to the low pKa values of PFAAs (Vierke et al. 2013), the vast majority of PFAAs present in flu-gases would be trapped in the condensate in these plants. Nevertheless, only low to sub ng/L levels of PFAAs were detected in the condensate samples (Table 7). It can thus be concluded that it is

highly unlikely that any significant amounts of PFAAs are emitted from Swedish waste incineration plants to the atmosphere.

5. Conclusion

Analysis of the samples from the waste incineration plants showed the presence of PFAAs in almost all samples. The results also showed that there were large variations in PFAA concentrations between the plants indicating that the cleaning processes used at the individual plants and the composition of the incinerated waste could have an impact on the amounts of PFAAs found in the end products. However, the concentrations found in all samples were generally low and waste incineration plants in Sweden are unlikely to contribute significantly to environmental emissions of PFAAs. This may be due to the high temperature maintained in modern incineration plants. However, there are a number of countries around the globe applying less advanced waste incineration processes than Sweden. Waste may be burned at relatively low temperatures and without flu gas cleaning. In these countries waste incineration could still be an important pathway of PFAAs to the environment.

6. Outlook

Future work should include further method development of the extraction method used for the slag, fly ash and bambergkaka to improve the recoveries and thereby the reliability of the analyses.

Further investigations of PFAAs from waste incineration should focus on the influence of the temperature in the incineration process on PFAA levels in slag, fly ash and condensate. This information is crucial in order to determine if PFAA emission from less advanced waste incineration plants than the ones investigated in the current study may have an impact on the local and potentially also global environment.

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Appendix A

1. Tested methods for slag, fly ash, and bambergkaka

Method S1
The sample drying and extraction procedure were identical to the procedure described for method S2. For extract cleanup, the concentrated extracts were transferred to Eppendorf tubes equipped with micro centrifuge filters (2μm) and passed through the filters by centrifugation at 13 000 rpm for 10 minutes. The clear extracts were evaporated to dryness and reconstituted in 100 μL of MeOH and 150 μL of 4 mM NH_4OAc in water. The final extract was vortex mixed and ultrasonicated for 5 minutes, transferred to a PP auto sampler vial for instrumental analysis and spiked with 50 μL of RIS-solution. A series of procedural blank experiments were performed and analyzed along with each batch of samples.

Method S3
The glassware and cartridges of the Soxhlet extractor were washed with MeOH by running the Soxhlet overnight (10 h). An aliquot of 1 g of homogenized, dry sample was weighed into the cartridge and spiked with 100 μL of the IS-solution to obtain an IS-concentration of 1 ng/g sample. Glass wool was placed on top of the sample in the cartridge. A volume of 200 mL of MeOH was used to extract the sample. The soxhlet extraction was done overnight (15 h). The extract was concentrated to 1 mL using a vacuum evaporator (Büchi, Flawil, Switerland). The concentrated extract was then transferred to a 13 mL PP-tube and a volume of 9 mL of milli-Q water was added. The extract was vortex mixed thoroughly. For extract clean up, the OASIS WAX SPE procedure described in detail for method S2 was employed. A series of procedural blank experiments were performed and analyzed along with each batch of samples.

2. Tested method for water samples

Method W1
On the day before extraction 50 mL of the sample were weighed into a 50 mL PP-test tube and spiked with 100 μL of the IS-solution to obtain an IS-concentration of 20 ng/L sample. The extraction and cleanup procedure were based on a method previously developed and published by (Ullah et al., 2011). On the day of extraction, a CUQAX 256 SPE column was washed and conditioned with 3 mL of MeOH with 0.1 vol% 1-methyl piperidine, 3 mL of MeOH, and 3 mL of Milli-Q water. The sample was ultrasonicated for 5 min before it was loaded onto the SPE column at a speed of approximately 1 mL/min. The analytes were eluted with 8 mL of 80:20 MeOH:acetonitrile with 2 vol% 1-methyl piperdine. The eluent extract was evaporated to dryness and reconstituted in 100μL of MeOH and 150 μL of 4 mM NH_4OAc in water. The final extract was vortex mixed and ultrasonicated for 5 minutes, transferred to a PP auto sampler vial for instrumental analysis and spiked with 50 μL of RIS-solution. A series of procedural blank experiments were performed and analyzed along with each batch of samples.

Appendix B

Compound names, MRM transition channels, cone voltages and collision energies

Native standards	Abbreviation	MRM transition (m/z)	Cone voltage (V)	Collision energy (eV)
Perfluorobutanoic acid	PFBA	213.0 > 169.0	20	10
Perfluorohexanoic acid	PFHxA	213.0 > 269.0	20	10
Perfluorooctanoic acid	PFOA	413.0 > 369.0	20	11
Perfluorononanoic acid	PFNA	463.0 > 419.0	24	11
Perfluorodecanoic acid	PFDA	513.0 > 469.0	26	11
Perfluoroundecanoic acid	PFUnDA	563.0 > 519.0	28	11
Perfluorododecanoic acid	PFDoDA	613.0 > 569.0	30	12
Perfluorohexane sulfonic acid	PFHxS	398.9 > 80.0	55	36
Perfluorooctane sulfonic acid	PFOS-80	498.9 > 80.0	65	42
Perfluorooctane sulfonic acid	PFOS-99	498.9 > 99.0	65	40
Perfluorodecane sulfonic acid	PFDS	598.0 > 80.0	80	46
Surrogate internal standards (IS)				
$^{13}C_4$-perfluorobutanoic acid	MPFBA	217.0 > 172.0	20	10
$^{13}C_3$-perfluorohexanoic acid	MPFHxA	315.0 > 270.0	20	10
$^{13}C_2$-perfluorooctanoic acid	MPFOA	417.0 > 372.0	22	11
$^{13}C_5$-perfluorononanoic acid	MPFNA	468.0 > 423.0	24	11
$^{13}C_2$-perfluorodecanoic acid	MPFDA	515.0 > 479.0	26	11
$^{13}C_2$-perfluoroundeacanoic acid	MPFUnDA	565.0 > 520.0	28	11
$^{13}C_2$-perfluorododecanoic acid	MPFDoDA	615.0 > 570.0	30	12
$^{13}C_2$-perfluorohexane sulfonic acid	MPFHxS	402.9 > 84.0	55	36
$^{13}C_4$-perfluorooctane sulfonic acid	MPFOS	502.9 > 80.0	65	42
Recovery internal standards (RIS)				
$^{13}C_8$-Perfluoro-n-octanoate	M8PFOA	421.0 > 376.0	22	11
$^{13}C_8$-Perfluoro-n-octane sulfonate	M8PFOS	506.9 > 80.0	65	42