PFAS in waste residuals from Swedish incineration plants

A systematic investigation

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In cooperation with Avfall Sverige

Preface

The overall goal of this project has been to investigate to which extent Swedish waste incineration plants contribute to emissions of PFAS (per- and polyfluoroalkyl substances) to the environment and within the emitted PFAS, which species are dominating. The project would not have been possible without the cooperation of more than twenty operators of waste incineration plants, who have provided samples of ashes and water for analysis. The high degree of participation shows a great interest in the questions from the operators, which has been valuable. The authors would also like to thank Minh Anh Nguyen and Robin Vestergren, previously working at IVL, who were instrumental in developing the project.

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Summary

Incineration is the dominant treatment for residual waste in Sweden. It is essential to reach complete thermal oxidation of chemical substances in the incineration process to destroy toxic substances contained in waste. Otherwise, there is a risk of toxic substances being released into the environment through incineration residuals. This project has investigated to which extent Swedish waste incineration plants emit PFAS (per- and polyfluoroalkyl substances) to the environment via bottom ash, fly ash and condensate water. Emissions were defined as a stream of substances that leaves the plants, irrespective of where this stream leads.

Of 38 incineration plants in Sweden, 27 (in total 31 furnaces) joined the project, answered questionnaires about operating parameters, and sampled incineration residuals. Instructions on carrying out the sampling were sent to the plant operators with a specified sampling protocol. The purpose of the sampling plan was to obtain samples that are representative of typical operating conditions covering most of the Swedish plants. Five samples from each matrix, fly ash, bottom ash, or condensate water, were collected during a two-week period to compensate for the variation over time. These samples were mixed (pooled) to obtain an average sample concentration closer to the actual average concentration.

The collected samples of bottom ash, fly ash and condensate were analysed for 27 different PFAS according to a methodology developed by IVL Swedish Environmental Research Institute, based on LC-MS / MS. The chemicals have been divided into PFSA, PFSA precursors, PFCA, and PFCA precursors.

Analysis showed detectable levels of PFAS-27 in the pooled bottom ash samples from 9 out of 31 furnaces, in concentrations between 0.22 to 12.76 µg/kg. PFCA precursors, especially 6:2 diPAP was the dominant type found in 6 of the 9 furnaces. For fly ash, there were detectable levels of PFAS-27 in 15 out of 31 furnaces, at concentrations between 0.18 to 37.71 µg/kg. In 12 of those 15 samples, the total PFAS-27 concentration was below 2 µg/kg. Three samples stand out from the others, with concentrations above 21.3 µg/kg. For condensate water, there were detectable levels of PFAS-27 in 13 out of 31 furnaces, at concentrations between 0.28 to 182.95 ng/L. The most dominant PFAS were total PFCA with a large representation of short-chain PFCA's.

Out of the 27 incineration plants in this project, five plants had no samples with PFAS-27 concentrations above the analytical limit of detection in any of the matrices. Generally, the results show low concentrations in the sampled matrices from most plants, with a few exceptions. The most considerable amounts of PFAS emissions are expected from the bottom and fly ashes due to the large amounts generated each year.

No apparent relationships were found between the analysed concentrations of PFAS in the sampling matrices and the operational data. Therefore, high incineration temperatures or a high proportion of a particular type of waste is not a guarantor of low concentrations of PFAS.

Sammanfattning

Avfallsförbränning är den vanligaste behandlingen av restavfall i Sverige. Vid förbränningen är det viktigt att nå fullständig oxidation av kemiska ämnen, så att giftiga ämnen i avfallet förstörs. Om så inte sker finns det risk att giftiga ämnen släpps ut i miljön via restprodukter. Detta projekt har undersökt i vilken utsträckning svenska avfallsförbränningsanläggningar släpper ut PFAS till miljön via bottenaska, flygaska och kondensatvatten. I det här projektet har all PFAS som lämnar avfallsförbränningsanläggningen betraktats som ett utsläpp, oavsett om det sker direkt till naturen eller exempelvis till en avfallshanteringsanläggning, eftersom själva riskanalysen inte ingått i projektet.

Av de totalt 38 förbränningsanläggningarna som finns i Sverige anslöt sig 27 till projektet, besvarade enkäter från projektet om driftsparametrar och provtog material för analyser. Instruktioner om hur provtagningen skulle utföras skickades till anläggningarna med ett definierat provtagningsprotokoll, som syftade till att ge prover som är representativa för typiska driftsförhållanden och som täcker de flesta av de svenska anläggningarna. Fem prover samlades in under en tvåveckorsperiod från varje matris, för att kompensera för variationen över tid. Dessa prover blandades (poolades) för att få en koncentration i provet som ligger närmare den sanna genomsnittliga koncentrationen.

De insamlade proverna av bottenaska, flygaska och kondensat analyserades med avseende på 27 olika PFAS-ämnen enligt en metod som utvecklats av IVL, baserad på LC-MS / MS. Kemikalierna kan delas in i typerna PFSA, PFSA prekursorer, PFCA och PFCA prekursorer.

Analysen visade detekterbara halter av PFAS-27 i bottenaskan från 9 av 31 pannor, i koncentrationer mellan 0,22 och 12,76 µg/kg. PFCA-prekursorer, särskilt 6:2 diPAP, var den dominerande typen som fanns i 6 pannor. För flygaska fanns det detekterbara halter av PFAS-27 i 15 av 31 pannor, i koncentrationer mellan 0,18 och 37,71 µg/kg. I 12 av dessa 15 prover låg den totala PFAS-27-koncentrationen under 2 µg/kg. Tre prover sticker ut från de andra, med koncentrationer över 21,3 µg/kg. Det fanns detekterbara halter PFAS-27 i kondensvatten från 13 av 31 pannor, i koncentrationer mellan 0,28 och 182,95 ng/L. Här dominerade PFCA med övervikt för de kortkedjiga PFCA:erna.

Av de 27 förbränningsanläggningarna i detta projekt hade fem anläggningar inga prover med PFAS-27-koncentrationer över detektionsgränsen. I allmänhet visar resultaten på låga koncentrationer i de provtagna matriserna från de flesta anläggningar, med några utstickande värden. De största mängderna PFAS förväntas komma från botten- och flygaska på grund av att det uppstår stora mängder av dessa material varje år.

Inga uppenbara samband hittades mellan de analyserade koncentrationerna av PFAS i provtagningsmatriserna och driftsuppgifterna. Det innebär att höga förbränningstemperaturer eller en hög andel av en viss typ av avfall inte per automatik är en garant för låga koncentrationer PFAS.

1   Background

Incineration is the dominant treatment for residual waste in Sweden (T. Clark, 2019). It is essential to reach complete thermal oxidation of chemical substances in the incineration process to destroy toxic substances contained in waste. Otherwise, there is a risk of toxic substances being released into the environment through the incineration residuals, fly ash, bottom ash and condensate water.

1.1   PFAS

Highly fluorinated substances or PFAS (per- and polyfluoroalkyl substances) is a collective name for a large group of synthetic chemicals (> 4500 individual substances) that contain a carbon chain where the hydrogen atoms are entirely or partially substituted by fluorine. Due to their high chemical and thermal stability, they have become attractive to use in several industrial and commercial applications. The same strong carbon-fluorine bond that gives these substances the beneficial technical properties also makes the substances hard to degrade in nature. Due to their persistence in the environment and long production history, they can be detected in humans and animals worldwide. Moreover, the substances can also be enriched in food chains, increasing the toxic effect due to their persistence. Measures have been taken at the national, regional, and global levels to reduce the use and distribution of PFAS, considering the risks to the environment and human health. Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the two most well-studied PFAS. PFOS was included in Annex B under the Stockholm Convention in 2009, and the global phasing out of production and use is soon complete. Restrictions have more recently been imposed on PFOA, which is now listed as a particularly dangerous substance in the REACH Regulation. In Sweden, the migration of PFAS into drinking water sources has received much attention, and several guideline values and action limits have been set.

Even though the direct emissions from the industrial production of PFOS and PFOA have been stopped, a large portion of these substances is still expected to emit during use and final disposal. Emissions of PFAS from landfills are estimated to be one of the most significant sources of PFAS to the environment in both Sweden and other parts of the world (Masoner et al., 2020, Singh et al., 2021). A slow release of relatively low molecular-weight PFAS substances (such as PFOA and PFOS) happens when perfluoropolymeric materials are broken down in the waste disposal. However, there is a lack of knowledge concerning the emissions of PFAS from waste incineration.

1.1.1   Combustion of PFAS

The knowledge on the fate of combusted PFAS is growing. At present, though, studies show different conclusions on the rate of combustion and at which temperatures this occur. Some experimental studies have shown 99.9% degradation of fluorinated polymers already at 750 °C. In contrast, other studies show that temperatures of 1000 °C are required to achieve complete thermal oxidation of PFOS and PFOA (Winchell et al., 2020, Lundin, 2017b). Moreover, the applicability of these studies on large-scale combustion is unknown. A recently completed project, which analysed condensate water and bottom ash from two plants in Sweden, showed that the total levels of PFCAs and PFSAs were below 5 ng/L (condensate water) and 1 µg/kg (bottom ash), respectively (Naturvårdsverket, 2016). At these levels, emissions from incineration

plants through condensate and bottom ash would be an insignificant contribution to the PFAS pollution in the environment. However, there is currently a lack of data from some facilities to assess whether the emissions vary with different process conditions or treatment technologies.

1.2   Operation of waste incineration plants

An incineration plant, which in most cases also serves as a waste-to-energy plant, is a waste management facility that combusts waste to produce heat or heat and electricity. Many countries, especially Sweden, have considered incineration plants a potential energy diversification strategy due to their low cost of energy production. Sweden has been a leader in waste-to-energy production over the past 20 years and extracts the largest amount of energy per ton waste in Europe, approximately 3Mwh per ton (Nilsson, 1993, Avfall Sverige, 2018). According to the EU framework directive for waste and the Swedish Waste ordinance, waste incineration with efficient energy recovery is considered recycling. Therefore, Swedish incineration plants are essential components in both waste recycling and energy production.
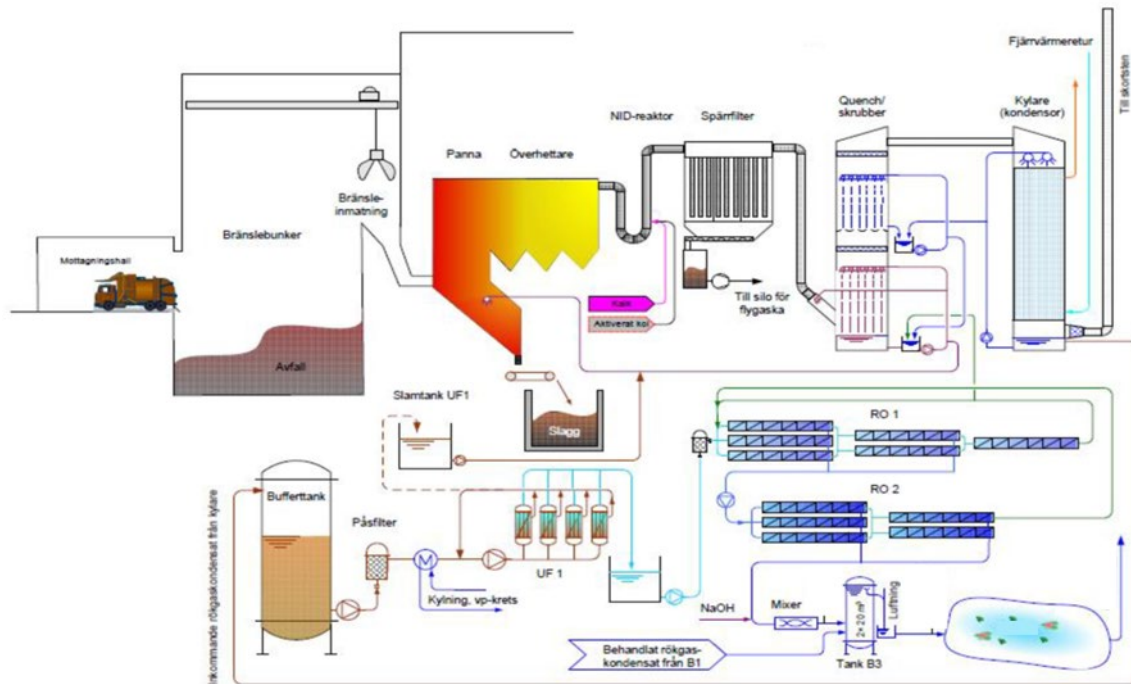
Figure 1. Process scheme of a Swedish incineration plant.

A typical waste incineration plant in Sweden (Fig.1) includes the following process steps, which are further described in sections below:

1. Waste storage and preparation for feeding;
2. Furnace for waste incineration;
3. Gas treatment: temperature reduction (heat recovery) and pollutant removal.

1.2.1   Waste storage and preparation for feeding

The most common way to store the waste is in piles, in a pit with a tipping floor. Before feeding, the over-size non-combustible and special wastes are removed. A waste crane or a bucket is

typically used for furnace feeding, which is operated manually. The operator makes the selection of waste to optimise the performance of the incineration, which means mixing combustible waste with, for example, expectedly wet waste streams.

1.2.2   Furnace for waste incineration

Combustion is a rapid, exothermic oxidation reaction between the waste and air (oxygen). An optimal working furnace can mineralise all organic substances to CO_2 and H_2O. Incomplete combustion due to low temperature or insufficient oxygen supply will result in the formation of CO or carbon-containing particles. All gases will leave the furnace as flue gas, while the incombustible particles constitute the fly ash. The incombustible waste residuals that remain in the bottom of the furnace after combustion form the bottom ash.

The three elements which need to be balanced to obtain optimal operation are temperature, airflow, and combustible waste. The temperature should be high enough to ensure complete combustion but not too high so that equipment is damaged or unwanted nitrogen oxides are formed. The optimum range has been found to be between 850-1200 °C depending on the types of waste incinerated. There is, however, limited information on the combustion rate of PFAS during these temperatures (Lundin, 2017a).

1.2.3   Flue gas treatment

The old incinerators were designed to remove particles and acid gases from the flue gas, but today this has been supplemented with removing dioxins and mercury. The first step of the flue gas treatment chain is to remove particles, which is most often solved by using bag filters (fabric filters). The particles trapped in the bag filter are the fly ash, one of the residues from the incineration plant. The flue gas then passes through a scrubber to wash away the acid gases and then cools in the condenser before being released into the atmosphere. The condensate consists of the moisture from the flue gas. It typically contains heavy metals and other inorganic substances (Noor et al., 2020), which are removed using various filtration systems (e.g. ultrafiltration, reverse osmosis) and pH adjustment before the condensate released.

2 Material and Methods

2.1 Incineration plants

Of the total of 38 incineration plants in Sweden, 27 joined the project and questionnaires (found in the appendix) were sent out where they were asked to specify certain operating parameters. Among the 27 incineration plants that joined in the study, one of them has three furnaces, and two of them have two furnaces, thus in total, 31 furnaces were included in the study. Two incineration plants (no. 8 and 27) represent plants where samples from two furnaces were pooled before analysis.

Part of the operational parameters for the furnaces are shown below:

Furnace type: 24 of the furnaces are of the type "grate furnace", four are of the type "fluidised bed furnace", and one is a rotating furnace. The two remaining furnaces (no. 8 and 27) represent plants that reported the use of both a "grate furnace" and a "fluidised bed furnace".
Temperature: The temperature inside the furnace during the sampling was between 850–1125 °C.
Waste type: 26 furnaces use both household and industrial waste, where the fraction of household waste in the plants ranged from 20 to 95 %. One furnace only uses household waste, and two furnaces only industrial waste. Two other furnaces receive all types of waste (household + industrial+ hazardous waste).

2.2 Sampling

The sampling of the three matrices; bottom ash, fly ash and condensate water, was carried out by the operational staff at the incineration plants. Instructions were sent to the plant operators (found in appendix 1) with a specified sampling protocol. The purpose of the sampling plan was to obtain samples that are representative of typical operating conditions covering most of the Swedish plants. Samples from 25-30 plants were estimated to be needed to cover differences in waste composition, different process designs and types of flue gas treatment.

It was expected that the content of the residues would vary over time, depending on the contents of the incinerated waste. Five samples were collected during a two-week period to compensate for the variation over time. These samples were mixed (pooled) to obtain an average sample concentration closer to the actual average concentration. The original samples were saved and analysed as individual samples in case of deviating values.

At the time of sampling, a field blank sample was taken at the plants as described in appendix 2, capturing background pollution from other sources. The period of sampling was between 2020-10 and 2021-03. The samples were stored at 4°C until the analysis was carried out.

2.3   Analysis

The collected samples of bottom ash, fly ash and condensate were analysed for 27 different PFAS according to a methodology developed by IVL, based on LC-MS / MS. Three blank samples and one quality control sample spiked with known amounts of native standards were processed and analysed in parallel with every batch of the real samples. Pooled samples were formed from collected samples of the same type condensate, bottom ash or fly ash and of the same furnace and analysed. When all pooled samples were analysed, any samples with deviating high levels of analytes were selected for re-analysis. The five individual samples constituting the pooled sample were analysed separately. The analysed PFA substances are shown in Table 1. The chemicals in the precursor group have been divided into PFSA precursors and PFCA precursors.

Table 1. Names, abbreviation, and individual PFAS class, along with internal standards used by the lab. Note that targets are referred to as "acids", although some may exist as anions in the environment.

Class	Native	abbreviation	Isotope-labelled standards
PFCA	Perfluorobutanoic acid	PFBA	13C4-PFBA
	Perfluoropentanoic acid	PFPeA	13C2-PFHxA
	Perfluorohexanoic acid	PFHxA	13C2-PFHxA
	Perfluoroheptanoic acid	PFHpA	13C4-PFOA
	Perfluorooctanoic acid	PFOA	13C4-PFOA
	Perfluorononanoic acid	PFNA	13C5-PFNA
	Perfluorodecanoic acid	PFDA	13C2-PFDA
	Perfluoroundecanoic acid	PFUnDA	13C2-PFUnDA
	Perfluorodecanoic acid	PFDoDA	13C2-PFDoDA
	Perfluorotridecanoic acid	PFTrDA	13C2-PFDoDA
	Perfluorotetradecanoic acid	PFTeDA	13C2-PFDoDA
	Perfluorohexanoic acid	PFHxDA	13C2-PFDoDA
	Perfluorooctanoic acid	PFOcDA	13C2-PFDoDA
PFSA	Perfluorobutane sulfonic acid	PFBS	18O2-PFHxS
	Perfluorohexane sulfonic acid	PFHxS	18O2-PFHxS
	Perfluorooctane sulfonic acid	PFOS	13C4-PFOS
	Perfluorodecane sulfonic acid	PFDS	13C4-PFOS
PFSA Precursor	Perfluorooctane sulfonamide	FOSA	13C4-PFOS
	6:2 fluorotelomer sulfonic acid	6:2 FTSA	13C4-PFOS
	8:2 fluorotelomer sulfonic acid	8:2 FTSA	13C4-PFOS
	N-methyl perfluorooctane sulfonamide acetate	MeFOSAA	13C4-PFOS
	N-ethyl perfluorooctane sulfonamide acetate	EtFOSAA	13C4-PFOS
PFCA Precursor	Hexafluoropropylene oxide	Gen-X	13C4-PFOA
	6:2 polyfluoroalkyl phosphate monoester	6:2 PAP	13C4-PFOA
	8:2 polyfluoroalkyl phosphate monoester	8:2 PAP	13C4-PFOA
	6:2 polyfluoroalkyl phosphate di-ester	6:2 diPAP	13C4-PFOA
	8:2 polyfluoroalkyl phosphate di-ester	8:2 diPAP	13C4-PFOA

2.3.1   Extraction procedure for condensate water

The water samples were fortified with 10 ng of labelled internal standards, see table 1. All water samples were extracted using Solid Phase Extraction (SPE) (Waters, Oasis WAX cartridges, 150

mg, 6cc). Before extraction, Oasis WAX cartridges were conditioned with 4 mL of 0.1% NH$_4$OH in MeOH, followed by 4 mL of MeOH and 4 mL of Milli-Q water. All samples were loaded onto the cartridge at a rate of ~2 drops/sec and then rinsed with 4 mL of ammonium acetate buffer. The cartridges were then dried and finally eluted with 4 mL MeOH followed by 4 mL of 0.1% NH$_4$OH in MeOH. The extract was reduced to 1 mL under a gentle nitrogen stream and then fortified with recovery standard and moved into a vial.

2.3.2   Extraction procedure for bottom and fly ashes

Circa 1 g of the dried homogenised sample was weighed into a 13 mL polypropylene centrifuge tube. After adding 10 ng of labelled internal standards, 5 mL of MeOH was added, the sample was vortex-mixed and placed in an ultrasonic bath for 15 min. After that, the sample was centrifuged for 5 min (1000xg), and the supernatant was transferred to a clean 13 mL polypropylene centrifuge tube. The extraction was repeated once, and the extracts were combined and reduced under nitrogen to a volume of 1 mL. An additional clean up step using SPE was performed to avoid the effect of bottom ash and fly ash matrices on the instrumental analysis. The 1 mL extract was mixed with 10 mL Milli-Q water and then vortex mixed. After that, the extract solutions were extracted by SPE (Waters, Oasis WAX cartridges, 150 mg, 6cc). Oasis WAX cartridges were conditioned with 4 mL of 0.1% NH$_4$OH in MeOH, followed by 4 mL of MeOH and 4 mL of Milli-Q water. All samples were loaded onto the cartridge at a rate of ~2 drops/sec and then rinsed with 4 mL of ammonium acetate buffer followed by 3 times washing with 4 mL Milli-Q water. The cartridges were then dried and finally eluted with 4 mL MeOH followed by 4 mL of 0.1% NH$_4$OH in MeOH. The extract was reduced to 1 mL under a gentle nitrogen stream, fortified with recovery standard and moved into a vial.

2.3.3   Instrumental Analysis

Targeted analysis was performed by LC-ESI-MS/MS (AB SCIEX API 4000) with a reversed-phase column (Thermo Scientific HyPURITY C8, 5 μm, 50 x 3 mm) using MeOH and Milli-Q water with 2 mM ammonium acetate buffer as mobile phase. An isolator column was inserted between the solvent mixer and the injector to separate potential contamination from the solvents to the sample. The system was operated in negative electrospray ionisation mode (ESI-). The ion source temperature was 600 °C, and the ion spray voltage was set to 4.0 kV. Qualification and quantification were carried out using Analyst 1.6 (SCIEX). Quantification was performed using internal standards (Table 1) via an 8-point calibration curve ranging from 0.088 to 20 ng/mL (linear).

2.3.4   Quality Control

Three procedural blanks (consisting of all reagents in 50 mL Milli-Q water) were extracted with water samples (condensate) following the same extraction protocol. Three procedural blanks (consisting of all reagents but no Milli-Q water) were extracted following the same extraction protocol for solid samples. Each batch of samples, whether from condensate, bottom ash or fly ash, received three procedural blanks. In addition, each batch also received a QC sample consisting of Milli-Q water fortified with 10 ng of each of the following native standards: PFOA, PFOS and 6:2 FTS. Finally, a random sample from each batch was selected for duplicate extraction and analysis. No detectable target analytes were measured in the procedural blanks

except for one batch out of 19 total analysed batches where detectable amounts of 6:2 FTS were in the procedural blanks, which led to a high LOD value for 6:2 FTS within this batch.

For target PFAS demonstrated in this report, a blank subtraction was performed using the procedural (reagent) blanks average. The analytical limit of detection (LOD) was calculated as three times the standard deviation of the blank signals.

2.4   Methodological uncertainties

The geographic representation of the study is considered good since a majority of the Swedish incineration plants have taken part. The distribution of waste composition and operating temperatures in our study thus realistically reflects that of the country. The temporal representativity is limited since sampling at each incineration plant occurred during a period of two weeks.

The analytical uncertainties are expected to be small and derive primarily from sub-sampling.

It is generally considered challenging to sample heterogeneous solid samples such as bottom and fly ash in a representative way. In bottom ash and fly ash, particles are not expected to distribute evenly but form aggregates that cannot easily be separated during sampling. In addition, different people carried out sampling at different locations, making it probable that instructions were interpreted or executed slightly different. The sampling of ashes is expected to be the most significant uncertainty with respect to the representativity of the solid materials. Sampling condensate water is not expected to have the same challenges.

Contamination from other sources is an uncertainty factor to consider, although the field blank samples will compensate for this to some extent. Studies (Ahrens et al., 2011) have shown that the air around the incineration plant has relatively high PFAS levels, which potentially contaminate the samples.

In this study, 27 PFAS were analysed. However, since combustion processes are involved, the ultimate fate of the fluorinated chemicals can be outside of these 27, which is not covered in this study, which leaves unknowns.

Since neither samples of incoming solid waste or released flue gas were taken, PFAS mass balance evaluation in the incineration plants cannot be calculated for this study. Hence, conclusions cannot be made regarding the PFAS removal efficiency of condensate water treatment or solid waste incineration. Those results are not in the domain of the study.

3   Results and discussion

In this chapter, the PFAS-27 concentrations in all samples, including blank samples, are presented. The samples with concentrations lower than the LOD (found in appendix 3) are shown as zero in the figures and averages.

Out of the 27 incineration plants in this project, five plants had no samples with PFAS-27 concentrations above the analytical limit of detection. Generally, the results show low concentrations in most plants, with a few outliers shown in Figure 2. Summary statics are shown in appendix 4. Results are explained in detail in the following sections.
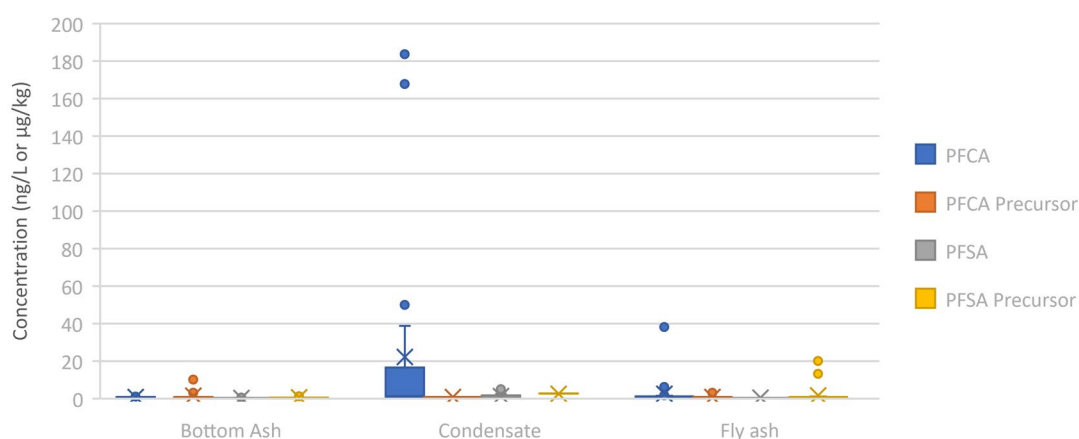
Figure 2. Boxplot showing the distribution of pooled sample concentrations of PFAS groups in different matrices for all furnaces. The upper and lower lines in the box represent the upper and the lower quartiles. The whiskers indicate variability outside of the upper and lower quartiles, the x marks the mean, and the dots are outlier values.

3.1   Field blank samples

None of the fly ash field blank samples had concentrations above the detection limit of the analysis (LOD). Only one of the bottom ash field blank samples (furnace no. 10) was above LOD, containing 0.75 µg/kg of a PFSA precursor.

A high value of a PFCA precursor was found in one of the condensate water field blanks, dominated by the substance 6:2 diPAP. It might derive either from the atmosphere as particles, dust, or due to the sampling. These results noticed in the field blank did not correspond with the result from the same furnace, which means that this contamination in the field blank was not systematic or constant. Apart from this field blank sample, another four field blank condensate water samples showed values marginally higher than the detection limit.

3.2 PFAS content in bottom ash

There were detectable levels of PFAS-27 in the pooled bottom ash samples from 9 out of 31 furnaces, in concentrations between 0.22 to 12.76 µg/kg (Fig. 2). PFCA precursors, especially 6:2 diPAP, were the dominant type found in 6 furnaces. The samples from furnace no. 28 contained besides 6:2 diPAP, also 8:2 PAP and 8:2 diPAP. Out of all analysed PFCA's, only PFHxA was detected in four pooled bottom ash samples at low concentrations (between 0.22 to 0.39 µg/kg).

PFSA was detected in three pooled bottom ash samples at concentrations between 0.36 to 0.41 µg/kg. The same samples also contained 6:2 FTS between 0.94 to 1.28 µg/kg.
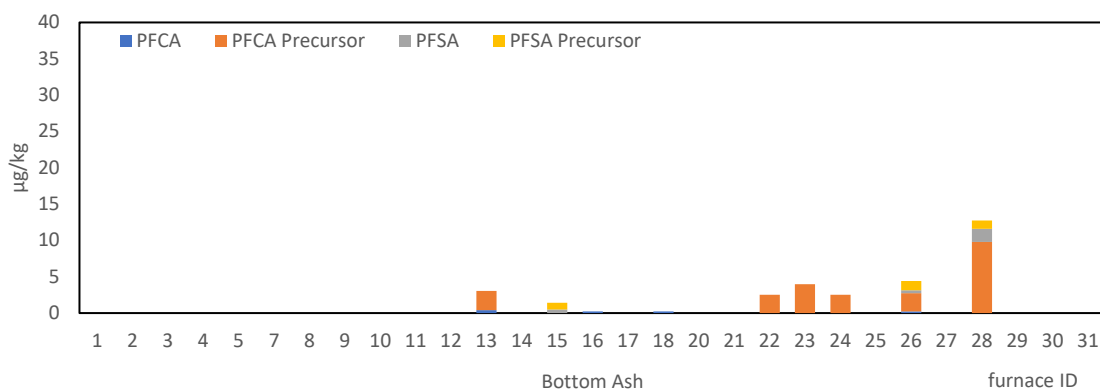

Figure 3. The concentration of total PFAS-27 and the contributions of different PFAS classes in bottom ash analysis results

3.3 PFAS content in fly ash

There were detectable levels of PFAS-27 in the pooled fly ash samples from 15 out of 31 furnaces, in concentrations between 0.18 to 37.71 µg/kg. In 12 of those 15 samples, the total PFAS-27 concentration was below 2 µg/kg. Three samples stand out from the others, with concentrations above 21.3 µg/kg (Fig. 3).
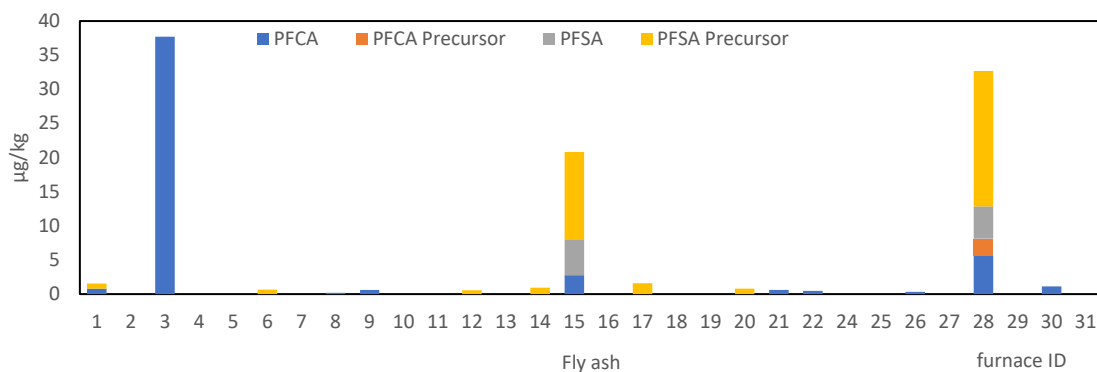

Figure 4. The concentration of total PFAS-27 and the contributions of different PFAS classes in fly ash analysis results

PFCA's were detected in 10 pooled samples in concentrations between 0.18 and 37,71 µg/kg. No detectable amount was noted for substances with a chain length of more than nine carbon atoms.

The detectable PFCA's, PFPeA and PFHxA, were the most frequently occurring in 8 and 7 samples, respectively.

Samples from two furnaces (15 and 28) belonging to the same incineration plant contained PFSA's, namely the substances PFBS, PFHxS and PFOS. The concentration of PFOS was the highest, with a concentration of 3.74 and 3.44 μg/kg in furnaces 15 and 28, respectively. Out of all analysed PFSA precursors, only 6:2 FTS and 8:2 FTS were detectable. 6:2 FTS was detected in eight pooled fly ash samples at concentrations ranging from 0.57 to 19.67 μg/kg. In comparison, 8:2 FTS was detected just in one pooled fly ash sample from furnace 28 at a concentration of 0.21 μg/kg.

Of the PFCA precursors, only 6:2 diPAP was detected in one pooled sample from furnace 28 at a concentration of 2.48 μg/kg.

3.4   PFAS content in condensate water

There were detectable levels of PFAS-27 in the pooled condensate water from 13 out of 31 furnaces, at concentrations between 0.28 to 182.95 ng/L (Fig. 4). The most dominant PFAS in the pooled condensate water samples were total PFCA with a large representation of short-chain PFCA's. It was further seen that only two samples contained barely detectable amounts of precursors. Furthermore, PFSA's were detected at low concentrations in five furnaces, mainly consisting of PFOS.

There are at least three possible explanations for the high concentrations of substances from the PFCA group, found in two of the plants: 1) the incinerated waste in the two outlier plants contained significantly higher amounts of PFAS at the time when the sample was taken, 2) the flue gas treatment in the two outlier plants is more efficient and hence captures the PFAS that others release or 3) the samples were contaminated.
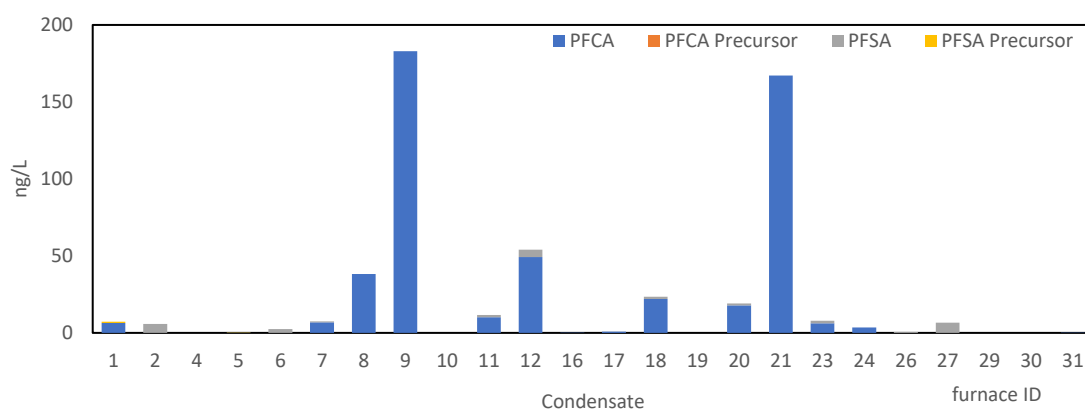
Figure 5. The concentration of total PFAS-27 and the contributions of different PFAS classes in pooled condensate water sample analysis. Missing furnace ID numbers (3,13, 14, 15, 22, 25 and 28) is due to 1) no condensate water produced in the flue gas treatment; 2) condensate water was treated together from several furnaces in the same incineration plant.

Since some of the pooled condensate samples contained high concentrations of PFAS (Fig. 5), individual samples from the furnaces were analysed, partly to confirm the analysis results for the pooled samples and partly to study how the PFAS concentrations vary over time.

The results showed that the total content of PFAS-27 for two of the furnaces was within a relatively large range. For furnace 21, the total PFAS-27 in the pooled condensate sample was 167 ng/L, while the individual samples ranged from 74 to 223 ng/L, with an arithmetic mean of 145 ng/L. In furnace 1, the concentration of total PFAS-27 in the pooled condensate sample was 7 ng/L, while the individual sampled revealed one outlier containing 156 ng/L, while the arithmetic mean for the other sample was 17.2 ng/L.

Large differences between pooled and individual samples can, to some extent, be related to the presence of PFCA precursors, especially 6: 2 diPAP, for which the LOD level is higher than for the other PFAS. In addition, the amount required of an individual sample to form the pooled sample is four times less than the amount of individual sample analysis. The analysis shows that outlier samples can greatly affect the pooled concentrations and variations over time between individual samples.

3.5 Connection of PFAS emissions to specific process conditions

Generally, no apparent correlations between the analysed concentrations of PFAS in the sampling matrices and the operational data were found.

Concerning furnace type, samples from 24 grate furnaces were included in the study. Samples from five of these did not contain concentrations over LOD. The other furnace types were not represented in sufficient numbers to be representative of a type. The results show that concentrations below LOD can be, but not necessarily are, achieved in a grate furnace, implying the importance of other factors than the furnace type.

Measurable concentrations of PFAS were found in the three matrices, irrespective of the incineration temperature. The two incinerators with the highest PFCA concentrations in the condensate samples had operating temperatures above 1100 °C, despite the general hypothesis that all organic substances combust at temperatures above 1000 °C.

The proportion between household waste and industrial waste did not show any apparent connection with the sample concentrations or the relative composition of the PFAS. High concentrations were found both in furnaces using only industrial waste and in furnaces using household waste.

3.6 Total annual PFAS emissions from incineration plants

An estimation of the total PFAS amounts emitted via bottom, fly ash and condensation water from Swedish incineration plants was made, based on measured concentrations and yearly amounts of each residual material reported by the plant operators. In this study, emissions were defined as streams of substances that leave the plants, irrespective of where these streams lead. Hence there is no distinguishment between emissions to nature and a waste management facility, and neither to whether PFAS is available or leachable or not. It was further assumed that

condensate water is released without treatment. However, this evaluation has a large degree of uncertainty due to the uncertainty concerning representativity over time.

Even though the PFAS concentration in the condensate water was high, the largest total emission of PFAS derives from the bottom- and fly ashes due to large production volumes, shown in Fig. 7. A. It should be noted that flue gas was not sampled in this study, which remains to be investigated in future studies. Ahrens et al. (2011) showed that flue gases could be a significant source of PFAS emissions from incineration plants.
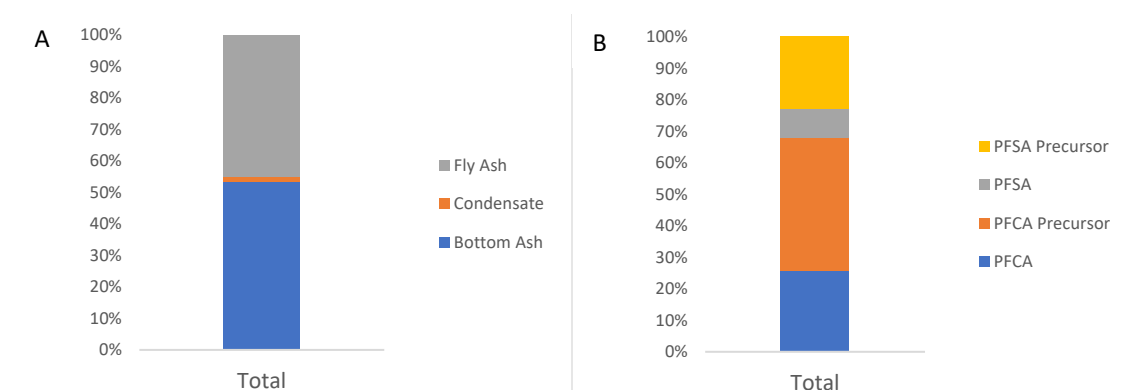
Figure 6. Estimation of PFAS emissions from the Swedish incineration plants: A) Relative contribution from different incineration residuals (bottom ash, fly ash and condensate). B) Relative composition of PFAS classes in the total potential annual emissions of PFAS in the studied Swedish incinerations.

The PFAS group which is emitted in the largest amounts is the PFCA precursors. (Fig. 7. B), since this was the dominating group in the bottom and fly ash samples. Assuming that the condensate water would be recycled or reused would have lowered the PFCA's contribution to the total emissions since these were almost exclusively found in condensate water.

For comparison, PFAS emissions from wastewater treatment plants (WWTPs) were measured by Eriksson et al. (2016) in the influent wastewater, effluent water and sludge from 3 Swedish municipal WWTPs (Henriksdal WWTP 737 000pe, Gässlösa WWTP 82 000 pe, Umeå WWTP 92 000pe) from 2012, 2014 and 2015. The results show that the sum of PFCA's and PFSA's in the sludge was in the range of 8-16 μg/kg (Henriksdal WWTP), 10-17μg/kg (Gässlösa WWTP) and 5-8 μg/kg (Umeå WWTP). These results are comparable with the analysis of the bottom and fly ashes obtained in this study. However, production volumes of bottom ash and fly ash are much higher than the wastewater sludge. Therefore, the total emission of PFCA and PFSA from bottom ash and fly ash will be larger than from wastewater sludge.

The sum of PFCA's and PFSA's in the influent amounted to 22-31 ng/l, in contrast to 27-70 ng/l in the effluent wastewater in the WWTP study. Higher concentrations of PFAS in the effluent were probably due to the breakdown of precursors or the release of chemicals from the sludge. These results are also comparable with the PFAS content in the condensate water. However, the amounts of produced condensate water are minor compared to the municipal wastewater amounts per year.

4   Conclusions

Out of the 27 incineration plants in this project mapped with respect to PFAS in the waste residuals, five plants had no samples with PFAS-27 concentrations above the analytical limit of detection. Generally, the results show low concentrations in the sampled matrices from most plants, with a few outliers.

The largest amounts of PFAS emissions, through the analysed matrices, are expected from the bottom and fly ashes due to the large amounts generated each year. The bottom ash was dominated by PFCA precursors such as 6:2 diPAP, while substances in the PFSA group dominated fly ash.

The condensate contained almost exclusively PFAS from the PFCA group. Even though the PFAS emission by the condensate water is less significant considering the low amounts generated each year, condensate water treatment needs to be paid special attention to because of its potentially high PFAS concentration.

No apparent relationship between high concentrations of analysed PFAS in the sampling matrices and the operational data, such as temperature, the composition of waste and furnace type, was seen. It means that high incineration temperatures or a high proportion of a particular type of waste did not guarantee low concentrations of PFAS.

5   Suggestions for further research

As noted, there are a few outliers in the dataset that could require some extra attention. If possible, an inventory should be made of materials in the condensate water system to investigate whether components pollute the condensate water. If this can be excluded, a sampling campaign investigating the temporal variability of PFAS concentrations in combination with better estimates of the composition of incinerated waste would be appropriate. Also, discussing results at an operator level might be an effective way of revealing differences and similarities in how the process is managed, possibly explaining some of the results in this investigation.

The degree to which PFAS are combusted and if there is a re-generation of PFAS after combustion is a question that needs to be investigated in a laboratory environment. Such a study would incinerate a known amount of PFAS in a controlled furnace and analyse the total emissions, both as total organic fluorine and PFAS.

Not being able to measure PFAS concentrations in the flue gases is a limitation of this study. Assume, for example, that the deviations noted regarding PFCA concentrations in condensate are explained by the fact that these plants have a more efficient condensation process and not by the fact that the incinerated waste contained higher concentrations of PFAS at the time. In that case, it could mean that the other plants release PFAS into the air, which can not be known without the possibility of measuring concentrations in the flue gases. Quantification of this potential emission route is thus needed to understand the fate of PFAS in incineration plants.

In this study, fly and bottom ash and condensate water from Swedish incineration plants were analysed for 27 PFAS. However, the ultimate fate of the fluorinated chemicals, especially since combustion processes are involved, would be a matter of interest and investigation. A study that will be performed at Stockholm University will analyse the total organic fluorine content of the samples from this project. The difference between PFAS-27 and total organic fluorine will reveal the extent of PFAS combustion.

References

AHRENS, L., SHOEIB, M., HARNER, T., LEE, S. C., GUO, R. & REINER, E. J. 2011. Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere. *Environmental Science & Technology,* 45**,** 8098-8105.

LUNDIN, L., JANSSON, S. 2017a. Destruction of persistent organic compounds in combustion systems. *Master thesis, Umeå University*.

LUNDIN, L. J., STINA 2017b. A desktop study on destruction of persistent organic compounds in combustion systems *Umeå University*.

MASONER, J. R., KOLPIN, D. W., COZZARELLI, I. M., SMALLING, K. L., BOLYARD, S. C., FIELD, J. A., FURLONG, E. T., GRAY, J. L., LOZINSKI, D., REINHART, D., RODOWA, A. & BRADLEY, P. M. 2020. Landfill leachate contributes per-/poly-fluoroalkyl substances (PFAS) and pharmaceuticals to municipal wastewater. *Environmental Science: Water Research & Technology,* 6**,** 1300-1311.

NATURVÅRDSVERKET 2016. Högfluorerade ämnen (PFAS) och bekämpningsmedel: en sammantagen bild av förekomsen i miljön, Redovisning av ett regeringsuppdrag. *Rapport* 6709.

NILSSON, K. 1993. Integrated waste management: A Swedish municipal case study. *Ekistics,* 60**,** 66-69.

NOOR, I.-E., MARTIN, A. & DAHL, O. 2020. Water recovery from flue gas condensate in municipal solid waste fired cogeneration plants using membrane distillation. *Chemical Engineering Journal,* 399**,** 125707.

SINGH, R. K., BROWN, E., MEDEDOVIC THAGARD, S. & HOLSEN, T. M. 2021. Treatment of PFAS-containing landfill leachate using an enhanced contact plasma reactor. *Journal of Hazardous Materials,* 408**,** 124452.

SVERIGE, A. 2018. Swedish Waste Management. *Report*.

T. CLARK, J. B., J. CHRISTIANSEN, J. FAGERQVIST, A-C. GRIPWALL, Å. HAGELIN, H. JANSSON, K. JÖNSSON, P. K. CARLSSON, S. LUNDGREN, B. MOUTAKIS, C. NILSSON, J. N. DJERF, C. STEINWIG, K. SUNDBERG, K. SVENSSON, P. SVENSSON, M. UMARK, J. WESTIN, P. WESTLING. 2019. Svenska Avfallshantering 2019. *Avfall Sverige Report*.

WINCHELL, L. J., ROSS, J. J., WELLS, M. J. M., FONOLL, X., NORTON JR, J. W. & BELL, K. Y. 2020. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review. *Water Environment Research,* n/a.

Appendix 1. Sampling instructions and protocols

The purpose of the sampling is to collect the combusting residuals from the incineration plant. The materials to be collected are

1. Bottom ash
2. Fly ash
3. Purified condensate water

The sampling period is 2 weeks, and during this period, samples must be taken every other day (5 samples in total).

NOTE: In some facilities, it can be difficult to take a fly ash sample every other day because the silo is not opened often. Then it may be ok to take a sample once every two weeks.

In conjunction with the collected samples, general information about the plant (type of boiler, condensate treatment plant, etc.) and operational parameters, e.g. type of waste, the temperature during incineration, amounts of bottom and fly ashes generated, needs to be communicated.

<u>Specific instructions:</u>

<u>What you need for each sample:</u>

• A new pair of blue nitrile gloves (sent by IVL)
• 2 x 1L plastic bottle (sent by IVL), for water sampling
• 1 x 250 ml bottle (sent by IVL), for bottom ash
• 1 x 250 ml bottle (sent by IVL), for fly ash
• A clean shovel, to take bottom ash samples
• A clean 10 L bucket for collecting and mixing bottom ash samples before transferring a subsample to the 250 ml bottle
• A clean stick (e.g. made of wood), to mix the bottom ash in the bucket
• A clean metal or glass bowl to collect the fly ash so that it can cool down before transferring it to the 250 ml bottle

<u>Before each sampling:</u>

Wear the new blue gloves (made of nitrile) before each sampling opportunity!

<u>After each sampling:</u>
Fill in the sampling protocol at the end of this document.

<u>1 - Condensate water sampling:</u>

1) Before sampling: rinse the bottles (2 x 1L plastic bottle) 3 times with the water to be sampled. Fill up to half, shake and rinse between each rinse
2) Then fill the bottles completely and tighten the cap
3) Place the sample in the dark in a refrigerator (4 ° C) until it is returned to IVL

2 - Sampling of bottom ash:
1) "Clean" the spade by submerging it in the bottom ash
2) Take eight samples with the shovel from a different place on the surface of the bottom ash pile. NOTE: Avoid large chunks. The purpose of taking samples from the surface is because the boiler has recently generated surface bottom ash
3) Collect all samples in the bucket
4) Use a clean stick to mix the bottom ash in the bucket
5) Fill a 250 ml plastic bottle (provided by IVL) with bottom ash
6) Place the sample in the dark in a refrigerator (4 ° C) until it is returned to IVL

3 - Sampling of fly ash:
1) Collect a quantity of fly ash in a metal or glass bowl
2) Allow the fly ash to cool
3) Fill a 250 ml plastic bottle (provided by IVL) with the cool ash
4) Place the sample in the dark in a refrigerator (4 ° C) until it is returned to IVL

Appendix 2. Questionnaire

Thank you for participating in the project and sampling campaign.

Here are some questions about the incineration plant. The information can help us evaluate the results later. Thanks for the cooperation!

1. Which type of furnace is installed in the plant? e.g. fluid bed furnace.

2. What was the temperature in the boiler, fuel gas flow, combustion airflow and waste residence time during the sampling sessions?

3. Information about the fuel (e.g. industrial waste and household waste) at the time of sampling.

4. What volumes of fly ash, bottom ash and condensate are generated annually?

5. Any further observations during the sampling occasions?

6. Can you provide us with a process scheme and mark where you took the samples?

Appendix 3. Analytical limits of detection

Table 1. Limits of detection (LOD) for individual PFAS in ash and water.

Substance	PFBA	PFPeA	PFHxA	PPFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
fly & bottom ash (µg/kg)	0.15	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
condensate water (ng/L)	0.15	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Substance	PFTrDA	PFTeDA	PFHxDA	PFOcDA	PFBS	PFHxS	PFOS	PFDS	FOSA
fly & bottom ash (µg/kg)	0.15	0.15	0.15	0.15	0.1	0.1	0.1	0.1	0.1
condensate water (ng/L)	0.15	0.15	0.15	0.15	0.1	0.1	0.1	0.1	0.1

Substance	6:2 FTS	8:2 FTS	Gen-X	Me-FOSAA	Et-FOSAA	6:2 PAP	8:2 PAP	6:2 diPAP	8:2 diPAP
fly & bottom ash (µg/kg)	0.1	0.1	0.1	0.1	0.1	0.5	0.5	0.2	0.2
condensate water (ng/L)	0.5	0.1	0.1	0.1	0.1	0.5	0.5	0.2	0.2

Appendix 4. Summary statistics

Table 2. Average, geometrical mean and standard deviation for the sum of PFAS concentrations in all pooled samples from all plants, per PFAS group. LOD values were replaced by half of LOD before calculation.

		Average	Geometrical mean	Standard deviation
Bottom ash (µg/kg)	PFCA	0.90	0.90	0.064
	PFCA Precursor	1.5	1.1	1.9
	PFSA	0.30	0.26	0.31
	PFSA Precursor	0.59	0.56	0.30
Condensate water (ng/L)	PFCA	22	4.1	48
	PFCA Precursor	0.75	0.75	0
	PFSA	1.3	0.65	1.9
	PFSA Precursor	2.5	2.4	0.57
Fly ash (µg/kg)	PFCA	2.5	1.2	6.7
	PFCA Precursor	0.83	0.79	0.43
	PFSA	0.54	0.28	1.2
	PFSA Precursor	1.7	0.75	4.1