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Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas

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HIGHLIGHTS

- Municipal incineration of PTFE shows no significant generation of studied PFAS.
- Using pilot scale equipment and paired t-testing minimizes background interference.
- PTFE produced mainly hydrofluoric acid and carbon dioxide during incineration.

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ABSTRACT

In recent years, concerns over some per- and polyfluorinated alkyl substances (PFAS) have grown steadily. PFAS are a large group of chemical substances with widely differing properties. While one class of PFAS, fluoropolymers, have been demonstrated to meet the OECD criteria for polymers of low concern during the in use phase of their lifecycle, questions remain regarding waste handling at the end of useful life for products containing fluoropolymers. To show that polytetrafluoroethylene (PTFE) can be almost fully transformed into fluorine (F) (as hydrofluoric acid (HF)) and to study the possible generation of low molecular weight per- and polyfluorinated alkyl substances (PFAS), PTFE combustion under typical waste incineration conditions at the BRENDA (German acronym for “Brennkammer mit Dampfkessel”) pilot plant at Karlsruhe Institute of Technology (KIT) was investigated. Results indicate that, within procedural quantitation limits, no statistically significant evidence was found that the PFAS studied were created during the incineration of PTFE. Therefore, municipal incineration of PTFE using best available technologies (BAT) is not a significant source of the studied PFAS and should be considered an acceptable form of waste treatment.

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1. Introduction

Concerns over certain per- and polyfluoroalkyl substances (PFAS) (also called per- and polyfluoroalkyl compounds (PFCs)) have grown since the May 16th, 2000 USEPA press release announcement of the phase out of perfluorooctane sulfonate (PFOS) due to its toxicity, environmental persistence and bioaccumulation (USEPA, 2000). This class of compounds have been found throughout the environment from a variety of industry and consumer sources

(Prevedouros et al., 2006; Rankin et al., 2016; Taniyasu et al., 2005). Today, many PFAS are under scrutiny, including perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates (PFASAs), perfluorooctane sulfonamides (PFOSAs) and perfluorooctane sulfonamidoethanols (PFOSEs). In addition to the manufacturing and intentional use of these compounds, other potential pathways where these PFAS might be generated are being studied (Prevedouros et al., 2006). One potential pathway identified for investigation is the waste handling of fluoropolymers at the end of useful life, specifically the municipal incineration of PTFE.

Due to its unique properties, PTFE is used in a wide range of products including wire insulation, gasket material, filtration and waterproof garments (Henry et al., 2018). At the end of useful life,

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these products are subject to different waste streams including landfilling which accounts for 56% w/w of waste treatment worldwide and incineration (IEA, 2014). The number of waste incineration facilities are increasing globally as the best available waste treatment technologies can be applied (Gehrmann et al., 2017; EC, 2010; 17 BImSchV, 2003). Although PTFE is inert in the environment due to its high chemical and thermal stability, municipal waste incinerators generate adequate temperatures to decompose PTFE (Taylor et al., 2014).

This study investigates the possible generation of a wide range of PFAS (Table 1) from PTFE incineration under standard municipal waste conditions. Extensive investigations at BRENDA pilot plant at KIT were conducted to validate that PTFE can be almost fully transformed to fluorine as hydrofluoric acid (HF) and a number of trace species in very low concentrations via incineration using the BAT.

2. Materials and methods

Due to the environmentally ubiquitous nature of the substances listed in Table 1 and the extreme sensitivity of the liquid chromatography with mass spectrometry (LC-MS/MS) detection methods, contamination of solvents, samples and blanks was a significant concern (Prevedouros et al., 2006; Sinclair et al., 2007; Taniyasu et al., 2005). To reduce the probability of producing false positive results, a three parallel step approach was taken. First, the experiment was scaled up to pilot plant incineration levels using the BRENDA facility (Fig. 1). The solid combustion material input was many orders of magnitudes larger than in lab based incinerator simulations. Second, to minimize potential external contaminants, combustion input materials were limited to natural gas, commercial premium wood pellets, PTFE polymer pellets and air. In addition, paired t-testing was used to identify the presences of

statistical differences between blank and PTFE spiked conditions (Van Belle et al., 1993).

For this study, compounds were chosen to represent a broad range of PFAS. Specific compounds in Table 1 were selected due to their occurrence in the environment, literature citations and availability of validated methods from commercial laboratories (Prevedouros et al., 2006; Sinclair et al., 2007; Rankin et al., 2016). While some of the compounds listed are less likely to form from the incineration of PTFE, the perfluoro-carboxylic acids, thirteen of which were included in this study, have been suggested as potential combustion products (Arito and Soda, 1977; Ellis et al., 2003).

2.1. BRENDA facility

The Institute for Technical Chemistry at KIT operates a rotary kiln test facility equipped with a boiler for heat recovery and a flue gas cleaning system which complies with German emission regulations (17 BImSchV, 2003). The pilot plant BRENDA (Fig. 1) provides scalable combustion research opportunities such as thermal behavior of end-of-life technical and consumer products. BRENDA has an overall thermal power of 2.5 MW, where 1.5 MW are from the rotary kiln and 1 MW from the post combustion chamber. (Nolte et al., 2005). For this study, PTFE and wood pellets were weighed and fed to the rotary kiln, while natural gas was supplied to the kiln and to the post combustion chamber. Table 1 in the Appendix summarizes all experimental process parameters.

The mass flow of wood pellets was kept constant at 100 kg/h using a connecting belt weigher and PTFE was added to the connecting belt at a rate of 0.3 wt% $\triangleq$ 300 g/h from a small dosing feeder to ensure uniform blending of the PTFE and wood pellets (Appendix Fig. 1). The range of fluorine concentration in typical municipal waste is 0.010%–0.035% (w/w dry solids) in Germany (EC, 2006). The level of PTFE for the study was chosen to maximize

Table 1
PFAS with procedural quantitation limits.

Compound	CAS number	Abbreviation	Quantitation limit $\mu\text{g}/\text{m}^3$
Perfluorobutanoic acid	375-22-4	PFBA [PFC C4]	6
Perfluoropentanoic acid	2706-90-3	PFPeA [PFC C5]	0.3
Perfluorohexanoic acid	307-24-4	PFHxA [PFC C6]	0.3
Perfluoroheptanoic acid	375-85-9	PFHpA [PFC C7]	0.3
Perfluorooctanoic acid	335-67-1	PFOA [PFC C8]	0.3
Perfluorononanoic acid	375-95-1	PFNA [PFC C9]	0.3
Perfluorodecanoic acid	335-76-2	PFDA [PFC C10]	0.3
Perfluoroundecanoic acid	2058-94-8	PFUdA [PFC C11]	0.3
Perfluorododecanoic acid	307-55-1	PFDoA [PFC C12]	0.3
Perfluoro-tridecanoic acid	72629-94-8	PFTriDA [PFC C13]	0.3
Perfluorotetradecanoic acid	376-06-7	PFTeDA [PFC C14]	0.3
Perfluorobutanesulfonic acid	375-73-5	PFBS [PFS C4]	0.3
Perfluorohexanesulfonic acid	355-46-4	PFHxS [PFS C6]	0.3
Perfluoroheptanesulfonic acid	375-92-8	PFHpS [PFS C7]	0.3
Perfluorooctanesulfonic acid	1763-23-1	PFOS [PFS C8]	0.3
Perfluorodecanesulfonic acid	335-77-3	PFDS [PFS C10]	0.3
Perfluorooctanesulfonamide	754-91-6	PFOSA	0.3
N-Methyl- Perfluorooctanesulfonamide	31506-32-8	N-Me-FOSA	0.3
N-Ethyl- Perfluorooctanesulfonamide	4151-50-2	N-Et-FOSA	0.3
N-Methyl-Perfluorooctane- sulfonamidoethanol	24448-09-7	N-Me-FOSE alcohol	0.3
N-Ethyl-Perfluorooctane- sulfonamidoethanol	1691-99-2	N-Et-FOSE alcohol	0.3
1H,1H,2H,2H-Perfluoro- octanesulphonic acid	27619-97-2	1H, 1H, 2H, 2H- PFOS	0.3
2H,2H,3H,3H-Perfluoro- undecanoic acid	34598-33-9	4HPFUnA	0.3
Perfluoro-3-7-dimethyl octane carboxylate	-	PF-3,7-DMOA	0.3
7H-Dodecafluoro heptane carboxylate	-	HPFHpA	6
2H,2H-Perfluoro decan carboxylate	-	H2PFDA	0.3
1H,1H,2H,2H-Perfluorohexan-1-ol	2043-47-2	4:2 FTOH	24
1H,1H,2H,2H-Perfluorooctan-1-ol	647-42-7	6:2 FTOH	24
1H,1H,2H,2H-Perfluorodecan-1-ol	678-39-7	8:2 FTOH	24
1H,1H,2H,2H-Perfluorododecan-1-ol	865-86-1	10:2 FTOH	24
Trifluoroacetic acid	76-05-1	TFA	0.4

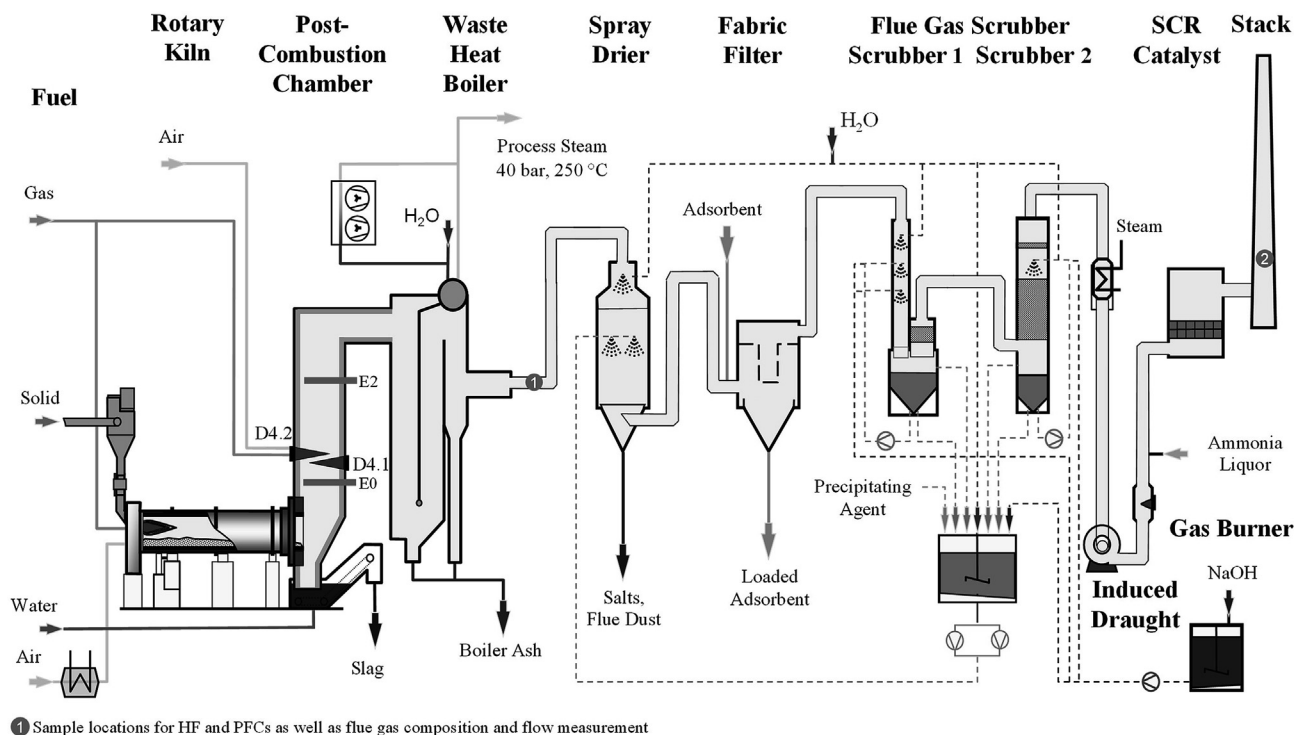


Fig. 1. Schematic of the BRENDA pilot combustion facility at KIT.

the mass fraction of PTFE to fuel while staying well below the 1% total halogen limit set by regulations (17 BImSchV, 2003).

Kiln incline and rate of revolutions were selected in a way to ensure that heat up, drying, pyrolysis and char burnout of the feedstock could be fulfilled (Gehrmann, 2005).

The combustion gases from the rotary kiln were fed into the post combustion chamber equipped with two combined burners for gases and secondary combustion air. The burners (D4.1 and D4.2) were staggered anti-parallel to each other. This configuration allowed for high turbulence and improved mixing of the combustion gases.

Regarding the influence of temperature and residence time in the post-combustion chamber on the decomposition rate of PFAS, the basic load of the rotary kiln was kept constant at approx. 1 MW, while the natural gas burners (D4.1 and D4.2) adjusted the temperature and residence time in the post-combustion chamber (Fig. 1). The experiment employed two post combustion chamber conditions to account for partial load (S1) and full load (S2) scenarios common at waste incineration facilities. The low load scenario (S1) ran at a temperature of 870 °C and residence time of 4.0 s, while the full load scenario (S2) ran at 1020 °C for 2.7 s.

To characterize the combustion behavior of the flue gases, samples were extracted via water-cooled lances at the level E0 (after the rotary kiln) and at the level E2 (after the supply of natural gas and air in the post combustion chamber).

The hot flue gases left the post-combustion chamber and entered the boiler, where they were cooled to approximately 300 °C. The flue gas then entered the pollution control devices which consisted of a spray dryer, a fabric filter, two scrubbers, and a SCR catalyst which met German emission regulation requirements (17 BImSchV, 2003).

2.2. Test materials

The PTFE pellets used for incineration were provided by W.L.

Gore & Associates GmbH, Putzbrunn; the wood fuel pellets by EC Bioenergie GmbH; and natural gas by Enercity Hanover. Detailed analyses of the combustion materials are presented in the Appendix.

2.3. Flue gas sampling methods

The flue gas samples were collected after the heat exchanger (boiler) but upstream of the spray dryer which is the beginning of the pollution control systems (see Fig. 1). This was the optimal location to find the compounds of interest because the flue gas temperatures decreased from 850 to 1000 °C to below 300 °C which allowed for potential condensation reactions, but excluded any dilution and/or extraction of the compounds from the pollution control systems.

Two methods were utilized to collect flue gases. The first method, based on USEPA Method 5 was chosen to collect fluorocarbon compounds of interest (see Table 1) during short-time measurements. The second method, based on VDI 2470 which includes filter units outside of the flue gas duct, was chosen to collect fly ash and HF (VDI 2470, 2011) using long time-measurements.

2.3.1. Test setup for fluorocarbons according to EPA method 5

The first method for flue gas collection utilized the isokinetic sampling train shown in Appendix Fig. 2 (USFR, 2016). Stack sampling procedures consistent with EPA Method 5 for stationary source sampling were followed, except the flue traverse collections points were limited to one axis due to obstructions to the secondary axis. Since the primary system flow measurements (from the modified EPA Method 5 sample train) agreed with the flow calculation within 0.06–4.56% and turbulent mixing occurs prior to the sampling zone (validated by high Re-numbers ($>10^5$)), this exception to the method did not impact the results of this study.

PFAS were sampled using a modified EPA Method 5 sampling train, utilizing three capture technologies, filtration, impinger

sampling and solid adsorbent sampling. Each sampling train was broken down into four samples: quartz fiber filter (1 each), 0.15 M NaOH impinger solutions (450–500 ml), XAD-2 Resin + PU foam (22–26 g), and a methanol rinse of the train glassware (150–250 ml). Each of the four samples was sent to a third party laboratory for analysis.

2.3.2. Test setup HF-analytics according to VDI 2470

Out-stack measurements of raw gas and post pollution control system gas at large-scale plants are performed according to VDI 2470 which is similar to the EPA Method 5 and is detailed described in the Appendix (Figs. 3 and 4).

The main difference between VDI 2470 and EPA Method 5 is the order of flue gas treatment. Per the VDI guideline, an empty impinger is used to collect the condensate after the filter, while the EPA Method uses the first two impingers to collect the condensate.

2.4. Laboratory analysis methods

PFAS analyses were carried out via Liquid Chromatography-Mass spectrometry (LC-MS/MS) at laboratories that offered commercially validated methods for the listed compounds (Table 1). SGS Institut Fresenius GmbH- Taunusstein, Germany (SGS) performed trifluoroacetic acid (TFA) sample analysis. All other PFAS analyses were completed at Intertek Consumer Goods GmbH, Fürth, Germany (Intertek).

Intertek performed liquid chromatography mass spectrometry (LC-MS/MS) blank and spike analyses using 0.5 µg/l standard for the majority of the compounds yielding between 43% and 128% recovery depending on the sampling matrix and compound. The fluorotelomer alcohols (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) were spiked with 25 µg/l yielding between 56% and 156% recovery depending on sampling matrix and compound. While a few of the compounds had low recoveries at the 0.5 µg/l level, the major of spike results were between 70 and 100% recovery. A list of spike recoveries for each of the sample collection matrixes is available in the supplemental data appendix.

VDI 2470 sampling analyses included four parts, fly ash total mass concentration, fly ash burnout (total carbon), the fluoride captured from the vapor stream and weight percent fluoride (F^-) in the fly ash. All analyses for VDI 2470 were carried out by KIT except for the weight percent fluoride in the fly ash, which was carried out by H.C. Starck using a pyrohydrolytic separation of the fluorine with the support of total ionic strength adjustment buffer I solution potentiometrically. This method is briefly described in Pyrohydrolysis in the Determination of Fluoride and Other Halides (Ware et al., 1954). Fly ash concentration in the flue gas was determined by the mass difference of the filters implemented in the long term sampling device in accordance with VDI 2470. The burnout of the fly ash (given as total carbon) was determined via a thermogravimetric analysis according to VDI 2465, part 2 and infrared spectroscopy (IR) detection. Analysis of F^- from the vapor stream was carried out using ion chromatography (IC), on a Thermo ICS 1000.

Total fluorine analysis of the wood pellets was performed by Eurofins Lab in Freiberg, Germany (Eurofins) by the means of a bomb digestion and ion chromatography of the captured condensates. The method is described in detail in DIN EN ISO 16994:2016–12. Eurofins is certified according to Deutsche Akkreditierungsstelle (DAkkS) (D-PL-14081-01-00).

2.5. Thermogravimetric analysis (TGA)

To estimate the thermal stability of the material, TGA was performed under nitrogen and air atmospheres with different heating rates. For more details on the methods, see the Appendix.

2.6. Quantitation limits (LOQ)

With the exception of TFA, quantitation limits were determined by the quality control procedures of the third party laboratories (i.e. Intertek and H.C. Starck). The procedural quantitation limits were calculated using the third party laboratory quantification limits for each sample type (quartz filter, impinger solution (NaOH), adsorbent media and methanol glassware rinse divided by the sample mass fraction then summed up and divided by the volume of flue gas sampled for each compound analyzed (Appendix, Tables 10 and 11). Procedural quantification limits were calculated for TFA based on field blank samples (DIN 32645, 2008). When the LOQ is analyzed, for further calculation the half of the LOQ is used (Japan MOE, 2001).

2.6.1. Statistics

Paired t-testing was utilized to determine if the addition of PTFE created a statistical difference from background levels and to minimize potential interference from external sources. Multiple pairs were analyzed and each pair contained two runs (a blank or control run with the incineration system running at the condition settings with 100 kg/h wood pellet solid fuel and a PTFE spiked run with 300 g/h PTFE pellets added to the wood pellet fuel). A 95% confidence interval was set to determine significance. Thus a p-value of 0.05 was required to determine if a signal could be distinguished when compared to a control (blank) run. It should be noted that all compounds listed in Table 1 were evaluated separately.

3. Results and discussion

This chapter is divided into results from analysis of the supplied materials (PTFE, wood pellets), combustion behavior, fluorine mass balance and the results from the PFAS analysis.

3.1. Analysis of the fuels

Wood pellet samples were collected from each shift and were analyzed in duplicate by Eurofins ($n = 15$). The primary elemental composition which included carbon and hydrogen showed a low standard deviation between 0.01 for hydrogen through 0.03 for all other elements. All fluorine values were below the detection limit of 0.001% with exception of one sample collected on February 11th 2018 (see Fig. 8 in the Appendix). In this case a third sample was collected and analyzed to verify that the single detectable analysis was an outlier.

The chemical content and the quality of the PTFE granules were proved with the help of Energy Dispersive X-ray Analysis (EDX) and Fourier-Transform Infrared Spectroscopy (FT-IR).

The Fluorine and Carbon concentration determined experimentally by the means of EDX (Fig. 9, Appendix) agreed with the theoretical values derived from the stoichiometric formula of PTFE – $[C_2F_4]_n$, i.e. 33.33 mol-% C and 66.67 mol-% F.

In one of the investigated granules, traces of Al (0.24 mol-%) were detected. In this case, contamination potentially occurred during the sample preparation.

In the FT-IR spectra of the granules only the characteristic bands of PTFE were presented (Fig. 10, Appendix). The most intense bands at approx. 1200 cm^{-1} matched the stretching vibrations of CF_2 at 1211 cm^{-1} and 1154 cm^{-1} (Fazullin et al., 2015). The band below 650 cm^{-1} showed the rolling vibrations and the planar deformation of CF_2 (Fazullin et al., 2015).

TGA indicated that the PTFE decomposition process appeared to start around 500 °C and was complete around 650 °C (Appendix, Tables 3 and 4; Figs. 9 and 10). Estimated half-life times at 800 °C

($\tau_{1/2} = \ln 2/k$ for first order reactions) were well below 0.1 s. Complete decomposition could be expected approximately at ten half-life times, equating to less than 1 s residence time at this temperature.

3.2. Combustion behavior

The mass flow of wood pellets and natural gas as well as the respective air ratios for combustion were adjusted to obtain enough thermal output, to avoid ash melting and to avoid loss of unburnt pellets into the deslagger (see Fig. 1), which was located after the rotary kiln. The air ratio for the natural gas, as the fuel with the greatest thermal output, was set below one ($\lambda = 0.7$), while the main air in the rotary kiln was set to a superstoichiometric value ($\lambda = 2.5$). Thus, the overall air ratio in the kiln was 1.43 without considering air leakage. This stoichiometry setting reduced the NO_x -emissions by about 40% compared to the combustion of natural gas ($\lambda = 2.0$) and gasification of wood pellets ($\lambda = 0.7$, Fig. 13 Appendix) at constant total air ratio in the rotary kiln.

Frequent visual observation of the solid movement towards the ash discharger confirmed no loss of solids into the discharger. This indicated an almost complete conversion of the PTFE and the wood pellets in the rotary kiln into the gas phase. From the profile measurements across the diameter of the post combustion chamber E2 (see Figs. 1 and 12 in the Appendix) average CO concentration as an indicator for the gaseous burnout for both settings were determined to values equal and below 1 mg/Nm³ referred to 11 vol.-% of O₂ independent of the CO release of the rotary kiln (measured at the level E0). The total carbon results, which were analyzed in one fly ash sample taken at S1 after the boiler supported the favorable burnout with 0.25 wt.-% of remaining carbon (see Table 5 in the Appendix). The concentrations of dust were in the range of 8–11 mg/m³ for setting S1 and about 6–7 mg/m³ for setting S2. Please note, the average ash content of the wood pellets

was 0.32 wt.-% when tested independently (see Fig. 5 of the Appendix). These results showed that the combustion was very efficient.

3.3. Fluorine balance

To generate the Fluorine balance, the dry flue gas flow after the boiler was needed. The measured wet flue gas flow from BRENDA and the water vapor measurement from the IR technique were used to calculate the fluorine balance.

The PTFE feeding rate was 300 g/h which corresponds to a mass flow of 228 g/h of fluorine (F). After combustion, fluorine leaves BRENDA in gaseous form, as HF and in solid form, as F-containing ash. Thus, the total fluorine mass flow (total F-export) leaving the system is the sum of the “gaseous” and the “solid” fluorine mass flows.

The difference in the water vapor concentration from combustion calculation (see Table 7 in the Appendix) to the other values relates to the missing measurement of the amount of water evaporated from the deslagger water bath after the rotary kiln.

From the wet flue gas flow from the process control system, the water vapor flow was subtracted from the measured water vapor concentration by IR technique. This concentration comprised the water from combustion and the evaporation from the deslagger water bath. Higher water vapor concentration, determined e.g. from gravimetric method during the long-term sampling of fly ash reduces the dry flue gas volume flow and lead to a lower fluoride outlet and decreased recovery rate (for the long-term sampling the values of the recovery rate are between 56 and 78 wt%). Low recovery rates were expected since fluorides are very reactive especially with silicates which are a main component of the refractory in BRENDA. The fluorine content in the fly ash could be neglected compared to the HF. The summed data for fluoride capture can be found in Fig. 2. The small black lines above the columns are the

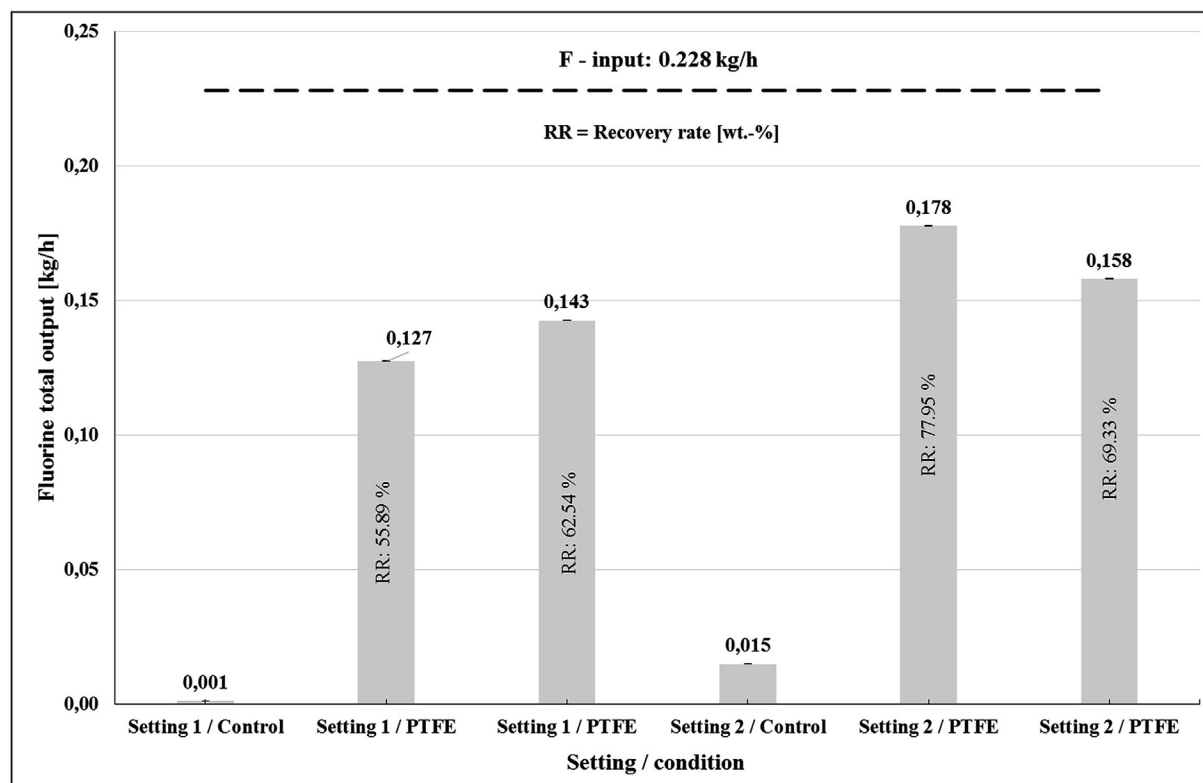


Fig. 2. Fluorine output and recovery rate of fluorine based on water vapor concentrations from long-term sampling.

errors according the error propagation. The errors were negligible.

Please see the Appendix for a detailed discussion of water vapor measurement including error propagation.

3.4. Per- and polyfluoroalkyl compounds (PFAS)

For each run, the concentrations of each substance were calculated by adding their masses found on the filter, in the NaOH, in the MeOH and on the XAD-resin and relating this to the dry gas volume sampled. As an example for the calculations, the measured concentrations of all substances and the respective concentrations at $\frac{1}{2}$ LOQ in each matrix are given in Fig. 3 for the control measurement of paired couple 1 (S1). Only the amount of PFOA in MeOH could be quantified to be about 90 ng/Nm^3 (dry). All other substances were below the LOQ and therefore assumed to be $\frac{1}{2}$ LOQ for further calculations.

By summarizing the concentrations of each substance in all matrices for each run, paired couples, as well as the settings could be compared (see Fig. 4). Due to the varying sample volumes, the LOQ differed for each run. For S1, paired couple 1 is shown. During the paired run, only minor changes in the concentration of PFOA could be observed compared to the control run. Additionally, the concentrations of PFDA and PFDoA were slightly above LOQ. No other substance could be found.

For S2, paired couple 8, no substance was visible above LOQ. Generally speaking, no significant differences can be observed between S1 and S2 with respect to the species detected and their concentrations.

With those results, paired *t*-test were conducted. Paired-*t*-tests are a statistical method to examine the difference of the mean values of two dependent samples and serves to evaluate a hypothesis. In this study, the difference of the concentrations of the PFAS investigated with and without the feed of PTFE was examined. The hypothesis states that the concentrations of the PFAS are independent of the feed of PTFE to the rotary kiln and thus the dispersion around the mean value can either be positive or negative. As a confidence interval, 95% was chosen. Therefore, if the probability value (*p*-value), which is often used to interpret *t*-tests, is > 0.05 , the hypothesis is correct, and no statistical difference exists between the concentrations with and without the feed of PTFE. For $p < 0.05$, the concentrations of the PFAS investigated are dependent on the feed of PTFE and the hypothesis is wrong.

The detailed results for PFOA for both experimental settings are shown in Table 2.

For both settings, the *p*-values are greater than 0.05, thus there is no statistical correlation in the difference of the concentration of PFOA whether or not PTFE is fed to the rotary kiln.

A summary for all PFAS detected in any matrix, for the experimental settings S1 and S2 is given in Table 3 as ng/Nm^3 (dry). Only 11 out of 31 compounds were detected. *P*-values could only be calculated, if the respective substance could be quantified in at least one matrix per measurement and at least 3 paired runs. Otherwise, no calculations could be performed, the PFAS concerned are labelled with “< LOQ”.

For all PFAS investigated, *p*-values were larger than 0.05 for either setting, or the concentrations were too low to be quantified

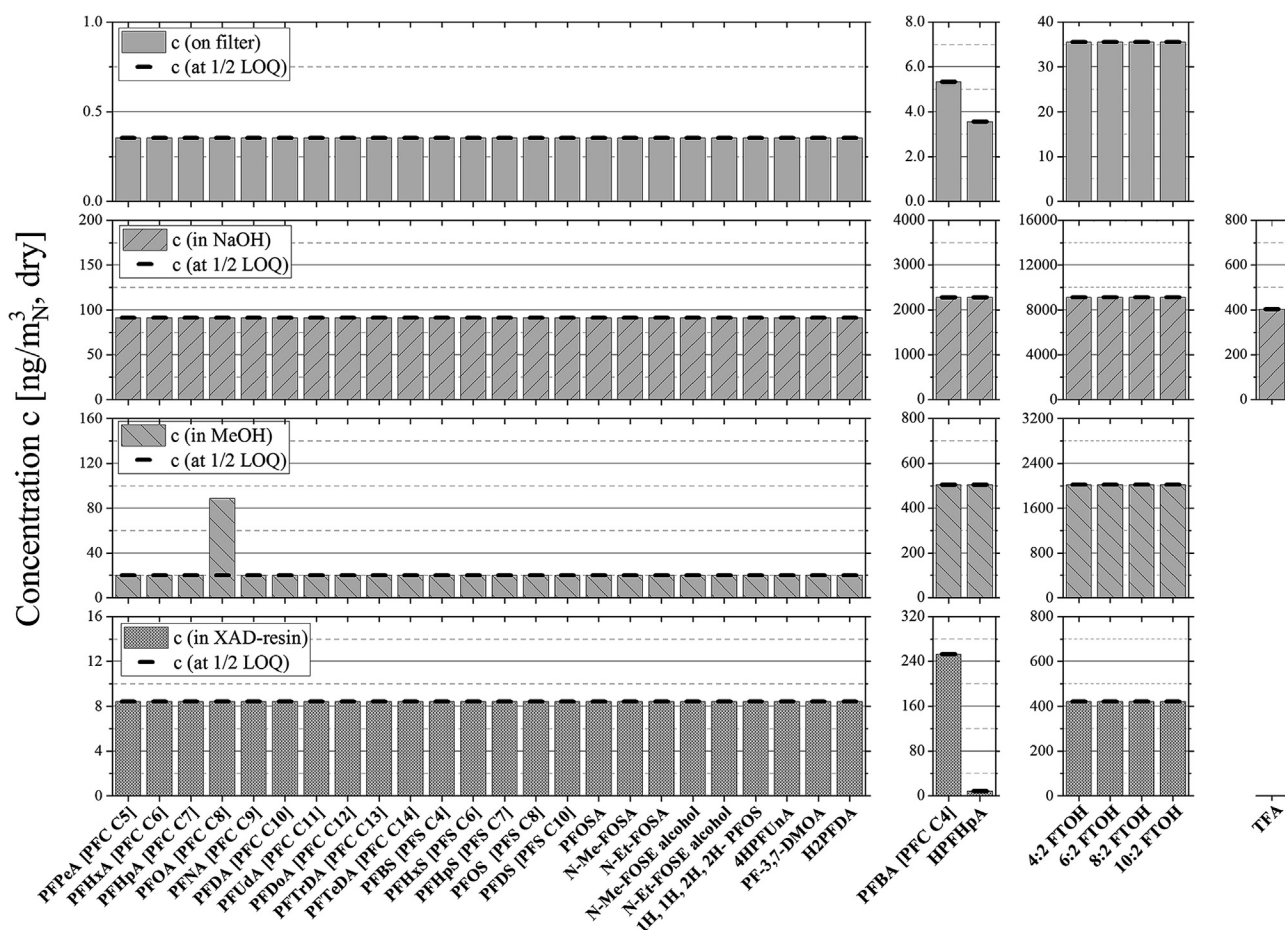


Fig. 3. Pattern of the species for each matrix for the control run of paired couple 1 (S1).

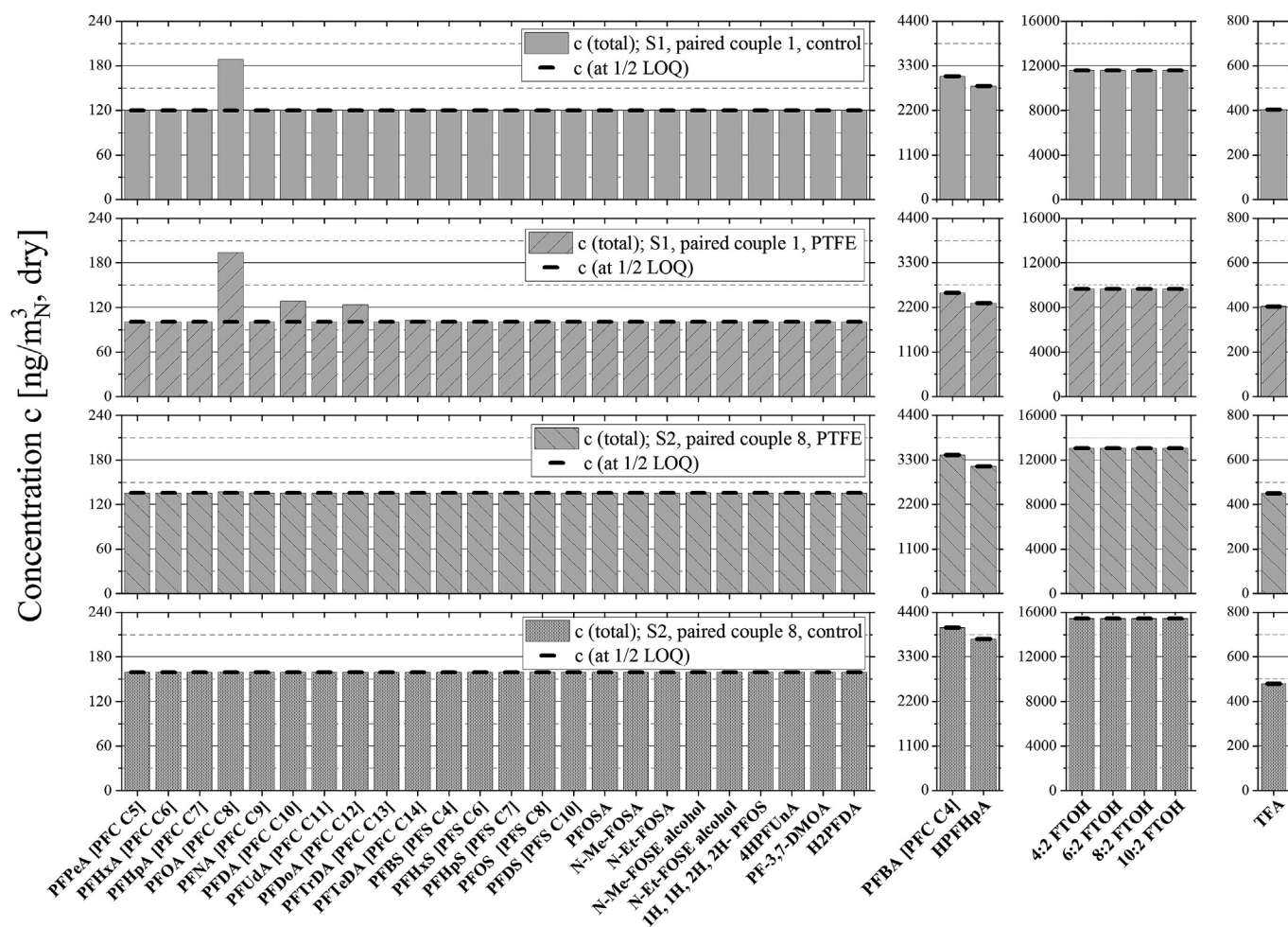


Fig. 4. Pattern of the species for PTFE spiked and control runs for paired couple 1 (S1) and paired couple 8 (S2).

Table 2
Results of t and P-values for PFOA.

Setting	Paired Couple	Type	Concentration [ng/Nm ³ , dry]	Difference (PTFE-Control) [ng/Nm ³ , dry]	t-value	p-value
S 1	1	Control	189	5	−0.624	0.564
		PTFE	194			
	2	PTFE	179	10		
		Control	169			
	3	PTFE	302	70		
		Control	232			
	4	Control	270	84		
		PTFE	354			
	5	Control	723	−539		
		PTFE	184			
S 2	6	Control	258	−70	−0.905	0.407
		PTFE	189			
	7	PTFE	644	487		
		Control	157			
	8	PTFE	137	−22		
		Control	159			
	9	Control	2743	−2600		
		PTFE	143			
	10	PTFE	175	32		
		Control	143			
	11	Control	413	−272		
		PTFE	141			

by the third party laboratories. Therefore no statistical correlation in the difference of the concentration of the PFAS whether or not PTFE was fed could be determined.

Additionally to the experiments at BRENDA spike and blank experiments with PFBA, PFHxA, PFOA, PFDA, PFDoA, PFTeDA and TFA were performed by the KIT and by the third party laboratories.

Table 3Results of all PFAS measured (ng/m3) and *P*-values for statistical comparison.

Abbrev.	Setting S1 (870 °C & 4 s)										p - value
	Pair 1		Pair 2		Pair 3		Pair 4		Pair 5		
	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE	
PFHxA [PFC C6]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	163 ^b	< LOQ	< LOQ
PFHpA [PFC C7]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	153 ^b	156 ^b	< LOQ
PFOA [PFC C8]	189 ^a	194 ^c	169 ^c	179 ^c	232 ^a	302 ^c	270 ^a	354 ^c	723 ^c	184 ^a	0.564
PFNA [PFC C9]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFDA [PFC C10]	< LOQ	128 ^a	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	153 ^b	< LOQ	< LOQ
PFUdA [PFC C11]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	152 ^b	< LOQ	< LOQ
PFDoA [PFC C12]	< LOQ	124 ^c	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	152 ^b	< LOQ	< LOQ
PFTrDA [PFC C13]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFTeDA [PFC C14]	< LOQ	102 ^b	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	154 ^b	< LOQ	< LOQ
PFBS [PFS C4]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
N-Me-FOSE alcohol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Abbrev.	Setting S2 (1020 °C & 2.7 s)										p - value		
	Pair 6		Pair 7		Pair 8		Pair 9		Pair 10			Pair 11	
	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE	Control	0.3% PTFE		Control	0.3% PTFE
PFHxA [PFC C6]	154 ^b	< LOQ	< LOQ	136 ^b	< LOQ	< LOQ	138 ^b	< LOQ	< LOQ	< LOQ	118 ^b	< LOQ	0.368
PFHpA [PFC C7]	< LOQ	< LOQ	< LOQ	135 ^b	< LOQ	< LOQ	138 ^b	< LOQ	< LOQ	< LOQ	116 ^b	< LOQ	0.424
PFOA [PFC C8]	258 ^c	189 ^c	< LOQ	644 ^c	< LOQ	137 ^b	2743 ^c	143 ^b	143 ^b	175 ^c	413 ^c	141 ^b	0.407
PFNA [PFC C9]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	128 ^b	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFDA [PFC C10]	< LOQ	145 ^b	< LOQ	133 ^b	< LOQ	< LOQ	130 ^b	< LOQ	< LOQ	< LOQ	117 ^b	< LOQ	0.536
PFUdA [PFC C11]	< LOQ	< LOQ	< LOQ	133 ^b	< LOQ	< LOQ	128 ^b	< LOQ	< LOQ	< LOQ	115 ^b	< LOQ	0.571
PFDoA [PFC C12]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	128 ^b	< LOQ	< LOQ	< LOQ	115 ^b	< LOQ	< LOQ
PFTrDA [PFC C13]	< LOQ	< LOQ	< LOQ	134 ^b	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
PFTeDA [PFC C14]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	131 ^b	< LOQ	< LOQ	< LOQ	115 ^b	< LOQ	< LOQ
PFBS [PFS C4]	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	141 ^b	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
N-Me-FOSE alcohol	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	136 ^b	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	140 ^b	< LOQ

^a Only found in MeOH, all other concentrations were assumed as 1/2 LOQ.^b Only found on Filter, all other concentrations were assumed as 1/2 LOQ.^c Only found in MeOH & on Filter, all other concentrations were assumed as 1/2 LOQ.

It turns out recovery rates are dependent on the matrix and the carbon chain length. For detailed results, please see the appendix (Table 12).

4. Conclusion

Of the 31 PFAS species studied only 11 were detected. When comparing the PFAS measurements, for the few compounds detected, no difference from baseline/control levels using paired *t*-testing for significance could be distinguished. Based on the PFAS levels detected and the randomness of the occurrence throughout the study, it is likely that the source of these signals are due to contamination of the samples from the environment. With procedural quantitation limits between 0.3 and 24 µg/Nm³ depending on compound and volume captured (see Table 1), these results give no significant evidence that the PFAS studied (Table 3) were created during the incineration of PTFE could be found. Therefore, it can be expected that municipal incineration of PTFE using BAT is not a significant source of studied PFAS and should be considered an acceptable form of waste treatment.

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Data Availability – All data and information used in this manuscript have been made available by the authors and are included in the paper and the Supplemental Data (Appendix).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.191>.

Disclosure statement

D. Pigeon is an employee of W.L. Gore, a global manufacturer of products made with fluoropolymers. K. Aleksandrov, H.J. Gehrman, M. Hauser, H. Mätzing, D. Stapf, and M. Wexler are affiliated with Karlsruhe Institute of Technology (KIT). KIT was retained and compensated by W.L. Gore to assist in conducting this study and writing of this paper. W.L. Gore & Associates, Inc. and Karlsruhe Institute of Technology donated employee and student time to support this work.

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