Title:

Determination of PFAS Compounds in Exhaust Gas and Residues from Combustion of Fluoropolymers in a Pilot Plant under Representative European Municipal Waste & Hazardous Waste Combustor Conditions

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1 **Determination of PFAS Compounds in Exhaust Gas and Residues from Combustion of**

2 **Fluoropolymers in a Pilot Plant under Representative European Municipal Waste &**

3 **Hazardous Waste Combustor Conditions**

4

5 **Abstract**

6   Concern related to the end-of-life phase of fluoropolymers (FP) emanates from the data

7 gaps on non-polymeric PFAS emissions, potentially generated from municipal and industrial waste

8 incinerators processing fluoropolymer waste. The goal of this study was to provide data to support

9 complete mineralization of fluoropolymer waste and insignificant generation of PFAS during

10 incineration of fluoropolymer applications at the end of life. This study demonstrated that FP in

11 incinerators operated according to the EU Directive regulations are converted to inorganic fluorides

12 (detected as hydrogen fluoride at recoveries between 70 to 80 wt. %) and carbon dioxide. Statistical

13 analysis of the PFAS measurements from the combustion runs demonstrated that PFOA was the

14 only quantified PFAS in the gas stream. Seven other PFAS were detected in the combustion runs

15 at levels below 0.5 ng/m^3 but were considered outliers in the statistical analysis. There was no

16 discernible effect of temperature on the mineralization of the FP and the decrease in temperature

17 from 1095°C to 860°C did not show evidence of an increase in PFAS or C_1-C_3 emissions.

18

19 **Graphical Abstract**

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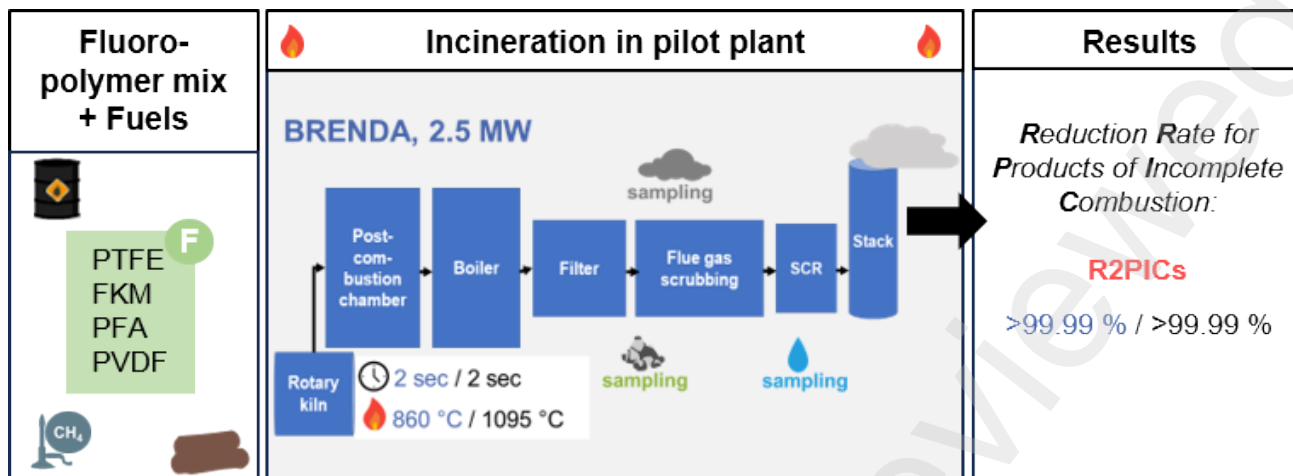
Introduction

23   Fluoropolymers (FP) are inert and high molecular weight substances which are thermally,

24 biologically, and chemically stable, insoluble in water, non-mobile, non-bioavailable, non-

25 bioaccumulative, and non-toxic. However, there are some concerns related to the lifecycle of FP,

26 mainly during manufacturing and end-of-life phases. Manufacturing concern is due to intentional

27 use of fluorinated polymerization aids. Hence, the fluoropolymer industry is working diligently to

28 develop non-fluorinated polymerization aids, thus limiting non-polymeric per- and polyfluoroalkyl

29 substances (PFAS) emissions.

30   In 2020, about 40 kilotons of fluoropolymer materials were sold to European Union (EU)

31 fluoropolymer product manufacturers (Conversio Market & Strategy GmbH, 2022).

32 Approximately 23.5 kilotons of fluoropolymer waste were collected, either in commingled waste

33 streams or in source-separated waste fractions. Almost 84% of FP were incinerated at the end of

34 their life in energy recovery or hazardous waste incineration units, 13% of collected fluoropolymer

35 waste was landfilled and about 3% was recycled. It was estimated that fluoropolymer waste was

36 only a tiny fraction (less than 0.01% by weight) in comparison to total plastic waste collected.

In February 2023, the EU Member States: Germany, The Netherlands, Sweden, Denmark, and Norway submitted the Annex XV restriction dossier on PFAS under EU Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) to the European Chemicals Agency (ECHA). FP were included in the scope of restriction proposal mainly due to concerns related to their manufacturing and end-of-life stages. The proposal clearly stated that PFAS emissions from incineration of FP were not clearly established or studied. As quoted in the Annex XV dossier, "The effectiveness of incineration to destroy PFAS and the tendency for formation of fluorinated or mixed halogenated organic by-products is not well understood (Lohmann et al., 2020). In general, PFAS emissions from waste incineration are not well studied, but it is clear efficiency of the destruction method depends on numerous (operational) conditions".

The objective of current study it to determine if fluoropolymer materials result in the formation of PFAS emissions downstream of a pilot incineration plant under representative European municipal solid waste and hazardous waste combustor conditions.

Materials and Methods

Incineration Pilot Plant BRENDA

Experiments were carried out at the pilot plant BRENnkammer mit DAmpfkessel (BRENDA), which was operated by the Institute of Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT). Pilot plants are a suitable tool for evaluation of waste behavior via incineration and for transfer of findings to industry. BRENDA (see Fig. 1) consists of a rotary kiln, a post combustion chamber, a boiler for heat recovery, and a flue gas cleaning system which complies with German emission regulations (17 BImSchV). The thermal output of the rotary kiln is 1.5 MW (max) while that of the post-combustion chamber is ~1 MW. Thus, the overall thermal

60   output of the plant is ~2.5 MW. The rotary kiln is equipped with a versatile multi-fuel feeding

61   system able to inject liquid, solid, as well as gaseous fuels. The length and inner diameter of the

62   kiln is 8.4 m and 1.4 m, respectively. The inclination of kiln can be adjusted between 0.5° and 3°.

63   Kiln rotation speed can be varied between 0.1 and 3 rpm. From the rotary kiln, the combustion

64   gases flow into the post-combustion chamber (PCC), which contains two natural gas burners,

65   staggered in an opposed manner and slightly shifted to each other (see Fig. 1). Gas temperature

66   and residence time in the PCC were adjusted with the help of the burners. Exiting the post-

67   combustion chamber, the hot exhaust gas enters the boiler where saturated steam at a pressure of

68   40 bar and temperature of 250°C is generated. The exhaust gas then cools and enters the flue gas

69   cleaning system, which includes a spray dryer, a baghouse filter, and an acidic and a neutral

70   scrubber. In the last stage of the gas cleaning system, nitrogen oxides are removed with a selective

71   catalyst reduction (SCR) catalyst unit. Finally, clean gas is released into the atmosphere through

72   the stack.

73   During Setting 1 (see Table 1 and Table S1, Supplemental Information), the rotary kiln was

74   operated with heating oil, wood chips and a small amount of natural gas, at total thermal power of

75   1.1 MW. In Setting 2, rotary kiln output power was reduced to 0.9 MW and the amount of natural

76   gas in PCC was increased from 22 m³/h to 35 m³/h per burner. Simultaneous increase in natural

77   flow rate and reduction of introduced air resulted in decrease in stoichiometry (air ratio). The

78   residual oxygen content in the flue gas at the PCC (location E2, Fig. S1) decreased from ~11% to

79   ~7% by volume dry. The carbon burnout, measured as CO, was in the low range (see Table S1), in

80   each case based on 11 vol.-% O_2. Good combustion conditions were ensured for all runs, including

81   those with FP fed to rotary kiln.

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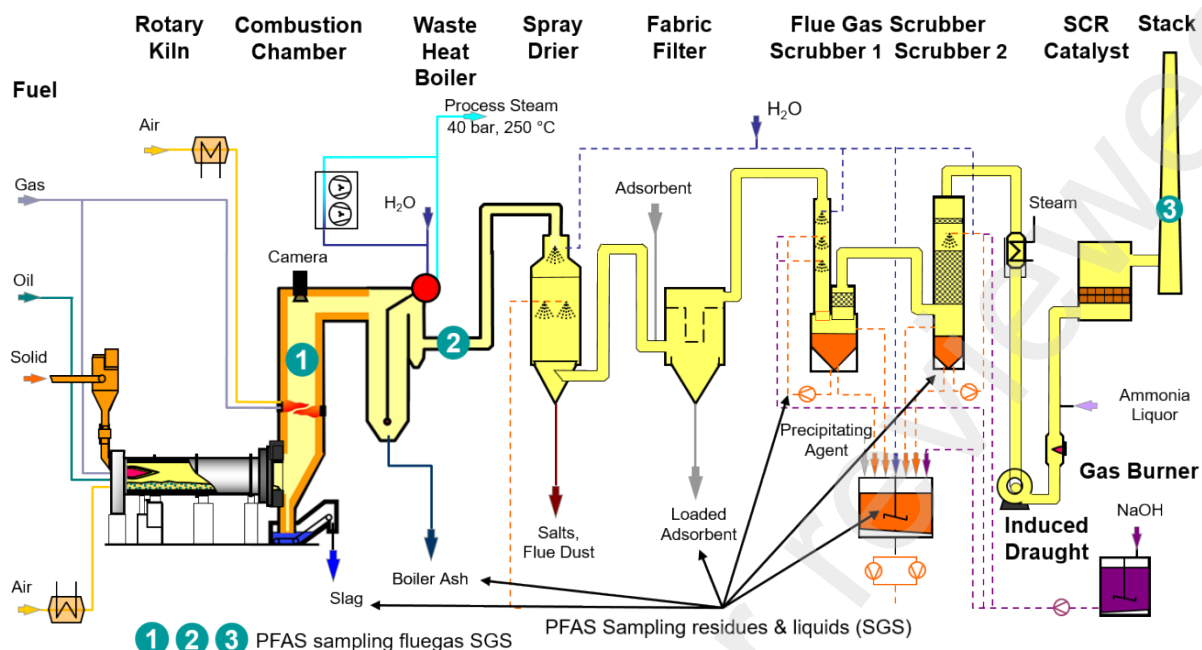
83
84 **Fig 1.** Layout of BRENDA incineration pilot-plant with PFAS sampling locations.

85 Feed Material

86   The feed material consisted of a mixture of polytetrafluoroethylene (PTFE), polyvinylidene

87 fluoride (PVDF), perfluoro alkoxy alkane (PFA) and fluoroelastomers (FKM) (see Table S2),

88 which represent more than 80% of global commercial production of FP.

89   Each fluoropolymer material was grinded in small pieces with a length from 3 mm to 6 mm

90 that allowed their mixing with wood chips before entering the rotary kiln. Throughout the

91 experiments, the total mass flow of feed FP was ~320 g/h, corresponding to a fluorine mass flow

92 of ~230 g/h. This fluorine mass flow rate assured that the fluorine concentration was below the

93 total halogen limit concentration of 1%, set by legislature. The base flow rate of natural wood chips

94 was 100 kg/h. The elemental composition of wood chips is given in Table S3. The background

95 level of fluorides in the wood chips was below the detection limit of 0.010 wt.%, indicating the

96 primary source of fluorine input was from the fluoropolymer feed.

97

Pilot-Plant Operational Parameters

99   The incineration of FP was studied for two sets of tests (Setting 1 and Setting 2, see Table

100   1). The purpose was to burn FP under conditions relevant to EU municipal and hazardous waste

101   combustors. The BRENDA pilot plant operation parameters are shown in Table S3, including

102   calculations of minimum gas residence time for the operational conditions and post combustion

103   chamber pilot plant geometry (see Fig. S1). For Setting 1, a temperature of 860°C was measured

104   and a residence time of 2 sec in the post-combustion chamber was calculated. For Setting 2, the

105   temperature in the PCC was increased to 1095°C while the residence time was maintained at 2 sec.

106   PFAS measurements were carried out with fluoropolymer input (Setting 1, RUN 2, and

107   Setting 2, RUN 5), as well as without fluoropolymer input (Setting 1, RUN 1 and RUN 3, and

108   Setting 2, RUN 4 and RUN 6) (see Table 1). This test sequence provided as assessment of the

109   system background PFAS concentrations for comparison with the PFAS measurements obtained

110   with fluoropolymer combustion.

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116   **Table 1**: Sequence and designations of tests at BRENDA pilot plant

Setting	Test Conditions		
	Background combustion with oil, natural gas and wood chips	Combustion with oil, natural gas, wood chips and FP	Background combustion with oil, natural gas and wood chips
	Start-up of pilot plant		
1	RUN 1	RUN 2	RUN 3

	Change of temperature in post-combustion chamber		
2	RUN 4	RUN 5	RUN 6
	Shut down of pilot plant		

117

Sampling Methods

119   Three gas sampling locations were chosen to measure PFAS emissions and to determine

120   potential PFAS sources at different stages of the combustion process, see Fig. 1 and Fig. S1,

121   respectively. The first sampling location was on the exit of the PCC, the second was downstream

122   the boiler, and the third was in the stack. The following analytes were measured: AOF - adsorbable

123   organic fluorine, IF - inorganic fluorine, TFA - trifluoroacetic acid, long-chain PFAS, and volatile

124   C_1-C_3 fluorocarbons. Sampling was conducted three times at each sampling point. Additional

125   liquid and solid samples that were collected and analyzed for long-chain PFAS included the

126   following: 1) the gas scrubber water upstream of SCR catalyst (wastewater from Scrubber 1 and

127   from Scrubber 2 and the neutral water fed to these scrubbers), 2) water from the wet deslagger, and

128   3) the solid residues from the filter and boiler.

129   Sampling was carried out with a sampling train designed with guidance from OTM-45 (see

130   Fig. S2). The sampling train involved the removal of the first XAD-2 cartridge in the OTM-45

131   sampling train due to low recovery rates for some of PFAS and its impact on TFA and IF analysis.

132   Since the XAD-2 cartridge had to be extracted with an ammonia/methanol solution, this extraction

133   creates a negative bias on the water-soluble TFA and IF sampling. The heated dust filter (see Fig.

134   S2) was followed by a condenser (only for sampling location 1), a single condensate impinger, two

135   water impingers, and a single 0.1M NaOH impinger (all impingers contained in an ice bath),

136   followed by a breakthrough XAD-2 cartridge. Further details of the sampling train are given in

137   the Supplemental Information – Sampling Methods.

7 | P a g e

138   According to OTM-45, a sample train field blank (STFB) blank was necessary for

139   previously used glassware. As there were only two sampling trains per sampling point available,

140   the glassware was cleaned for each sampling point prior to the next measurement. All glassware

141   was cleaned. However, not every cleaning was proofed with a blank, as the number of STFBs to

142   be carried out for all measuring points would have significantly increased the total number of

143   analyses. Thus, the STFBs were only obtained at sampling location 1, when changing from

144   background to feeding FP and feeding FP back to background to certify the cleaning performance

145   for all cleaned glassware. Location 1 was chosen because of the expected highest levels of PFAS.

146   A summary of collected blanks is given in Table S7.

147   Sampling times for AOF, IF, TFA and PFAS were about 3 h with an average isokinetic

148   volume of 3.2 m_N^3. Sampling for the C_1-C_3 fluorocarbons was done with Tedlar® bags using

149   guidance from Other Test Method - 50 (2024). The sampling time was 5-10 min.

150   <u>Analytical Methods</u>

151   Ultrahigh-pressure liquid chromatography tandem mass spectrometry (UPLC/MS/MS)

152   was used to measure the long-chain PFAS collected in all sampling train components. The quartz

153   filter was also analyzed for IF by ion selective electrode (ISE). Samples collected in the impingers

154   were also analyzed for TFA using UPLC/MS/MS, for IF by ISE, and AOF using Combustion Ion

155   Chromatography with Conductivity Detection (C-IC-CD). The AOF measurements were not

156   considered reliable and are not reported here. ISE was used to analyze impinger samples collected

157   at the three sampling locations for fluoride ion and converted to HF concentrations. The

158   measurements were biased low at the boiler exit location based on comparison with the Tunable

159   Diode Laser (TDL) HF measurements (see below). Further details of the C-IC-CD and the ISE

160   measurements are given in the Supplemental Information. Samples collected in Tedlar® bags were

161 analyzed for C_1-C_3 fluorocarbons by GC-MS. TDL spectroscopy was used to measure HF at the

162 boiler exit.

163 <u>Statistical Data Analysis and FP Mixture Reduction Rate</u>

164 The PFAS and C_1 - C_3 fluorocarbon results reported as "non detect" were assigned a

165 concentration equal to zero according to the (Compendium of water sampling, measurement and

166 analysis 2024) in the Netherlands. To show the impact of the limit of quantitation (LOQ) on the

167 PFAS measurements, calculations were also performed where PFAS values were set to 50% of the

168 LOQ (Japan, Manual 2001), these results are reported in the Supplemental Information.

169 To prevent "outliers" from distorting the overall results, the median (50th percentile)

170 approach was applied (see Supplemental Information) for the flue gas sampling. FP mixture

171 Reduction Rate for Products of Incomplete Combustion (R2PIC) was calculated from Eqn. (2), see

172 Supplemental Information for more details.

173

174 **Results**

175 <u>Evaluation of PFAS Emissions</u>

176 Fluorine mass emission rates from measurements of long-chain PFAS, TFA, and C_1-C_3

177 fluorocarbons are presented in Fig. 2 with "non detect" assigned with a concentration equal to zero.

178 Because of the different units of the PFAS concentrations in the flue gas and the liquid and solid

179 samples (ng/m^3, ng/l and ng/kg respectively), the different concentrations were converted into mass

180 emission rates with their specific volume or mass flow (see Supplemental Information, Eqn. 1).

181 The data for the flue gas are presented using a logarithmic scale.

182 Exhaust gas, scrubber water and solid residue measurements are shown from the

183 combustion tests at 860°C and 1095°C. Fig. 2 shows that only a single PFAS, PFOA, was detected

184 in the flue gas in RUN 5, PFBS in the solid residue, and PFOS in the wastewater. PFBS and PFOS

185 were detected only in Setting 1. Other PFAS were not detected at or above the LOQ.
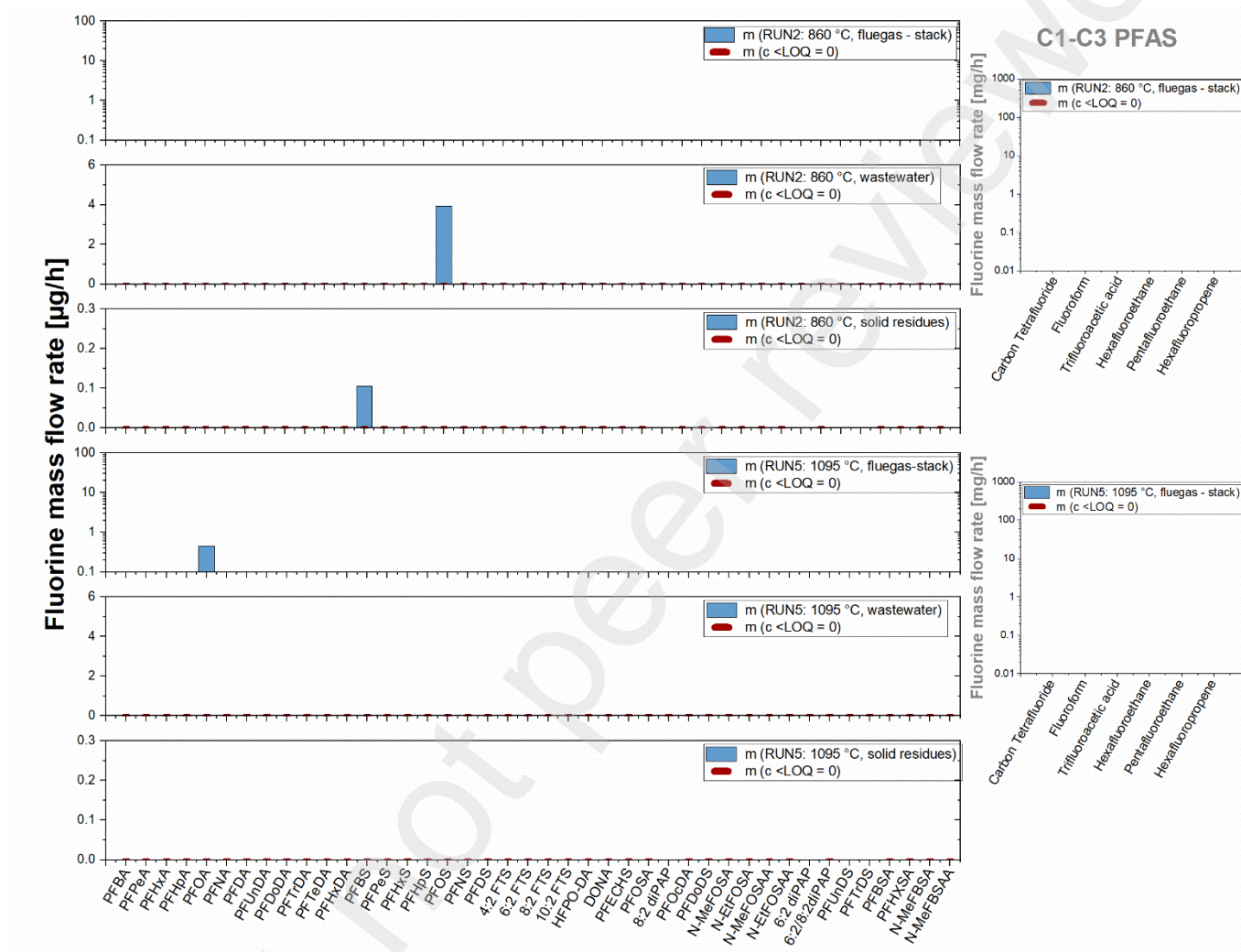
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187 Fig. 2: Fluorine mass emission rates measured in a flue gas, scrubber wastewater, and solid

188 residues for combustion tests at 860°C and 1095°C.

189

190 The PFAS abbreviations are explained in the Supplemental Information.

191

192 <u>Fluorine Mass Balance</u>

193   The feed rate of the fluoropolymer mixture was 0.320 kg/h for each test, which corresponds

194   to a fluorine mass flow of 0.230 kg/h (inlet). A TDL was used to determine HF concentrations at

195   the exit of the boiler (see Fig. 1, sampling location 2). The measured HF concentrations were

196   converted to a fluorine mass flow rate exiting the system (boiler outlet). The fluorine recovery rate

197   was then determined by the ratio of the fluorine mass flow at the outlet divided by the fluorine

198   mass flow rate at the inlet x 100.

199   The results of these measurements provide an indication of fluorine recovery as HF. This

200   is a reasonable assumption given the large amounts of hydrogen provided during the combustion

201   process. As shown in Fig 3, for setting 1, RUN 2, the fluorine recovery was ~80%. The

202   corresponding fluorine recovery rate for Setting 2, RUN 5 was ~70%. The calculated recoveries

203   are based on the averaged values for HF profile measurements, see Fig. S6.

204   Fluoride ion measurements at the stack converted to HF concentrations were below the

205   maximum limit of 1 mg/m_N^3 according to the EU regulations.

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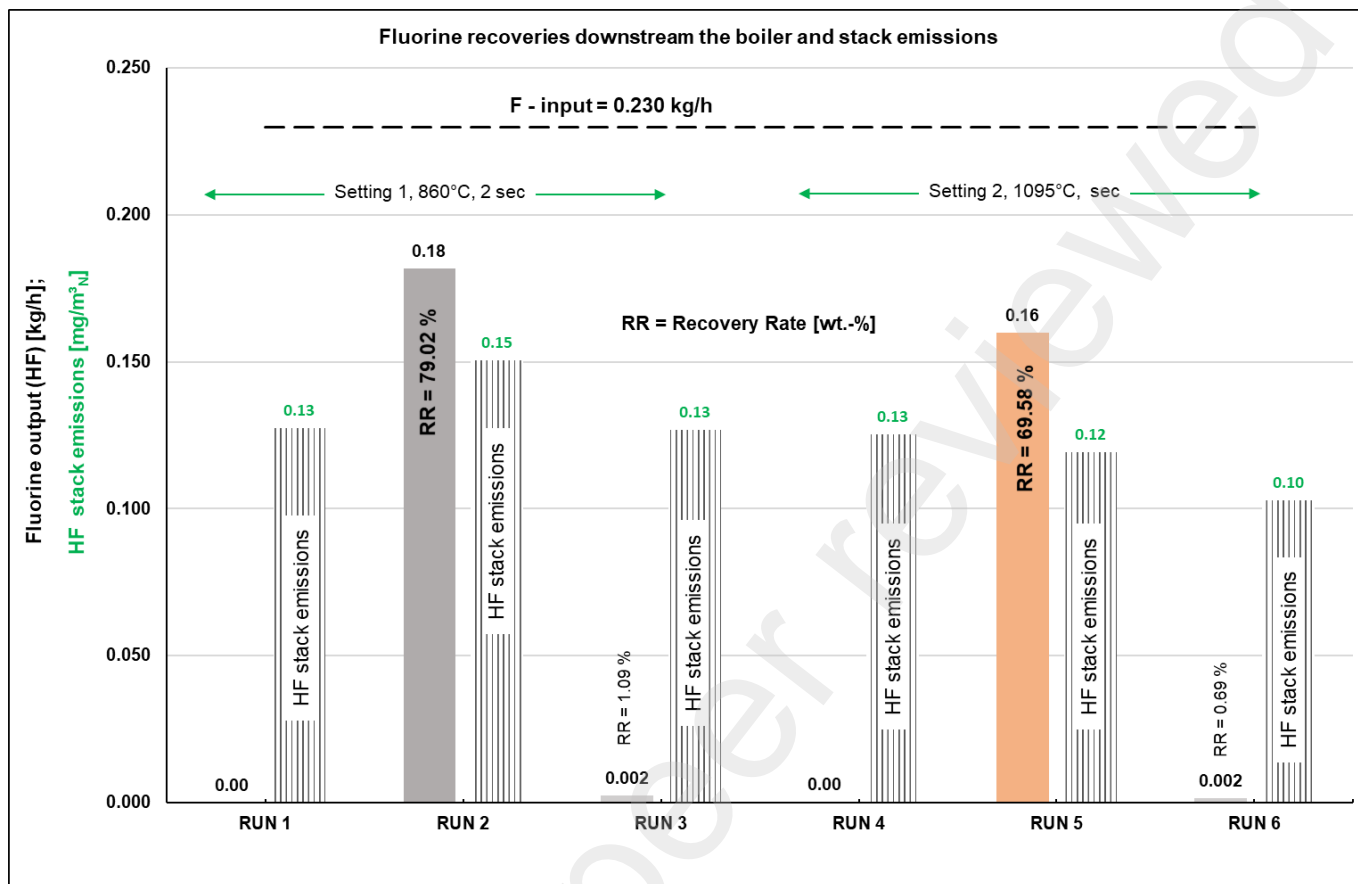
Fig. 3: Total fluorine output measured in-situ with TDL at the boiler exit and from stack emission ISE measurements. The HF stack emissions are normalized to 11 Vol.-% of O_2.

Discussion

FP Degradation and PFAS Emissions

The impact of temperature and residence time on the degradation of fluoropolymers was investigated in one prior published pilot-scale study of the combustion of PTFE (see Aleksandrov et al. 2019). Tests were performed at temperature of 870°C and residence time of 4 sec and at temperature of 1020°C and residence time of 2.7 sec, respectively. Statistical evaluation of the results as a function of operational conditions found no significant difference in measured PFAS

223 concentrations. Furthermore, measured PFAS emissions were not found to vary with or without

224 PTFE feeding.

225   In the current study, a constant residence time was obtained by varying operating

226 temperature (see Supplemental Information). At constant residence time (2.0 s), the increase in gas

227 temperature had no significant influence on PFAS emissions.

228   Statistical analysis of the PFAS emissions measurements indicated that PFOA was the only

229 PFAS that was detected above the LOQ. PFOA was quantified in the stack gas sample in the

230 1095°C FP combustion test (see Fig. 2). This result is not considered definitive, however, as PFOA

231 was also detected in 10 other combustion test samples where the FP was not fed (at levels ranging

232 from 0.04-1.19 ng/m^3). Statistical analysis of the wastewater and ash residue samples indicated

233 that PFBS and PFOS were detected above the LOQ. These results are also questionable given that

234 the FP fed did not contain measurable amounts of sulfur. The source of the PFBS and PFOS may

235 be memory effects or the presence of traces of sulfur in the wood chips fed to support the

236 combustion process.

237   These results are supported by data published in Taylor et al. (2014), where these authors

238 investigated the release of PFOA emissions to the environment in a bench-scale combustion

239 system. In that study, fluorotelomer-based polymers were incinerated in the presence of methanol

240 fuel. Experiments were carried out at 1000°C and residence time of 2 sec. No PFOA concentrations

241 above LOQ of 54 ng/m$_N^3$ for 7% O_2 were detected.

242   The National Institute for Public Health and the Environment of the Netherlands recently

243 investigated to what extent and under what conditions fluoropolymers are thermally degraded and

244 what kind of incineration byproducts are formed (Bakker et al, 2021). In this review, PTFE was

245 found to be the most stable fluorine-containing polymer. For PTFE, it was concluded that complete

246   thermal decomposition is achieved at a temperature of about 800°C. It was, therefore, assumed that

247   other fluorine-containing polymers also thermally decompose completely at a temperature of

248   800°C. Temperatures at the pyrolysis and combustion fronts in the waste-burning bed range from

249   900°C to 1100°C, which is well above 800°C, the temperature at which the complete thermal

250   decomposition of PTFE is achieved.

251   <u>Emission of C_1-C_3 fluorocarbons</u>

252   The only prior bench-scale study of low molecular weight fluorocarbon emissions from

253   combustion of fluoropolymers was reported by Garcia et al. (2007). In this work, percent yields

254   of CF_4, C_2F_6, and C_3F_6 were reported for fuel-rich (sub-stoichiometric) thermal degradation of

255   PTFE at 850°C. The Garcia et al. (2007) study contrasts with the current work in that no flame or

256   hydrogen-containing fuel source was present. Shields et al. (2023) presented similar emission

257   measurements in a pilot-scale study of aqueous film forming foam (AFFF) combustion. In that

258   study, emission concentrations were $\mu g/m^3$ or lower for sampling conducted at temperatures of

259   970°C and above but increased as high as mg/m^3 at temperatures of 870°C and below, suggesting

260   that fluorocarbon intermediates may form at lower incinerator temperatures.

261   The current work was conducted at temperatures of 860°C and 1095°C under excess air

262   combustion conditions representative of municipal and hazardous waste incinerators in the EU.

263   For both test conditions, carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6), and

264   hexafluoropropylene (C_3F_6) were not detected at a LOQ of 11 ppbv, 5 ppbv, and 1 ppbv,

265   respectively. The current work suggests that low molecular weight fluorocarbons are not formed

266   as products of incomplete combustion (PIC) from burning fluoropolymers under representative

267   municipal and hazardous waste incineration conditions.

268   <u>PFAS Emissions from Municipal and Hazardous Waste Incinerators</u>

269   In Germany, residues from flue gas treatment, for example boiler and filter ashes, are

270   disposed in mines, reducing impact to the environment. Even if PFAS concentrations would be

271   higher than the limits given by the regulations according to EU-Directive 2020/784, no harmful

272   impact could be expected. The limits, e.g. for PFOA in residues, are 25 µg/kg for materials,

273   mixtures and products. For operational conditions relevant to municipal and hazardous waste

274   incineration, Awad et al. (2021) found in full-scale waste incinerators a sum of measured PFAS

275   yielded an average of 3.3 µg/kg for bottom ash and 5.6 µg/kg for fly ash. These data are a factor

276   of 10 higher compared to the values found in the current tests, with 0.53 µg/kg up to 0.64 µg/kg,

277   in the filter ash for PFBS.   The recent survey of Björklund et al. (2023) studied a commercial

278   waste-to-energy plant where PFAS were measured in a flue gas. In addition to bottom ash samples,

279   gypsum and process water were analyzed for PFAS. Like Awad et al. (2021), analyses were

280   carried out by Industrial Emissions Directive (IED) 2010/75/EU (2010). For bottom ash, the sum

281   of 8 detected PFAS resulted in 0.23 µg/kg, while for flue gas the concentration of 4.6 ng/m³$_{dry, N}$ at

282   11 vol. % O$_2$ was obtained. Bjorklund et al. (2023) identified PFAS in all residual streams, with

283   short-chain PFCAs (mainly PFBA and PFHxA) being dominant. PIC measurements were not

284   included in any of the studies.

285   In the current study, PFAS emissions were measured from the PCC exit, the boiler exit,

286   and at the stack. Fig. 4 shows the influence of the evaluation of the LOQ on the fluorine mass

287   emission rates in flue gas at the corresponding sampling locations (see Fig. 1), calculated using the

288   statistical approach outlined above (see Supplemental Information). PFAS values in the flue gas

289   below LOQ are defined to be zero (Fig. 4), and ½ LOQ was applied for each PFAS species below

290   LOQ for the data shown in the Supplemental Information in Fig. S5.
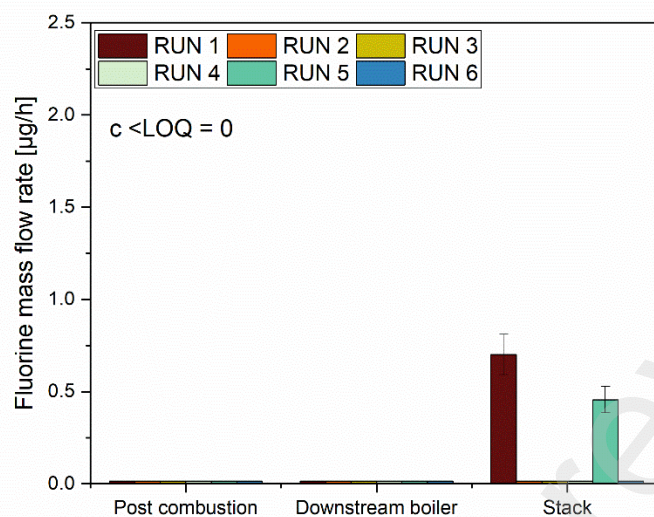
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292   Fig. 4: Influence of PFAS analysis on the fluorine mass flow in flue gas at sampling locations .

293

294   Fluoropolymers were fed into the rotary kiln during the Setting 1, RUN 2 and Setting 2,

295   RUN 5. For the evaluation with $c < LOQ \equiv 0$ (Fig. 4), PFAS were not detected in the post

296   combustion chamber and downstream the boiler for all RUNs. This supports the hypothesis that

297   for PFAS no "de novo synthesis" exists. Stack measurements for RUN 1 and RUN 5 indicated

298   PFOA detection near the level of the LOQs. It is possible that the flue gas treatment system induces

299   some kind of memory effect, where PFAS, for still unknown reasons, is retained for a certain time,

300   and, afterwards, is released again. For the evaluation with $c < LOQ \equiv \frac{1}{2} LOQ$, see Supplemental

301   Information, Fig. S5.

302   The influence of the evaluation methodology, especially for the implementation of LOQs,

303   is of great importance for the evaluation of PFAS emissions and should be considered in future

304   work. We recommend PFAS values $< LOQ$ be set to zero.

305   <u>Fluorine Mass Balance</u>

306   A recent critical review (Longendyke et al., 2022) indicated a lack of data on the closure

307   of the fluorine mass balance as related to the thermal degradation products of PFAS and related

308   waste streams. The current study focused on better understanding of fluoropolymer combustion in

309   incinerators which have been operated during the last several decades. This work set out to

310   determine if current operation conditions were sufficient to provide complete mineralization of the

311   input fluorine.

312   Ideally, the fluorine added to the fluoropolymer mixture should react with hydrogen from

313   the incinerated biomass and natural gas, forming HF and CO_2. However, it is known that fluorine

314   reacts readily with silica (SiO_2, silica oxide) and alumina (Al_2O_3, alumina oxide). Yamada et al.

315   (2005) found that the use of HF as surrogate might be complicated, as HF could react with the

316   reactor tube walls, which contained silica. Yamada et al. observed that the amount of silicon

317   tetrafluoride (SiF_4), measured in fluorotelomer-based (acrylic polymer) combustion tests, increased

318   with temperature. It was concluded that SiF_4 was not formed by sample combustion, but by reaction

319   of HF with fused silica reactor surfaces. As SiO_2 and Al_2O_3 are the main constituents of BRENDA

320   pilot plant refractory materials, it was likely that their reaction with fluorine was responsible for

321   reduced fluorine recovery, measured experimentally with the TDL. This explains why fluorine

322   mass balance as a measurement of HF is not viable.

323   Fluoropolymer Reduction Rate for Products of Incomplete Combustion

324   The Reduction Rate for Products of Incomplete Combustion R2PIC, calculated according

325   to Eq. (2), Supplemental Information, was determined to be greater than 99.99% for both

326   combustion tests. There was no measurable effect of PCC temperature on fluoropolymer R2PIC

327   number. The results do suggest that a temperature of 860°C is sufficient for complete

328   mineralization of fluoropolymers. In related work, PFAS destruction efficiencies at the pilot-scale

329   have been recently reported by Shields et al. (2023). In these studies where individual PFAS were

330   feed into the system, the highest decomposition rates (>99.9999%) were achieved by direct

331   injection in the flame (1963°C and by 1180°C at a residence time of ~3 sec). High destruction rates

332   were reached for PFOS, PFHpS, PFHxS, PFPeS and PFBS, which are comparable with the findings

333   here. All other decomposition rates were in the range 94.03% and 99.9996% for various

334   temperatures and residence time.

335

Conclusions

337   Concern related to the end-of-life phase of fluoropolymers emanates from the data gaps on

338   non-polymeric PFAS emissions, potentially generated from municipal and industrial waste

339   incinerators processing fluoropolymer waste. Prior to this study, there was insufficient data to

340   prove complete mineralization of fluoropolymer waste and insignificant generation of PFAS during

341   incineration of fluoropolymer applications at the end of life.

342   The study clearly demonstrated that fluoropolymers in incinerators operated according to

343   the EU Directive regulations are converted to inorganic fluorides and carbon dioxide. Inorganic

344   fluorides were detected as hydrogen fluoride (between 70 to 80 wt. %). There was no discernible

345   effect of temperature on the mineralization of the FP and testing at 860°C versus 1095°C did not

346   show evidence of an increase in PFAS or C_1-C_3 emissions. Statistical analysis of the combustion

347   runs demonstrated that PFOA was the only detectable PFAS in the gas stream. Seven other PFAS

348   were detected in the FP combustion runs at levels below 0.5 ng/m^3 but were considered outliers in

349   the statistical analysis. There was no discernible effect of temperature on the mineralization of the

350   FP and the decrease in temperature from 1095°C to 860°C did not show evidence of an increase in

351   PFAS or C_1-C_3 emissions.

352   The main reason to include fluoropolymers in the EU PFAS restriction proposal was

353   persistence (resistance to degradation) in the environment. The absence of organic fluorides and

354   more specifically PFAS in tests representative of hazardous and municipal waste incineration

355   confirms very high (likely complete) mineralization of fluoropolymers and provides critical data

356   in support for exempting fluoropolymers from the EU REACH PFAS restriction proposal.

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