

23 **Keywords**

24 Combustion, dioxins, inhibition, organic compounds, polyurethane

25

26 **1. Introduction**

27 Waste incineration is a controversial topic due to unintentionally formation of toxic
28 polychlorodibenzo-*p*-dioxins/furans (PCDD/Fs) during the process. The emission of
29 PCDD/Fs can be high when incinerating chlorinated waste. For this reason, many studies
30 have been focused on the study of the mechanism of PCDD/F formation and technologies
31 to minimize their emission.

32 It is known that the possible pathways for PCDD/F formation during thermal processes
33 are: (i) some PCDD/F contained in the incoming feed could pass through due to an
34 incomplete destruction during combustion, (ii) reaction with dioxin precursors in the gas
35 phase at temperatures between 400 and 800 °C, (iii) formation at low temperature (in the
36 post-combustion zone between 200-400 °C) that involves: the *de novo synthesis* that uses
37 carbon and chlorine in fly ash to form PCDD/Fs or simultaneous oxidation and
38 chlorination of aromatic hydrocarbons via catalytic-assisted by transition metal ions like
39 Cu and Fe (Huang and Buekens, 1995). Pathway (i) has a rare occurrence in incinerators
40 because combustion temperatures higher than 850 °C and residence times higher than 2 s
41 destroy all chlorinated organic molecules (Weber, 2007).

42 Due to the toxicity of these compounds, a large number of studies have been focused on
43 possible methods to control PCDD/F emissions. Control techniques can be classified into
44 two types, the first group of control techniques is focused on collecting and removing
45 these compounds from flue gases after their formation, which involves high investment
46 and operating costs. The second group of control methods is focused on minimizing
47 PCDD/F formation; therefore they seem to be the most economical and environmentally-
48 friendly control methods (Samaras et al., 2000). This group includes techniques like

49 control of waste composition, pre-treatment for cleaning solid fuels, optimization of the
50 combustion parameters and addition of inhibition compounds.

51 The most common additives for inhibition of PCDD/F formation in thermal processes are
52 N- and S- containing compounds, and alkaline sorbents. Since the post-combustion zone
53 is the main critical point of the formation of PCDD/Fs, many researchers have carried out
54 experiments at the temperature range of post-combustion zone by impregnating model fly
55 ash with inhibitors or injecting the inhibitors into the flue gas (Fu et al., 2015; Hajizadeh
56 et al., 2012; Yan et al., 2014). However, adding organic compounds in the post-
57 combustion zone could result in an increase of CO emissions in the flue gases.

58 The possible mechanisms of inhibition with N-containing compounds would be: i)
59 formation of stable metal nitride bonds, such as copper nitrides (Luna et al., 2000), thus
60 blocking active sites of metals and reducing their catalytic activity (Hajizadeh et al.,
61 2012), ii) reaction of the N-additives and their degradation products with PCDD/F
62 precursors (Kuzuhara et al., 2005) or with the chlorine present in the post-combustion
63 zone, avoiding the reaction of carbon and chlorine in fly ash to form PCDD/Fs (Zhan et
64 al., 2016), iii) alteration of the acidity of fly ash, specially with NH_3 due to their alkalinity,
65 thereby losing aromatic chlorine by base-catalyzed elimination (Pandelova et al., 2005),
66 iv) combustion of N-containing compounds to form NO_2 , which is a stronger oxidant than
67 oxygen, favoring the oxidation of organic compounds and precursors (Marie-Rose et al.,
68 2009).

69 Neither polyurethane foam (PUF) waste nor pyrolysis oxidative gas from PUF waste have
70 been found in the literature as inhibitors of dioxin formation in the combustion of
71 chlorinated compounds, although several N-containing compounds have demonstrated

72 their inhibitor effect in the PCDD/F formation and only few studies can be found
73 regarding the use of waste with high N content as inhibitor. PUF is the main component
74 of an important type of mattresses, which generates large amounts of bulky waste in
75 Europe and its main end is the landfill (Turner, 2014). PUF waste shows management
76 problems, but its high N content could inhibit the PCDD/F formation in thermal treatment
77 of chlorinated waste, such as PVC cables, improving the management of both types of
78 waste. No papers have been found about the study of PUF waste for this purpose as
79 commented previously.

80 Another promising management treatment for biomass or polymer waste such as PUF is
81 pyrolysis, which obtains energy and chemical products of high added value, solving also
82 the issue of the large amount of waste generation. Regarding the chemical products
83 obtained, recently, several researchers have focused on the production of carbonaceous
84 nanoparticles (CNPs), due to their large number of applications in high value
85 manufacturing technologies (Dubey et al., 2014; Jander et al., 2019; Maroufi et al., 2017;
86 Santhiago et al., 2018; Tripathi et al., 2014). However, the production of CNPs is limited
87 and expensive at the moment. Nevertheless, pyrolysis of fuel with significant nitrogen
88 content such as PUF produces gaseous NH_3 at high levels (Garrido et al., 2016; Moreno
89 and Font, 2015), which has been found as an effective inhibitor of the PCDD/F formation
90 (Hajizadeh et al., 2012; Liu et al., 2015; Ruokojärvi et al., 2004). In addition, it must be
91 noted that the first stage of combustion is a pyrolysis process, in which NH_3 formation
92 can be high if the nitrogen content of the fuel is significant. Therefore, NH_3 produced in
93 combustion of PUF or in a previous pyrolysis (oxidative pyrolysis) can act as inhibitor as
94 commented previously.

95 This work aimed for the study of PCDD/F inhibition by prior addition of N-containing
96 compounds to a model waste (a mixture of sawdust and PVC) in a laboratory reactor, in
97 order to control properly the operating conditions. Other compounds were also analyzed
98 to study the effect of PCDD/F inhibitors on other pollutants evolved in the combustion
99 process. The inhibitors studied were PUF and gases from the oxidative pyrolysis of PUF.
100 The mentioned model waste was selected to assure that a considerable amount of
101 chlorinated compounds could be evolved.

102 **2. Experimental section**

103 *2.1. Characteristics of materials and experimental procedure*

104 The materials employed for the combustion runs were: PUF from mattress waste, which
105 was collected from a Municipal Solid Waste Treatment Plant, sawdust from wood, which
106 was supplied by Energías Renovables Tarazona S.A. (Albacete, Spain), and PVC resin
107 Etinox-450. Major elements (C, H, N, S) of the PVC resin were analyzed by a Leco Micro
108 TuSpec Elemental Analyzer and the characterization of PUF and sawdust and the
109 methods used were presented in previous works (Conesa and Soler, 2017; Garrido et al.,
110 2016). For comparison purposes, the results are shown in Table 1. The high N content of
111 PUF is noteworthy since its nitrogen degradation products could act as inhibitors of
112 PCDD/F formation in thermal processes. On the other hand, the Cl content in PVC is also
113 remarkable. A synthetic waste was obtained with sawdust and PVC (95 wt% and 5 wt%,
114 respectively), so a model waste with high Cl content could lead to a high PCDD/F
115 formation during combustion.

116 **Table 1**

117 The experiments of combustion were carried out at 850 °C in a laboratory-scale horizontal
118 tubular quartz reactor previously described in detail by Font et al (2003). A small amount
119 of sample (around 60 mg) is introduced inside a reactor with controlled temperature, and
120 in the latter part of the reactor some quartz raschig rings are placed, which promote the
121 secondary cracking reactions. Synthetic air (79% nitrogen, 21% oxygen) was used in the
122 experiments. These set-ups were carried out under substoichiometric conditions (ratio
123 $\text{CO}/(\text{CO} + \text{CO}_2)$ around 0.1) to promote the formation of incomplete combustion
124 products. The outlet gas was passed through a Tedlar bag or XAD-2 resin to collect the
125 compounds of interest for their analysis.

126 In each experiment, the exact amount of each material was added to the crucible used in
127 the reactor, in order to assure the composition of the feeding material. The mixture of the
128 different materials was carried out manually with a glass rod to obtain a uniform feeding.

129 Three different experiments were carried out with the synthetic waste as fuel: M0, M1
130 and M2. The M0 experiment was carried out without inhibitors in order to observe the
131 PCDD/F levels during combustion of the synthetic waste used and to compare the effect
132 of the inhibitors afterwards. The M1 experiment studied the effect of the first inhibitor,
133 the addition of 5 wt% of PUF to the synthetic waste. This percentage was selected taking
134 into account the results of Fu et. al (2015), who observed a PCDD/F decrease of 97.7%
135 by adding inhibitors to ash with a molar ratio $(\text{N}+\text{S})/\text{Cl}$ 0.47, or 0.19 as weight ratio. In
136 the M1 experiment, the N/Cl weight ratio in the mixture was 0.11 in order to observe the
137 inhibition effect with an intermediate ratio. The M2 experiment studied the effect of the
138 second inhibitor, the addition of gases from the oxidative pyrolysis of PUF to the inlet
139 gas, containing NH_3 and other N- compounds which can act as inhibitors of the PCDD/F
140 formation. In order to obtain these gases from oxidative pyrolysis of PUF, a previous

141 experiment of thermal decomposition of PUF was carried out in the same reactor at 850
142 °C, obtaining a mixture of gases with 1.8 vol% of O₂. These gases obtained were mixed
143 with air for the M2 combustion runs, at a ratio of approximately 24% of oxidative
144 pyrolysis gases and 76% of air. The flowrate was 225 mL/min (25°C and 1 atm) for the
145 M0 and M1 experiments (solids + air) and 300 mL/min (25°C and 1 atm) for the M2
146 experiment (solids + gas mixture with pyrolysis gas). The duration was 4 min for the M0
147 and M1 experiments and 3 min for the M2 experiment, to assure that the sample was
148 totally burned and the compounds evolved were collected correctly. The residence time
149 was 3.5 s for the M0 experiments and M1 and 5 s for the M2 experiment.

150 Gases from oxidative pyrolysis of PUF used for the M2 experiment show high NH₃, HCN
151 and nitrogen oxides content (Table 2), which were also found in previous works as
152 effective inhibitors of PCDD/F formation (Hajizadeh et al., 2012; Kuzuhara et al., 2005;
153 Marie-Rose et al., 2009). The variations of the composition correspond to the standard
154 deviation between analyses from 3 different oxidative pyrolysis runs. Since some of these
155 compounds are hazardous, its presence in the latter combustion experiments was taken
156 into account.

157 **Table 2**

158 From the outlet gas obtained in the combustion experiments mentioned above, PCDD/Fs
159 and dl-PCBs (dioxin-like polychlorinated biphenyls) were analyzed, but also Cl₂ and
160 other different compounds, such as NH₃, HCN, NO_x, HCl, volatile and semivolatile
161 organic compounds. Among the semivolatile organic compounds, PCDD/F precursors
162 such as chlorobenzenes (ClBzs) and chlorophenols (ClPhs), as well as priority polycyclic
163 aromatic hydrocarbons (PAHs), were specially taken into account.

164 Additional information about the gases evolved in the combustion of these materials has
165 been obtained through thermogravimetric analysis (TG) coupled with both mass
166 spectrometer (MS) and Fourier-transform infrared (FTIR) spectrometer, in order to
167 corroborate the results obtained with the horizontal tubular quartz reactor.

168 The TG-MS analyses were carried out in a Mettler Toledo TGA/SDTA851e/LF/1600
169 (TG-DTA) with an alumina crucible in series with a Pfeiffer Vacuum Quadrupole Mass
170 Spectrometer (QMS) Thermostar GSD301T. The sample mass used was approximately 5
171 mg. Runs were performed at a heating rate of 30 °C/min with a flow rate of 100 mL/min
172 of He:O₂ (4:1). This atmosphere was selected in order to determine the evolution of CO
173 avoiding the overlap of m/z ions from N₂. The response of the different ions was divided
174 by that of helium (m/z = 4) and subtracted from that corresponding to the beginning of
175 the run.

176 The TG-FTIR analyses were carried out in a TG STA6000 (PerkinElmer) with a ceramic
177 crucible at a heating rate of 50 °C/min coupled to a Nicolet 6700 FTIR spectrometer.
178 Resolution in FTIR was set at 4 cm⁻¹ and spectra were collected at 32 scans in the range
179 400-4000 cm⁻¹. TGA measurements were performed using around 5 mg of sample.

180 *2.2. Methodologies of analysis*

181 Triplicate combustion experiments were carried out for the analyses of NH₃, HCN, HCl,
182 Cl₂, volatile compounds and organic semivolatile compounds, whereas analyses of
183 PCDD/Fs and dl-PCBs were carried out in duplicate. In addition, blanks of the
184 experiments and the apparatus used were also carried out prior to the corresponding runs.

185 Apart from their analysis in the combustion experiments, NH₃, HCN, HCl, Cl₂ and other
186 gases and volatile compounds were analyzed in the flue gas from the oxidative pyrolysis
187 of PUF.

188 *2.2.1. Sampling and analysis of ammonia, hydrogen cyanide, hydrogen chloride and*
189 *chlorine.*

190 The U.S. EPA CTM 027 method was followed for sampling and analysis of ammonia
191 emissions (EPA, 1997). This method consists of passing the evolved gases through two
192 impingers containing a sulphuric acid solution (0.1 N) in order to retain the released
193 ammonia. The amount of ammonium in the solution was analyzed by ion chromatography
194 (Dionex DX500).

195 The U.S. EPA OTM 029 method was followed for sampling and analysis of hydrogen
196 cyanide emissions (EPA, 2011). This method consists of passing the evolved gases
197 through two impingers containing a 0.1N NaOH solution and HCN is trapped by the alkali
198 solution as cyanide ion (CN⁻). The amount of cyanide in the solution was analyzed by ion
199 chromatography (Dionex DX500).

200 The U.S. EPA 051 method was followed for sampling of hydrogen chloride and chlorine
201 emissions, by the use of impingers like in the previous cases. In acidified absorbing
202 solutions, the HCl gas is solubilized and forms chloride ions (Cl⁻). The acidified solution
203 used was 0.1N sulphuric acid solution. The Cl₂ gas was sampled in alkaline absorbing
204 solution (0.1N NaOH solution) (EPA, 1996a). The U.S. EPA 9057 method was followed
205 for the determination of HCl and Cl₂ by the analyses of obtained solutions by ion
206 chromatography (Dionex DX500) (EPA, 1996b).

207 2.2.2. *Sampling and analysis of gases and volatile compounds.*

208 Gases evolved were collected in Tedlar[®] bags. O₂, N₂, H₂, CO and CO₂ were analyzed
209 in an Agilent 7890A Gas Chromatograph coupled to a Thermal Conductivity Detector
210 (GC-TCD) equipped with a first packed column (HayeSep Q) with 80/100 mesh and a
211 second packed column (MolSieve 5A) with 80/100 mesh. A Shimadzu GC-17A Gas
212 Chromatograph coupled to a Flame Ionization Detector (GC-FID) with a capillary
213 column Alumina KCl Plot was used to analyze the aliphatic hydrocarbons C₁-C₆ (with
214 low boiling points). In addition, for the analysis of other non-condensable organic
215 compounds, an Agilent 6890N Gas Chromatograph was used, coupled to an Agilent
216 5973N mass spectrometer (GC-MS) with a DB-624 capillary column (30 m x 0.25 mm x
217 1.4 μm).

218 Tedlar[®] bags were also needed to collect the gases for the analyses of nitrogen oxides
219 (NO and NO₂), which were carried out with a calibrated IM-2800 portable gas analyzer
220 (Environmental Equipment Germany GmbH).

221 2.2.3. *Sampling and analysis of organic semivolatile compounds.*

222 The gas stream passed through an adsorptive trap containing XAD-2 resin to retain PAHs,
223 ClBzs, ClPhs and other semivolatile compounds. Before extraction, internal standards
224 were added, specifically 5 μL of deuterated PAH Mix 26 (Dr. Ehrenstorfer-Schäfers,
225 Augsburg, Germany), 10 μL of ¹³C-labelled ClPh and 10 μL of ¹³C-labelled ClBz
226 (Wellington Laboratories, Ontario, Canada). The resins were extracted with a mixture of
227 dichloromethane/acetone, using Accelerated Solvent Extraction, according to the U.S.
228 EPA method 3545A (EPA, 2007a). The extracts obtained were concentrated and finally
229 the recovery standard anthracene-d₁₀ (AccuStandard, New Haven, USA) was spiked.

230 The 16 priority PAHs and other semivolatile organic compounds were quantified
231 according to the U.S. EPA method 8270D (EPA, 2007b). Analyses of PAHs were carried
232 out in an Agilent 6890N Gas Chromatograph coupled to an Agilent 5973N Mass
233 Spectrometer (GC-MS) with a HP-5MS capillary column (30 m x 0.25 mm x 0.25 μ m)
234 by the isotope dilution method. The identification of semivolatile compounds was done
235 by comparing unknown mass spectra with NIST database reference spectra and a
236 semiquantitative determination of the yield was calculated with the response factors of
237 the deuterated internal standard with the nearest retention time. The SIR mode was used
238 for the analyses of ClPhs and ClBzs, confirming each isomer with the ratio between the
239 areas of the primary and secondary ions.

240 2.2.4. *Sampling and analysis of PCDD/Fs and dioxin-like PCBs.*

241 Samplings of PCDD/Fs and dl-PCBs were also carried out passing the flue gases through
242 an adsorptive trap containing XAD-2 resin. However, for analysis of PCDD/Fs and dl-
243 PCBs, between 6 and 20 consecutive combustions were carried out (being retained their
244 emissions by the same XAD-2 resin), in order to amplify the signal in the analysis.

245 The resin extractions and the following purification and clean-up of the extracts for the
246 simultaneous analyses of 2,3,7,8-substituted PCDD/Fs and 12 dioxin-like PCBs were
247 carried out according to a modification of the U.S. EPA Method 1613, taking into account
248 the U.S. EPA Method 1668 (Moltó et al., 2006).

249 The purified extracts were analyzed with a Thermo Finnigan MAT95 XP High-
250 Resolution Mass Spectrometer connected to a Thermo Finnigan Trace GC 2000 Gas
251 Chromatograph. A J&W DB-5MS (60 m x 0.25 mm x 0.1 μ m) capillary column was used

252 for PCDD/F determination and a DB-XLB (60 m x 0.25 mm x 0.25 μ m) for dl-PCBs
253 determination.

254 **3. Results and discussion**

255 Table 3 shows the results corresponding to the formation of carbon oxides, nitrogen
256 oxides, NH₃, HCN, HCl, chlorine and the main light hydrocarbons in M0 and M1
257 combustion runs. The results for the M2 experiment, however, are shown separately in
258 Table 4 since this was carried out with an addition of a percentage of gases from the
259 oxidative pyrolysis of PUF into the inlet gases (flow gas to carry out the combustion).
260 This gas introduces carbon oxides, nitrogen oxides, NH₃, HCN, etc. into the reactor.
261 Therefore, this different initial condition of the combustion experiment must be
262 considered in order to evaluate the results accurately. For this consideration, Table 4
263 shows the composition of the inlet gas, the composition of the outlet gas and the
264 difference between both of them. Inlet gas for M0 and M1 combustion runs basically
265 contains air, therefore it does not need to be analyzed in these experiments.

266 **Table 3**

267 **Table 4**

268 Comparing the inlet gas with the outlet one in the M2 combustion, Table 4 shows that
269 obviously carbon oxides increase in flue gas due to the solid fuel combustion. Inlet gas
270 shows a high content of light hydrocarbons, although these compounds were oxidized
271 during combustion, some of them were completely oxidized and the rest of them reduced
272 their yield significantly. Inlet gas for M2 combustion shows a significant content of NH₃
273 and HCN, although these compounds were oxidized during the M2 run. Even though they

274 were not completely consumed, their decrease was quite considerable (Table 4). In
275 addition, an increase of NO was observed in flue gases from M2 combustion compared
276 to the composition of its inlet gas. It is known that the oxidation of NH₃ and HCN
277 produces nitrogen oxides, which could explain their increase. Specifically, Marie-Rose et
278 al. (2009) explained that the ammonia adsorbed in the strong acid sites of particles reacts
279 with the oxygen that is also adsorbed and they form NO_(g) (Eq. 1) and NO formed is
280 quickly oxidized into NO_{2(g)} (Eq. 2).



283 In addition, Glarborg and Miller (1994) proved that the main oxidation route for HCN
284 forms NCO (Eq. 3) and the products of the subsequent reactions of NCO depend on the
285 gas composition and temperature (Eqs. 4-7).



291 The previous equations could explain the great decrease in the emission factors of
292 nitrogen compounds observed in Table 4 concerning the M2 experiment. Comparing the

293 different combustion runs, according to Tables 3 and 4 the CO/(CO + CO₂) ratios are
294 slightly lower in the experiments carried out with inhibitors, but the three ratios are around
295 0.10. This indicates that the oxygen conditions for the three combustion processes were
296 substoichiometric and similar, what could occur at some points of a commercial waste
297 incinerator.

298 Marie-Rose et al. (2009) suggested that the presence of NH₃ seems to favor the formation
299 of coke and also the decrease of the CO₂ formation. At low temperature (ca. 300 °C), NH₃
300 adsorbs on the strong acid sites. Therefore, the oxidation of organic molecules into carbon
301 dioxide is reduced, but the formation of PCDD/Fs could also be reduced due to the
302 blocking of these strong acid sites. Concerning this matter, Tables 3 and 4 show that the
303 lowest yield of CO₂ corresponded to the M2 experiment, due to the significant ammonia
304 content in the inlet gas of this experimental run.

305 The yield of NO_x slightly increases in the experiments carried out with the inhibitor, but
306 despite this increase, the NO_x emissions obtained do not exceed the permitted limits of
307 the Directive 2010/75/EU on industrial emissions for waste incineration plants (daily
308 average emission limit: 200 mg/Nm³ of NO and NO₂, expressed as NO₂).

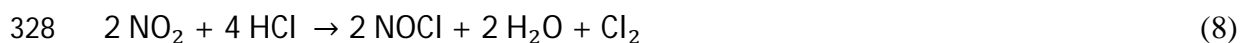
309 M1 experiment shows a higher HCN content in its flue gases comparing with the content
310 obtained in flue gases of M0 experiment (Table 3). Flue gases from M2 experiment also
311 show a higher NH₃ and HCN content, although it must be noted that inlet gas for this
312 experiment shows a significant NH₃ and HCN content as mentioned before, which were
313 greatly oxidized during combustion run (Table 4).

314 It must be considered that combustions with excess oxygen consume the HCN and NH₃
315 formed. Nevertheless, if there is not sufficient oxygen, a higher N content in the materials

316 to burn (due to the inhibitor used) will produce a higher HCN and NH₃ content in the flue
317 gases. It must be taken into account that these experiments were carried out under
318 substoichiometric conditions, therefore, HCN and NH₃ emissions will be probably
319 negligible if combustions were carried out with excess oxygen.

320 It is also noteworthy that there are decreases in the yield of some main light hydrocarbons
321 in the experiments carried out with inhibitors.

322 Concerning HCl and Cl₂ yields, the values obtained were relatively similar for M0 and
323 M1 experiments. However, a higher difference was observed in the flue gases obtained
324 in M2 experiment. The higher Cl₂ content in flue gases from M2 combustion could be
325 due to the formation of NO (by NH₃ and HCN). Subsequently, this NO is quickly oxidized
326 into NO₂ and the formed NO₂ can react with HCl and produces Cl₂ (Eq. 8) (favored
327 reaction).



329 Additional information about these combustion processes were obtained with TG-FTIR
330 and TG-MS analyses. The main results obtained from TG-FTIR and their discussions are
331 shown in Appendix A, and it can be concluded that combustion experiments carried out
332 with inhibitors produce lower yield of volatile organic compounds, which corroborates
333 the results obtained in the horizontal quartz tubular reactor.

334 Concerning TG-MS analysis, an interesting result obtained must be discussed. Fig. 1
335 shows the intensities of ions corresponding to HCl (*m/z* 36) and Cl₂ (*m/z* 70) from the
336 TG-MS runs for M0 and M1 combustions. It can be observed that the formation of Cl₂ in
337 M0 combustion is negligible. This result is in agreement with that obtained in the

338 laboratory-scale reactor (Table 3). On the other hand, TG-MS results show that the Cl₂
339 formation increases and the HCl formation decreases for M1 combustion, comparing with
340 the results of M0 combustion. The addition of PUF with high nitrogen content to the fuel
341 is the reason of this result, as previously mentioned, since high nitrogen content in the
342 fuel can form a significant yield of NO₂ and consequently, the formed NO₂ can react with
343 HCl and produces Cl₂.

344 **Figure 1**

345 Table 5 shows the emission factors of the PAHs obtained, the total yield of semivolatile
346 compounds and ClBz and ClPh yields. Emissions of the PAHs studied were also lower
347 in the experiments carried out with the inhibitors. Naphthalene, acenaphthylene,
348 phenanthrene and fluoranthene were the majority PAHs obtained in all cases.
349 Furthermore, other 51 semivolatile compounds were identified and quantified and they
350 are shown in Table B1 of Appendix B. Their total yields were also lower in M1 and M2
351 combustion experiments (with the inhibitors).

352 **Table 5**

353 Table 6 shows the PCDD/F and dl-PCB yields and the total toxicity equivalence (TEQ)
354 in the combustion runs. Values for TEQ were calculated using the toxicity equivalency
355 factor given by the World Health Organization (WHO) (Van den Berg et al., 2006).

356 **Table 6**

357 The results suggest that the addition of PUF to the model waste and the addition of the
358 gases from the oxidative pyrolysis of PUF reduce PCDD/F and dl-PCB formation.

359 Although the yield of Cl₂ is the highest one in the M2 combustion experiment, PCDD/F
360 and dl-PCB formation is the lowest. The reason could be the low yield of organic products
361 of incomplete combustion obtained in the M2 combustion experiment (Tables 4 and 5).

362 From Table 6, it can be observed that the yields of toxicity equivalent of PCDFs are much
363 higher than that corresponding to PCDDs. This trend is mainly observed in M0
364 experiment (combustion of model waste) and this was also the tendency during the
365 combustion of PVC (Font et al., 2010).

366 Taking into account that yields of ClBzs and ClPhs are similar in the three runs, probably
367 the interaction of the N-compounds takes place in the reactions of these precursors leading
368 to a formation of PCDD/Fs and dl-PCBs. By inhibiting the formation, ClBzs and ClPhs
369 do not react.

370 **4. Conclusions**

371 The addition of polyurethane foam to the model waste and the addition of the gases from
372 the oxidative pyrolysis of PUF inhibit PCDD/F and dl-PCB formation in combustion. The
373 first alternative reduces the formation of PCDD/Fs by 85.7% and dl-PCBs by 81.2% in
374 toxicity WHO-TEQ, and the second one 99.6% and 99.99% respectively. Both
375 alternatives are interesting, being the direct addition of PUF waste the simplest one. The
376 addition of gases from oxidative pyrolysis increases the inhibition potential.

377 Both addition of PUF and gases from its oxidative pyrolysis to the synthetic waste
378 produce higher yield of NH₃, HCN and NO_x in thermal processes, but the presence of
379 NH₃ and HCN in the flue gases from combustion is easier to control than PCDD/Fs and
380 dl-PCBs, and NO_x levels do not surpass the emission limit. In addition, significant yield

381 reductions of organic volatile and semivolatile compounds have been obtained in the
382 experiments carried out with the inhibitors studied. This is due to the presence of NO_x in
383 these experiments, since NO₂ is a stronger oxidant than oxygen and consequently reduces
384 products of incomplete combustion. In addition, the presence of N-compounds and the
385 reduction of products of incomplete combustion can also cause a decrease of PCDD/F
386 and dl-PCB formation.

387 The proposed alternatives could help to avoid the PCDD/F and dl-PCB formation during
388 incineration of waste with a high Cl content such as PVC cables, and at the same time
389 they allow the treatment of bulky waste such as used mattresses.

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393 **References**

394 Conesa, J.A., Soler, A., 2017. Decomposition kinetics of materials combining biomass
395 and electronic waste. *J Therm Anal Calorim* 128, 225-233.

396 Dubey, P., Tripathi, K.M., Sonkar, S.K., 2014. Gram scale synthesis of green fluorescent
397 water-soluble onion-like carbon nanoparticles from camphor and polystyrene foam. *RSC*
398 *Advances* 4, 5838-5844.

399 EPA, 1996a. Method 0051. Midget impinger HCl/Cl₂ emission sampling train., United
400 States Environmental Protection Agency, Washington, DC.

401 EPA, 1996b. Method 9057. Determination of chloride from HCl/Cl₂ emission sampling
402 train (methods 0050 and 0051) by anion chromatography., United States Environmental
403 Protection Agency, Washington, DC.

404 EPA, 1997. Procedure for Collection and Analysis of Ammonia in Stationary Sources
405 (CTM-027). United States Environmental Protection Agency, Washington, DC.

406 EPA, 2007a. Method 3545A. Pressurized Fluid Extraction (PFE). United States
407 Environmental Protection Agency, Washington, DC.

408 EPA, 2007b. Method 8270D. Semivolatile Organic Compounds by GC/MS., United
409 States Environmental Protection Agency, Washington, DC.

410 EPA, 2011. OTM 29. Sampling and Analysis of Hydrogen Cyanide Emissions from
411 Stationary Sources, Other Test Method 29, United States Environmental Protection
412 Agency, Washington, DC.

413 Font, R., Aracil, I., Fullana, A., Martín-Gullón, I., Conesa, J.A., 2003. Semivolatile
414 compounds in pyrolysis of polyethylene. *Journal of Analytical and Applied Pyrolysis* 68–
415 69, 599-611.

416 Font, R., Gálvez, A., Moltó, J., Fullana, A., Aracil, I., 2010. Formation of polychlorinated
417 compounds in the combustion of PVC with iron nanoparticles. *Chemosphere* 78, 152–
418 159.

419 Fu, J.-Y., Li, X.-D., Chen, T., Lin, X.-Q., Buekens, A., Lu, S.-Y., Yan, J.-H., Cen, K.-F.,
420 2015. PCDD/Fs' suppression by sulfur–amine/ammonium compounds. *Chemosphere*
421 123, 9-16.

422 Garrido, M.A., Font, R., Conesa, J.A., 2016. Pollutant emissions during the pyrolysis and
423 combustion of flexible polyurethane foam. *Waste Management* 52, 138-146.

424 Glarborg, P., Miller, J.A., 1994. Mechanism and modeling of hydrogen cyanide oxidation
425 in a flow reactor. *Combustion and Flame* 99, 475-483.

426 Hajizadeh, Y., Onwudili, J.A., Williams, P.T., 2012. Effects of gaseous NH₃ and SO₂ on
427 the concentration profiles of PCDD/F in flyash under post-combustion zone conditions.
428 *Waste Management* 32, 1378-1386.

429 Huang, H., Buekens, A., 1995. On the mechanisms of dioxin formation in combustion
430 processes. *Chemosphere* 31, 4099-4117.

431 Jander, H., Borchers, C., Böhm, H., Emelianov, A., Schulz, C., 2019. Structure of
432 carbonaceous nanoparticles formed in various pyrolysis systems. *Carbon*.

433 Kuzuhara, S., Sato, H., Tsubouchi, N., Ohtsuka, Y., Kasai, E., 2005. Effect of Nitrogen-
434 Containing Compounds on Polychlorinated Dibenzo-p-dioxin/Dibenzofuran Formation
435 through de Novo Synthesis. *Environmental Science & Technology* 39, 795-799.

436 Liu, X., Wang, J., Wang, X., Zhu, T., 2015. Simultaneous removal of PCDD/Fs and NO_x
437 from the flue gas of a municipal solid waste incinerator with a pilot plant. *Chemosphere*
438 133, 90-96.

439 Luna, A., Amekraz, B., Morizur, J.P., Tortajada, J., Mó, O., Yáñez, M., 2000. Reactions
440 of Urea with Cu⁺ in the Gas Phase: An Experimental and Theoretical Study. *The Journal*
441 *of Physical Chemistry A* 104, 3132-3141.

442 Marie-Rose, S.C., Belin, T., Mijoin, J., Fiani, E., Taralunga, M., Chaucherie, X., Nicol,
443 F., Magnoux, P., 2009. Destruction of PAH and dioxin precursors using selective
444 oxidation over zeolite catalysts. Influence of the presence of ammonia in the flue gas.
445 *Applied Catalysis B: Environmental* 93, 106-111.

446 Maroufi, S., Mayyas, M., Sahajwalla, V., 2017. Nano-carbons from waste tyre rubber:
447 An insight into structure and morphology. *Waste Management* 69, 110-116.

448 Moltó, J., Font, R., Conesa, J.A., 2006. Study of the Organic Compounds Produced in the
449 Pyrolysis and Combustion of Used Polyester Fabrics. *Energy & Fuels* 20, 1951-1958.

450 Moreno, A.I., Font, R., 2015. Pyrolysis of furniture wood waste: Decomposition and
451 gases evolved. *Journal of Analytical and Applied Pyrolysis* 113, 464-473.

452 Pandelova, M.E., Lenoir, D., Kettrup, A., Schramm, K.-W., 2005. Primary Measures for
453 Reduction of PCDD/F in Co-Combustion of Lignite Coal and Waste: Effect of Various
454 Inhibitors. *Environmental Science & Technology* 39, 3345-3350.

455 Ruokojärvi, P.H., Asikainen, A.H., Tuppurainen, K.A., Ruuskanen, J., 2004. Chemical
456 inhibition of PCDD/F formation in incineration processes. *Science of The Total*
457 *Environment* 325, 83-94.

458 Samaras, P., Blumenstock, M., Lenoir, D., Schramm, K.W., Kettrup, A., 2000. PCDD/F
459 prevention by novel inhibitors: Addition of inorganic S- and N-compounds in the fuel
460 before combustion. *Environmental Science and Technology* 34, 5092-5096.

461 Santhiago, M., Garcia, P.S., Strauss, M., 2018. Bio-based nanostructured carbons toward
462 sustainable technologies. *Current Opinion in Green and Sustainable Chemistry* 12, 22-
463 26.

464 Tripathi, K.M., Sonker, A.K., Sonkar, S.K., Sarkar, S., 2014. Pollutant soot of diesel
465 engine exhaust transformed to carbon dots for multicoloured imaging of *E. coli* and
466 sensing cholesterol. *RSC Advances* 4, 30100-30107.

467 Turner, J., 2014. Recycling special: Europe. *European Bedding Industries' Association*
468 *Magazine*, pp. 28-34.

469 Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M.,
470 Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D.,
471 Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006.
472 The 2005 World Health Organization reevaluation of human and mammalian toxic
473 equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences* 93,
474 223-241.

475 Weber, R., 2007. Relevance of PCDD/PCDF formation for the evaluation of POPs
476 destruction technologies – Review on current status and assessment gaps. *Chemosphere*
477 67, S109-S117.

478 Yan, M., Qi, Z., Yang, J., Li, X., Ren, J., Xu, Z., 2014. Effect of ammonium sulfate and
479 urea on PCDD/F formation from active carbon and possible mechanism of inhibition.
480 *Journal of Environmental Sciences* 26, 2277-2282.

481 Zhan, M., Chen, T., Lin, X., Fu, J., Li, X., Yan, J., Buekens, A., 2016. Suppression of
482 dioxins after the post-combustion zone of MSWIs. *Waste Management* 54, 153-161.

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Table 1. Characterization of the materials used.

Analysis on dry basis	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	Cl (wt%)
Sawdust	51.6	6.5	<0.01	<0.01	41.9	0.12
PVC	39.0	4.9	<0.01	<0.01	<0.01	56.2
PUF	57.8	7.4	5.95	0.01	23.4	0.04

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Table 2. Composition of the gases from the oxidative pyrolysis of PUF

PUF oxidative pyrolysis gases	
H ₂ (vol%)	12.5 ± 0.5
O ₂ (vol%)	1.8 ± 0.8
N ₂ (vol%)	84.5 ± 0.2
CO ₂ (vol%)	0.21 ± 0.01
CO (vol%)	0.93 ± 0.06
NO _x (mg/kg PUF)	2430 ± 260
NH ₃ (mg/kg PUF)	8650 ± 1040
HCN (mg/kg PUF)	20610 ± 1340

489

490

491 **Table 3.** Gases and organic volatile compounds evolved in M0 and M1 combustion
 492 runs.

COMPOUND	mg compound/kg dry solid fuel	
	M0 (wood/PVC)	M1 (wood/PVC/PUF)
CO ₂	1607000 ± 48000	1655000 ± 249000
CO	200000 ± 49000	187000 ± 21000
Ratio CO/(CO + CO ₂)	0.11 ± 0.02	0.10 ± 0.01
NO	480 ± 20	920 ± 110
NO ₂	480 ± 80	170 ± 180
NO _x	950 ± 60	1090 ± 150
NH ₃	4 ± 2	15 ± 5
HCN	580 ± 20	1180 ± 130
HCl	8000 ± 1800	9040 ± 2460
Cl ₂	200 ± 40	380 ± 160
Methane	18400 ± 1280	14580 ± 3370
Ethane	90 ± 10	20 ± 10
Ethene	1830 ± 920	460 ± 150
Acetylene	2250 ± 200	20 ± 40
1,3-Butadiene	60 ± 10	nd
Benzene	5900 ± 600	1470 ± 1040
Toluene	210 ± 200	nd

493

494

495 **Table 4.** Composition of the inlet gas for M2 combustion (expressed as mass of added
 496 compounds per mass of dry solid fuel to be combusted), yield of the main gases evolved
 497 in M2 combustion and difference of the main gases between outlet and inlet yields.

COMPOUND	mg compound/kg dry solid fuel		
	Inlet gas for M2 combustion	Outlet gas from M2 combustion	Difference between outlet and inlet yields
CO ₂	39500 ± 3000	1385000 ± 251000	1346000 ± 178000
CO	46600 ± 4100	131000 ± 34000	85000 ± 24000
Ratio CO/(CO + CO ₂)	0.54 ± 0.04	0.09 ± 0.02	
NO	490 ± 230	1230 ± 410	740 ± 330
NO ₂	< 1	< 29	< 29
NO _x	490 ± 160	1260 ± 290	770 ± 240
NH ₃	6200 ± 2090	2130 ± 450	- 4060 ± 1510
HCN	16430 ± 1190	1000 ± 210	- 15430 ± 850
HCl	Negligible*	7940 ± 1630	7940 ± 1150
Cl ₂	Negligible*	6650 ± 4780	6650 ± 3380
Methane	126600 ± 8500	3800 ± 100	-122800 ± 6000
Ethane	7280 ± 440	10 ± 20	-7270 ± 310
Ethene	105300 ± 6400	440 ± 330	-104900 ± 4500
Propane	500 ± 80	nd	-500 ± 50
Propene	20600 ± 1700	nd	-20600 ± 1200
Acetylene	9130 ± 480	170 ± 100	-8950 ± 400
n-Butane	1400 ± 110	nd	-1400
1-Butene	360 ± 120	nd	-360 ± 90
Isobutene	280 ± 60	nd	-280 ± 40
Propyne	1850 ± 140	nd	-1850 ± 100
1,3-Butadiene	9130 ± 1110	100 ± 180	-9030 ± 790
1-Butyne	3660 ± 1110	nd	-3660 ± 790
Benzene	28100 ± 600	1500 ± 170	-26600 ± 500
Toluene	6510 ± 1160	1310 ± 460	-5200 ± 880

498 * Negligible: HCl and Cl₂ were not analyzed for inlet gas due to the low Cl content in
 499 PUF.

500

501 **Table 5.** 16 EPA priority PAHs, total semivolatile compounds, chlorobenzenes and
 502 chlorophenols evolved in combustion experiments

COMPOUND	mg compound/kg dry sample		
	M0 (wood/PVC) (n = 3)	M1 (wood/PVC/PUF) (n = 3)	M2 (wood/PVC/PUF pyrolysis gases) (n = 3)
Naphthalene	193.8 ± 94.6	67.8 ± 26.0	83.9 ± 53.0
Acenaphthylene	99.1 ± 66.6	21.7 ± 13.5	26.0 ± 19.6
Acenaphthene	0.4 ± 0.4	nd	nd
Fluorene	1.0 ± 0.5	nd	nd
Phenanthrene	134.5 ± 79.8	31.3 ± 15.7	26.2 ± 19.6
Anthracene	14.5 ± 7.4	2.2 ± 0.6	1.6 ± 1.2
Fluoranthene	43.1 ± 29.7	9.0 ± 4.2	8.5 ± 7.6
Pyrene	28.6 ± 13.0	3.5 ± 1.7	6.0 ± 5.4
Benzo(a)anthracene	8.9 ± 5.1	1.1 ± 0.6	0.3 ± 0.1
Chrysene	22.6 ± 10.8	3.3 ± 1.7	1.1 ± 0.3
Benzo(b)fluoranthene	9.1 ± 3.1	1.8 ± 0.5	2.6 ± 1.7
Benzo(k)fluoranthene	4.4 ± 1.6	0.7 ± 0.6	0.9 ± 0.7
Benzo(a)pyrene	4.0 ± 1.4	0.41 ± 0.04	0.6 ± 0.5
Indeno(1,2,3-cd)pyrene	3.4 ± 2.8	0.04 ± 0.07	0.3 ± 0.4
Dibenz(a,h)anthracene	0.4 ± 0.5	nd	nd
Benzo(g,h,i)perylene	1.6 ± 0.9	0.06 ± 0.06	0.2 ± 0.4
Total 16 PAHs	569.5	142.9	158.0
Total semivolatile compounds	1156.3	443.3	480.6
<i>Chlorobenzenes (µg/kg dry basis)</i>			
MONO-	35900 ± 8700	15400 ± 5700	27700 ± 8700
DI-	2800 ± 500	1500 ± 500	3900 ± 1700
TRI-	66 ± 27	36 ± 11	103 ± 56
TETRA-	7 ± 2	7 ± 1	6 ± 4
PENTA-	2 ± 1	10 ± 3	nd
HEXA-	40 ± 30	22 ± 2	20.0 ± 0.4
Total	38845	16918	31722
<i>Chlorophenols (µg/kg dry basis)</i>			
MONO-	1850 ± 520	1550 ± 430	1350 ± 590
DI-	750 ± 440	440 ± 150	780 ± 290
TRI-	43 ± 24	25 ± 4	15 ± 7
TETRA-	2.3 ± 0.4	14.9 ± 2.6	1.7 ± 2.1
PENTA-	26 ± 11	19 ± 3	17 ± 3
Total	2676	2043	2156

sample) in combustion experiments

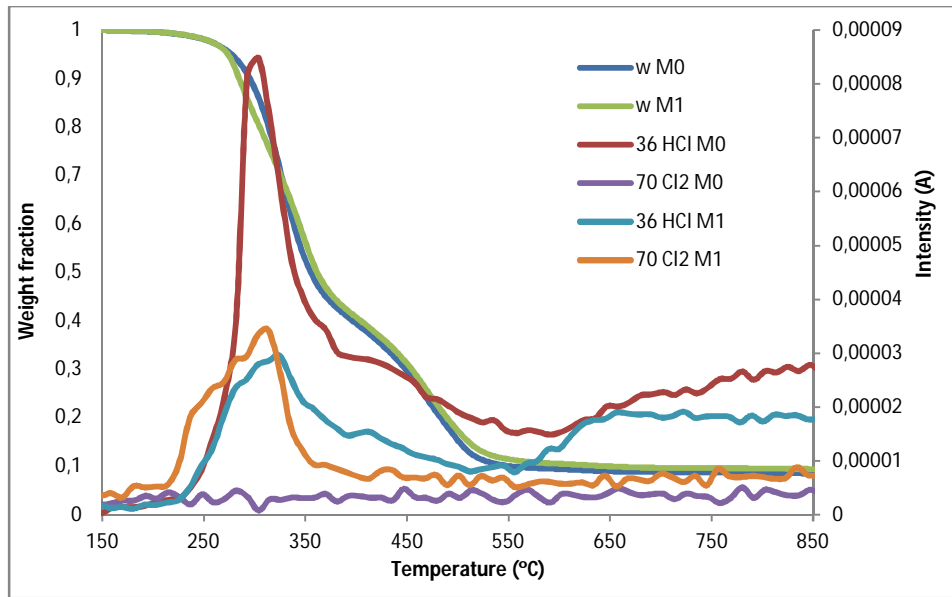
COMPOUND	ng WHO-TEQ/kg dry sample			LOB*
	M0 (wood/PVC) (n = 2)	M1(wood/PVC/PUF) (n = 2)	M2 (wood/PVC/PUF gases) (n = 2)	
2378-TCDF	0.7 ± 0.9	0.2 ± 0.3	nd	0.006
12378-PeCDF	0.9 ± 1.3	0.2 ± 0.3	0.05 ± 0.08	0.001
23478-PeCDF	118 ± 49	24 ± 12	nd	0.01
123478-HxCDF	52 ± 34	5.6 ± 2.0	nd	0.008
123678-HxCDF	74 ± 47	10.0 ± 0.4	nd	0.008
234678-HxCDF	146 ± 66	19 ± 3	1.2 ± 1.7	0.009
123789-HxCDF	112 ± 82	16 ± 1	nd	0.02
1234678-HpCDF	51 ± 32	4.9 ± 0.3	0.9 ± 1.2	0.001
1234789-HpCDF	13 ± 10	0.6 ± 0.8	nd	0.002
OCDF	0.7 ± 0.5	0.05 ± 0.07	0.03 ± 0.05	0.0001
2378-TCDD	nd	nd	nd	0.06
12378-PeCDD	nd	0.6 ± 0.8	nd	0.1
123478-HxCDD	0.2 ± 0.3	nd	nd	0.03
123678-HxCDD	2.2 ± 3.0	0.2 ± 0.3	nd	0.03
123789-HxCDD	0.1 ± 0.2	nd	nd	0.1
1234678-HpCDD	1.1 ± 1.6	0.2 ± 0.3	nd	0.01
OCDD	nd	nd	nd	0.001
Total PCDFs	569.3	81.7	2.1	
Total PCDDs	3.6	0.9	nd	
Total PCDD/Fs	572.9	82.6	2.1	
Reduct. Rate (%)	-	85.7	99.6	
PCB-77	$3.2 \cdot 10^{-3} \pm 7.9 \cdot 10^{-4}$	$5.9 \cdot 10^{-4} \pm 8.3 \cdot 10^{-4}$	$2.0 \cdot 10^{-4} \pm 2.9 \cdot 10^{-4}$	$6.5 \cdot 10^{-6}$
PCB-81	nd	$7.1 \cdot 10^{-4} \pm 1.0 \cdot 10^{-3}$	nd	$2.1 \cdot 10^{-5}$
PCB-126	9.7 ± 4.0	1.6 ± 0.8	nd	$4.7 \cdot 10^{-3}$
PCB-169	nd	0.2 ± 0.1	nd	$2.0 \cdot 10^{-3}$
PCB-105	$6.9 \cdot 10^{-4} \pm 1.5 \cdot 10^{-4}$	nd	nd	$1.8 \cdot 10^{-5}$
PCB-114	nd	nd	nd	$1.5 \cdot 10^{-5}$
PCB-118	nd	$5.3 \cdot 10^{-5} \pm 7.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-4} \pm 2.1 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$
PCB-123	nd	$6.6 \cdot 10^{-5} \pm 9.4 \cdot 10^{-5}$	$1.8 \cdot 10^{-4} \pm 2.6 \cdot 10^{-4}$	$4.3 \cdot 10^{-6}$
PCB-156	$2.2 \cdot 10^{-3} \pm 1.1 \cdot 10^{-3}$	$6.7 \cdot 10^{-5} \pm 9.5 \cdot 10^{-5}$	nd	$7.9 \cdot 10^{-6}$
PCB-157	$6.8 \cdot 10^{-4} \pm 9.6 \cdot 10^{-4}$	$8.2 \cdot 10^{-5} \pm 1.2 \cdot 10^{-4}$	nd	$8.4 \cdot 10^{-6}$
PCB-167	$3.4 \cdot 10^{-4} \pm 4.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-5} \pm 1.8 \cdot 10^{-5}$	$1.0 \cdot 10^{-5} \pm 1.49 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
PCB-189	$3.0 \cdot 10^{-3} \pm 2.1 \cdot 10^{-3}$	nd	nd	$5.9 \cdot 10^{-6}$
Total PCBs	9.71	1.83	$5.5 \cdot 10^{-4}$	

Reduct. rate (%)	-	81.2	99.9
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505 * LOB: Limit of Blank.

506 nd: result below LOB.

507



508

509 **Figure 1.** Intensities of ions corresponding to HCl and Cl₂ in TG-MS runs for M0 and
 510 M1 combustion.

511