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Emissions of PBDD/Fs, PCDD/Fs and PBDEs from

flame-retarded high-impact polystyrene under

thermal stress

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13 ABSTRACT

The emissions of polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and their chlorinated analogues (PCDD/Fs) during the thermal treatment of a high impact polystyrene (HIPS) TV casing were investigated. The halogenated compounds were analyzed in the original material and in the gases emitted during its treatment at temperatures between 50 and 250 ºC. DecaBDE was the primary PBDE in the TV casing, which also contained high levels of PBDFs (ppm range). At the lower treatment temperatures, non-

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20 modified PBDEs evaporated from the samples. Conversely, at 200 ºC or above, debromination

21 reactions led to the formation of additional tri- through nonaBDE. The formation of new PBDD/Fs

22 was also detected in the gas phase when the plastic was heated to 200 or 250 ºC, with higher yields

23 of furans than dioxins. This appreciably increased the toxic equivalent (TEQ) levels of the gas

24 phase relative to those seen in the untreated sample. In all cases, the levels and TEQ contributions

25 from PCDD/Fs were negligible compared to those for brominated analogues.

26 KEYWORDS: thermal transformation, HIPS, BFRs, PBDEs, PBDD/Fs, PCDD/Fs.

27 1. INTRODUCTION

28 Enormous quantities of electrical and electronic products are disposed of around the world every

29 day. This e-waste is of major environmental concern due to the toxicity of some of its components

30 (Herat, 2008) such as brominated flame retardants (BFRs). According to the European Flame

31 Retardants Association (EFRA), the electronics industry is the largest consumer of BFRs; it uses

32 them in computers, printed circuit boards and components such as connectors, plastic cabinets and

33 cables. Polybrominated diphenyl ethers (PBDEs) have been extensively used for this purpose,

34 mainly in the form of additive flame retardants that are not chemically bound to the plastic and are

35 therefore comparatively readily released into the environment (Tasaki et al., 2004).

36 Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) are present as impurities in

37 technical BFR mixtures, particularly in PBDE mixtures (Hanari et al., 2006), and may leak along

38 with the BFRs from the flame-retarded products during their lifetime. In addition, PBDEs may be

39 transformed into PBDD/Fs during combustion processes or under thermal stress such as that

40 caused by extrusion, molding or shredding (Weber and Kuch, 2003), which may occur during

41 production or recycling. The total quantity of PBDD/Fs formed during thermal processes depends

42 largely on the abundance of precursor compounds and the specific conditions of the thermal

43 treatment. Precursors that can form PBDD/Fs by a simple elimination step (e.g. PBDEs) are thus

44 most prone to form PBDD/Fs (Weber and Kuch, 2003). In fact, when PBDEs are used as flame

45 retardants, reactions involving the condensation or recombination of fragments are one of the main

46 reasons for the presence of PBDD/Fs in thermally treated plastics (Ebert and Bahadir, 2003).

47 Recent studies (Duan et al., 2012) have shown that the combustion of brominated and chlorinated

48 compounds is the main source of dioxins (Söderström and Marklund, 2002; Barontini et al., 2005;

49 Lai et al., 2006; Gullett et al., 2007; Altarawneh et al., 2009). However, there have been relatively

50 few empirical studies on dioxin formation during the conventional dismantling and processing of

51 e-waste. There is a particular lack of information relating to low-temperature thermal processing

52 and PBDD/F emissions (Duan et al., 2012).

53   The aim of this study was to examine the emissions of PBDEs, PBDD/Fs and PCDD/Fs from

54   flame-retarded high impact polystyrene (HIPS) in the back cover of a TV set when heated to

55   temperatures between 50 and 250 ℃, which are similar to the temperatures the polymer may reach

56   during production (e.g. extrusion and molding) and recycling processes (e.g. hammer milling,

57   impact grinding, granulation, etc.), as well as during accidental overheating (e.g. partial fires).

58   2. MATERIAL AND METHODS

59   2.1. Samples

60   Pieces of flame-retarded HIPS from a TV back cover produced in the early 90's were used in this

61   study. The elemental composition of the cover is provided in the Supplementary material (Table

62   S1). Its relatively high contents of bromine (Br, 9.2 wt %) and antimony (Sb, 4.1 wt %) are

63   probably due to the flame retardants in its plastics. BFRs are usually added to polymers in high

64   proportions, and antimony trioxide (Sb_2O_3) is often used in combination with BFRs and other

65   halogenated flame retardants due to the synergistic effects obtained (WHO, 1997).

66   2.2. Experimental setup and sampling

67   The thermal treatment experiments were carried out in a vertical stainless steel reactor (diameter

68   75 mm, length 750 mm) that is described in detail elsewhere (Lundin et al., 2011). For each run,

69   once the desired temperature (i.e. 50, 100, 150, 200 or 250 ℃) had been reached, a crucible

70   containing the sample (a 10 g piece of the TV plastic, supported on quartz glass wool), was placed

71   in the middle of the reactor. Air was introduced into the reactor via a constant downward flow

72   (1.35 L/min), and the outgoing gases were sampled continuously over 30 minutes. Experiments

73   were performed in duplicate at each temperature, along with two blank runs at 150 and 250 ℃.

74   Measurements of the temperature in the gas phase during the experiments showed that the desired

75   temperature was maintained within ±5 ℃, with one exception: during the second run at 150 ℃, the

76   temperature fluctuated between 100 and 150 ℃ during the first 10 minutes. This increased the

77   variation in the results obtained for these replicates as shown in Section 3.

78   During each experiment, the gas phase was continuously sampled using the cooled probe

79   polyurethane foam (PUF) plug technique according to the EN 1948:1-3 standards

80   (European Committee for Standardization, 2006).

81   2.3. Analytical procedure

82   All samples, including samples of the original TV casing and the emission samples, were analyzed

83   with respect to PBDEs, PBDD/Fs and PCDD/Fs.

84 The analytical method allowed for the congener-specific determination of 10 tri- to
85 decabrominated diphenyl ethers and the corresponding total PBDE content. The samples were also
86 analyzed for 17 different 2,3,7,8-substituted tri- to octaBDD/F congeners and total PBDD/F
87 content. Finally, the PCDD/F analysis included the quantitative determination of 23 different
88 2,3,7,8-substituted mono- to octaCDD/F congeners and the corresponding total homologues.

89 Flue gas condensates and impinger solutions were combined and diluted to 2 L with Milli-Q water.
90 The mixture was filtered through a glass fiber prefilter combined with a membrane filter (0.45 μm
91 pore size) and then extracted through a C_{18} solid-phase extraction disk (SPE) (Envi-Disk,
92 Supelco). The prefilter, membrane filter, SPE disk, aerosol filter, and PUFP were extracted in a
93 Soxhlet-Dean-Stark apparatus with 400 mL toluene for 24 hours to efficiently recover all target
94 compounds. Untreated TV casing samples were dissolved in tetrahydrofuran, treated in an
95 ultrasonic bath for 60 minutes to ensure dissolution and extracted overnight at room temperature;
96 the polymer was precipitated by n-hexane addition and removed by filtration. Prior to extraction,
97 samples were spiked with a $^{13}C_{12}$-labeled multi-analyte internal standard (IS) solution. All extracts
98 were concentrated down to 1 mL by rotary evaporation.

99 The extracts were purified and fractionated on two sequential gravity fed liquid chromatography
100 columns. First, the extract and 3 x 1 mL n-hexane rinses were applied to a 16 mm i.d. multi-layer
101 silica gel column, consisting of 3 g of basic silica gel (SiO_2, 70-230 mesh, Merck, thoroughly
102 mixed with 20 % KOH (w/w) dissolved in methanol, then washed with methanol and
103 dichloromethane), 1.4 g of silica gel (SiO_2, 70-230 mesh, Merck, washed with methanol and
104 dichloromethane and thermally activated at 130 °C), 4 g of acid silica gel (activated SiO_2, 70-230
105 mesh, Merck, thoroughly mixed with 40 % H_2SO_4 (w/w)), and 3 g of anhydrous Na_2SO_4. The
106 column was eluted with 130 mL of n-hexane, and the eluate was collected and concentrated down
107 to 1 mL using a TurboVap II concentration workstation (Zymark Corp.). Then, this eluate and
108 3 x 1 mL n-hexane rinses were applied to a 16 mm i.d. Florisil® column containing 5 g of Florisil®
109 (deactivated with 1 % H_2O) and topped with 3 g of anhydrous Na_2SO_4. In this column, PBDEs
110 were eluted with 90 mL of n-hexane after which PBDD/Fs and PCDD/Fs were eluted with 150 mL
111 n-hexane:DCM (40:60 v/v). Both fractions were concentrated in 40 μL tetradecane using the
112 TurboVap II station and subjected to a nitrogen blow-down for final sample concentration.

113 The final samples were analyzed for the target compounds in three separate HRGC/HRMS runs
114 using a Waters AutoSpec ULTIMA NT 2000D high resolution mass spectrometer. PCDD/Fs were
115 separated on a DB5−MS column (60 m x 0.25 mm x 0.25 μm) under the following conditions:
116 splitless injection at 280 °C and GC oven temperature programmed at 190 °C (2 min hold),
117 3 °C/min to 278 °C and 10 °C/min to 315 °C (5 min hold). PBDD/Fs and PBDEs were separated

118   on a shorter DB5−MS column (15 m x 0.25 mm x 0.10 µm) using the following conditions: PTV

119   injection (in pulsed splitless mode) programmed from 190 ℃ to 320 ℃ at 700 ℃/min and GC

120   oven temperature programmed at 190 °C (1 min hold) and 7 °C/min to 320 °C (4 min hold).

121   All compounds were quantified using the isotope dilution method. Recoveries of the spiked IS-

122   compounds were calculated using a recovery standard (RS) solution that was added to the samples

123   before injection into the gas chromatograph. PCDD/F and PBDD/F recoveries were well within

124   the limits specified in EN 1948:1-3 (European Committee for Standardization, 2006): 30 – 150 %

125   for tetra- to hexa-substituted congeners and 20 – 150 % for hepta- to octa-substituted congeners

126   with the exception of monoCDFs, for which recoveries of 12 – 16 % were achieved. The

127   recoveries of PBDEs met the criteria specified in US-EPA method 1614 (US EPA, 2007): 25 –

128   150 % for tri- to nonaBDE and 20 – 200 % for decaBDE.

129   Care was taken to avoid directly exposing samples to light during all experiments and analytical

130   steps in order to prevent the photodegradation of brominated compounds.

131   3.   RESULTS AND DISCUSSION

132   3.1. TV casing

133   3.1.1.   PBDE concentrations

134   Only small amounts of the tri- to hexabrominated PBDEs were detected in the TV casing (Table

135   1). The most abundant congeners were hepta- to decaBDEs, with BDE-209 accounting for 67 % of

136   the total PBDE content. The presence and relative abundances of these congeners suggests that the

137   material was manufactured using a commercial DecaBDE mixture as the flame retardant (Alaee et

138   al., 2003; La Guardia et al., 2006), although technical DecaBDE mixtures usually contain more

139   than 90 % BDE-209. The higher amounts of octa- and nonabrominated congeners found in the TV

140   casing in this study may be due to the transformation of the PBDEs originally present in the

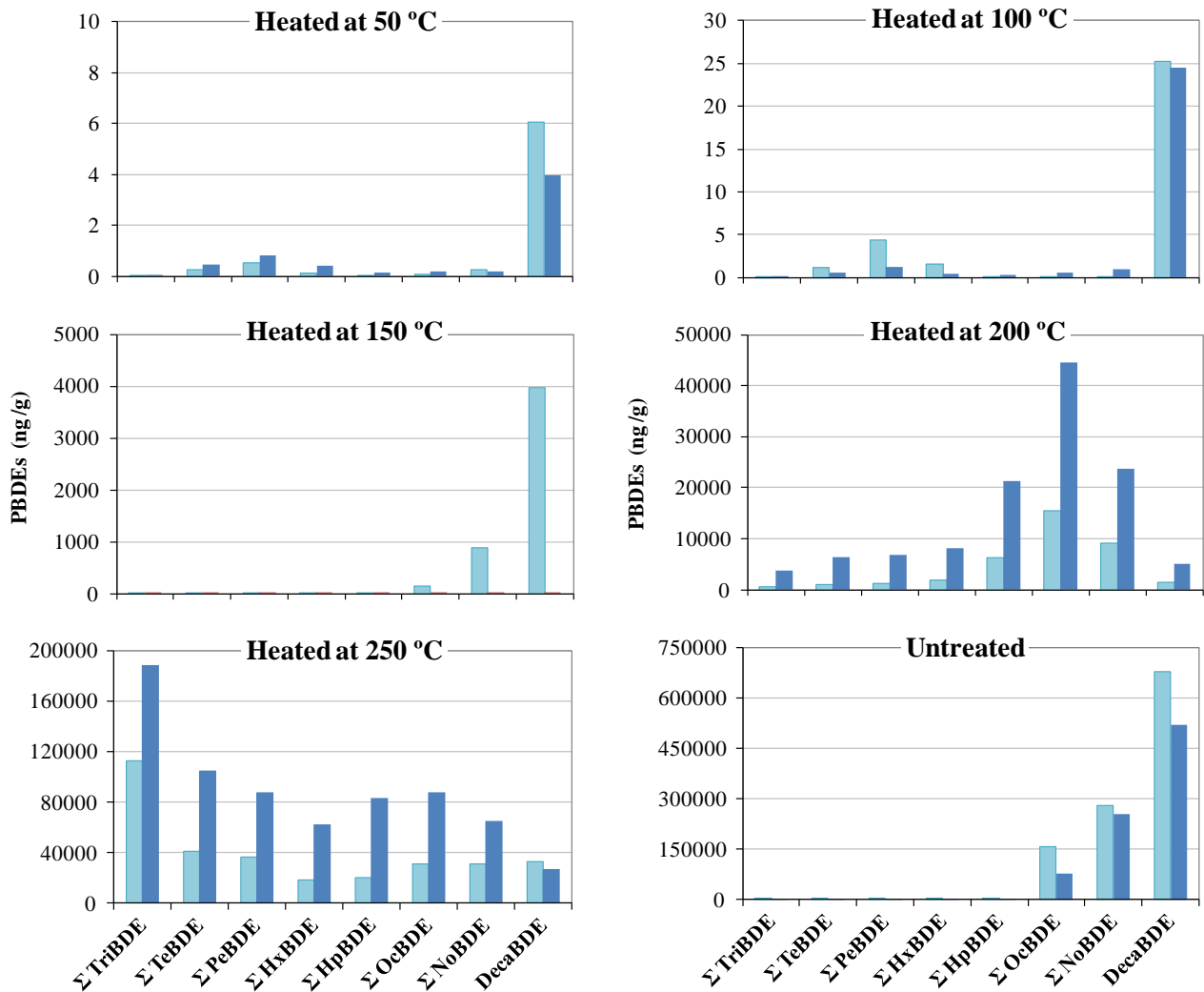141   product (Kajiwara et al., 2008).

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Table 1. PBDE congeners (ng/g) in the flue gas samples (normalized against the amount of heated plastic) and in the untreated TV casing samples. Results for duplicate runs are shown in each case.

	50 ºC		100 ºC		150 ºC		200 ºC		250 ºC		untreated	
TriBDE #28	0.01	0.01	0.03	0.04	2.6	1.2	35	200	11000	18000	76	71
TeBDE #47	0.25	0.45	1.0	0.56	2.9	2.4	27	130	2800	5500	18	15
PeBDE #99	0.42	0.68	3.6	1.0	1.7	6.9	67	360	2200	5200	9.1	9.5
PeBDE #100	0.09	0.14	0.67	0.22	0.32	1.3	29	170	1700	3800	1.7	1.9
HxBDE #153	0.06	0.22	0.79	0.26	2.9	1.3	240	970	2600	6900	300	280
HxBDE #154	0.05	0.09	0.63	0.16	0.35	1.0	310	1600	3700	11000	6.9	4.0
HpBDE #183	0.02	0.15	0.06	0.20	11	0.38	1400	4600	4200	19000	3800	3400
OcBDE #196	0.02	0.05	0.03	0.17	84	0.39	1700	4300	3000	13000	120000	55000
NoBDE #206	0.10	0.08	0.05	0.38	530	1.0	2700	6000	6000	16000	210000	200000
DcBDE #209	6.0	4.0	25	24	4000	21	1600	5000	33000	27000	680000	520000
Total PBDEs	7.0	5.9	32	27	4600	37	8100	23000	70000	130000	1010000	780000

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3.1.2. PBDE homologue profiles

149 The plastic casing contained large quantities of PBDEs, exceeding the limit of 0.1 wt %

150 established in the RoHS Directive (European Comission, 2011). DecaBDE accounted for 60% of

151 the total PDBE content of the TV casing (Figure 1). NoBDE and ocBDE were also present,

152 accounting for 25 – 30 % and 9 – 14 %, respectively, of the total PBDE content in the duplicate

153 runs. Minor amounts of less heavily brominated diphenyl ether homologues were also detected

154 (around 5 000 ng/g in total).

155 Figure 1. PBDE homologue profiles (ng/g) in the flue gas samples (normalized against the amount

156 of heated plastic) and in the untreated TV casing samples (duplicate runs).

3.1.3. PBDD/F concentrations

158 As shown in Table 2, the average 2,3,7,8-substituted PBDD/F content of the TV casing was

159 5 450 ng/g, with furans accounting for more than 98% of the total. The most prevalent congeners

160 were OBDF and 1,2,3,4,6,7,8-HpBDF; the only brominated dioxin detected was OBDD. The

161   PBDD/F content of the untreated sample is similar to the values reported by other authors (Sakai et
162   al., 2001), who measured PBDD/F contents of 3 000 ng/g in waste TV casing materials
163   manufactured between 1987 and 1995.

Table 2. Contents of PBDD/F congeners and total PCDD/Fs (ng/g) in the flue gas samples (normalized against the amount of heated plastic) and the original TV casing samples (duplicate runs).

	WHO_{2005}-TEF	50 ºC		100 ºC		150 ºC		200 ºC		250 ºC		untreated	
2,3,8-TriBDF		0.002	0.02	0.003	0.02	0.15	0.03	20	110	3200	4300	9.3	8.4
2,3,7,8-TeBDF	0.1	0.003	0.03	0.003	0.02	0.09	0.02	67	340	3000	3100	6.3	5.2
1,2,3,7,8-PeBDF	0.03	0.003	0.005	0.002	0.007	0.08	0.02	100	370	740	1300	1.4	1.3
2,3,4,7,8-PeBDF	0.3	0.001	0.007	0.001	0.01	0.13	0.02	75	320	720	1200	3.3	3.5
1,2,3,4,7,8-HxBDF	0.1	0.002	0.008	0.005	0.02	0.6	0.06	760	2300	9400	13000	31	34
1,2,3,4,6,7,8-HpBDF	0.01	0.02	0.02	0.02	0.07	7.4	0.15	6100	10000	24000	31000	1200	1200
OBDF	0.0003	0.03	0.02	0.01	0.07	21	0.10	4700	5000	13000	16000	4200	3900
1,3,7+1,3,8-TriBDD		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,3,7-TriBDD		nd	nd	nd	nd	nd	nd	nd	0.39	4.9	5.9	nd	nd
2,3,7,8-TeBDD	1	nd	nd	nd	nd	0.001	0.001	1.3	5.7	140	150	nd	nd
1,2,3,7,8-PeBDD	1	nd	nd	nd	nd	0.003	0.001	2.4	8.0	120	110	nd	nd
1,2,3,4,7,8+1,2,3,6,7,8-HxBDD	0.1	nd	nd	nd	nd	0.03	0.002	nd	2.3	nd	nd	nd	nd
1,2,3,7,8,9-HxBDD	0.1	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpBDD	0.01	nd	nd	nd	nd	0.26	0.001	3.1	5.7	9.8	7.60	nd	nd
OBDD	0.0003	nd	nd	nd	nd	4.6	nd	30	36	130	120	89	66
Total PBDFs		0.06	0.11	0.04	0.22	29	0.40	12000	18000	54000	70000	5500	5200
Total PBDDs		nd	nd	nd	nd	4.9	0.005	37	58	400	390	89	66
Total PBDD/Fs		0.05	0.11	0.04	0.22	34	0.41	12000	18000	54000	70000	5600	5300
Total WHO_{2005}-TEQ (PBDD/Fs)		0.0011	0.0060	0.0010	0.0090	0.210	0.020	170	490	2000	2600	18	18
Total PCDFs		0.28	0.35	0.39	0.32	0.39	0.30	0.51	0.74	0.60	0.86	24	24
Total PCDDs		0.001	0.004	0.001	0.007	0.005	0.002	0.002	0.004	nd	nd	0.07	0.01
Total PCDD/Fs		0.28	0.35	0.39	0.33	0.40	0.30	0.51	0.74	0.60	0.86	24	24
Total WHO_{2005}-TEQ (PCDD/Fs)		0.0004	0.0007	0.0005	0.0007	0.0003	0.0005	0.0028	0.0100	0.0300	0.0500	0.0029	0.0040

nd: not detected or <LOD

3.1.4. PBDD/F homologue profiles

164 As illustrated in Figure 2, the total PBDD/F content of the TV casing ranged from 6 700 to

165 7 000 ng/g and was completely dominated by furans (99 %). OBDD was the only PBDD congener

166 found in this sample whereas furans with every possible degree of bromination (i.e. tri− through

167 octa−) were detected, with OBDF (59 − 60 %) and HpBDF (17 − 18 %) being the most abundant

168 homologues. The PBDD/Fs present in the plastic probably had multiple origins: some would have

169 been present as impurities in the technical PBDE-mixtures used (Hanari et al., 2006), some would

170 have been formed during the production of the plastic cover (Luijk et al., 1992), and others would

171 have been formed by transformation processes arising from the everyday use of the TV (Kajiwara

172 et al., 2008). Similar PBDD/F profiles have previously been observed in commercial DecaBDE

173 mixtures (Ren et al., 2011).
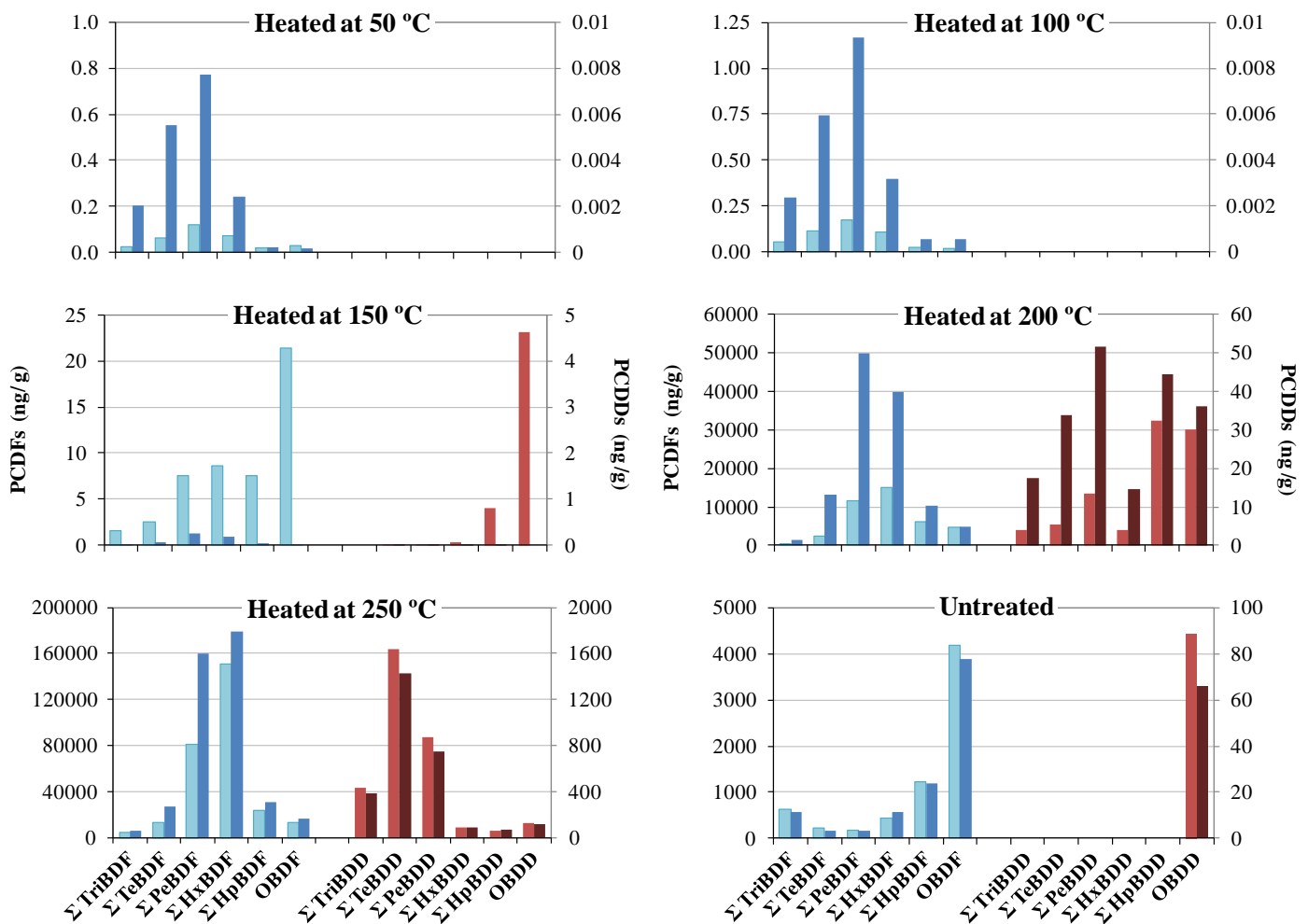
174 Figure 2. PBDD/F homologue profiles (ng/g) in the flue gas samples (normalized against the

175 amount of heated plastic) and the original TV casing samples (duplicate runs). Furan levels are

176 shown on the left-hand axes and dioxin levels on the right.

177   3.2. Gas phase

178   3.2.1.   PBDE concentrations

179 As shown in Table 1, at low treatment temperatures of 50 or 100 ℃, decaBDE accounted for
180 almost the entire PBDE content of the exhaust gases, suggesting that mainly unmodified PBDEs
181 were emitted from the plastics under these conditions.

182 At 150 ℃, BDE#209 (nona), #196 (octa) and #183 (hepta) start to emerge in the exhaust gases,
183 indicating a slight debromination of BDE#209 at this temperature. At 200 ℃, BDE#206, #196,
184 and #183 were emitted at similar levels to BDE#209 and less brominated congeners also started to
185 appear, indicating further debromination. Finally, at 250 ℃ all PBDEs were emitted in larger
186 amounts than at the lower temperatures. While BDE#209 and BDE#28 dominated the pattern, the
187 other six congeners were emitted in equal amounts. Treatment at 250 ℃ thus seems to cause both
188 extensive emissions of the original flame retardants and extensive debromination.

189 Treatment at 250 ℃ increased PBDE emissions by an order of magnitude compared to the results
190 observed at 200 ℃, increasing the yields of every analyzed isomer.

191   3.2.2.   PBDE homologue profiles

192 The homologue profiles in the flue gas samples differed from the PBDE profile found in the
193 original TV casing (Figure 1). At temperatures between 50 and 150 ℃, PBDE emissions were
194 dominated by decaBDE, indicating a release of unchanged PBDEs from the plastics. At higher
195 temperatures there was a shift towards less brominated PBDEs, indicating the occurrence of
196 debromination. At 200 °C, octaBDE was the most abundant congener (around 40 %), followed by
197 nona- and heptaBDEs. At the highest temperature (250 °C), PBDE emissions increased by around
198 a factor of ten compared to the second highest temperature and debrominated congeners became
199 even more dominant in the homologue profile: triBDEs accounted for 27 – 34 % of the total PDBE
200 content.

201   3.2.3.   PBDD/F concentrations

202 As shown in Table 2, no 2,3,7,8-substituted PBDD congeners were detected at 50 or 100 ℃ and
203 the amount of furans was low. At 150 ℃ 1,2,3,4,6,7,8-HpBDF, OBDF and OBDD were present in
204 the gas phase to a greater extent, in keeping with their abundance in the plastic, but their
205 concentrations remained very low. Increasing the treatment temperature further to 200 ℃
206 increased the abundance of 2,3,7,8-substituted PBDF congeners in the gas phase to between 15
207 and 30 % of the total PBDF content, while 2,3,7,8-dioxins accounted for 29 – 42 % of the total

208   PBDDs. The contribution of the 2,3,7,8-substituted congeners to the total PBDD/F content

209   decreased at 250 ºC (17 – 19 % for furans and 13 – 14 % for dioxins).

210   1,2,3,4,6,7,8-HpBDF, OBDF and OBDD dominated the PBDD/F profiles in the gas samples at all

211   investigated temperatures, and at the higher temperatures (i.e. 200 and 250 °C) they were present

212   at higher levels than in the untreated plastics, reflecting new PBDD/F formation. These were

213   probably formed from PBDEs via the precursor pathway (Weber and Kuch, 2003). In a study on

214   PBDD/F formation from PBDEs in electronic waste, Zennegg et al. (2014) also observed the

215   formation of new PBDD/Fs in TV monitor samples heated at 225 ºC for up to 10 min in a torque

216   rheometer. However, the increase in that case was less pronounced than in our samples, probably

217   because of the difference in treatment temperature and duration.

218   The WHO_{2005}-TEQ concentration of PBDD/Fs in the TV casing was 18 ng/g, and treatment at 200

219   and 250 ºC resulted in the release of 170 – 490 and 2 000 – 2 600 ng WHO_{2005}-TEQ/g plastic,

220   respectively. Depending on the temperature, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF or 1,2,3,4,6,7,8-

221   HpBDF were the congeners that made the greatest contribution to the total toxicity. These results

222   are in agreement with the findings of Duan et al. (2011), who reported emission factors for

223   PBDD/Fs formed during the incineration of scrap printed circuit boards (PCBs). These researchers

224   found that for untreated PCB samples, 1,2,3,4,7,8-HxBDF and 1,2,3,4,6,7,8-HpBDF made the

225   greatest contributions to the toxicity value (34 % and 55 % of the total TEQ PBDD/Fs,

226   respectively) and these congeners, together with 2,3,4,7,8-PeBDF, were also the most toxic ones

227   generated in samples heated to 250 ºC.

228   3.2.4.   PBDD/F homologue profiles

229   Heating the plastic caused both PBDFs and PBDDs to be emitted into the gas phase (Figure 2). As

230   expected from a thermal process, furans were dominant in the gas phase, with PBDDs accounting

231   for only 10 % of the total PBDD/F content at 150 ºC and less than 1.5 % at 200 and 250 ºC.

232   No PBDDs were detected at 50 or 100 ºC, while the PBDF concentrations under these conditions

233   were below the ppb range. This indicates that at the lower treatment temperatures, the emissions

234   from the plastic are mainly due to the evaporation of its original PBDF content, so the less

235   brominated (i.e. more volatile) congeners are predominant in the gas phase.

236   Raising the treatment temperature to 150 ºC increased the emissions of brominated dioxins and

237   furans, but the emitted concentrations were still lower than those in the plastic. In addition to the

238   evaporation of the PBDD/Fs that were originally present in the material, some OBDD

239   debromination occurred. Consequently, HxBDDs and HpBDDs were detected in the gas phase.

240   PBDF emissions increased sharply on raising the treatment temperature to 200 or 250 ℃, by

241   factors of 6-18 and 42-63, respectively, relative to their original concentrations in the plastic.

242   There was also an increase in PBDD emissions, but it was only at 250 °C that their total gas phase

243   concentration exceeded the PBDD (OBDD) concentration in the plastic. These results indicate that

244   no appreciable formation of PBDDs from PBDEs occurred at treatment temperatures of 200 ℃ or

245   below.

246   Figure 2 shows that the PBDF homologue profiles were identical at 50 and 100 ℃, became

247   dominated by OBDF at 150 ℃, and then shifted again at 200 and 250 °C to become dominated by

248   penta- and hexa-brominated congeners. The PBDD homologue profile shifted as the treatment

249   temperature increased: it consisted exclusively of hepta- and octabrominated dioxins at 150 ℃ but

250   was dominated by tri-, tetra- and pentabrominated congeners at 250 ℃.

251   Luijk et al. (1991) have previously conducted pyrolysis experiments using HIPS containing the

252   DecaBDE/Sb_2O_3 flame retardant system. Their results also showed that the yields of PBDDs were

253   considerably lower than those of PBDFs when the samples were thermally stressed. According to

254   these authors, the radical depolymerisation process is stabilized by the brominated diphenyl ethers,

255   which start to debrominate in the polymer melting phase and abstract hydrogens from the polymer

256   backbone. The exchange of bromine and hydrogen in DecaBDE gives rise to more reactive (less

257   brominated) PBDEs, thus enhancing PBDF formation. The high PBDF yields in the gas samples

258   can also be explained by the presence of the synergist Sb_2O_3 (Dumler et al., 1990), since this metal

259   oxide can catalyze the elimination of HBr/Br_2 in the condensation steps leading to the formation of

260   PBDFs from PBDEs.

261   Different hypotheses have been proposed to account for the formation of PBDDs during PBDE

262   thermolysis. In their comprehensive review of the formation pathways of PBDD/Fs from BFR in

263   thermal processes, Weber et al. (2003) discuss two possible explanations. The first was proposed

264   by Buser (1986) and Luijk et al. (1991), and invokes intra-molecular oxygen insertion to account

265   for the formation of PBDDs from PBDEs. Conversely, Lenoir et al. (1994) postulated the

266   degradation of PBDEs to polybrominated phenols and polybrominated benzenes followed by

267   phenol dimerisation.

268   3.2.5.   PCDD/F concentrations

269   In comparison to PBDD/Fs, the concentrations of the chlorinated analogues in both the original

270   plastic and the flue gases were very low.

271   Even though the mean concentration of total chlorinated homologues measured in the TV casing

272   was 125 ng/g, the PCDD/F emissions from the different runs remained below 10 ng/g for all

273 treatment temperatures up to 200 ºC and only rose to 42-56 ng/g at 250 ºC. As was observed for

274 the PBDD/Fs, PCDFs were much more abundant than PCDDs: dioxins accounted for only 1 % of

275 the total PCDD/F content.

276 A mean of 3.45 pg WHO_{2005}-TEQ PCDD/Fs /g plastic was determined for the TV casing (Table

277 2). The low temperature treatments (50-150 ºC) produced lower emissions of PCDD/F-TEQ

278 200 ºC had similar TEQ-levels to the plastic while treatment at 250 ºC generated emissions with a

279 ten-fold higher PCDD/F-TEQ value. In all cases, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF,

280 1,2,3,6,7,8-HxCDF or 2,3,4,6,7,8-HxCDF were the congeners that made the greatest contribution

281 (between 62 and 100 %) to the total TEQ value.

282 4. CONCLUSIONS

283 DecaBDE was the dominant PBDE detected in the TV casing. At lower temperatures, thermal

284 stress caused an evaporation of unmodified PBDEs from the plastic. However, debromination

285 reactions occurred at temperatures of 200 ºC or above, causing the formation and emission of

286 additional tri- through nonaBDEs.

287 The flue gases generated during thermal stressing of the samples at 200 and 250 ºC contained great

288 concentrations of PBDD/Fs, thereby confirming the role of PBDEs as precursors in the formation

289 of brominated dioxins and furans. The emitted dioxin profile was dominated by furans. The

290 PBDD/F homologue profile in the original TV casing was dominated by highly brominated PBDFs

291 but those for the flue gas samples exhibited a shift towards less brominated congeners.

292 It can be concluded that the heating of the studied plastics produced high yields of PBDD/Fs,

293 leading to higher TEQ values than in the original material. These results should be considered

294 when assessing production or recycling processes for materials containing brominated flame

295 retardants such as PBDEs because these emissions could pose a risk to workers and cause serious

296 environmental pollution.

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Supplementary Material