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1 **Evaluation of polybrominated diphenyl ether (PBDE) flame retardants from various**
2 **materials in professional seating furnishing wastes from French flows.**

3

4 Florence Portet-Koltalo^{1*}, Nicolas Guibert¹, C. Morin¹, Florence de Mengin-Fondragon²,
5 Adèle Frouard²

6

7 1 Normandie University, UNIROUEN, COBRA Laboratory UMR CNRS 6014, 55 rue Saint
8 Germain, 27000 Evreux, France.

9 florence.koltalo@univ-rouen.fr; nicolas.guibert@wanadoo.fr; [christophe.morin@univ-](mailto:christophe.morin@univ-rouen.fr)
10 rouen.fr

11

12 2 VALDELIA, 93 rue du Lac, 31670 Labège, France

13 florence.demengin@valdelia.org; adele.frouard@valdelia.org

14

15 * Author to whom correspondence should be addressed:

16 e-mail: florence.koltalo@univ-rouen.fr ; Tel.: +33-232-291-535

17

18

19 **Abstract**

20

21 Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants that are used in
22 polymeric materials. Due to their adverse health effects, the use of recycled wastes has been
23 forbidden if the total PBDE content exceeds 0.1% (w/w). The objective was to estimate the
24 proportion of PBDEs in professional seating furnishing wastes to identify the materials in
25 which the content of PBDEs (and particularly BDE-209) could exceed the limit to eliminate
26 them from recycling. An analytical process (microwave extraction followed by purification
27 and chromatographic analysis) was adapted to assess with a unique methodology the amounts
28 of eight PBDEs in materials that result from various seating wastes, such as hard plastics,
29 foams and accompanying textiles. X-ray fluorescence (XRF) was used to rapidly predict
30 critical PBDE concentrations via Br. From 100 samples, the total PBDE content did not
31 exceed the current tolerated threshold. The examined materials contained only trace levels of
32 former PBDE formulations, and BDE-209 was identified at higher amounts, mainly in hard
33 plastics, but these amounts were less than 312 mg kg⁻¹. Since XRF was not reliable for
34 quantitative measurements and was not specific, no direct correlation could be identified
35 between Br and PBDE levels. Br was strongly associated with As in all the materials, but the
36 presence of PBDEs was not clearly associated with the presence of other metals that are used
37 in flame retardants.

38

39 **Key words**

40 Polybrominated diphenyl ethers; waste furnishings; hard plastics; foams; soft furnishings

41

42 **1. Introduction**

43 Polybrominated diphenyl ethers (PBDEs) are a class of synthetic brominated compounds that
44 are used as flame retardants (FRs), primarily in plastic polymers and textiles, to meet
45 flammability standards of consumer electronics, textiles and furnishings. Each is composed of
46 a diphenyl ether skeleton that is substituted by 1 to 10 bromines. They can accumulate in
47 soils/sediments or bioaccumulate and have adverse health effects (Shaw et al., 2010; Li et al.,
48 2012; Zhang et al., 2019).

49 Penta-, Octa- and Deca-BDE are the three major commercial PBDE formulations. Although
50 much more widely employed in North America, Penta-BDE has also been used in Europe,
51 mainly in polyurethane foams (PUF) for furniture and automobile equipment (Drage et al.,
52 2018). Octa-BDE has been used mainly in plastics for electrical and electronic equipment
53 (EEE), PC, TV monitors and printers (Charbonnet et al., 2020). Deca-BDE has been used for
54 dense plastics (for housings of TVs and computers), furniture upholstery, textiles and drapes
55 (for high-risk occupational areas) (Alcock et al., 2003; Drage et al., 2018). During
56 manufacturing, PBDEs are added to products for fire control. As they are not chemically
57 grafted, they can be easily released into the environment through dust (Cowell et al., 2017;
58 Nkabinde et al., 2018), leaching or decomposition of plastic/foam wastes due to high
59 temperatures or UV exposure. The levels of PBDEs in the environment have increased as a
60 result of their widespread use and their persistence (Shaw and Kannan, 2009). Penta- and
61 Octa-BDEs were listed under the Stockholm Convention on Persistent Organic Pollutants in
62 2009, and Deca-BDE was added to this list in 2017. Penta- and Octa-BDEs are supposed to be
63 completely eliminated by 2030, with specified exceptions being permitted before that date for
64 articles that contain recycled materials. In France, the 2004-1227 decree stipulated that from
65 2005, Penta- and Octa-BDE could not be used in manufactured products at concentrations
66 above 0.1% (w/w), which is not sufficient for the realization of flame retardant efficiency and

67 requires the replacement by other FRs. Deca-BDE remains under production for limited uses
68 but these exemptions will expire in 2036. The European Directive 2003/11/CE banned the use
69 of recycled wastes if the sum of tetra- to hepta-BDEs exceeds 0.1% w/w (1000 mg kg⁻¹). If so,
70 wastes must be specially treated to remove those PBDEs prior to recycling. As Deca-BDE
71 was recently introduced under the Stockholm Convention, it is likely that it will also be more
72 severely restricted, especially BDE-209 (with 10 bromines), which is the main congener.

73 Waste recycling sites have attracted attention worldwide as potential sources of PBDEs,
74 especially in the US, China, and the UK but also in developing countries (Petreas and Oros,
75 2009; Stubbings et al., 2016; Ahn et al., 2017; Yu et al., 2017; Babayemi et al., 2018). The
76 flow of PBDEs in wastes has been examined mainly in EEE wastes (e-wastes) and sometimes
77 in end-of-life vehicles, in plastic packaging and household products, in construction or
78 demolition wastes (Petreas and Oros, 2009; Duan et al., 2016; Chen et al., 2010; Choi et al.,
79 2017, Pivnenko et al., 2017; Xiu et al., 2019). But to the best of our knowledge, no study has
80 focused on end-of-life professional seating furniture, which represents the largest tonnage of
81 office wastes in France. France, like other countries, requires the use of mildly flammable
82 materials (M3 category) in seating furniture for establishments that service the public, which
83 leads to the addition of FRs into the seating components to satisfy this requirement. This is
84 especially the case for materials that were produced before 2005. Therefore, it is now
85 imperative, especially for sectors that organize the collection and recycling of end-of-life
86 seating furniture, to identify the materials in which PBDEs could exceed the current
87 concentration limit of 1000 mg kg⁻¹ to eliminate those materials from recycling. Notably,
88 BDE-209 must be controlled, as Deca-BDE remains in use and can possibly enter flows of
89 recycled materials.

90 As discussed, various complex matrices can contain PBDEs. The analytical procedures for
91 PBDE detection are complex and involve sample pretreatment, extraction, clean-up and

92 chromatographic separation, coupled to mass spectrometry detection if the multiple congeners
93 must be identified and quantified (Ionas et al., 2015). A variety of extraction techniques can
94 be employed but they are not sufficiently selective and the extracts contain many interfering
95 compounds (Vilaplana et al., 2008; Binici et al., 2013). Subsequently, a wide variety of
96 adsorbents can be utilized to purify the extracts before injection into chromatographic systems
97 (Li et al., 2009). Therefore, analytical methodologies must be adapted according to the
98 materials to be analysed, as no standardized methodology is available for PBDEs (Mingwu et
99 al., 2016).

100 Far less specific, X-ray fluorescence (XRF) can detect elements such as elemental bromine,
101 and this technique has been relatively successful in screening brominated FRs (Gallen et al.,
102 2014; Sharkey et al., 2018). This technique can also have the advantage of linking
103 contamination from brominated FRs to that from other heavy metals (Xu et al., 2015).

104 In this study, a complete analytical process for analysing a mixture of 7 PBDEs and BDE-209
105 was adapted to assess with a unique methodology their concentrations in various materials,
106 such as hard plastics, furniture foams and soft furnishings from furnishing element wastes.
107 Therefore, the objective was to estimate for the first time the proportion of PBDEs, with a
108 particular focus on BDE-209, within various professional seating furnishing waste streams.
109 Furthermore, XRF was evaluated and compared to the tedious and expensive
110 chromatographic analytical tool to evaluate its ability to rapidly predict critical PBDE
111 concentrations in seating element wastes. In addition, an attempt was made to correlate
112 measured PBDE levels to levels of various associated metals, which could increase the
113 potential toxic effects of those materials.

114

115 **2. Materials and methods**

116 **2.1. Sample collection**

117 Two sampling campaigns (November 2018 and March 2019) were conducted to collect
118 representative current nondomestic seating furniture wastes from dedicated recycling sites in
119 France. These furniture wastes, which originated from furniture that was used in public
120 places, represent approximately 80% of office wastes that are addressed to agencies such as
121 VALDELIA (Labège, France), which specializes in recycling furnishings from establishments
122 that service the public. Of these wastes, 70% is office chairs (7922 tons in 2018 in France)
123 and 22% is armchairs (2544 tons in 2018). In France, the professional furnishing waste
124 recovery target was recently increased to 80%, of which 45% must be recycled (2018-2021);
125 therefore, it appeared critical for an eco-agency such as VALDELIA to understand which
126 types of materials could exceed the PBDE concentration limit, especially in seating wastes,
127 which represent the majority of office wastes. Hundreds of professional seating waste items
128 were accumulated in two French centres of treatment and valorisation of wastes in November
129 2018 and March 2019. For these two collection campaigns, a loading bucket (5 m³) was used
130 to extract the seating wastes from the centres of the piles. To obtain a random and
131 representative collection, this process was repeated 5 times for each sampling campaign. A
132 total of 100 office chair or armchair waste items were extracted from the secondary piles.
133 Various materials were separated from these samples: 21 accompanying textiles (or leather or
134 imitation leather), 36 foams (seat upholsteries) and 43 hard plastics (from various parts of the
135 seats, such as wheels, armrests, bearing legs, and back supports). At least 150 g of each
136 material was kept in sealed bags and stored in the dark.

137 The CEDEN consultancy (Bois-Guillaume, France), which specializes in wastes and energy
138 studies, collected other types of seating waste samples and kindly made their general results
139 available (Table S1 in supplementary materials). In our study, the collection campaigns were
140 conducted to obtain representative seating waste flows, mainly with office chairs and
141 armchairs representing the highest tonnage. In contrast, CEDEN collected more specific

142 wastes such as cinema armchairs and mattresses (Table S1), and their results are presented
143 here just to show that other minority seats, produced in the 1990s, might pose problems for
144 recycling.

145

146 2.2. Chemicals and standards

147 Hexane, toluene, methanol, methylene chloride, propan-2-ol, acetone, of HPLC grade, were
148 provided by Fisher Scientific (Illkirch, France). Sodium sulfate, silica gel (0.035-0.070 mm
149 diameter), sulphuric acid (>95%) came from Merck (St Quentin-Fallavier, France). A mixture
150 of 8 PBDEs of primary interest (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154,
151 BDE-183, BDE-209) was furnished by Interchim (Montluçon, France). ¹³C-BDE-99 and ¹³C-
152 BDE-209, used as labelled internal standards (IS) for quantification and ¹³C-BDE-183, used
153 as surrogate standard (SS), were furnished by BCP Instruments (Oullins, France). The
154 certified reference material ERM-EC591 (PBDEs in polypropylene) came from Merck.

155

156 2.3. Sample preparation, extraction and clean-up

157 All materials (plastics, foams, and soft furnishings) were cut into small pieces of
158 approximately 1-2 cm² and ground and sieved (<0.5 mm diameter) using a Polymix system
159 (Kinematica, Germany). Then, the powders (mixed with fine fibres for textiles) were dried
160 (12 h, 35°C) and stored in the dark.

161 Before solvent extraction, the samples were spiked with 10 µL ¹³C-BDE-183 (50 mg L⁻¹) for
162 evaluating sample losses. Some samples (2 g) were extracted with an automated hot-Soxhlet
163 (Büchi B-811, Switzerland) using 150 mL solvent (toluene or methylene chloride) for 6h30.
164 Microwave-assisted extraction (MAE) (ETHOS X, Milestone, USA) was used to extract a 1 g
165 sample using 30 mL hexane/propan-2-ol 50/50 (v/v) under stirring, with a 10 min rise and 60
166 min at 130°C (power = 800 W).

167 The extracts were pressed so that extraction solvents (and hexane as a rinsing solvent) could
168 pass through a cellulose filter. Then, the solution was centrifuged at 5000 rpm for 10 min. The
169 supernatant was filtered through a 0.45- μm PTFE filter. Octanol (50 μL) was added as a
170 solvent keeper, and the filtrate was evaporated to dryness (30 mBar) with a Mivac system
171 (Genevac, UK) and reconstituted in 425 μL hexane and 25 μL acetone.

172 For purification, silica gel was prepared: It was rinsed with methylene chloride, activated for
173 1h at 180°C and after cooling, sulphuric acid was added (30% w/w). A glass column (200 \times 15
174 mm) was filled with 1 g dry sodium sulphate, 2 g acidified silica gel and 1 g sodium sulphate
175 and rinsed with 10 mL hexane. Then, 500 μL of the sample extract was spiked at the top of
176 the glass column. When the extracts were too viscous, evaporation tubes were rinsed twice
177 again with a mixture of 450 μL hexane and 25 μL acetone, which was spiked at the top of the
178 column. Thereafter, the deposited sample was eluted with 20 mL hexane. The eluate was
179 filtered through a 0.2- μm PTFE filter, and after the addition of 50 μL octanol, it was
180 evaporated to dryness and reconstituted with 420 μL toluene, 10 μL ^{13}C -BDE-99 (50 mg L^{-1})
181 and 20 μL ^{13}C -BDE-209 (25 mg L^{-1}).

182

183 2.4. Instrumental analysis

184 A gas chromatograph (7890B series, Agilent, USA) that was coupled with a mass
185 spectrometer (7000C) was used for the analyses. Samples of 1 μL were injected in splitless
186 mode (285°C) in an ultra-inert liner and with He as a carrier gas (1.5 mL min^{-1}). Separation
187 was performed using a 15 m \times 0.25 mm DB-5MS capillary column (0.1- μm film thickness)
188 from Agilent. The oven temperature was programmed at 110°C for 1 min, increased to 250°C
189 (40°C min^{-1}), to 290°C (15°C min^{-1}) and to 310°C (20°C min^{-1}) for 7 min. The transfer line
190 was set to 310°C. The MS detector was operated at 70 eV in electronic impact (EI) mode,
191 with an ion source at 300°C. Quantification was based on selected ion monitoring to realize

192 higher sensitivity (Table S2). It was performed by internal calibration using seven-point
193 calibration curves and ^{13}C -BDE-99 as an IS for all the target PBDEs, except BDE-209, for
194 which ^{13}C -BDE-209 was used. The detection was linear over the 0.05-3 mg L⁻¹ concentration
195 range ($r^2 > 0.990$) for all PBDEs, with the exception of BDE-209 (0.5-30 mg L⁻¹). The GC-MS
196 instrumental limits of detection (LODs) and quantification (LOQs) were estimated based on
197 signal/noise ratios (S/N) of 3/1 and 10/1, respectively. From BDE-28 to BDE-183, LODs and
198 LOQs were respectively in the range 0.003-0.012 mg L⁻¹ and 0.011-0.039 mg L⁻¹. For BDE-
199 209, instrumental LOD and LOQ were respectively 0.080 and 0.262 mg L⁻¹ (Table S2).

200 A fluorescence-X spectrometer (ARL Quant'X, ThermoFisher Scientific, France) was used to
201 analyse small pieces of materials (approximately 3 cm²) at the Department of Chemistry,
202 University of le Mans, France. Plastics were prepared with a slight abrasion of the solid
203 surface. Then, dust was removed from the surface of each sample with a Kimwipe.
204 Measurements were conducted under vacuum for 60 s. The LOD was 10 mg kg⁻¹ for Br.

205

206 2.5 Statistical analyses

207 Statistical analyses were conducted using R2020 software (Microsoft Inc. USA). ANOVA
208 tests were performed to compare two means through the variances of two independent
209 populations using Fisher's distribution and one p-value to support or reject the null
210 hypothesis. In the case in which the data followed a non-normal distribution, nonparametric
211 Kruskal-Wallis tests were performed, and population comparisons were conducted with the
212 Dunn test. Microsoft XLSTAT 2013 software was used for principal component analysis
213 (PCA).

214

215 3. Results and discussion

216 3.1. Adaptation of a single analytical procedure for hard plastics, furniture foams and soft
217 furnishings.

218 As no standardized methodology is available for PBDE analysis, different analytical protocols
219 have been described in the literature that differ according to the materials to be analysed. In
220 this study, a single complete analytical process was adapted for the quantitative analysis of
221 PBDEs in both hard plastics, furniture foams and soft furnishings from seating wastes, in
222 consideration of the substantial disparity of their unknown components.

223 The GC-MS procedure was performed in accordance with established (but not standardized)
224 procedures. But here, increasing the temperature of the MS source from 230 to 300°C resulted
225 in doubling of the peak area for BDE-209. The LOD for BDE-209 (Table S2) was consistent
226 with the LOD that was reported by Li et al. (2009), who also used GC-MS in EI mode.

227 The extraction step had to be adapted due to the variety of the analysed materials. Two
228 extracting apparatuses were tested. Hot-Soxhlet, which is an improved system compared to
229 the traditional Soxhlet, enables heating to be applied to the extraction cavity. Thus, this
230 technique can markedly reduce the Soxhlet extraction duration (less than 8h instead of 18h)
231 (Oukebdane et al. 2010; Duan et al., 2016). In this study, only toluene and methylene chloride
232 were tested, as Li et al. (2009) showed that hexane or mixtures of hexane and acetone were
233 not suitable for the extraction of BDE-209 from various plastic materials. It appeared that
234 toluene was not suitable because in some plastic materials and accompanying textiles, it
235 dissolved parts of the materials after only 6h30 hot extraction and generated too many
236 colloidal particles, thereby dramatically decreasing the SS recovery. The use of methylene
237 chloride generated less colloidal particles but did not enabled us to obtain satisfactory SS
238 recoveries. Then, MAE was tested with solvent mixtures such as hexane/propan-2-ol 50/50
239 (v/v) and toluene/methanol 75/25 (v/v) (Ranz et al., 2008; Vilaplana et al., 2009). A polar
240 solvent was necessary for the *in situ* instantaneous transformation of microwaves into heat.

241 For comparison, the same hard plastic from a desk chair was extracted with 20 mL of these
242 two solvent mixtures for 30 min at 130°C under stirring. The recovery of SS was $59.4\pm 4.5\%$
243 ($n=3$) using toluene/methanol and $65.4\pm 3.9\%$ ($n=3$) using hexane/propan-2-ol. Increasing the
244 volume of hexane/propan-2-ol to 30 mL enabled us to obtain an SS recovery of $76.1\pm 2.7\%$
245 ($n=3$).

246 After extraction, filtration through cellulose filters, centrifugation, filtration through PTFE
247 filters and evaporation (Section 2.3), the samples still contained more or less viscous colloidal
248 particles, which could not be injected for GC-MS. The presence of these problematic
249 interfering compounds was independent of the type of material. Thus, the extracted solutions
250 still required clean-up. Columns of acidic silica or activated silica between two layers of
251 sodium sulphate (to remove water) were tested. First, 1 g of each silica gel was tested.
252 However, as discussed by Li et al. (2009), activated silica columns led to “dirty” GC-MS
253 analysis, especially at the beginning of the analysis. Via the use of 1g of acidified silica gel
254 columns and 10, 15, 20 or 30 mL hexane as the eluent, 72.4, 73.6, 85.5 and 85.6%,
255 respectively, of the SS was efficiently recovered when standard PBDEs and SS were spiked at
256 the top of the column. When real samples were tested, 1 g acidified silica was not sufficient
257 for purifying the extracts. Hence, 2 g acidic silica was tested. In this case, the SS recovery that
258 was obtained with 30 mL hexane elution ($80.1\pm 5.8\%$, $n=3$) did not differ significantly from
259 that obtained with 20 mL elution ($76.1\pm 2.7\%$, $n=3$) (ANOVA test, $p\text{-value}>0.05$); thus, 20
260 mL elution with hexane was utilized.

261 It is important to note that after the extraction and evaporation steps and before column clean-
262 up (Section 2.3), the extracts were reconstituted in hexane that contained 25 μL acetone, and
263 the tube walls could also be rinsed twice with hexane/acetone mixtures, which is unusual in
264 processes that are developed for analysing PBDEs in plastics or dusts, for example. In this
265 study, the characteristics of the polymers and additives in the plastics, foams and textiles were

266 highly disparate and unknown. Various samples could contain large amounts of colloidal
267 particles after extraction, thereby casting doubt on the quantification. The addition of acetone
268 for reconstituting the evaporated sample and rinsing the tube walls appeared essential for
269 dissolving PBDEs from colloids and obtaining higher recoveries.

270 The overall analytical process was evaluated via repeated analyses of a certified reference
271 material (ERM-EC591) that contains PBDEs in a polypropylene material. As presented in
272 Table 1, the measured values were in the same range as the values of the certificate.
273 Moreover, the extraction recoveries were satisfactory, namely, 84-104.5%, and were
274 consistent with recoveries that were obtained by Abdallah et al. (2017). To ensure that the
275 results could not be affected by the variability of the extracted materials, four additional
276 experiments were conducted on the same day to determine the intraday repeatability for two
277 types of materials. Moreover, four experiments were conducted on different days to evaluate
278 the reproducibility (intermediate precision) (Table 1). The repeatability and reproducibility
279 were satisfactory, with values of <19% for the target PBDEs and for BDE-209. Table 1
280 presents the LODs (S/N=3) and LOQs (S/N=10) that were obtained after the overall
281 procedure of extraction, purification and GC-MS analysis of a hard plastic. They were lower
282 than those that were obtained by Binici et al. (2013) but exceeded those that were obtained by
283 Abdallah et al. (2017), particularly for BDE-209, which is more strongly affected by thermal
284 degradation. However, they were considered satisfactory since they enabled the quantification
285 of all the target PBDEs at levels of substantially less than 1000 mg kg⁻¹.

286 Table S3 in the supplementary materials presents the raw results of the 200 analyses (each
287 sample was analysed in duplicate) of the seating furniture wastes. Considering the mean
288 values for the 100 samples, the relative standard deviations (RSDs) for the BDE-209 analyses
289 were <11%, with the exception of samples in which BDE-209 was under the LOQ (Table S4).

290

291 3.2. PBDEs in seating furnishing wastes

292 According to the analyses of the 100 samples, none contained a single BDE or the Σ_8 BDEs
293 above the critical limit of 1000 mg kg⁻¹ (Table S4). No soft furnishings contained BDE-209
294 above the LOQ (1 mg kg⁻¹). Only 2 foam samples and 16 hard plastics contained BDE-209
295 above 1 mg kg⁻¹, which represented 5.6% of the foams and 37.2% of the plastics. Only hard
296 plastics contained BDE-209 above 10 mg kg⁻¹ (11 samples above 10 mg kg⁻¹ and 4 samples
297 above 100 mg kg⁻¹, with the highest concentration being 311.9 mg kg⁻¹). The levels of PBDEs
298 that were detected in plastics of seating furnishing wastes were substantially lower than those
299 that could be measured in plastics from e-wastes, where many samples could exceed the
300 maximum permissible contents (1000-29,000 mg kg⁻¹ for Octa-BDE, 860-237,000 mg kg⁻¹ for
301 Deca-BDE) (Sindikú et al., 2015). Even plastics from current consumer products (mainly
302 plastics that encase electronic components) could contain excessive amounts of Octa-BDE or
303 Deca-BDE (1000-88,600 mg kg⁻¹), which could further be detected in plastic wastes and
304 recycling (Gallen et al., 2014). The nondetectability or very low levels of PBDEs in foams or
305 textiles that were used in professional seating furnishings were in accordance with previous
306 studies on domestic soft furnishings and foams, where single BDEs were in the same low
307 concentration ranges as in this study and their levels did not exceed 42 mg kg⁻¹ (Stubbings et
308 al., 2016). However, according to Drage et al. (2018), the level of BDE-209 could reach 7800
309 mg kg⁻¹ in various furniture foam fillings.

310 As presented in Table 2, most of the median amount values were at the zero level that
311 corresponds to non-detectable values; thus, PBDEs could not be detected in more than 50% of
312 the samples. The mean amounts of the tri- to hexa-BDEs were very low in all the samples
313 (0.016-0.470 mg kg⁻¹) and did not differ significantly from one another (Kruskal-Wallis test,
314 p-values>0.05). However, the mean amounts of the BDE-209 and BDE-183 were

315 significantly higher in plastic materials than in textiles and foams (Kruskal-Wallis test, p-
316 values<0.05).

317 In textile and foam materials, only the mean amounts of BDE-47 and BDE-99 were similar
318 (Kruskal-Wallis test, p-values>0.05) but significantly different from those of the other BDEs
319 (Kruskal-Wallis test, p-values<0.05). In contrast, the mean amounts of BDE-209 in plastic
320 materials were significantly higher than those of BDE-28, BDE-100; BDE-99, BDE-153 and
321 BDE-154 (Kruskal-Wallis test, p-values<0.05), and the mean amounts of BDE-47 and BDE-
322 99 were similar to those in the other materials (Kruskal-Wallis test, p-values>0.05).

323 Higher amounts of the 8 target PBDEs could be detected in the hard plastics, which contained
324 91.5% of the target PBDE amounts (Figure 1A). Most flame retardants are typically added at
325 a 5-30% w/w level to efficiently inhibit combustion and burning of the materials (Gallen et
326 al., 2014; Ionas et al., 2015; Drage et al., 2018); thus, the levels that were detected in our
327 study were too low to conclude that the various materials were directly treated with PBDEs.
328 Even BDE-209 was more likely derived from recycled plastic materials, where it
329 progressively weakened.

330 Figure 1B shows that the BDE congeners were not uniformly distributed in the various
331 materials. The most-brominated BDEs, namely, BDE-209 and BDE-183, were detected
332 mainly (in various amounts) in hard plastics; hexa-brominated BDEs (BDE-153 and BDE-
333 154) were partitioned among hard plastics and foams; four- and penta-brominated BDEs
334 (BDE-47, BDE-99, and BDE-100) were detected in foams and textiles; and the three-
335 brominated BDE-28 was detected mostly in hard plastics. BDE-47 and BDE-99 represented,
336 on average, 58.0 and 26.7%, respectively, of the PBDE content in textiles and 31.0 and
337 46.0%, respectively, of PBDE content in foams, whereas BDE-209 represented 95.1% of the
338 PBDE content in hard plastics.

339 The distribution of PBDEs in current professional seating furniture wastes is in accordance
340 with historical or recent uses of commercial PBDE formulations. Indeed, commercial Penta-
341 BDE, which is composed mostly of BDE-47 and BDE-99, was mainly used in Europe in PUF
342 for furniture and automotive applications. It is not surprising to detect these two major
343 congeners in office chair and armchair foams. However, their very low amounts (mean values
344 of 0.795 and 1.2 mg kg⁻¹ for BDE-47 and BDE-99, respectively (Table 2)) may indicate that
345 the PBDEs have migrated out of the products over their lifecycles because the amounts do not
346 correspond to the percent by weight levels that are required to impart flame retardancy.
347 Alternatively, their very low amounts may indicate that they were not in the initial
348 composition of the foams. It seems that large amounts of Penta-BDE could be found in foam
349 furniture items mainly prior to 2005 (Shaw et al., 2014). So here BDE-47 and BDE-99
350 originated from other sources, such as passive sorption from the indoor environment
351 (Stubbings et al., 2016). Indeed, foams such as PUF are used as active or passive samplers for
352 PBDEs in air monitoring (Aliyeva et al., 2018).

353 In textiles, commercial Octa-BDE has never been used, but Deca-BDE could be used in the
354 past (Shaw et al., 2014; Ionas et al. 2015). Here, BDE-209 could be found only at trace levels
355 (Table 2) and was apparently not used in the analysed textiles, probably replaced by other
356 brominated FRs (Shaw et al., 2014). As for BDE-209, BDE-153 and BDE-183 were detected
357 at trace levels in rare samples (5/21 textile samples), and it was likely due to a migration of
358 these congeners from the plastics of the chairs or to passive sorption from the indoor
359 environment. BDE-47 and BDE-99, which could be detected in more textile samples, had
360 mean values of only 0.239 and 0.110 mg kg⁻¹, respectively (Table 2). Therefore, these very
361 low amounts (of the same order of magnitude as in foams) may indicate that Penta-BDE
362 formulation was not in the initial composition of the textiles and originated from other sources
363 (migration from foams or passive sorption from the environment).

364 In plastics, commercial Octa-BDE, which is composed mostly of BDE-197, BDE-183 and
365 BDE-153, was employed in housings of EEE made of acrylonitrile butadiene styrene (ABS)
366 polymer. However, ABS was also used in plastics for office chairs. Commercial Deca-BDE,
367 which is composed mainly of BDE-209, could still be recently employed in high impact
368 polystyrene (HIPS) in EEE and also in ABS. Therefore, it is not surprising to detect BDE-
369 209, BDE-183 and BDE-153 in the plastics of office chairs. In the 20 samples in which BDE-
370 209 could be detected, the 7 other PBDEs represented only 1.5% of the total amount, and only
371 one hard plastic sample contained significantly more (73.8%) of the other BDEs (particularly
372 BDE-183) than BDE-209. Therefore, the levels of BDE-183 and BDE-153 that were detected
373 in hard plastics, which perhaps originated from commercial Octa-BDE application, were
374 marginal compared to that of BDE-209, which has only recently been restricted.

375 The presence of BDE-28 in plastics represented only 0.15% on average of the BDE-209
376 content. Polybromodiphenyl ethers can be subject to debromination, namely, to the
377 replacement of bromine on the aromatic ring with hydrogen (Wei et al., 2013). Therefore,
378 higher bromodiphenyl ether congeners may be converted to lower congeners. The higher
379 BDE-209 congener is more likely to be the precursor of tetra- to nona-BDEs, but BDE-28
380 more likely originates from the debromination of BDE-183, BDE-154, BDE-153, BDE-99,
381 BDE-100 or BDE-47 (Wei et al., 2013).

382 Finally, only two foam samples contained BDE-209 at a relatively high level (2 and 4 mg kg⁻¹)
383 ¹). As there is no known treatment of PUF by Deca-BDE, this suggests migration of BDE-209
384 from plastics that underlay foam via direct contact (Drage et al., 2018).

385 PCAs were conducted to attempt to correlate the PBDE amounts in the various materials.
386 Table S5 presents the correlation matrices (with the Pearson correlation coefficients (r)) from
387 four PCAs for all the samples, for the plastics only, for the foams only and for the textiles
388 only. Components F1 and F2 of the PCAs accounted for 75.0%, 74.9%, 90.7% and 64.3%,

389 respectively, of the total variance. As described previously, BDE-47 and BDE-99 were
390 strongly correlated with each other ($r=0.990$) when all the materials were considered, and they
391 were also strongly correlated with BDE-100 and BDE-154 ($0.926 < r < 0.989$) (Table S5A).
392 These BDEs likely originated from the same source, which is probably the previous
393 application of commercial Penta-BDE. BDE-153 was more strongly correlated with BDE-183
394 ($r=0.870$) and likely originated from the previous application of commercial Octa-BDE.
395 However, BDE-209 was not correlated with any of the other target PBDEs for any of the
396 analysed materials (Tables S4B, C, and D): When BDE-209 was present in the materials, its
397 source differed from the sources of the other PBDEs. Therefore, it is likely that the other low-
398 brominated PBDEs did not originate from the decomposition of BDE-209. BDE-28 was never
399 correlated with BDE-209, even in plastics ($r=0.078$), where it was more prevalent (Table
400 S5B). Therefore, its higher prevalence in plastic materials (even in very low amounts)
401 compared to textiles or foams could not be explained by successive BDE-209 debrominations.
402 In contrast, BDE-28 was correlated ($0.962 < r < 0.999$) with the other main PBDEs (especially
403 BDE47, BDE-99 and BDE-154) in foams and textiles, and it is more probable that it
404 originated from the same source.

405 The presence of BDE-209 at high levels ($100-312 \text{ mg kg}^{-1}$) was relevant mainly for plastic
406 materials from office seating and armchair wastes, which constitute the main flow of furniture
407 wastes from establishments that service the public in France. Nevertheless, according to the
408 results from the CEDEN office (Table S1) regarding other less abundant furniture wastes,
409 such as mattresses and performance hall armchairs, higher amounts of BDE-209 could also be
410 detected in foams or textiles, especially for cinema armchairs that were manufactured before
411 1998, where BDE-209 could be measured at 3550 mg kg^{-1} .

412

413 3.3. Correlation with X-ray fluorescence of Bromine and other metals

414 XRF spectroscopy was conducted on the various materials of the seating furniture wastes for
415 three main reasons: (i) to evaluate its ability to rapidly predict high critical PBDE
416 concentrations in various materials from seating wastes via Br to rapidly eliminate them from
417 recycling; (ii) if not possible, to evaluate its ability to screen only samples that necessitate a
418 confirmation of the presence of PBDEs with GC-MS. Due to the capability of XRF of
419 detecting high levels of Br, this screening could enable a substantial reduction of analytical
420 costs; and (iii) to correlate the presence of Br (and possibly PBDEs) with the presence of
421 other associated metals, which could increase the potential toxic effect of materials that are
422 intended for recycling.

423 Thirty-nine elements were analysed with XRF in the 100 samples. Table S6 presents the
424 amounts of 28 of them. Bromine was analysed to correlate its amount to the amounts of
425 PBDEs in the various materials from seating wastes. Indeed, Br can represent 58.9 to 83.3%
426 of the total molar weight of the target PBDEs (Table S2). However, although XRF enables the
427 rapid, simple and nondestructive detection of bromine, it is nonspecific and subject to
428 substantial variations due to the nonhomogeneous distribution of elements within the
429 materials.

430 Figure 2A shows that there was no correlation ($r^2=0.004$) between Br levels and the total level
431 of the 8 target PBDEs when considering all the analysed materials. There was no correlation
432 when materials were analysed by family (plastics, foams, textiles) and so no correlation
433 between Br and BDE-209 levels in plastics ($r^2=0.002$) (Figure 2B). However, as mentioned by
434 Sharkey et al. (2018), XRF had a high bromine LOD (10 mg kg^{-1}), which substantially
435 exceeds the LODs that were determined for GC-MS analyses of PBDEs. Thus, XRF could not
436 detect low amounts of PBDEs and indicated 0 when PBDEs were present at trace levels.
437 When only samples with $\Sigma_8\text{PBDEs}>10 \text{ mg kg}^{-1}$ were considered (12 samples/100), the
438 correlation between the Br amount and the PBDE amount was more significant but not strong

439 ($r^2=0.450$) (Figure 2C). This essentially concerned samples in which Br amount was >150 mg
440 kg^{-1} .

441 Therefore, XRF alone (via Br analysis) is not sufficient for evaluating the amount of PBDEs
442 (or BDE-209) that is possibly present in a material. Indeed, XRF measurements can be
443 artificially altered due to the nonhomogeneous distribution of Br in a solid material, especially
444 when only a small piece is analysed. Hence, one plastic sample showed a significant PBDE
445 amount (33 mg kg^{-1}), and no bromine was detected by XRF. In contrast, 14 samples had
446 substantially larger amounts of Br than PBDEs (1000 times). In this study, only a small
447 number of BDEs were analysed via GC-MS among 209 possible congeners; octa-BDEs from
448 the former commercial Octa-BDE formulation and nona-BDEs, which are possible
449 degradation products of BDE-209, were not analysed. Moreover, other brominated FRs could
450 be used in seating furniture materials, such as hexabromocyclododecane (HBCDD) (which is
451 also limited by EU legislation), decabromodiphenyl ethane and tetrabromobisphenol A
452 (TBBPA) (Stubbings et al., 2016; Abdallah et al., 2017; Pivnenko et al., 2017). HBCDD is
453 frequently used in polystyrene foams, whereas TBBPA is used in plastics such as ABS
454 (Gallen et al., 2014). Therefore, XRF measured all the brominated compounds, without
455 distinguishing between PBDEs and the other brominated FRs and their degradation products.
456 Other groups of flame retardants can be used to treat products, such as chlorinated
457 organophosphate flame retardants (OPFRs). PCA was conducted to attempt to correlate the
458 presence of P and Cl to the presence of PBDEs in the seating waste materials. No correlation
459 was identified in plastics or textiles. In contrast, the presence of P and Cl was positively
460 correlated in foams with the presence of the 7 other PBDEs (excluding BDE-209), with $r=$
461 0.678 and 0.462 , respectively. Therefore, it is likely that in foams, commercial Penta-BDE
462 was associated with OPFRs. According to Stubbings et al. (2016), OPFRs such as tris(2-
463 chloroisopropyl)phosphate could be quantitatively measured in PUF.

464 Finally, other compounds that contain metals could serve as FRs: ABS polymers and PUF
465 could contain magnesium hydroxide, sodium antimonate, zinc borate, aluminium trihydrate or
466 barium tetraborate. PUF could also contain neoalkoxytri(dioctylphosphate)titanate or
467 molybdcic acid. Ferric oxide could also be used as FR. Therefore, Al, Ba, Mg, Ti, Sb, Zn, Fe
468 and Mo were screened in the seating wastes. Figure 3 presents PCA results regarding the
469 correlation of their amounts to the amount of PBDEs. In plastics, BDE-209 was weakly
470 correlated with Fe and Ba ($r=0.500$), and Br was more strongly correlated with Sb ($r=0.679$)
471 (Figure 3A and Table S7 for Pearson coefficients). Antimony oxide could be used as a
472 synergist, together with PBDEs, to enhance the flame retardant properties. However, for
473 seating wastes, it appears that Sb was correlated with Br but not to BDE-209. Xu et al. (2015)
474 also found that BDE-209 was not directly correlated with Sb in e-wastes. Additionally, Ti and
475 Fe were correlated with each other ($r=0.605$) in plastics.

476 In foams, BDE-209 was strongly correlated with Mg ($r=0.894$), but no correlation was
477 identified for the other PBDEs (Figure 3B and Table S7). Additionally, Al/Fe and Ti/Ba were
478 correlated together ($r=0.807$ and $r=0.997$, respectively). Finally, in textiles, the 7 PBDEs
479 (excluding BDE-209) were strongly correlated with Mg ($r=0.996$), thereby suggesting that
480 magnesium hydroxide could have been associated with Penta-BDE as FR. Additionally,
481 Al/Ti, Al/Fe and Ti/Fe were correlated together ($r=0.878$, $r=0.914$ and $r=0.921$, respectively)
482 (Figure 3C and Table S7).

483 Finally, various metals and metalloids (Cr, Cu, Zn, Pb, Cd, Ni, Cu, and As), which are
484 typically investigated as toxic metals in the environment, were examined to attempt to
485 correlate their amounts in seating material wastes to those of Br, BDE-209 and the 7 other
486 PBDEs. Cd and Pb can be used in plastics and foams as stabilizers, and Co, Cd, Cr, Pb, Cu,
487 and Zn can be present in pigments. Figure 3D shows that considering all the materials, Br was
488 strongly correlated with As ($r=0.971$), and Co with Ni ($r=0.707$) (Table S7). This strong

489 correlation between Co and Ni was also identified in dust from e-waste workshops (Xu et al.,
490 2015). Considering only plastics, Br was strongly correlated with As ($r=0.989$), BDE-209
491 appeared to be slightly correlated with Co, Cr and Pb ($r=0.527$, 0.413 and 0.310 ,
492 respectively), and Br/Cd and As/Cd were also correlated together ($r= 0.545$ and 0.547 ,
493 respectively). In foams, Br was totally correlated with As ($r=1.000$), and only a weak
494 correlation between the 7 PBDEs and Zn was identified ($r=0.352$). However, many metals
495 were strongly correlated: Cr/Co, Cr/Ni, Cr/Cu, Co/Ni, Co/Cu and Ni/Cu ($0.866 < r < 0.996$). In
496 textiles, Br was strongly correlated with As ($r=0.983$), and no correlations between PBDEs
497 and any metals were identified. However, Cu/Zn and Co/Pb were strongly correlated together
498 ($r=0.842$ and 0.975 , respectively).

499 Based on these results, it seems that the presence of Br was strongly associated with the
500 presence of As in all the materials of the seating wastes. Arsenic could be used as a biocide in
501 PVC plastics or foams in the 0.001-1% (w/w) range, but its association with Br is unclear.
502 The levels of As in the urine of workers from e-waste plastic recycling activities were found
503 to significantly exceed those in the urine of workers from reference sites; hence, recycling
504 workers are also exposed to this element (Hahladakis et al. 2018). Finally, no strong
505 correlation between PBDEs and Cd or Pb was identified, in contrast to that observed in e-
506 waste dust (Xu et al., 2015).

507

508 **4. Conclusions**

509 In a legislative context, the total amounts of PBDEs that were detected in 100 pieces of
510 materials from professional seating furniture wastes did not exceed the EU proposed threshold
511 of 1000 mg kg^{-1} . One exception was reported from the parallel collection of the CEDEN
512 office and concerned cinema armchairs that were manufactured before 1998. The French
513 market underwent a disruption in approximately 2005 with the interdiction of the use of

514 Penta- and Octa-BDE formulations in new materials, and professional seating furniture that
515 has entered the French waste stream seems to contain only trace levels of PBDEs in materials
516 that were treated with the previous BDE formulations (which is referred to as “legacy”
517 contamination). The presence of BDE-209 was identified at significant higher levels
518 (although $<1000 \text{ mg kg}^{-1}$), which demonstrates that circular material flows may be
519 contaminated for extended periods. BDE-209 levels will need to be tracked in seating
520 furniture wastes in the future, as the EU will likely decrease its threshold level to 500 mg kg^{-1}
521 by July 16, 2021 in wastes to be recycled.

522 It seems that BDE-209 contamination may occur mainly through the use of recycled plastics
523 in office seating furniture and through migration to other materials by contact. According to
524 the results of the CEDEN Office, professional seating furniture that was manufactured before
525 2005 could contain BDE-209 levels that exceed the current limit. Therefore, it is possible that
526 no treatment (removal) is necessary for the wastes from professional chairs and armchairs that
527 were produced after 2005, but this should be confirmed via additional analyses. As a
528 precaution, monitoring of the presence of PBDEs (particularly BDE-209) in more furnishing
529 wastes (especially plastic wastes that are routed to recycling) that were produced before and
530 after 2005 and that originate from other countries seems necessary.

531 In light of the rapidity and low cost of measurement using XRF, this technique could be used
532 as a nondestructive method to rapidly screen samples and separate suspected samples with
533 large amounts of Br ($>150 \text{ mg kg}^{-1}$). However, GC-MS must be conducted to confirm the
534 presence of BDE-209 if this FR is the target compound to measure in seating waste materials.
535 Indeed, no direct correlation was identified between Br and BDE-209 levels since XRF was
536 not reliable for quantitative measurements and was not specific; other brominated FRs or
537 degradation products may be responsible for high Br responses. Therefore, the use of XRF as
538 a pre-screening technique, which is easy to implement *in situ*, could decrease the analytical

539 costs that are related to the quantification of BDE-209 or other regulated brominated FRs,
540 such as HBCDD. Finally, the XRF results demonstrated that the presence of Br was strongly
541 associated with the presence of As in all the materials of the professional seating wastes, for
542 which the reason has yet to be determined, and that the presence of PBDEs was not clearly
543 associated with the presence of other metals.

544

545 **Supplementary materials**

546 Seven tables (Tables S1, S2, S3, S4, S5, S6 and S7) are given in the supplementary materials
547 of this paper.

548

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704

705 Table 1: Overall procedural limits of detection and quantification (S/N=3 and 10, respectively); Certified and measured values from a certified
 706 reference material (ERM-EC591); Repeatability of the overall analytical process established from a foam and a hard plastic sample,
 707 reproducibility established from a hard plastic sample.

PBDEs	LOD (mg kg ⁻¹)	LOQ (mg kg ⁻¹)	ERM-EC591 (certificate)	ERM-EC591 ^a Mean ± SD (mg kg ⁻¹) (RSD %) (n=4)	Repeatability (foam) Mean ± SD (mg kg ⁻¹) (RSD %) (n=4)	Repeatability (hard plastic) Mean ± SD (mg kg ⁻¹) (RSD %) (n=4)	Reproducibility (hard plastic) Mean ± SD (mg kg ⁻¹) (RSD %) (n=4)
BDE-28	0.006	0.020	2.5±0.4	2.1±0.3 (14.3%)	n.d. ^b	n.d. ^b	n.d. ^b
BDE-47	0.003	0.010	245±23	239±25 (10.5%)	0.016±0.001 (3.9%)	0.014±0.001 (6.6%)	0.014±0.001 (5.9%)
BDE-100	0.002	0.006	66±7	61±9 (14.8%)	n.d. ^b	0.020±0.003 (13.6%)	0.018±0.003 (15.3%)
BDE-99	0.002	0.008	320±40	312±52 (16.7%)	0.008±0.001 (5.7%)	0.067±0.011 (16.5%)	0.054±0.010 (18.6%)
BDE-153	0.002	0.005	44±6	46±7 (15.2%)	n.d. ^b	0.906±0.082 (9.1%)	0.909±0.054 (6.0%)
BDE-154	0.001	0.005	26±4	27±4 (14.8%)	n.d. ^b	0.254±0.040 (15.6%)	0.227±0.041 (17.9%)
BDE-183	0.004	0.013	87±8	88±8 (9.1%)	n.d. ^b	3.717±0.310 (8.3%)	3.923±0.331 (8.4%)
BDE-209	0.314	1.047	780±90	766±42 (5.5%)	3.039±0.264 (8.7%)	8.964±0.496 (5.5%)	8.806±0.415 (4.7%)

708 (a) Extracts diluted by 100 before injection into GC-MS

709 (b) n.d. : not detected

710

711 Table 2: Mean and median (with min and max) amounts (mg kg⁻¹) of each PBDE in all the
 712 100 analysed samples and in each type of material (textiles, foams, hard plastics).

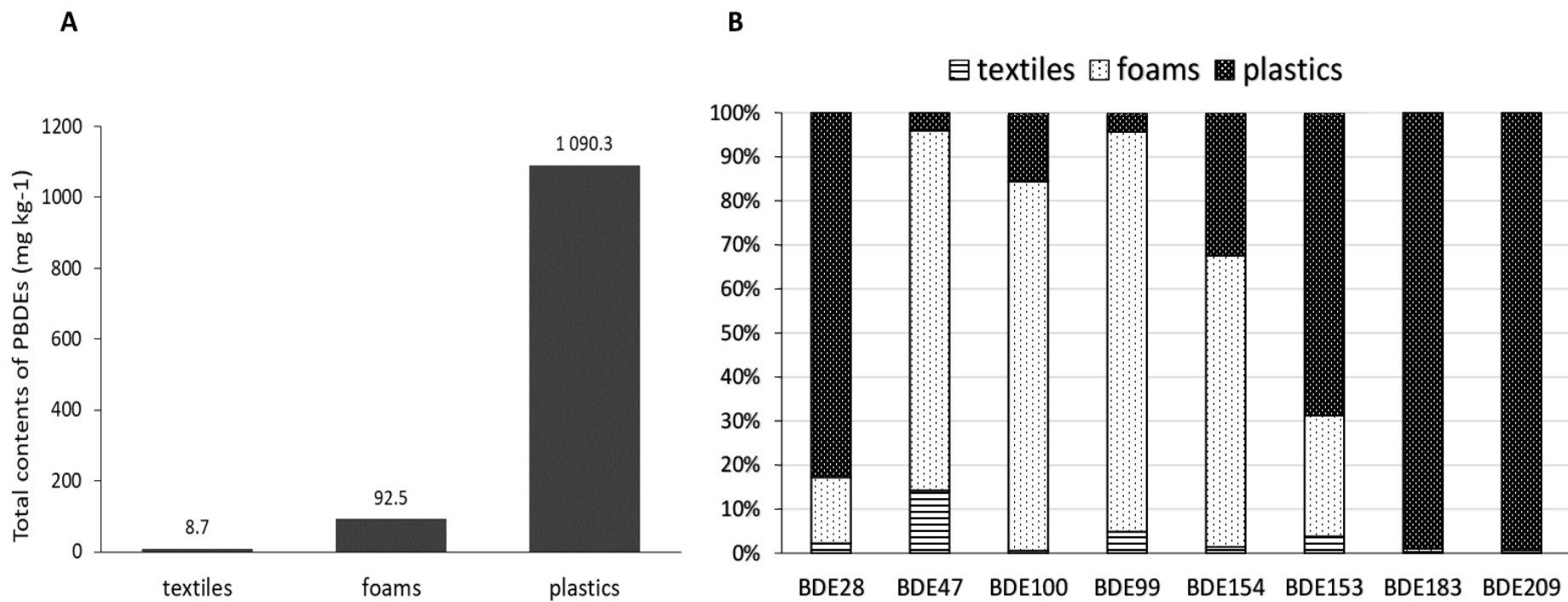
713

		BDE- 28	BDE- 47	BDE- 100	BDE- 99	BDE- 154	BDE- 153	BDE- 183	BDE- 209
All	<i>mean</i>	0.017	0.351	0.096	0.470	0.045	0.136	0.371	10.4
materials	<i>median</i>	<LOD	0.014	<LOD	0.014	<LOD	<LOD	<LOD	<LOD
(n=100)	<i>min*</i>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<i>max</i>	0.870	23.5	6.7	35.4	2.4	5.8	30.4	311.9
Textiles	<i>mean</i>	0.002	0.239	0.003	0.110	0.003	0.025	0.005	0.027
(n=21)	<i>median</i>	<LOD	0.009	<LOD	0.010	<LOD	<LOD	<LOD	<LOD
	<i>min*</i>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<i>max</i>	0.036	4.6	0.032	1.8	0.049	0.381	0.087	0.562
Foams	<i>mean</i>	0.007	0.795	0.224	1.2	0.082	0.104	0.008	0.167
(n=36)	<i>median</i>	<LOD	0.013	<LOD	0.008	<LOD	<LOD	<LOD	<LOD
	<i>min*</i>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<i>max</i>	0.135	23.5	6.7	35.4	2.4	3.0	0.158	4.0
Plastics	<i>mean</i>	0.031	0.033	0.035	0.047	0.034	0.217	0.854	24.1
(n=43)	<i>median</i>	<LOD	0.015	<LOD	0.017	<LOD	<LOD	<LOD	<LOD
	<i>min*</i>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<i>max</i>	0.870	0.655	1.1	0.818	0.853	5.8	30.4	311.9

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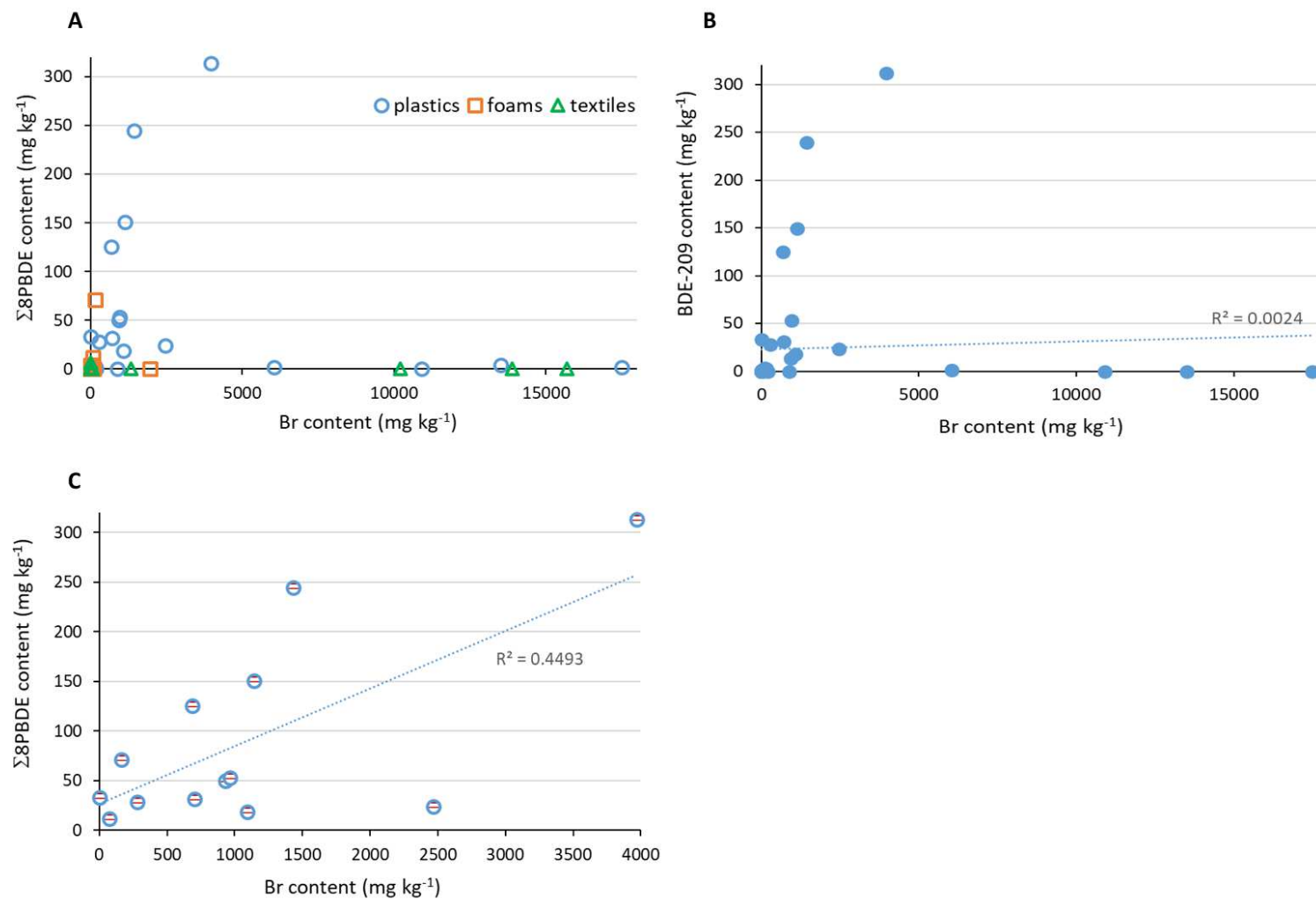
716 Figure 1: A: Cumulative distribution of the total PBDE amount (Σ_8 BDEs in mg kg^{-1}) in the various materials and B: BDE congeners relative
 717 distribution in amount (%) in the various materials, from the 100 sub-samples from seating wastes.



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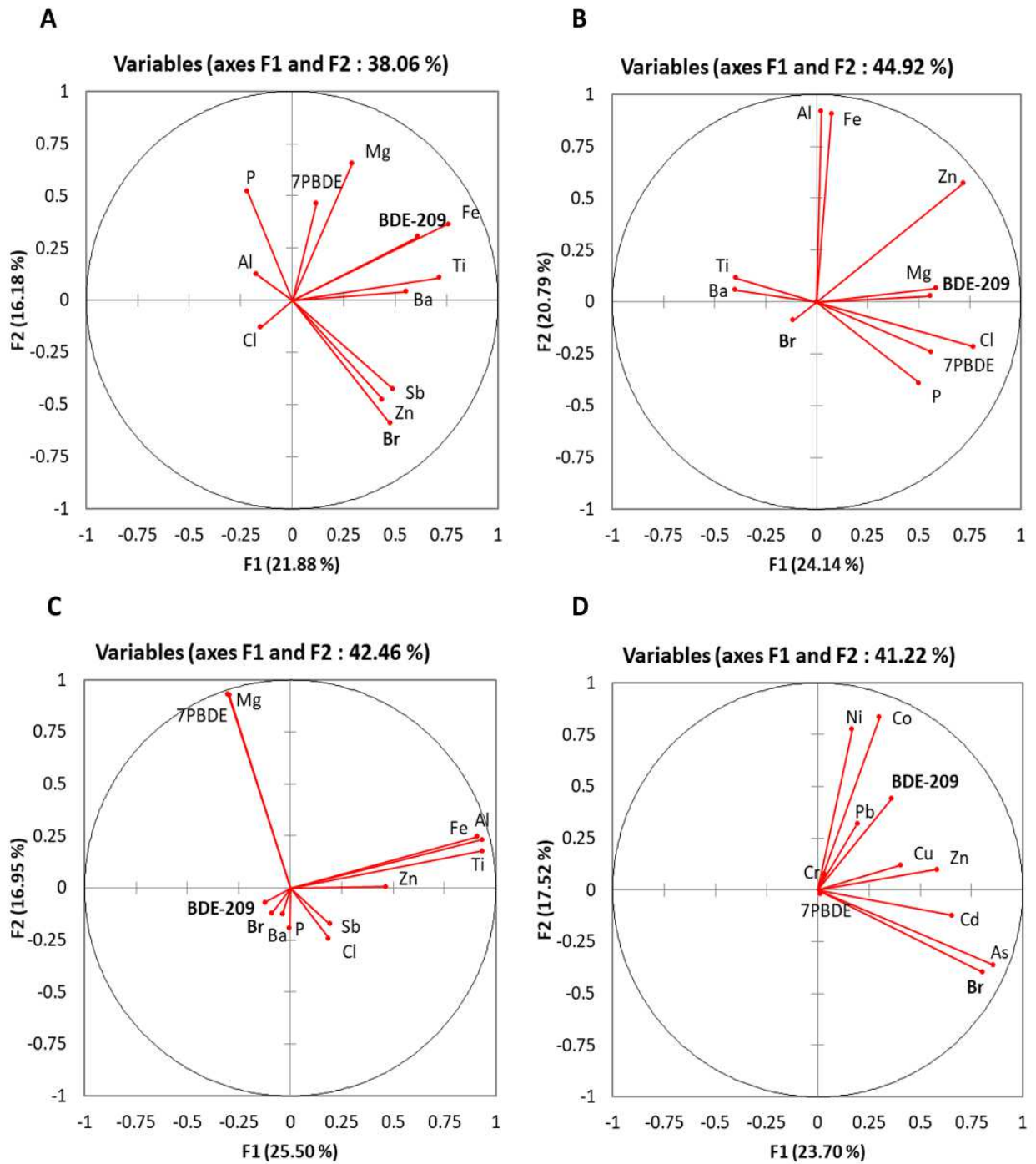
719

720 Figure 2: Correlations between Br amount measured by XRF and A: Σ_8 PBDEs amount in the 100 samples; B: BDE-209 amount in plastics; C:
721 Σ_8 PBDEs amount, only for samples with Σ_8 PBDEs > 10 mg kg⁻¹.



722

723 Figure 3: PCAs linking metals potentially present as flame retardants and PBDEs in A:
 724 plastics; B: foams; C: textiles. D: correlation between PBDEs and toxic metals generally
 725 studied in the environment, in the 100 seating waste materials.



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