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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.

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Abstract

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

Key words

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

1. Introduction

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

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

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

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

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

2. Materials and methods

2.1. Sample collection

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

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

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

2.2. Chemicals and standards

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

2.3. Sample preparation, extraction and clean-up

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

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

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

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

2.4. Instrumental analysis

A gas chromatograph (7890B series, Agilent, USA) that was coupled with a mass spectrometer (7000C) was used for the analyses. Samples of 1 μ L were injected in splitless mode (285°C) in an ultra-inert liner and with He as a carrier gas (1.5 mL min⁻¹). Separation was performed using a 15 m×0.25 mm DB-5MS capillary column (0.1- μ m film thickness) from Agilent. The oven temperature was programmed at 110°C for 1 min, increased to 250°C (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 was set to 310°C. The MS detector was operated at 70 eV in electronic impact (EI) mode, with an ion source at 300°C. Quantification was based on selected ion monitoring to realize

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

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

2.5 Statistical analyses

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

3. Results and discussion

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

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

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

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

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

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

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

3.2. PBDEs in seating furnishing wastes

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

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

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

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

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 molybdic 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

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

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

4. Conclusions

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

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

Supplementary materials

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

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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).

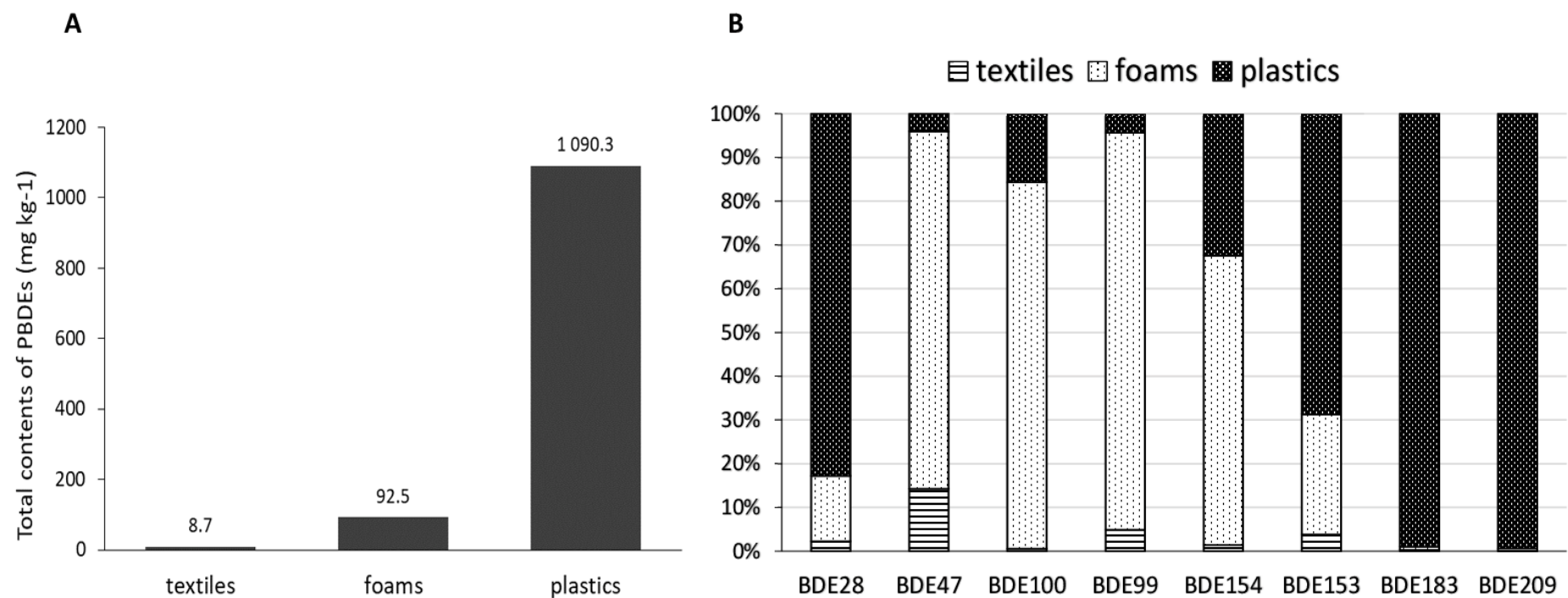
713

		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

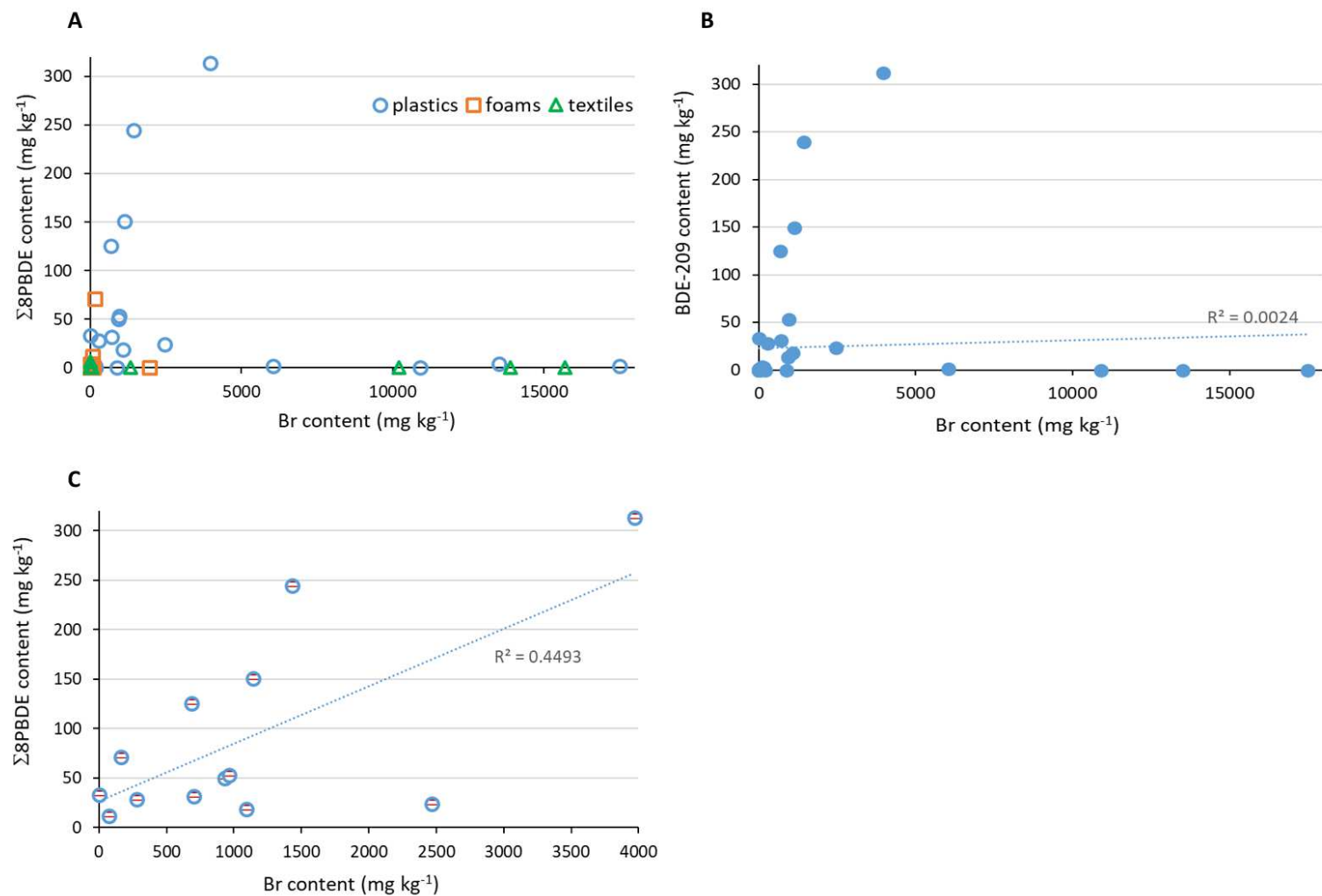
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715

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.

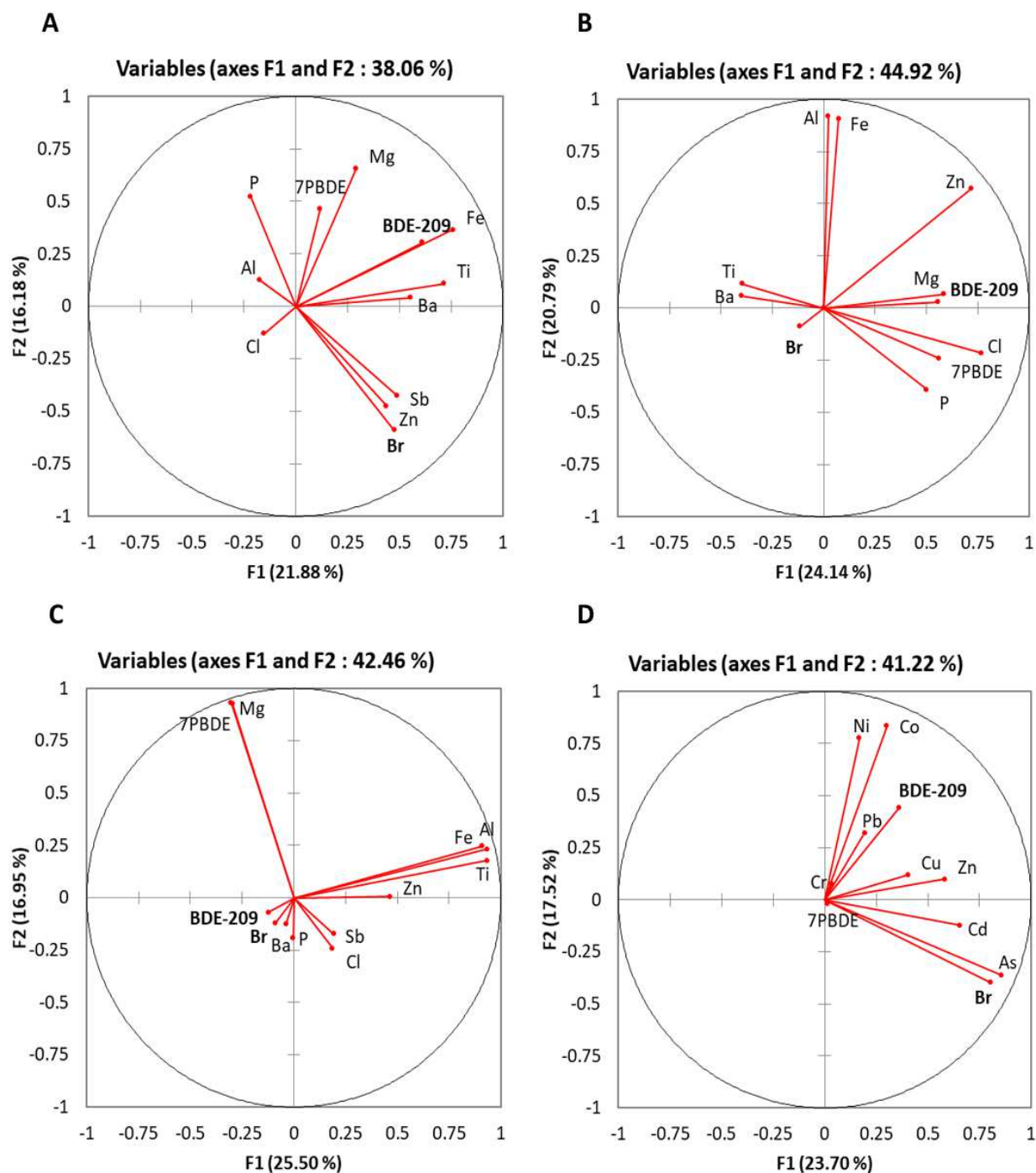


720 Figure 2: Correlations between Br amount measured by XRF and A: Σ_8 PBDEs amount in the 100 samples; B: BDE-209 amount in plastics; C:
 721 Σ_8 PBDEs amount, only for samples with Σ_8 PBDEs > 10 mg kg⁻¹.



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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