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BROMINATED DIPHENYL ETHER IN INDOOR DUST

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Introduction

With the rapidly growing use of combustible polymer material, e.g. for IT/TV casings, mattresses, upholstered furniture, the use of flame retardants like brominated diphenyl ether (BDE) has also increased strongly. They can release into the environment during their production, use or after disposal. BDE are synthesized by brominating diphenylether in the presence of a catalyst. Three commercial products are available: Penta (PeBDE) (world market demand estimates in 1999 8,500 t/a), octa (OcBDE) (3,800 t/a) and decabromdiphenylether (DeBDE) (55,000 t/a)[1]. The technical products contain residues of lower brominated BDE congeners. In order to protect health and environment the use and the placing on the market of preparations and articles containing Pe and OcBDE in concentrations > 0.1% by mass will be prohibited in the European Union from August 15, 2004. For DeBDE risk reduction strategies are aspected not later than June 30, 2003[2]. The objective of this study is to get more information about the release of these compounds from consumer products during their use and the exposure routes of humans.

Materials and Methods

Sample Collection. Dust from vacuum cleaner bags was collected from 40 private households in Germany from May to September 2001[4] and from August 2002 to January 2003.

Chemical Analysis. 10 g dust was extracted by Soxhlet extraction (Knöfler-Böhm hot extractor) with toluene. 10% of the extract was spiked with six $^{13}C_{12}$-BDE standards (20 ng BDE 28, 47, 99, 153, 183 and 200 ng BDE 209), one of each degree of bromination. The extract was cleaned by a four column clean-up (SiO_2-$AgNO_3$, H_2SO_4, NaOH, Macro Al_2O_3, Bio-Beads S-X3, Mini Al_2O_3), spiked with the injection standard (20 ng 4,4'-dibromoctafluorbiphenyl) and reduced to 100 µl. 1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC-EI-LRMS (GC 8000Top-MS Voyager, ThermoQuest) using a DB-5MS (15 m x 0.25 mm, 0.1 µm). The two most intensive mass of the bromine cluster (TrBDE: M^+. Te-DeBDE: M^+-2Br) were measured for each homologue group. The identification of BDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the $^{13}C_{12}$-labelled internal standards. Method blanks were analysed.

Results and Discussion

BDE were analysed in all indoor dust samples in considerable amounts. The data set shows a large variation of concentrations caused by a small number of very high values (hot spots) (mean many times over the 50-percentile) (Table 1). Three hot spots of BDE 47, 99, 100 (application of technical PeBDE), 153 and 154 (application of technical Pe and/or OcBDE) were detected (Figure 1-3), one hot spot of BDE 183 (application of technical OcBDE) (Figure 4) and two of BDE 209 (Figure 5). BDE 209 is the dominating congener in 35 samples, BDE 99 in 4 samples. The maximum values are much higher (BDE 47 x 11, BDE 85 x 7, BDE 99 x 17, BDE 100 x 9, BDE 153 x 7, BDE 154 x 19, BDE 209 x 3) as those already reported for office dust[5]. The source of BDE contamination of indoor dust is unknown with the exception of the maximum DeBDE value, which was detected in dust from a mattress. Abrasion of particles from polyurethane foam or textile back coatings seem to be a very important source. For PCDD/F the exposure routes of

humans are well characterized (food intake 94%, inhalation 5% and dermal contact 1%). For BDE inhalation and dermal contact could be more important. Long time inhalation of gas phase BDE 47, 99 and 153 from flame retardant polyurethane foam mattresses at body temperature 37.5°C (higher vapor pressure) could explain the high values detected in 5% of human blood samples from Sweden[6]. In this work 7.5% from 40 indoor dust samples contain high levels of technical Pe and/or OcBDE. A report about the emissions of Br, Cl and P flame retardants from building materials and consumer products in test chambers is in preparation[3].

Table 1: BDE in indoor dust – statistics

	BDE [ng/g]									
	28	**47**	**49**	**85**	**99**	**100**	**153**	**154**	**183**	**209**
n	15	40	12	17	40	39	38	38	40	39
Min	0.2	3.3	0.5	0.1	2.6	0.5	0.4	0.3	0.9	18.6
Max	4.4	1910	282	74.7	2850	314	420	210	464	19100
Mean	0.9	122	25.8	7.1	180	20.8	30.7	13.8	23.3	980
10Perc	0.3	5.6	0.5	0.2	5.7	1.0	1.7	0.6	2.2	149
50Perc	0.6	17.1	1.0	1.1	23.9	4.2	6.0	2.7	6.1	265
90Perc	1.7	71.6	16.4	14.2	96.0	17.5	20.4	10.4	39.0	969

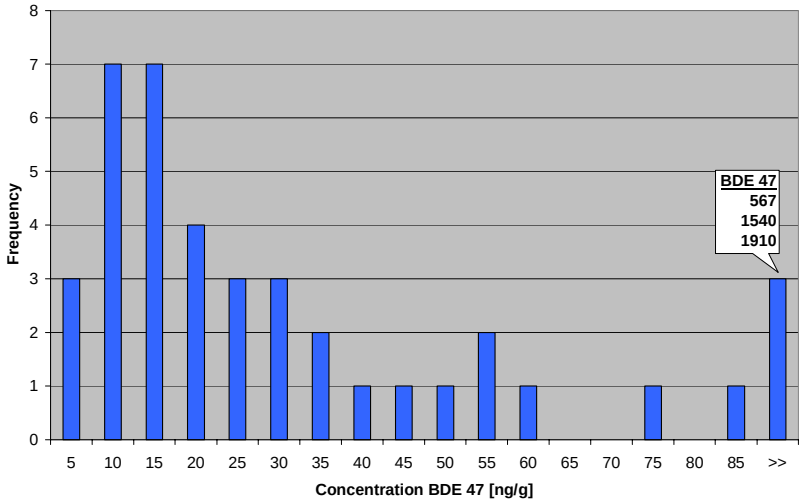

Figure 1: Histogram BDE 47 (2,2',4,4'-TeBDE) (n=40) in indoor dust. Three hot spots of BDE 47 of 567, 1540 and 1910 ng/g were detected.

References

1. BSEF 2001. Bromine Science and Environmental Forum
2. Directive 2003/11/EC of the European parliament and of the council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether)
3. FEA 2003. Federal Environmental Agency, Germany. Emissions of Flame Retardants from Building Materials and Consumer Products, project no. 299 65 321, in preparation
4. Knoth, W., Mann, W., Meyer, R., Nebhuth, J., 2002. Polybrominated Diphenylether in House Dust, Organohalogen Compounds 58, 213-216.

5. Leonards, P.E.G., Santillo, D., Brigden, K., van der Veen, I., v. Hesselingen, J., de Boer, J., Johnston, P., 2001. Brominated Flame Retardants in Office Dust Samples. The Second International Workshop on Brominated Flame Retardants, Stockholm, 299-302.
6. Van Bavel, B., Hardell, L., Kitti, A., Liljedahl, M., Karlsson, M., Pettersson, A., Tysklind, M., Lindström, G. 2002. High Levels of PBDEs in 5% of 220 Blood Samples from the Swedish Population, Organohalogen Compounds 58, 161-164.

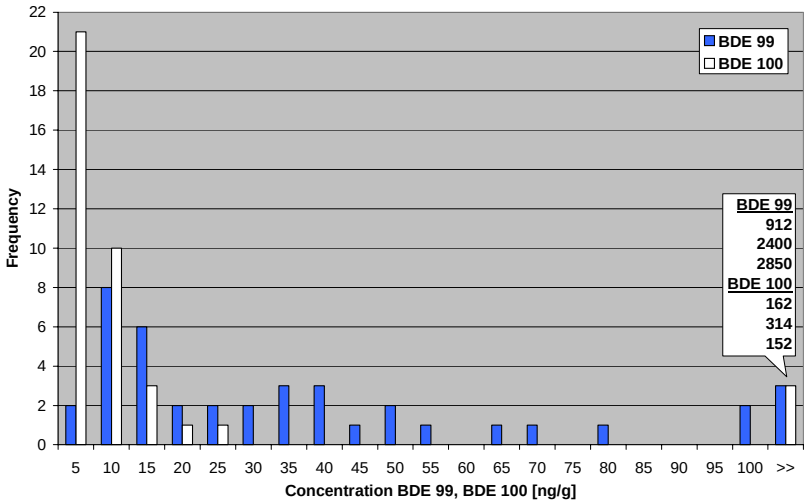

Figure 2: Histogram BDE 99 (2,2',4,4',5-PeBDE) (n=40) and BDE 100 (2,2',4,4',6-PeBDE) (n=39) in indoor dust. Three hot spots of BDE 99 of 912, 2400 and 2850 and of BDE 100 of 162, 314 and 152 ng/g were detected.

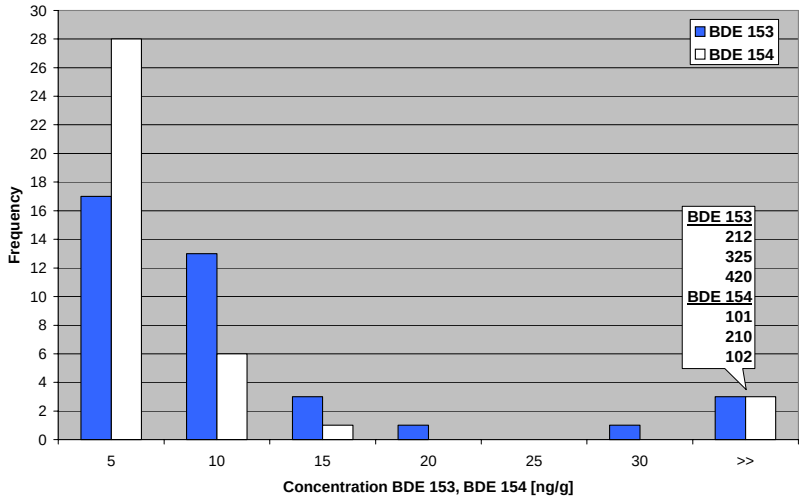

Figure 3: Histogram BDE 153 (2,2',4,4',5,5'-HxBDE) (n=38) and BDE 154 (2,2',4,4',5,6'-HxBDE) (n=38) in indoor dust. Three hot spots of BDE 153 of 212, 325 and 420 and of BDE 154 of 101, 210 and 102 ng/g were detected.

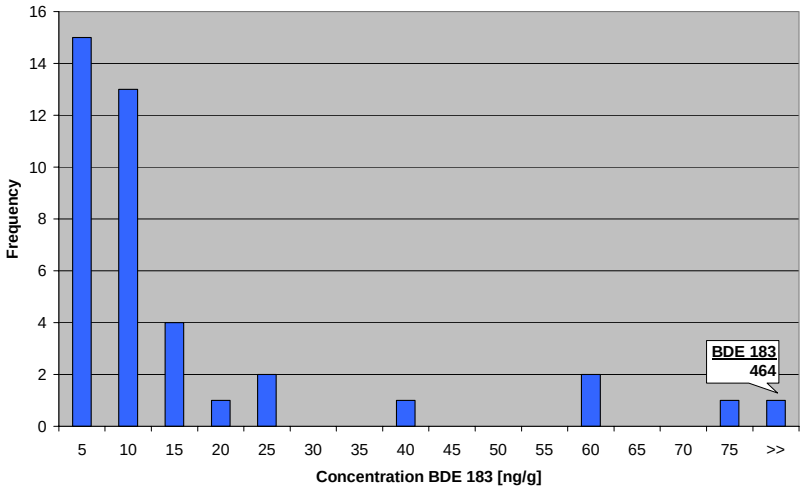

Figure 4: Histogram BDE 183 (2,2',3,4,4',5',6-HpBDE) (n=40) in indoor dust. One hot spot of BDE 183 of 464 ng/g was detected.

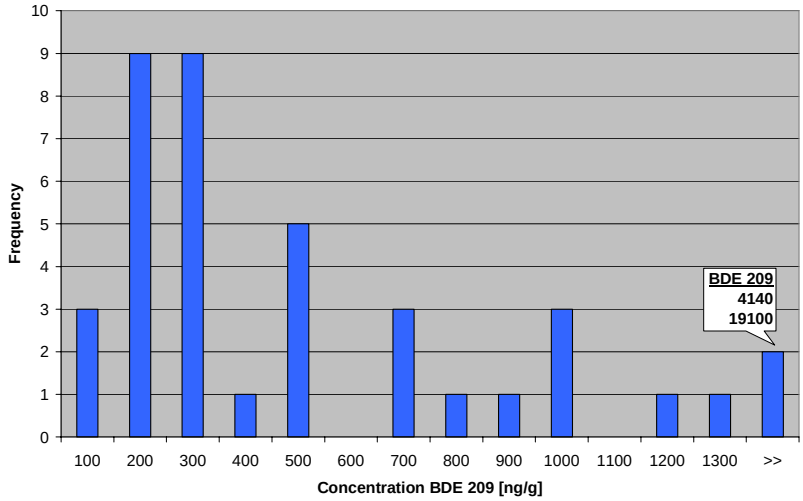

Figure 5: Histogram BDE 209 (DeBDE) (n=39) in indoor dust. Two hot spots of BDE 209 of 4140 and 19100 ng/g were detected.