

POLYBROMINATED FLAMES RETARDANTS

POLYBROMINATED DIPHENYLETHER IN HOUSE 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 retardants² like polybrominated diphenylethers (PBDE) has also increased strongly. They can release into the environment during their production, use or after disposal. PBDE are synthesized by brominating diphenylether in the presence of a catalyst. Three commercial products are available: Pentabromodiphenylether (world market demand estimates in 1999 8,500 t/a), octabromodiphenylether (3,800 t/a) and decabromodiphenylether (55,000 t/a)¹. The technical products contain residues of lower brominated PBDE congeners⁷. Tri to HexaBDE bioaccumulate in the food chain and were detected in Swedish human breast milk^{5,4} and human blood from Germany⁶. The aim 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 Method

10 g dust from vacuum cleaner bags of private households in the Rhein-Main area were extracted by Soxhlet extraction (Knöfler-Böhm hot extractor) with toluene. 10 % of the extract was spiked with five ¹³C₁₂-PBDE standards (20 ng BDE 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, spiked with the injection standard (200 ng ¹³C₁₂-OCDD) and reduced to 100 µl (Figure 3). 1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC-EI-LRMS (Te-HpBDE: GC 8060-MS MD 800, Fisons. BDE 209: GC 8000Top-MS Voyager, ThermoQuest) using a DB-5MS (Te-HpBDE: 30 m x 0.25 mm, 0.1 µm. BDE 209: 15 m x 0.25 mm, 0.1 µm). The two most intensive mass of the bromine cluster (M⁺-2Br) were measured for each homologue group. The identification of PBDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the ¹³C₁₂-labelled internal standards. To estimate the contribution of vacuum cleaner and bag to the PBDE contamination of dust, a new bag was analysed (Blank 1) and the vacuum cleaner, used for sampling S048, was run with a new bag for 15 min, cooling-off period 45 min, for a total time of 24 h (Blank 2). Quantification was only done if sample data was at least twice the blank data.

Results and Discussion

PBDE were detected in all house dust samples in considerable amounts. The two highest BDE 209 concentrations were found in sample no. S042 (4.14 mg/kg) and S058 (19.1 mg/kg) (Figure 1), the two highest BDE 99 concentrations in sample no. S062 (2.85 mg/kg) and S063 (0.912 mg/kg) (Figure 2). BDE 209 was the dominating congener in 22 samples, BDE 99 in 2 samples (S062 and S063) (Table 1). The maximum values are much higher (BDE 47 x 11, BDE 85 x 7, BDE 99 x 17, BDE 100 x 5, BDE 153 x 7, BDE 154 x 9, BDE 209 x 3) as those already reported for office dust³. PBDE leak from consumer products treated with this flame retardant and may reach via the pathway house dust, waste water, sewage sludge and its land-application the food chain to humans.

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Table 1. PBDE in House Dust - Concentration and Statistics

| Sample No. | BDE [ng/g] | | | | | | | | |
|---|------------|------|------|------|------|------|------|------|-------|
| | 47 | 49 | 85 | 99 | 100 | 153 | 154 | 183 | 209 |
| S040 | 34,6 | n.d. | 1,1 | 47,7 | 7,2 | 6,1 | 6,1 | 3,9 | 1220 |
| S041 | 81,7 | n.d. | 1,8 | 66,5 | 10,5 | 7,2 | 5,7 | 5,5 | 1150 |
| S042 | 15,3 | n.d. | 1,2 | 30,2 | 6,8 | 29,7 | 7,5 | 71,4 | 4140 |
| S043 | 14,1 | n.d. | 0,3 | 6,5 | 2,0 | 2,3 | 0,8 | 2,6 | 176 |
| S045 | 13,8 | 1,0 | 1,2 | 20,9 | 2,8 | 8,5 | 2,0 | 37,0 | 403 |
| S046 | 4,8 | n.d. | n.d. | 5,7 | 1,0 | 3,2 | 1,0 | 11,1 | 917 |
| S047 | 24,9 | 1,0 | 1,1 | 32,3 | 7,4 | 6,1 | 3,8 | 7,3 | 226 |
| S048 | 25,8 | 0,5 | 0,1 | 6,4 | 2,0 | 4,4 | 0,5 | 5,1 | 622 |
| S049 | 3,3 | n.d. | n.d. | 2,6 | 0,5 | 0,4 | 0,3 | 0,9 | 137 |
| S050 | 8,9 | n.d. | 0,4 | 11,4 | 2,4 | 2,3 | 1,1 | 6,6 | 175 |
| S051 | 25,2 | 0,8 | 1,8 | 45,4 | 7,3 | 6,6 | 4,3 | 4,8 | 741 |
| S052 | 46,1 | 1,8 | n.d. | 51,4 | 9,4 | 6,4 | 4,9 | 3,2 | 328 |
| S053 | 5,6 | 1,1 | 0,3 | 5,5 | 1,0 | 1,9 | 0,6 | 5,6 | 265 |
| S054 | 4,7 | n.d. | n.d. | 4,2 | 0,9 | 1,2 | 0,4 | 4,8 | 255 |
| S055 | 16,7 | n.d. | 0,7 | 19,6 | 4,0 | 2,5 | 1,9 | 1,8 | 235 |
| S056 | 10,4 | n.d. | n.d. | 11,2 | 2,1 | 2,7 | 1,1 | 8,5 | 658 |
| S057 | 55,4 | 2,3 | 3,8 | 95,9 | 20,2 | 12,8 | 9,7 | 10,0 | 241 |
| S058 | 9,3 | 0,8 | 0,2 | 8,0 | 1,6 | n.a. | n.a. | 4,3 | 19100 |
| S059 | 6,7 | 0,5 | n.d. | 7,4 | 1,4 | n.a. | n.a. | 8,7 | 600 |
| S060 | 5,4 | 0,5 | n.d. | 5,7 | 1,1 | 1,0 | 0,7 | 1,9 | n.a. |
| S061 | 9,3 | n.d. | 0,9 | 15,9 | 3,0 | 2,8 | 1,4 | 5,2 | 264 |
| S062 | 1910 | 282 | 74,7 | 2850 | 152 | 420 | 102 | 59,5 | 924 |
| S063 | 567 | 18,0 | 29,8 | 912 | 162 | 212 | 101 | 464 | 242 |
| S064 | 14,5 | n.d. | 0,5 | 22,5 | 3,7 | 6,9 | 2,8 | 10,0 | 173 |
| S065 | 15,1 | n.d. | n.d. | 11,6 | n.d. | 2,9 | 1,0 | 7,4 | 271 |
| n | 25 | 12 | 17 | 25 | 24 | 23 | 23 | 25 | 24 |
| Min. | 3,3 | 0,5 | 0,1 | 2,6 | 0,5 | 0,4 | 0,3 | 0,9 | 137 |
| Max. | 1910 | 282 | 74,7 | 2850 | 162 | 420 | 102 | 464 | 19100 |
| Mean | 117 | 26 | 7 | 172 | 17 | 33 | 11 | 30 | 1394 |
| 50-Perc. | 14,5 | 1,0 | 1,1 | 15,9 | 2,9 | 4,4 | 1,9 | 5,6 | 300 |
| 90-Perc. | 71,1 | 16,4 | 14,2 | 84,1 | 17,3 | 26,3 | 9,3 | 50,5 | 1200 |
| 10-Perc. | 5,0 | 0,5 | 0,2 | 5,6 | 1,0 | 1,4 | 0,5 | 2,2 | 175 |
| Blank 1 | 1,8 | n.d. | n.d. | 1,0 | 0,2 | 0,2 | n.d. | 0,4 | 48,6 |
| Blank 2 | 1,6 | n.d. | n.d. | 0,7 | 0,2 | 0,1 | n.d. | 0,2 | 5,3 |
| dominating congener | | | | | | | | | |
| Blank 1: Vacuum cleaner bag new | | | | | | | | | |
| Blank 2: Vacuum-clean 15 min, cooling-off period 45 min, total 24 h | | | | | | | | | |
| sampling site, vacuum cleaner and bag same as for sampling S048 | | | | | | | | | |

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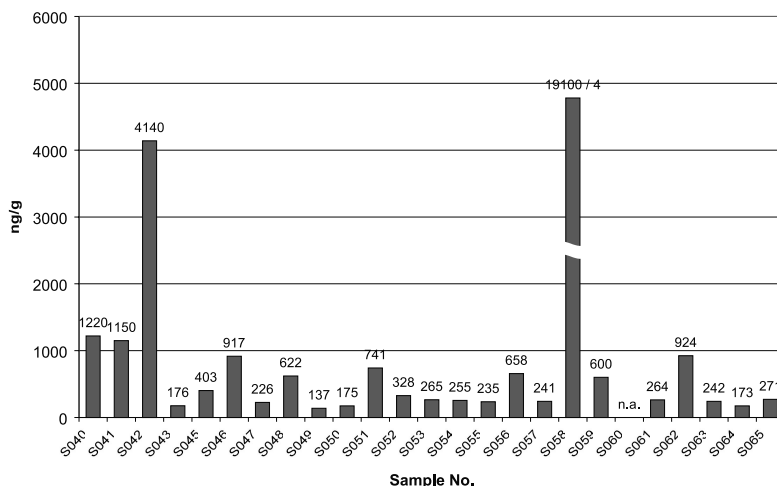


Figure 1. Concentration of BDE 209 in 24 House Dust Samples

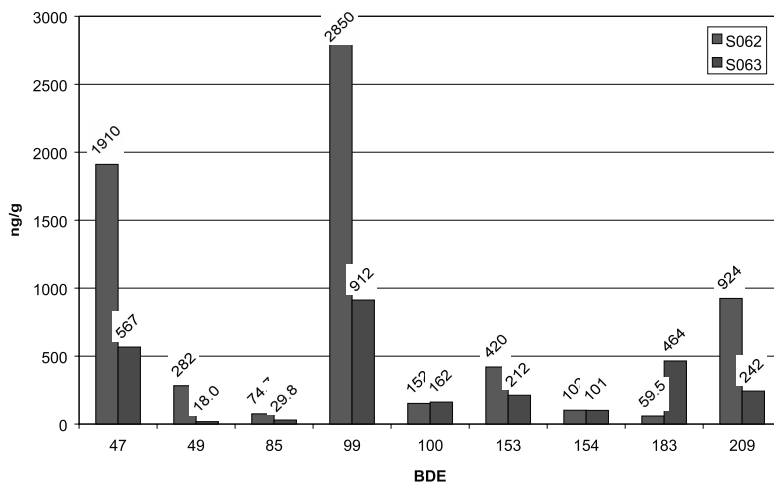


Figure 2. PBDE Profiles in House Dust Samples S062 and S063

References

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2. FEA 2001. Federal Environmental Agency, Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Vol. I: Results and Summary Overview. Texte 25/01 (in German). Texte 40/01 (translated into English). Vol. II: Flame-Retardant Finishings of Selected Products – Applications-Focused Analysis: State of the Art, Trends, Alternatives. Texte 26/01 (in German). Vol. III: Toxicological and Ecotoxicological Substance Profiles of Selected Flame Retardants. Texte 27/01 (in German).

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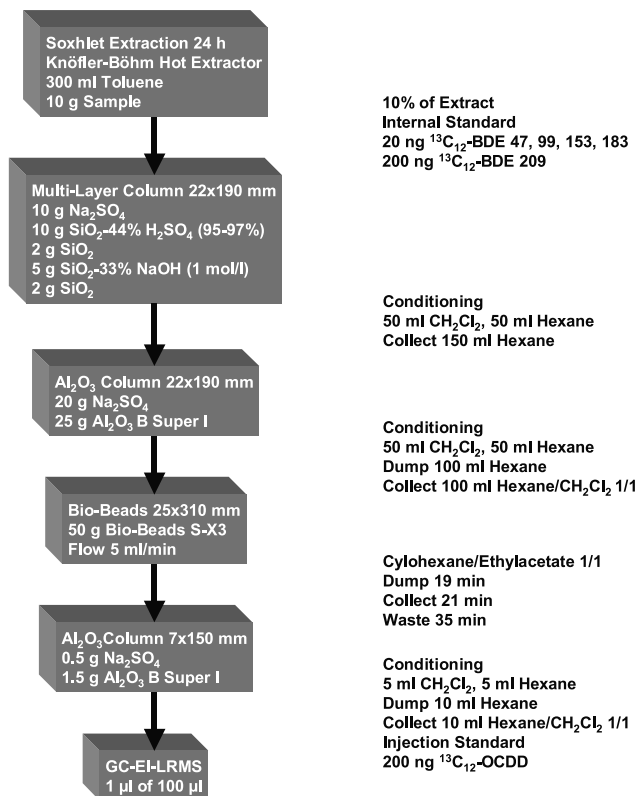


Figure 3. Extraction and Clean-Up

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