Polybrominated diphenyl ether (PBDE) in Italian ryegrass exposed near to Bavarian shredder plants

Antonia Wanner, Ludwig Peichl, Jutta Köhler, Silke Schädel, Arnold Rupprich, Wolfgang Körner
Bavarian Environment Agency, Buergermeister-Ulrich-Strasse 160, D-86179 Augsburg, Germany

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants applied to many common products like computers, television sets, white goods and textiles which are used for example in cars. Many of these products end their cycle of life in a shredder plant. Due to high concentrations of PBDE measured in indoor air in electronic dismantling plants [Sjödin et al. 2001], it was assumed that the immission of PBDE near shredder plants is elevated as well. In 2005, PBDE concentrations were determined in standardized Italian ryegrass cultures exposed on and nearby the plant premises of three shredder plants of different age, all located in the state of Bavaria, Germany.

Materials and Methods

Standardized cultures of Italian ryegrass were disposed at five different locations on (location 1-3) and nearby (location 4-5) the premises of three different shredder plants named A, B and C according to the German guideline VDI 3957 part 2. Five time series of grass cultures were exposed for four weeks each from midth of May until beginning of Oct. Grass cultures serve as passive samplers for monitoring of particle-bound and gaseous semivolatile persistent organic pollutants in ambient air.
At the end of the exposure period the grass was cut, wrapped in aluminum foil and stored in a refrigerator till analysis. At first material was freeze-dried. After the addition of $^{13}C_{12}$-labeled PBDE standards (BDE 28, -47, -99, -100, -153, -154, -183, -209) the samples were Soxhlet extracted with toluene for 20 h. Clean-up of the extracts included column chromatography with acid and basic silica, gel permeation chromatography (Bio-Beads SX-3) and chromatographic separation on basic aluminum oxide as described elsewhere [Schütz 2004]. The volume of the final extract was reduced by a stream of nitrogen and $^{13}C_{12}$-BDE 138 was added as recovery standard.
Analysis of PBDE was carried out by HRGC/MS on a 15 m x 0.25 mm RTX-5 Sil MS capillary column (film thickness 0.10 µm).

Results and Discussion

Total concentrations of PBDE (sum of eight main congeners) in ryegrass ranged between 1.15 µg/kg dry mass and 450 µg/kg dry mass, depending on its exposure location (see figure 1). Highest concentrations were analyzed in samples from shredder C, the oldest one of the three plants, especially from location C1, which was in close vicinity to the shredder and other activities such as sieving and open storage of residues from the shredder process. Unfortunately, there was no exposure of grass cultures at C1 in the first and second period.
At plant B, where parts of the facility are located indoor, the lowest PBDE concentrations were detected. But even these levels were higher than those measured in Italian ryegrass samples from one rural and one urban background monitoring station from 2002 to 2004 (mean: 0.33 µg/kg dry mass). In summary, PBDE concentrations in grass cultures on and nearby the plant premises of three shredder plants were between one and three orders of magnitude higher than background levels.
In Table 1, mean concentrations of the eight analyzed PBDE congeners are depicted. Highest concentrations were found for BDE 209 (1.22-214 µg/kg dry mass) followed by BDE 47 (0.44-16.9 µg/kg dry mass) and BDE 99 (0.30-26.5 µg/kg dry mass). This correlates with the congener pattern of technical PBDE mixtures and their annual amount of production before Penta- and OctaBDE were banned in Europe in August 2004.

Figure 2 shows the congener pattern of PBDE for the three plants. For this diagram all values of one shredder plant (all five locations and five sampling periods) are averaged.
The dominant congener is, as mentioned before, BDE 209 with 80 %, 53 % and 72 %, respectively. Thus, it is assumed that plant B processes more material containing Penta- and OctaBDE and plant A and C are processing mainly common products containing DecaBDE.

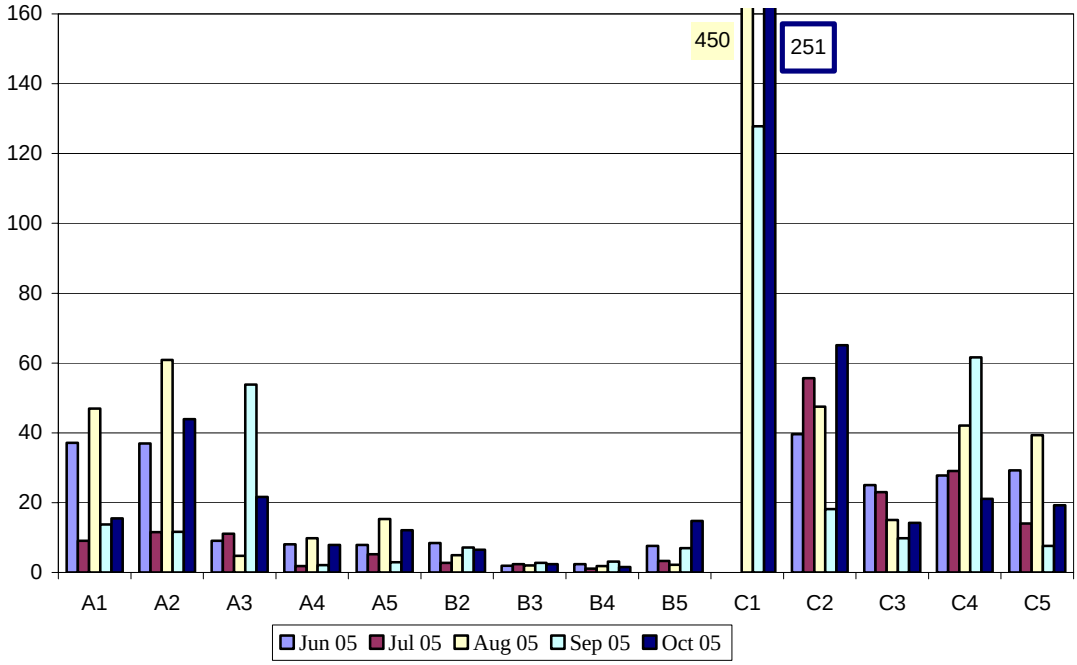

Figure 1. Total concentration in µg/kg dry mass of PBDE (eight congeners) in Italian ryegrass from locations around three different shredder plants sampled after four weeks of exposure in 2005.

Table 1. Mean PBDE concentrations in ryegrass in µg/kg dry mass at the different exposure locations

	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 209
A1	0.07	1.47	0.22	1.24	0.11	0.16	0.33	20.9
A2	0.07	1.83	0.37	2.10	0.21	0.31	0.60	27.5
A3	0.05	1.66	0.33	2.02	0.20	0.32	0.54	15.0
A4	0.02	0.58	0.09	0.51	0.05	0.07	0.12	4.49
A5	0.03	0.84	0.13	0.73	0.07	0.11	0.24	6.56
B2	0.12	1.16	0.20	1.03	0.12	0.15	0.19	2.99
B3	0.04	0.48	0.07	0.35	0.04	0.04	0.06	1.22
B4	0.06	0.44	0.06	0.30	0.03	0.04	0.07	1.24
B5	0.06	0.94	0.15	0.85	0.08	0.12	0.18	4.58
C1	0.67	16.9	4.28	26.5	2.39	4.17	7.57	214
C2	0.16	3.85	0.82	5.21	0.50	0.82	1.43	32.4
C3	0.06	1.35	0.26	1.57	0.16	0.29	0.67	13.1
C4	0.15	3.43	0.65	3.99	0.39	0.71	1.55	25.5
C5	0.08	1.74	0.37	2.28	0.22	0.40	0.79	16.0

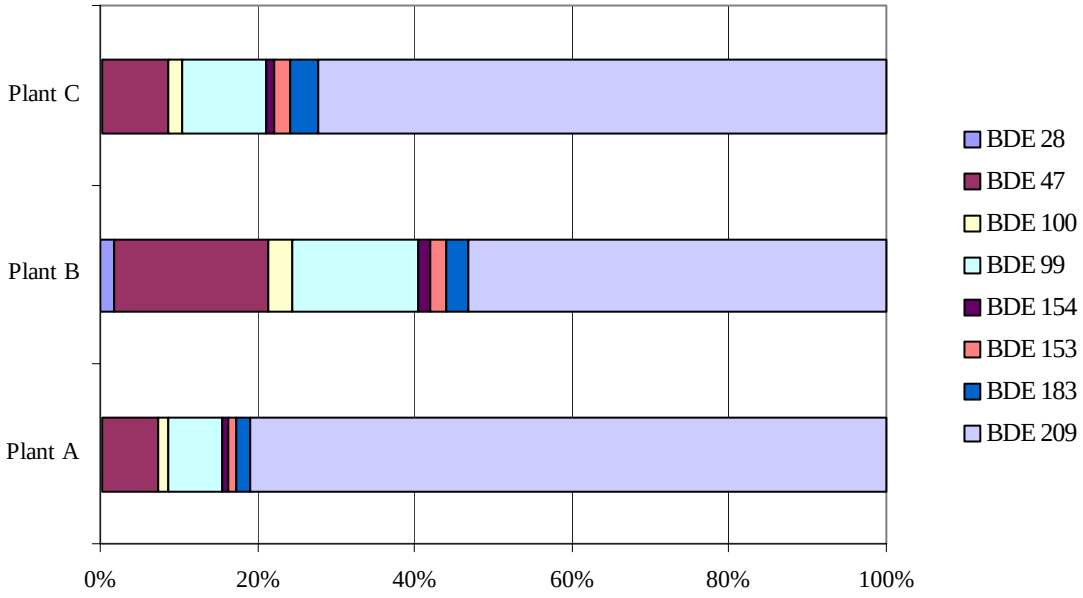

Figure 2. PBDE congener pattern in ryegrass from locations around three different shredder plants

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