Polybrominated Diphenyl Ethers (PBDEs) in House Dust in Beijing, China

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Abstract Eleven house dust samples were collected in Beijing to quantify 42 different polybrominated diphenyl ethers (PBDEs). Total PBDEs concentrations ranged from 140 to 1,300 ng g⁻¹. The dominant PBDEs congener identified was BDE 209, which made up more than 70 % of all PBDEs congeners. Concentrations of PBDEs in Chinese house dust were lower than in other countries. The most polluted areas were electronics shops and households. It is likely that PBDEs exposure is a potential threat for Beijing residents, particularly toddlers.

Keywords China · Contamination · House dust · PBDEs

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals used extensively as flame retardants in a wide variety of plastics, textiles and electronic components (Chen et al. 2012). Technical PBDEs are synthesized by the electrophilic substitution of diphenyl ethers. There are three commercial formulations of PBDEs: penta-, octa- and decabrominated diphenyl ethers, which are named based on their bromine content (de Wit 2002). PBDEs have the potential for endocrine disruption, bioaccumulation, carcinogenic

and mutagenic activities, and long-range transport (Knoth et al. 2007). Recently, certain commercial mixtures of PBDEs (penta- and octa-formulations) were banned in Europe because of their persistence and potential environmental or human health risks (Kemmler et al. 2003). However, in Asia the demand for PBDEs has rapidly increased and all commercial PBDEs mixtures are used without regulation (Tan et al. 2007).

The sources of human exposure to PBDEs remain poorly understood. Direct human exposure via the inhalation of dust, or particulate matter, is a significant exposure pathway, which allows PBDEs to enter the upper respiratory tract. Fine and ultrafine particles can also reach lung alveoli. Since PBDEs can easily accumulate on particles, contaminated house dust could have a significant impact on public health and increase the risk of PBDEs inhalation, ingestion or direct skin contact (Wu et al. 2007). Because they spend more time indoors than adults, toddlers are more exposed to house dust and may be more affected by PBDEs contamination. Despite the potential for negative health outcomes, studies on PBDEs contamination in house dust are rare and much more information is needed to better identify their environmental impact.

This study investigated the composition and profiles of PBDEs in house dust samples obtained from different house types in Beijing, China. The main objectives were to quantify PBDEs concentrations, identify the potential sources of house dust and explore potential threats from human exposure to PBDEs in house dust.

Materials and Methods

A standard solution (EPA method 1614) of 39 PBDEs congeners (Accustandard, New Haven, CT, USA), BDE

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205 and 206 (Cambridge Isotope Laboratories, Andover, MA, USA) and BDE 209 (the Laboratory of Dr. Ehrenstorfer, Augsburg, Germany) were used to quantify 42 PBDEs. The congeners studied included mono- through deca-brominated BDEs. Specifically, the congeners quantified were: mono-BDEs (BDE 1, 2 and 3), di-BDEs (BDE 7, 8, 10, 11, 12, 13 and 15), tri-BDEs (BDE 17, 25, 28, 30, 32, 33, 35 and 37), tetra-BDEs (BDE 47, 49, 66, 71, 75 and 77), penta-BDEs (BDE 85, 99, 100, 116, 118, 119 and 126), hexa-BDEs (BDE 138, 153, 154, 155 and 166), hepta-BDEs (BDE 181, 183 and 190) and BDE 205, 206 and 209. All solvents used in this study were pesticide grade (J. T. Baker, USA). Silica gel (100–200 mesh, Qingdao Haiyang Chemical Factory, Shandong, China) was rinsed with methanol followed by dichloromethane, baked at 70°C for a minimum of 3 h, activated for 6 h at 550°C and stored in desiccators. Anhydrous sodium sulfate, sulfuric acid, sodium hydroxide and silver nitrate were analytical grade (Beijing Chemical Factory, Beijing, China). Anhydrous sodium sulfate was activated for 6 h at 600°C and stored in desiccators.

House dust samples were collected from 11 houses including a storage room, a dining room, three offices, three electronics shops and three homes in Beijing. Dust samples were collected from the filters of air conditioning units (ACUs) according to the sampling method of Tan et al. (2007). The samples were transferred to pre-cleaned amber glass bottles and stored at –18°C. Extraction was normally carried out within 72 h. Plastic materials were avoided throughout the collection procedures.

Three grams of each house dust sample were weighed and then homogenized using anhydrous sodium sulfate. The samples were then extracted by ultrasonication using 40 mL of hexane/dichloromethane (1:1, v/v) for 4 min and separated by centrifugation. The extracts were then collected and this procedure was repeated three times. The extracts were reduced to 2 mL using a rotary evaporator. The concentrated extracts were then cleaned using a multilayer silica gel column packed from the bottom to the top with 2 g of silver nitrate silica gel (10 %, w/w), 1 g of activated silica gel, 3 g of basic silica gel, 1 g of activated silica gel, 4 g of acidic silica gel (44 % concentrated sulfuric acid, w/w), 4 g of acidic silica gel (22 % concentrated sulfuric acid, w/w), 1 g of activated silica gel and 1 cm of anhydrous sodium sulfate. The multilayer silica gel column was cleaned using 100 mL hexane. The extracts were eluted using 100 mL hexane/dichloromethane (1:1, v/v) and reduced to 2 mL using a rotary evaporator. The concentrated eluents were then transferred to a Kuderna–Danish concentrator and reduced to 20 µL under a gentle N₂ stream. Analytes were protected from light by wrapping containers with aluminum foil or by storage in amber glassware throughout the extraction, cleanup and analysis procedures.

The 42 PBDEs were analyzed using an Agilent 6890 series gas chromatograph (GC) coupled with an Agilent 5973 mass spectrometer (MS) (Agilent Technologies, Palo Alto, CA, USA) using a 15 m DB-5MS capillary column (15 m × 0.25 mm, internal diameter; 0.25 µm film thickness). The MS used the negative chemical ionization source in the SIM mode. Both the MS ion source and the quadrupole temperature were set to 150°C and the electron energy was 70 eV. Methane was used as the chemical ionization moderating gas and helium was used as the carrier gas. The GC temperature program began at 80°C and was held for 1 min, then increased to 200°C at a rate of 10°C min^{–1}, and finally increased to 300°C at a rate of 20°C min^{–1} where it was held for 5 min. The GC was equipped with a split-splitless injector that was held at a constant temperature of 270°C and samples were injected in the pulsed splitless mode. The compounds were monitored at m/z 79 and 81 (for all PBDE congeners except BDE 209) and m/z 486.7 and 488.7 (for BDE 209).

A laboratory method control group was also analyzed to ensure there were no interferences or cross-contamination. Also, a procedural blank was run in parallel for every set of six samples to further check for interferences and cross-contamination. Duplicate samples were analyzed along with the initial samples as an additional quality control tool to ensure valid results. Instrument stability and relative response factor variance were determined by analyzing the calibration standard solutions in each sample batch.

Quantification of PBDEs was performed using an external standard method. Three quality control criteria were used to ensure correct identification of the target compounds. First, the GC retention times matched those of the standard compounds within ±0.05 min. Second, the signal-to-noise ratio was greater than 3, and finally, each compound had two monitored ions and the isotopic ratios between the quantification and confirmation ions were within ±15 % of the theoretical values. The SRM sample (NIST 2585) was analyzed to validate the analytical method employed. The results were satisfactory, with z-scores of ≤1 for all congeners. The limits of detection (LOD) for the PBDEs ranged from 0.001 to 0.05 ng g^{–1} (dry weight) for di- to nona-PBDEs and an LOD of 0.1 ng g^{–1} (dry weight) was found for BDE 209.

Results and Discussion

Polybrominated diphenyl ethers were identified in each of the house dust samples. Some PBDEs were detected in all of the samples, highlighting the wide occurrence of these compounds in indoor environments. Total PBDEs concentrations ranged from 140 to 1,300 ng g^{–1} (dry weight) in the house dust (Table 1).

Table 1 Total concentration of PBDEs in each sample

Sample no.	Di-BDEs	Tri-BDEs	Tetra-BDEs	Penta-BDEs	Hexa-BDEs	Hepta-BDEs	Octa-BDEs	Nona-BDEs	BDE 209	ΣPBDEs
1. Storage	0.19	0.69	2.6	3.8	2.2	4.6	0.37	32	260	310
2. Dinner room	0.04	0.59	3.3	2.0	1.2	3.5	0.26	29	99	140
3. Office 1	0.46	2.3	9.8	4.4	2.3	2.8	0.08	17	130	170
4. Office 2	0.15	0.56	4.8	7.1	3.8	4.5	0.09	23	230	270
5. Office 3	0.54	4.9	31	31	11	14	0.25	36	990	1,100
6. E. shop ^a 1	0.31	1.2	8.0	19	10	18	0.45	55	1,100	1,200
7. E. shop ^a 2	0.04	1.0	8.8	9.6	3.5	5.6	0.07	19	790	830
8. E. shop ^a 3	0.02	1.7	4.5	10	7.6	12	0.33	25	550	610
9. Home 1	0.01	1.3	3.8	3.3	2.6	4.7	0.05	21	1,300	1,300
10. Home 2	N.D. ^b	24	76	31	8.2	7.5	0.20	20	680	850
11. Home 3	4.3	16	47	23	5.7	3.9	0.06	15	480	600

(unit: ng g⁻¹)^a Electronics shop^b Not detected

The dominate PBDEs congener detected in this study was BDE 209, which accounted for more than 70 % of the total PBDEs in all of the samples. BDE 206, 47, 99 and 183 were the next most abundant congeners. The PBDEs congener profiles of the house dust samples were similar to those measured from surface soil in some Chinese urban area (Li et al. 2008, 2009).

The most polluted area was home 1 (total PBDEs concentration of 1,300 ng g⁻¹), followed by electronics shop 1, office 3, home 2, electronics shop 2, electronics shop 3 and home 3. The lowest concentrations were found in the dining room and storage, and at office 1 and 2. The abundance of PBDEs in the homes and electronics shops was likely because many electronic products featuring PBDEs (used in circuit boards and casings) were used. The concentrations of PBDEs in office 3 were much higher than in the other offices because office 3 had more electronic products than the other offices.

The results of this study were compared with those reported elsewhere. PBDEs concentrations were much lower than those in Singapore (Tan et al. 2007), Ottawa, Canada (Wilford et al. 2005), Washington DC, USA (Stapleton et al. 2005) and Birmingham, UK (Harrad et al. 2008). The concentrations of PBDEs, except BDE 209, were also much lower than those in Toronto, Canada (Harrad et al. 2008). There have been few studies on house dust in China. Total PBDEs and BDE 209 concentrations in this study were much lower than those in Guangzhou, Haikou, Wuhan, Shenzhen and Hong Kong, China (Chen et al. 2011; Huang et al. 2010; Kang et al. 2011). This work suggested that PBDEs pollution was lower in northern China than in southern China. The possible reason was that

the temperature in northern China was lower than that in southern China, PBDEs possibly released less to indoor environment in these area.

To investigate potential sources and distributions, Pearson correlation analyses were performed for selected house dust PBDEs congeners. These PBDEs congeners had higher concentrations, and were studied more by researchers. The coefficients ranged between 0.028 and 0.995 for BDE 47 versus BDE 183 and BDE 209 versus ΣPBDEs, respectively. The higher correlation coefficients were BDE 153 versus BDE 154 (0.974), BDE 153 versus BDE 183 (0.925) and BDE 154 versus BDE 183 (0.914). These indicated that BDE 153, 154 and 183 may have a common source and similar environmental behavior. The strongest relationship of BDE 209 with the sum of PBDEs indicated that BDE 209 was the most significant contributor to total PBDEs concentrations. Based on their abundances, it was likely that PBDEs contamination in house dust was strongly associated with the use of three commercial PBDEs flame-retardant mixtures.

Humans are exposed to pollutants via numerous pathways, including diet and ingestion (inhalation and dust ingestion). Butte and Heinzow (2002) found correlations between PBDEs concentrations in human matrices and house dust, indicating that dust ingestion cannot be ignored. PBDEs contamination in this study of house dust indicated that there was potential for Beijing residents to be exposed to PBDEs. People, especially toddlers, spend most of their time indoors, increasing the potential threats of PBDEs exposure. This makes estimating the daily intake of PBDEs in house dust necessary. Since no local data were available to assess daily PBDEs intake via house dust

Fig. 1 Contributions to PBDEs exposure via diet, inhalation and dust ingestion for toddlers and adults assuming an average and high dust ingestion rate for toddlers, and an average and high dust ingestion rate for adults

ingestion in China, the method described by Wilford et al. (2005) was used assuming that the average and high dust ingestion rates were 55 and 200 mg day⁻¹, respectively, for toddlers, and 4.16 and 100 mg day⁻¹, respectively, for adults. The PBDEs intake was calculated to be 37 ng day⁻¹ (average) and 140 ng day⁻¹ (high value) for toddlers and 2.8 ng day⁻¹ (average) and 68 ng day⁻¹ (high value) for adults. Because there were no local data available to identify daily PBDEs intake via food ingestion in China, a value of 44 ng day⁻¹, derived from Ryan and Patry (2001), was used. A toddler's PBDEs exposure via dietary intake was estimated to be 57 % of an adult's (Kiviranta et al. 2004), and was calculated to be 25 ng day⁻¹. The exposure via dietary intake was based on a single value and was a rough estimation. For daily PBDEs intake via inhalation, we adopted median values of 0.33 and 2.0 ng day⁻¹ for toddlers and adults, respectively (Wilford et al. 2005). From Fig. 1, when we used the average dust ingestion rate, diet was the major source of PBDEs exposure for adults, contributing to approximately 90 % of the total PBDE intake. This was concordant with the study of Ni et al. (2012). When the high dust ingestion rate was used, dust ingestion contributed approximately 60 % PBDEs exposure, more than diet. House dust, which was not the dominant adult exposure pathway for PBDEs, was still a potential health risk for adults. Conversely, dust ingestion was the major exposure pathway for toddlers, with contributions ranging from 60 % to 84 % depending on the ingestion rate used. Toddlers may be more susceptible to PBDEs-contaminated house dust than adults, but more work is needed to fully evaluate toddler susceptibility. We suggest that, researchers in China should focus on more accurately quantifying the daily intake of PBDEs from dust, diet and inhalation.

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