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Composition, Distribution, and Characterization of Polybrominated Diphenyl Ethers in Sandstorm Depositions in Beijing, China

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Abstract This study was conducted to determine the concentration of 8 polybrominated diphenyl ethers (PBDEs) in sandstorm depositions in Beijing, China. The PBDE concentrations in 10 samples collected in Beijing ranged from 8.47 to 29.02 ng g^{-1}, with BDE-209 as the predominant congener (>85%). Principal component analysis revealed that the major source of PBDEs in Beijing may be potentially associated with deca-BDE. Furthermore, increasing PBDE contamination was observed from northwest to east Beijing. Finally, possible factors affecting contamination of the sandstorm depositions were subsequently explored revealing a significant correlation between ΣPBDEs and the minimum particle size of the sandstorm deposition samples.

Keywords Beijing · China · Pollution · Polybrominated diphenyl ethers · Sandstorm deposition

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals widely used as flame retardants in a wide variety of plastics, textiles and electronic components (Pirard and Pauw 2007). Technical PBDE are synthesized by electrophilic substitution of diphenylether. Therefore 2,2′,4,4′-PBDE isomers dominate in the three commercial formulations: penta-, octa-, and decabromo-diphenylether, named after their mean bromine content (de Wit 2002). PBDEs have the potential for endocrine disruption, bioaccumulation, and long-range transport (Boon et al. 2002; Moon et al. 2007). Recently, certain commercial mixtures of PBDEs (penta and octa formulations) were banned in Europe because of their persistence and potential environmental and human health risks (Kemmlein et al. 2003). However, the demand for PBDEs has been increasing rapidly, and in Asia all commercial BDE mixtures are used without regulation (Tan et al. 2007).

The sources of human exposure to PBDEs remain poorly understood. Natural and anthropogenic organic chemicals are transported within the atmosphere, while deposition events are important in helping remove them (Bidleman 1988). Furthermore, sandstorms which distribute a great number of particles are a special atmospheric occurrence and are frequent in northern China. For example, northern China experienced 11 sandstorms in 2006, one of which covered approximately one-eighth of China and deposited about 330,000 tons of sand and dust in Beijing (Han et al. 2007; Lin and Chen 2007). The regional characteristics of sand and dust sources are mainly arid or semiarid regions covered by deserts or land undergoing desertification in northern China (Wang et al. 2006). Wind-blown sand and floating-dust not only remain in the areas where sandstorms occur, but also extend to neighboring areas. The wind-blown sand extends either northeastward or southeastward, but floating-dust mainly extends southeastward to low-latitude regions such as the East China Plain (Wang et al. 2003). Beijing, the capital of China, is one of the main cities affected by sandstorms, and is one of the most densely populated cities in the world with more than 12 million people. Since PBDEs can easily accumulate on particles, contamination of sandstorm deposition has a direct impact on public health, increasing the risk of

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human exposure via inhalation, ingestion or direct skin contact (Wu et al. 2007). Due to the paucity of data on levels of PBDEs in sandstorm depositions in China, this study investigated the composition, distribution, and characterization of PBDEs in sandstorm deposition samples obtained from urban areas of Beijing. The main objective of this study was to identify the possible sources of pollution in the sandstorm depositions of Beijing.

Materials and Methods

A serious sandstorm that developed in a Mongolian cyclone blew over Beijing on April 16, 2006 (Han et al. 2007). During the sampling period, the climate in Beijing was dominated by temperate semi-wet monsoon conditions, and the mean temperature was 14°C. We obtained sandstorm deposition samples from 10 urban sites in Beijing, China (Fig. 1) on April 17, 2006. The area of the sampling region was 750 km^2. Samples were collected from platforms (0.5–1.0 m high with an area of and 3 m^2) during the daytime (between 8:00 A.M. and 6:00 P.M. [10 h day^{-1}]) when there was no precipitation. Composite samples comprised of three subsamples obtained at each sampling site were then transferred into precleaned amber glass bottles and stored at 4°C until they were extracted, which was usually done within 72 h. We then analyzed the particle size distributions of the sandstorm deposition samples using a Laser Particle Size Analyzer (Mastersizer 2000, Malvern Co., United Kingdom).

A standard solution of PBDE congeners (EO-5278) (Cambridge Isotope Laboratories, USA) was used to quantify the following mono- through hepta-brominated BDEs: BDE-28, 47, 99, 100, 153, 154, 183, and 209. Eight $^{13}C_{12}$-labeled (EO-5277) congener PBDEs and two congener $^{13}C_{12}$-labeled (EO-5275) PCBs were purchased from Cambridge Isotope Laboratories for use as internal surrogate standards and injection standards, respectively. Standard reference material (SRM) NIST-2585 (reference house dust for organic contaminants analysis) was obtained from NIST, USA. All solvents used were pesticide grade (J. T. Baker, USA).

Five grams of each sandstorm deposition sample was weighed then ground with anhydrous sodium sulfate into a free-flowing powder. The samples were extracted with 30 mL of hexane/dichloromethane (1:1, v/v) by ultrasonication for 4 min then separated by centrifugation. This process was repeated three times. Before extraction, 1 ng $^{13}C_{12}$-labeled (EO-5277) PBDE was added as a surrogate standard. The concentrated extracts were then cleaned on a 15-mm i.d. column packed from the bottom to top with 2 g silver nitrate ($AgNO_3$) silica (10%, w/w), 1 g activated silica gel, 3 g basic silica gel (EPA Method 1614, Section 7.5.1.3), 1 g activated silica gel, 4 g acid silica gel (44% concentrated sulfuric acid, w/w), 4 g acid silica gel (22% concentrated sulfuric acid, w/w), 1 g activated silica gel, and 1 cm anhydrous sodium sulfate. The first fraction was eluted with 100 mL hexane then the PBDEs were eluted with 70 mL of hexane/dichloromethane (1:1, v/v). The elution was evaporated with a rotary evaporator and then reduced to 50 μL under a gentle N_2 stream for analysis. Before PBDEs analysis, 1 ng $^{13}C_{12}$-labeled (EO-5275) PCBs was added as an injection standard.

High-resolution GC/MS analysis of the PBDEs was performed on an Autospec Ultima mass spectrometer coupled with an Agilent 6890N gas chromatograph equipped with a CTC PAL autosampler. Ionization was performed with an EI source at an electron voltage of 35 eV according to the optimization parameters of the instrument. The source temperature was 280°C and the resolving power of the analyzer was 10,000. The mass spectrometer was operated in selected ion monitoring (SIM) mode to analyze all PBDE congeners except BDE-209. Gas chromatographic separation prior to MS was performed with a 30 m DB-5MS

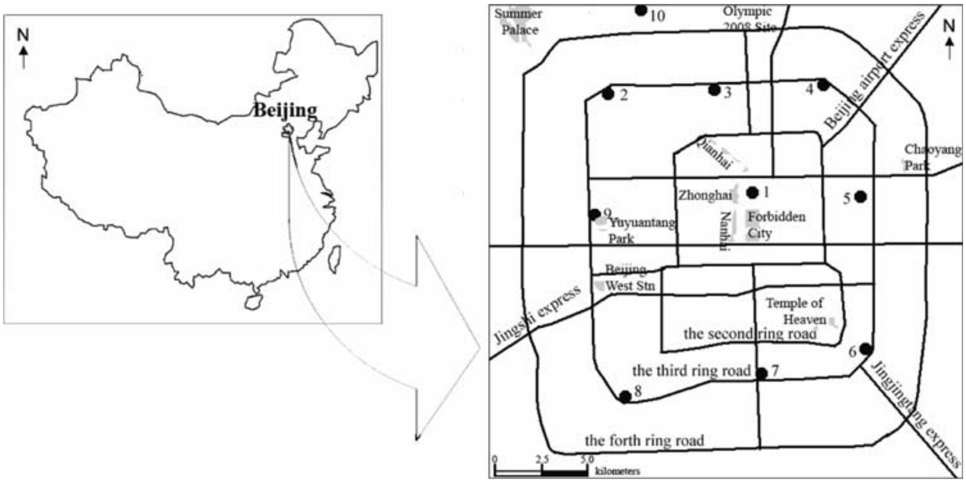


Fig. 1 Sampling sites of sandstorm deposition in urban areas of Beijing

(30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. The GC injector was held constant 290°C. The GC column was maintained at 100°C for 2 min then ramped at 15°C min^{-1} to 230°C, further ramped at 5°C min^{-1} to 270°C, then finally at 10°C min^{-1} to 330°C. The total run time was approximately 24 min. Quantification of the samples was performed using an internal standard method and following EPA 1614 QA/QC protocols (USA EPA, 1999).

Analysis of BDE-209 was carried out with an Agilent 6890 series gas chromatograph coupled with an Agilent 5973 mass spectrometer using negative chemical ionization (NCI) in the SIM mode. The ion source and interface temperatures were set to 150 and 300°C, respectively. The GC was equipped with a split-splitless injector held constant at 265°C. Gas chromatographic separation was performed on a 15 m DB-5MS (15 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column. The GC column was maintained at 80°C for 1 min then ramped at 10°C min^{-1} to 200°C, further ramped at 20°C min^{-1} to 300°C and held at this temperature for 15 min. The total run time was 32 min. Quantification of the samples was performed using the isotope dilution method. The compounds were monitored at 492.7 and 494.7 m/z (for ^{13}C-BDE-209) and 486.7 and 488.7 m/z (for BDE-209). BDE-209 was quantified at 486.7 and 494.7 m/z. The response factor relative to ^{13}C-BDE-209 with recovery determined for ^{13}C-surrogate was also used to quantitate BDE-209 in the samples.

A laboratory method control group was run to demonstrate the lack of interference and cross-contamination. In addition, a procedural blank was run in parallel for every set of six samples to further check for interference and cross-contamination. Duplicate samples were analyzed in the laboratory along with the regular 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 PBDE was performed using an internal standard method except for BDE-209. Three quality control criteria were used to ensure correct identification of the target compounds: (1) GC retention times matched those of the standard compounds within ±0.05 min; (2) the signal-to-noise ratio was greater than 3:1; (3) each compound had two monitored ions. Isotopic ratios between quantification and confirmation ions were within ±15% of theoretical values. The limits of detection (LOD) for PBDE (di- to hepta-BDEs) were within the range of 0.003–0.07 ng g^{-1} (dry weight). Recovery of the $^{13}C_{12}$-labeled (EO-5275) PBDEs surrogate was within the range of 40%–60%. Recovery of the surrogate was satisfactory and no correlation of analytical data applied to the samples. Analysis of BDE-209 was conducted using an isotope dilution method. The results met the criteria and the LOD of BDE-209 was 0.1 ng g^{-1} (dry weight). The recovery of $^{13}C_{12}$-BDE-209 in all samples was in the range of 65%–95%. The results met the acceptance criteria specified in the US-EPA method 1614-draft (25%–150%).

The SRM sample (NIST-2585) was analyzed to validate the analytical method employed. The results were satisfactory, with a z-score of ≤ 1 for all congeners (range: 0.32–0.86 for the PBDEs, $p < 0.05$). Recovery of the $^{13}C_{12}$-labeled (EO-5275) PBDE surrogate was in the range of 50%–60% with the NIST-2585 sample, which also met the acceptance criteria specified in the US-EPA method 1614-draft (25%–150%).

Statistical analysis was carried out with SPSS 13.0 for windows (SPSS, Chicago, IL, USA). Principal component analysis (PCA) is a multivariate statistical technique used to derive new components (principal components [PCs]) as a linear combination of the original variables, while principal components (PCs) attempt to preserve the statistical relationships present in the original data. In present study, inter-species variations in the PBDE congeners were investigated using PCA. The initial variables considered were the concentration values of the PBDE congeners. The PBDEs values were normalized to a percentage of the sum all congeners. Rotation was used in the PCA through the varimax method to facilitate interpretation of the results.

Results and Discussion

PBDEs were identified in 10 sandstorm deposition samples. The total PBDE concentrations (defined as the sum of BDE-28, 47, 99, 100, 153, 154, 183, and 209) ranged from 8.47 to 29.02 ng g^{-1} (median: 14.06 ng g^{-1}, dry weight) (Table 1). The highest concentration was found at site 5 (29.02 ng g^{-1}, dry weight) and the lowest value was found at site 7 (8.47 ng g^{-1}, dry weight). There are few previous studies on sandstorm deposition. Furthermore, sandstorm deposition directly influences surface soil. Therefore, we compared the soil concentrations of PBDEs reported elsewhere in the literature. In comparison with other areas of China, the median concentration in the present study was much lower than those obtained in an e-waste pollution area in southeast China (33–974 ng g^{-1}, dry weight) (Leung et al. 2007). Compared to soils from some developed countries, on the other hand, the levels were higher than those in surface soil in the United Kingdom and Norway (65 and 12000 pg kg^{-1}, dry weight, respectively) (Hassanin et al. 2004).

Of the PBDE homologues, the dominant PBDE detected in this study was BDE-209, accounting for over 85% of the total in all sampling locations, followed by BDE-183 (median: 2.4%) and BDE-47 (median: 2.1%) (Table 1). Lower brominated congeners were detected at relatively low concentrations. The ratio of BDE-47 to BDE-99

Table 1 Total concentration of PBDEs in each sample

Sample	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	ΣPBDEs
1	0.14	0.31	0.18	0.02	0.11	0.06	0.29	12.67	13.97
2	0.15	0.37	0.20	0.03	0.15	0.08	0.58	12.53	14.35
3	0.10	0.25	0.12	0.02	0.10	0.05	0.33	9.16	10.33
4	0.12	0.30	0.16	0.03	0.16	0.13	0.48	13.57	15.25
5	0.13	0.32	0.25	0.04	0.66	0.18	1.86	25.13	29.02
6	0.13	0.26	0.14	0.03	0.11	0.06	0.33	14.84	16.15
7	0.28	0.59	0.20	0.04	0.08	0.05	0.20	9.12	8.47
8	0.08	0.14	0.08	0.01	0.05	0.03	0.10	11.76	12.38
9	0.15	0.26	0.11	0.02	0.08	0.05	0.18	7.42	10.79
10	0.09	0.22	0.12	0.02	N.D.	N.D.	0.15	13.40	14.16

Data are in units of ng g^{-1}; N.D., not detected

detected in the sandstorm deposition samples was 1.8 as a median, while Bromkal 70-5DE as a typical penta-BDE product shows a ratio of about one for these two congeners (Sjödin et al. 1998). The PBDE congener profile of the sandstorm deposition was similar to that of technical deca-BDE products (Saytex 102E and Bromkal 82-0DE) (La-Guardia et al. 2006). This profile is reasonable since BDE-209 firmly bound to particles due to its low volatile property. BDE-209 was also the main PBDE homologue in an e-waste pollution area in southeast China (Leung et al. 2007). The main PBDE homologue in atmospheric deposition samples from Korea (93%) (Moon et al. 2007) and house dust from Singapore was also BDE-209 (88%) (Tan et al. 2007), highlighting the prevalent use of deca-BDE as a flame retardant in Asia.

Correlation analysis was performed to investigate the sources of the PBDE congeners in the dry deposition samples (Table 2). Significant correlations existed among low-brominated congeners including BDE 47, 99, 100, 153, and 154. However, high-brominated congeners (including BDEs 183 and 209) showed no significant correlation with low-brominated congeners. This pattern suggests that the sources of lower molecular-weight PBDEs are different from high-brominated congeners (Moon et al. 2007). These findings are consistent with the findings of a previous study conducted in Korea (Moon et al. 2007). The strong relationship between BDE-209 and the sum of the PBDEs can be explained by the predominance of BDE-209 in the total PBDE concentration. The major source of the PBDEs was therefore thought to be a currently used Deca-BDE product in Beijing.

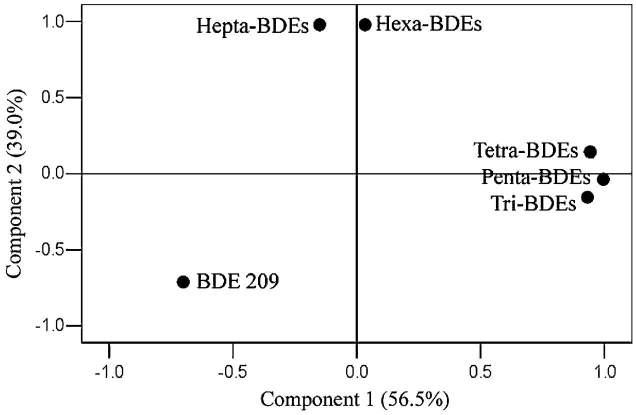


Fig. 2 Two-dimensional principal-component loading plot obtained from the data correlation matrix of 10 sandstorm deposition samples in Beijing

Table 2 Spearman's rank correlation coefficients between different congeners ($p < 0.05$)

	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183	BDE209
BDE47	0.818							
BDE99	0.552	0.903						
BDE100	0.479	0.806	0.855					
BDE153	0.273	0.624	0.721	0.697				
BDE154	0.358	0.709	0.782	0.782	0.988			
BDE183	0.261	0.600	0.721	0.612	0.939	0.903		
BDE209	0.097	0.103	0.442	0.527	0.600	0.588	0.491	
ΣPBDE	0.152	0.152	0.442	0.503	0.673	0.661	0.564	0.927

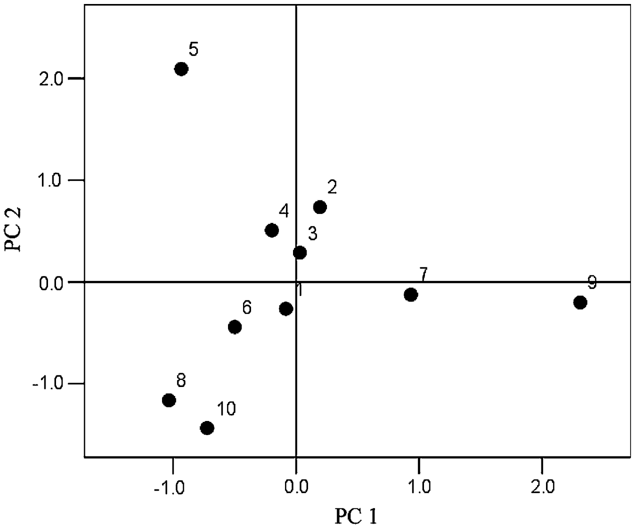
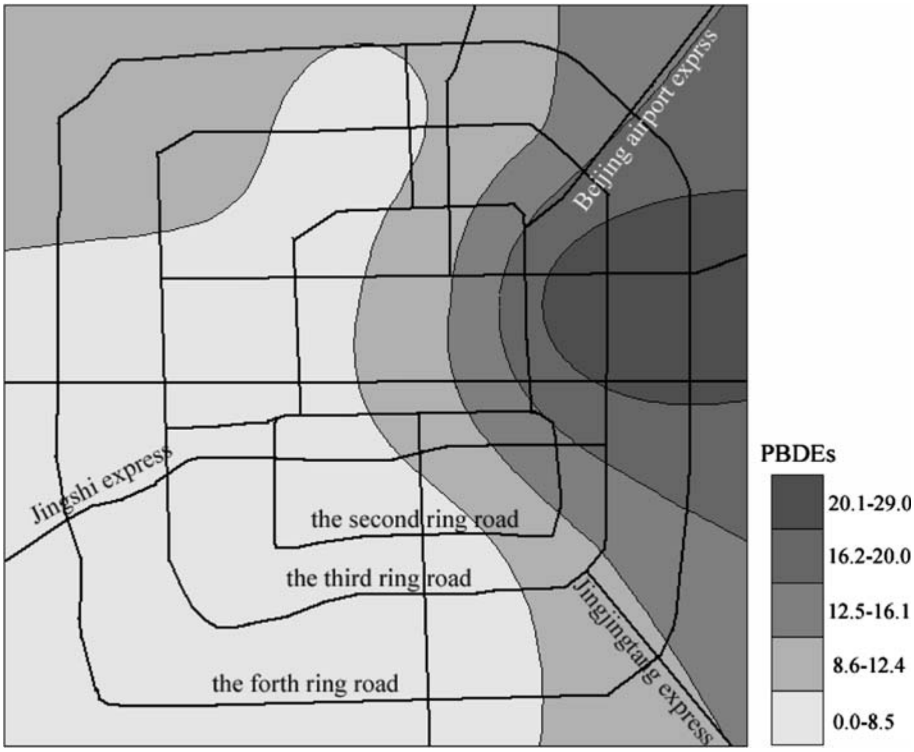


Fig. 3 Two-dimensional principal-component score plot obtained from the data correlation matrix of 10 sandstorm deposition samples in Beijing

PCA progress was also performed to evaluate similarities or differences between the PBDE congener patterns of each sample; all data were normalized to percent of ΣPBDEs. PCs were determined by an eigenvalue of over 1. By processing, two extracted PCs could explain 95.5% of the data variance. A loading plot and score plot rotation were obtained after varimax. Component 1 in Fig. 2 accounted for 56.5% of the total variance and was characterized most positively by tri-, tetra-, penta-BDEs and was most negatively characterized by BDE-209, while component 2 accounted for 39.0% and was characterized by Hexa- and Hepta-BDE congeners. The score plot (Fig. 3) indicated that the compositions of PBDEs in the Beijing samples were similar, possibly originating from the same source. The PBDEs found in Beijing could therefore be classified into one main group relatively highly contaminated by BDE-209. A clear clustering of samples was also observed, showing that BDE-209 is indeed the dominant contaminant in Beijing. Deca-BDE mixture is the most widely used commercial mixture, and comprises 97% BDE-209 (Schecter et al. 2005). This is consistent with the prevalent use of deca-BDE as a flame retardant in Beijing.

The distribution of ΣPBDEs in the sandstorm deposition samples is shown in Fig. 4, revealing an increasing trend from northwest to east Beijing. It is interesting to explore a correlation between ΣPBDEs and the minimum particle sizes of the sandstorm deposition samples. The particle size distributions of the sandstorm deposition samples were analyzed using a Laser Particle Size Analyser, when the particles suspended in water. A significant correlation existed between the ΣPBDEs and minimum particle sizes ($r = 0.80, p < 0.05$). This indicated that the ΣPBDEs were associated with the particle size distribution and that they were removed through the scavenging of particulates (Butt et al. 2004). Furthermore, Beijing, as mentioned above, was relatively highly contaminated by BDE-209, suggesting that PBDEs are strongly associated with the degree of urbanization (Stapleton et al. 2005).

Fig. 4 Distribution of ΣPBDEs in urban areas of Beijing (data units in the figure are nanograms per gram)



Another possible reason is the influence of the northwest wind during the study period. As a result, BDE-209 from local sources could have been absorbed by smaller atmosphere particles that mixed with the passing sandstorm deposition before being transported and deposited in eastern areas of Beijing, resulting in higher concentrations.

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