LEVELS AND TRENDS OF POLYBROMINATED DIPHENYLETHERS IN AIR AND SOIL OF HARBIN IN CHINA

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Abstract
This study presents for the first time, to our knowledge, a set of concurrently sampled data in both ambient air and topsoil for polybrominated diphenyl ethers (PBDEs) in Chinese city. Both air and soil samples were collected from 6 locations on a transaction across Harbin, a city in northeast of China in 2006. Concentration levels of total PBDEs (BDEs 28, 47, 99,100， 153, and 154) ranged from 2 to 35 pg/m^3 with a mean of 15 pg/m^3 in air samples, and from 3 to 41 pg/g with a mean of 16 pg/g dry weight in soil samples, which were low in comparison to those in other cities. In both air and soil samples, concentrations clearly decrease with increasing distance from the city center, supporting the existence of a phenomenon of urban "pulse". This indicated that PBDEs volatilized from treated products indoors in the city are a source of PBDEs found in outdoor air and soil within and surrounding the city. The higher ratios of BDE 47/99 in air than in soil were also observed in this study, supporting the hypothesis that PBDEs volatilize from treated products indoors, and transports outdoors, where congener 99 undergoes preferential atmospheric deposition and accumulation in soil.

Introduction
Polybrominated diphenyl ethers (PBDEs) are congeners of a class of environmental contaminants that have been present in the environment for decades. PBDEs were first identified in the River Viskan in Sweden[1] and have since then been recognized as an environmental contaminant with a global distribution[2,3]. These compounds have been found in measurable amounts in different environmental media (sediment, air, soil, water and various organisms) and in human tissues.[4,5]

Major commercial products principally contain penta-, octa-, and deca-BDE mixtures. The penta-product contains a mixture of tetra- to hexa-BDEs including BDE 47, 99, 100, 153 and 154, as well as trace amounts of BDE 17 and BDE 28. The octa-product consists primarily of BDE 183, followed by BDE 153 and BDE 154, whereas the deca-product is mostly composed of BDE 209 (>97%).[6,7] The annual worldwide consumption of PBDEs was about 70,000 metric tons, of which 49% was used in North America, 37% in Asia, and 12% in Europe[8]. In China, the domestic production of PBDEs was 10,000 t in 2000. The domestic demand of PBDEs has increased at a rate of 8% annually in China[9].

This study reports concentrations of a number of PBDE congeners in outdoor air samples (using PUF disk passive air samplers) and also topsoil samples taken from 6 locations on a transection across Harbin in China, by covering distances from spatial variation between a range of rural, suburban, and urban locations. We focused on BDEs 28, 47, 99,100, 153, and 154. These congeners were selected for: (i) they have been identified as the most abundant in air [10] and soil [11], and (ii) they are the principal congeners monitored in previous comparable studies[12,13].

Materials and Methods

Air Sampling. Six sampling sites were chosen including one background tow rural and three urban sites. Passive air samplers (i.e., polyurethane foam PUF disks) were employed. These have been used successfully in other studies[10, 14]. Prior to deployment, disks were washed thoroughly in tap and distilled water sequentially to remove loose material, then extracted in hexane using a Soxhlet apparatus for 48 h to remove any target or interfering compounds. Following extraction, disks were desiccated to remove solvent, spiked with known quantities of PCBs 65 and 155 as

QA/QC standards to provide a measure of contaminant loss during sampling, and stored in pre-cleaned foil in airtight solvent-cleaned glass jars. On deployment, disks were removed from the jars on site and transferred into the shelters. At the end of each sampling period, disks were removed from shelters and stored in solvent-cleaned aluminum foil in airtight glass jars at 4°C until extraction. Conversion of contaminant masses per sample into concentrations in air requires knowledge of the air sampling rate of the PUF disk samplers employed and the sampler deployment time. Examination of the literature relating to sampling rates of similar PUF disk sampler configurations employed outdoors led us to select a sampling rate of 3.5 m^3 day^{-1} for PBDEs.

Soil Sampling. Soil samples were collected at the same locations as the air samples, at the end of each air sampling period. At each sampling event, 3 subsamples were taken using a soil corer to 5 cm from the same 10 m×10 m area immediately adjacent to the air sampler. Samples were pooled, transported back to the laboratory, immediately transferred to clean, solvent-rinsed, amber glass storage bottles, sealed, and stored at -20 °C until analysis. Before extraction, soil samples were homogenized. An accurately weighed 20 g
subsample was mixed with anhydrous sodium sulfate (20 g), and transferred to a clean Soxhlet apparatus.

Results and Discussion

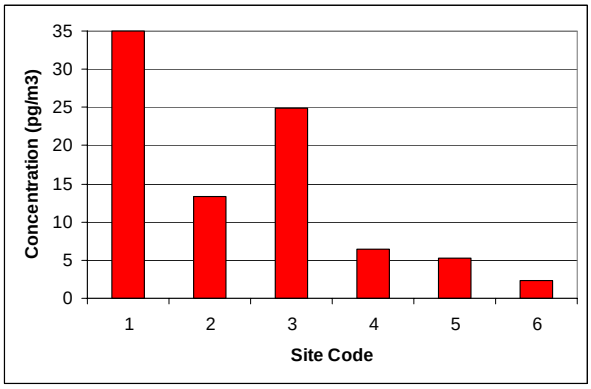

Fig.1 Spatial variation of total PBDE congeners concentrations (pg/m^3) in air samples

PBDE Concentrations in Air. BDE-28, 47, 99, 153 and 154 are detected in all samples across Harbin, and the results are showing in Table 1, but BDE-100 could not be detected in all the air and soil samples. Total PBDE values were generally low, ranged from 2.4 to 35 pg/m^3, similar to the results in Japan, Korea, Singapore, and most of China[15], the West Midlands of the UK[13], Great Lakes basin [16], and Toronto[14], but lower than that from Guangzhou background (105 pg/m^3) [17]. Table 1 also indicates that BDE-47 and 99 are predominant congeners in passive air samples accounting from 24 to 50% of the amount for total five congeners.
Spatial variation of total PBDE congener concentrations in air samples is depicted in Figure 1. A clear "urban pulse" was revealed in this study, in which concentrations are highest at urban areas (Sites 1-3), and decrease with distance from the urban sites, the suburban (Sites 4 and 5) and then the background site (Site 6).

TABLE 1. Concentrations(pg/m^3) of PBDEs in Air Samples

site/reference	28	47	99	153	154	∑BDE	47:99 ratio
1 (Urban)	2.61	18.29	6.94	3.81	3.32	34.97	2.64
2 (Urban)	1.13	6.8	4.41	0.45	0.57	13.37	1.55
3 (Urban)	3.8	12.84	6.52	0.79	0.91	24.85	1.97
4 (Rural)	1.13	3.48	1.29	0.22	0.33	6.46	2.7

5 (Rural)	1.08	2.33	1.32	0.29	0.23	5.24	1.77
6 (Background)	0.93	0.6	0.6	nd	0.28	2.41	1
Mean	1.78	7.39	3.513333	1.112	0.94	14.55	

PBDE Concentrations in Soil.
Table2 summarizes concentrations (pg/g dry weight (dw)) of PBDEs in soil samples taken in this study. The total concentration levels of PBDEs in soil samples, ranged from 2.72 to 40.73 pg/g dw with a mean of 16.3 pg/g dw were lower than those in West Midlands of the UK. While BDE congeners 28, 47, 99, 153 and 154 were the major constituents of BDEs in the air samples, while only BDE28, 47 and 99 could be detected in soil samples, and BDE 153 and 154, both belong to penta-product, could hardly be found in soil sample. In addition, Figure 2 reveals that total BDE concentrations in the soil samples, as those in air samples shown in Figure 1, were also reveal a clear "urban pulse".

TABLE 2. Concentrations(pg/gdw) of PBDEs in Soil Samples

site/reference	28	47	99	153	154	∑BDE	47:99 ratio
1 (Urban)	3.24	7.66	8.52	2.93	nd	22.35	0.90
2 (Urban)	4.30	0.31	0.59	nd	nd	5.20	0.53
3 (Urban)	2.15	9.11	29.47	nd	nd	40.73	0.31
4 (Rural)	2.01	2.84	8.59	nd	nd	13.43	0.33
5 (Rural)	1.47	4.63	7.43	nd	nd	13.53	0.62
6 (Background)	1.13	1.57	nd	nd	nd	2.70	nd
Mean	2.38	4.35	10.92	2.93	nd	16.32	

Sources of PBDEs. In line with previous indications[12, 14], the existence of the "urban pulse" observed in this study is strong evidence that urban areas act as sources of PBDEs. The source of PBDEs in the outdoor air measured in this study could be from indoor environments contaminated with PBDEs due to the use of stuffs containing PBDEs, such as furnishings and electronic goods, in urban areas, resulted in significant emissions when these environments exchange air with outdoors.
As previously reported[13], the higher ratios of BDE 47:99 in air than in soil were also observed in this study (see Tables 1 and 2). Harrad and Hunter[13] gave their explanation that PBDEs volatilize from treated products indoors, and transports outdoors, where congener 99 undergoes preferential atmospheric deposition and accumulation in soil. This is due to the higher K_{OA} of BDE 99 relative to BDE 47.

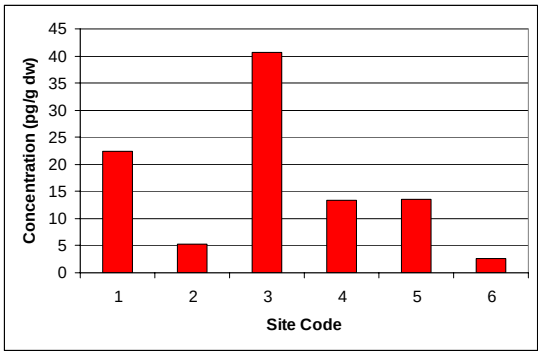

Fig.2 Spatial variation of total PBDEs concentrations (pg/g dw) in soil samples.

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