LEVELS AND DISTRIBUTION OF POLYBROMINATED DIPHENYL ETHERS IN URBAN ROAD DUST FROM YANGTZE RIVER DELTA, CHINA

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Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used as flame retardants in various polymers. Due to various health and environmental threats posed by PBDEs, penta-BDE and octa-BDE commercial products were listed as POPs under the Stockholm Convention. Previous studies have highlighted the occurrence of PBDEs in the urban environment, especially in gases or particles of the urban atmosphere. Particulate PBDEs of the urban atmosphere can be accumulated in road dust via atmospheric deposition[1]. Road dust is thought as environmental reservoirs for POPs in the urban environment[2]. Road dust POPs may have adverse effects on the aquatic ecosystem through urban stormwater runoff, and may lead to contamination of vegetables and food chains. In addition, road dust POPs will go back to the atmosphere carried by the wind or volatilization. It was reported that road dust could constitute over 10% of PM2.5 in the atmosphere of urban environment[3].The fugitive dusts can pose serious risks to humanhealth through inhalation[4], especially for street sweepers, pedestrians, street vendors and traffic policemen. Therefore, POPs pollution in road dust has been a serious concern for the urban environment. Suzhou, Wuxi and Nantong are the emerging industrial cities in the Yangtze River Delta, China. Currently they are facing serious aerosol particulate pollution problems due to the rapid growth of industrial productions, including various combustion processes, traffic congestions, and the large-scale construction activities. Investigating the occurrence and the level of PBDEs pollution in road dust of these cities can help us better understand the environmental fate and behaviour of PBDEs in the urbanized areas.

Materials and methods

Three land use classes including the industrial area, the residential/commercial area and the suburb park were chosen as the representative sampling sites. Road dust samples were collected from the same type of road surface (i.e., pavements with cement brick). Samples were collected from a rectangular block (2 × 10 m) along the road by sweeping with a small brush.

The mixed standards of eight native PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209) and $^{13}C_{12}$-PCB209 were obtained from Accustandard Inc. (USA). The mixed standards of eight $^{13}C_{12}$-labeled PBDEs were obtained from the Cambridge Isotope Laboratories, Inc. (USA). All solvents used (Methylene dichloride, n-hexane and acetone) were of pesticide grade (Tedia, USA).

ASE with solvent containing hexane and dichloromethane (1:1, v/v) were chosen as the sample extraction method for the samples. An aliquot of 5.0 g of sieved fractions of road dust mixed with 5.0 g of acid washed copper powder was added to extraction cell of ASE300 (Dionex, USA). Prior to extraction, all samples were spiked with surrogate standard to monitor the analytical recovery efficiency. The majority of the lipids were removed by adding concentrated H_2SO_4 to each extract. Then, the concentrated extracts were further cleaned individually by a multilayer silica gel column (10 mm i.d.) packed with, from the bottom to top, a little absorbent cotton, anhydrous Na_2SO_4 (1 g), activated silica (1 g), florisil (2 g), activated silica (1 g), sodium hydroxide/silica (3 g 33%, w/w), activated silica (1 g), sulfuric acid/silica (8 g 44%, w/w), activated silica (1 g), and anhydrous Na_2SO_4 (1 g). The silica gel column was pre-eluted with 80 mL of hexane prior to adding to the extract. The fraction eluted with hexane and dichloromethane (8:2, v/v, 120 mL) was intended for the collection of the PBDE congeners. Finally, the eluants were concentrated to approximately 200 µL. An internal standard, 50 ng $^{13}C_{12}$-PCB-209, was added to the final extract prior to the instrumental analysis.

Extracts were analyzed for BDE-209 using GC/MS (QP2010Shimadzu, Japan) operated negative chemical ionization (NCI) with methane as reagent gas and ZB-5HT MS column (15 m × 0.25 mm × 0.1 µm). Pulsed-splitless injection (180 kPa, 1 min) was used to minimize degradation of BDE-209 in the injector liner. The initial oven temperature was 100°C for 1 min and raised at 30 °C/min to 240°C, then raised at 20 °C/min to 320°C and held for 5 min. Extracts were analyzed for 7 BDE congeners using electron ionization (EI) and with a DB-5 MS column (30 m × 0.25 mm × 0.25 µm). The initial oven temperature was 60°C for 1 min and raised at 30 °C/min to

220°C, then raised at 10 °C/min to 310°C and held for 5 min.

The surrogate in all the samples ranged from 50% to 128%. Concentrations of BDE congeners in all samples were corrected by recoveries of $^{13}C_{12}$- labeled BDEs. Procedural blanks were analyzed and no target compounds were detected except BDE-209. The limit of the detection of the method (MDLs) for 7 BDE congeners ranged from 0.1 to 0.2 µg/kg and 4.0 µg/kg for BDE-209. Concentrations of BDE-209 in all samples were corrected by subtracting value of blank.

Results and discussion

Descriptive statistics for the content of PBDEs in the road dust samples (n = 58) are summarized in Table 1 . The detection frequency for 8 BDE congeners was between 51.7% and 100% in the road dust samples. The high detection frequency may suggest that these compounds have become ubiquitous in outdoor environments. The concentrations of Σ_7PBDEs and BDE-209 in the road dust samples ranged from ND to 35.5 µg/kg (4.34 µg/kg as geometric mean), and 4.01 to 1439 µg/kg dw (163 µg/kg as geometric mean), respectively. The concentration of the Σ_7PBDEs and BDE209 in this study were higher than that reported around world rencent years. It is worth to mention that the level of BDE-209 observed in the present study was comparable to that in home dust from Europe[5] (60–467 µg/kg),only lower than that in soil near the PBDEs production area, Laizhou, China[6] (576 µg/kg). The findings suggested that the higher PBDEs contaminant in road dust of these cities was serious, and should be considered in human exposure assessments in the future.

Table 1. Descriptive data of PBDEs in road dust from Suzhou, Wuxi and Nantong (µg/kg dw).

	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209
Detection (%)	93.1	96.6	51.7	65.5	70.7	72.4	87.9	100
Mean	0.45	1.79	0.32	1.75	0.59	1.11	3.03	322
Geomean	0.24	1.03	0.45	1.36	0.50	0.96	1.92	163
Median	0.20	1.03	0	0.67	0.24	0.53	1.62	272
Maximum	5.62	18.7	3.09	16.8	4.42	7.66	18.7	1439
Minimum	ND	ND	ND	ND	ND	ND	ND	4.01
St. Dev.	0.796	2.91	0.59	3.49	0.82	1.48	4.05	361

ND: less than the method detection limit.

BDE-209 was the major BDE congeners, accounting for 96.7% (89.4–99.8%) to Σ_8PBDEs in the road dust samples. Levels of individual 7 BDE congeners in all samples were approximately 1–2 orders of magnitude lower than the BDE-209. The results were consistent with the dominance of commercial deca- BDE mixtures accounting for most of the PBDE mixture production and usage in China. Recent studies demonstrated that BDE-209 in urban ambient air mainly come from combustion sources[7]. During the combustion processes, BDE-209 could form or not be completely destroyed[7,8]. In addition, Fugitive emissions from PBDE-containing products indoors or from disposal of PBDE-containing products could also contribute BDE-209 to the outdoor environment. Except for BDE-209, BDE-183 was the main congener among 7 BDE congeners in all samples. Like BDE-209, BDE-183 has a tendency to strongly attach to particles, and dry deposition flux of BDE-183 is higher than lighter brominated PBDEs. Furthermore, since BDE-183 is a marker congener of the octa-BDE products, higher than that in the Penta-BDE products (0.1% in DE-71 and 0.33% in Bromkal 70-5DE, respectively)[9]. The results indicated that the octa-BDE products may have been used in in the Yangtze River Delta, whose amounts are much lower than deca-BDE products.

BDE-47, 99, 100, 153, and 154 were usually found in the technical penta-BDE mixture (La Guardia *et al.*, 2006). In the present study, the mean values of BDE-47 and 99 contributed 29.5% and 29.4% to Σ_6PBDEs in the road dust samples, respectively. The compositional pattern of 6 BDE congeners found in the road dust samples was not completely consistent with that of the commercial penta-BDE product (Fig. 1). Compared with the penta-BDE product and other urban environmental matrices collected from China, the results indicated that the proportions of BDE-28 of Σ_6PBDEs in the road dust were lower than that in the air, but greater than that in Bromkal 70-5DE (0.12%), DE71 (0.23%) and other matrices. It was reported that BDE-28 is often primarily associated with the gas phase in the urban atmosphere[10]. The results indicated that road dust could accumulate gas-phase and particle-phase PBDEs from the surrounding air. Moreover, relatively higher proportion of BDE-153 was found in the road dust samples than in Bromkal 70-5DE, DE-71(Fig. 1). Previous research reported that BDE-153could form during the metallurgical processes[11], and BDE-153 also could be from Octa-BDE sources,

as commercial Octa-BDE mixtures contain BDE-153 [9].

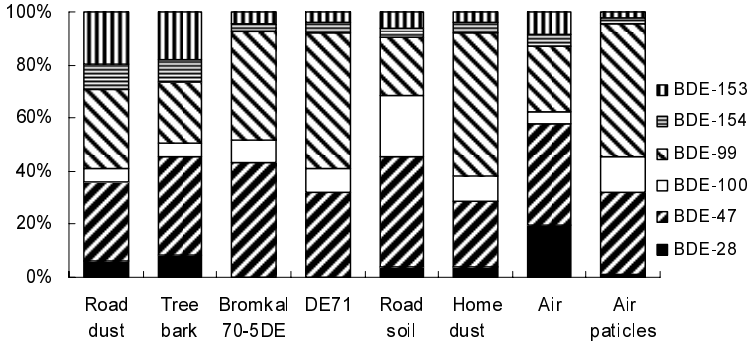

Fig. 1. PBDE congener profile comparison between the penta-BDE technical mixture and other matrix.

Fig. 2 showed that the levels of dust PBDEs in each city. The mean concentration of Σ_8PBDEs in the road dust samples followed the order of Nantong > Suzhou > Wuxi. The highest concentration was observed in the industrial area of Nantong, and the lowest concentration was observed in the suburb park in the dust samples. This suggested that the road dust samples could play important roles in identifying PBDEs depositional regions and exploring spatial trends. The road dust usually stays on the surface of pavements for a short period of time, reflecting mainly the present air pollution.

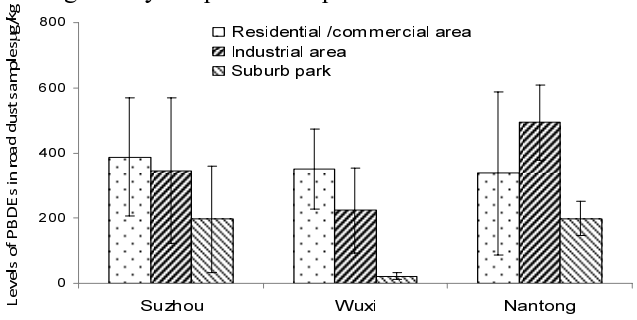

Fig. 2. Levels of Σ_8PBDEs in road dust samples collected from Suzhou, Wuxi and Nantong. Error bars correspond to one standard deviation.

The mean concentration of Σ_8PBDEs in the road dust samples collected from the commercial/residential areas has the same order of magnitude as that from the industrial areas. The road dust contamination in the suburb parks was the least among different land use areas. However, the concentration of PBDEs in the commercial/residential areas was found to be higher than in the industrial areas in Suzhou and Wuxi. PBDE contributions to the atmosphere from vehicles emissions should not be ignored. Previous studies found that while no commercial PBDE mixtures were added to the motor vehicles fuels, PBDEs were still found in their flue gases and exhausts[7,8]. Particulate PBDEs caused by vehicle-based exhausts in the commercial/residential areas might be a major contributor to the road dust. Another plausible explanation is that the relatively high PBDEs in the road dust collected from the commercial/residential areas might be associated with the size of particulates. Some researches indicated that the proportion of fine particles in the urban dusts is higher than in the industrial dusts[12], because of the higher fine particulates depositional fluxes in the urban areas than in the industrial areas[13]. Meanwhile, PBDEs are distributed disproportionally between the fine and coarse fractions (i.e., more PBDEs in the fine fraction than in the bigger coarse particles fraction[14]). Other study showed that fine particulate matters in urban atmosphere were identified mainly from automobiles and coal combustion sources[15], which contain numerous PBDEs, especially to BDE-209. Therefore, high concentrations of PBDEs in the road dust were founded in the commercial/residential sites. Conversely, high concentration of PBDEs detected in the road dust samples from industrial areas of Nantong indicated significantly higher PBDEs emissions from plants located in this area.

In this study, the contents of soil TOC ranged from 2.73% to 25.2%, and the correlation coefficients between individual PBDE and soil TOC were calculated by Pearson correlation analysis, and the results are presented in Table2. Low correlations were found between the concentrations of $\sum_8$PBDE and TOC contents in the present study(r = 0.024-0.193). This result may be attributed to the unhomogeneous dust samples in different sites, and also impacted by transport, mixing, degradation, depositional mechanisms associated with PBDEs. In addition, relatively good correlations were found among the PBDEs (including 28, 47, 100, 99, 154, 153), with correlation coefficient ranging from 0.608 to 0.952, indicating a common source and similar environmental behavior. However, BDE-209 and BDE-183 showed relatively moderate correlation with less highly brominated congeners, correlation coefficient were ranging from 0.420 to 0.728 and 0.470 to 0.787 respectively. This pattern suggests that the sources of lower molecular-weight PBDEs are possibly different from the sources of BDE-209 and BDE-183.

Table 2. Spearman's rank correlation coefficients between total organic carbon (TOC) and individual PBDEs

	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209
BDE-28								
BDE-47	0.772							
BDE-100	0.660	0.858						
BDE-99	0.608	0.903	0.952					
BDE-154	0.806	0.796	0.820	0.768				
BDE-153	0.795	0.797	0.758	0.756	0.935			
BDE-183	0.704	0.653	0.502	0.470	0.780	0.787		
BDE-209	0.587	0.547	0.455	0.420	0.689	0.625	0.728	
TOC	0.193	0.099	0.027	0.024	0.144	0.098	0.150	0.177

Correlation is significant at the 0. 05 level (2-tailed).

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