



Monitoring of Airborne Polybrominated Diphenyl Ethers in the Urban Area by Means of Road Dust and Camphor Tree Barks

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ABSTRACT

Urban road dust and camphor tree bark samples were collected in June of 2009 from Suzhou, Wuxi and Nantong in the Yangtze River Delta, China. Eight polybrominated diphenyl ether (PBDE) congeners (BDE-28, 47, 100, 99,154, 153, 183 and 209) were measured to determine the levels and compositional profiles in the samples. The concentrations of Σ_7 PBDEs and BDE-209 ranged from N.D to 35.5 $\mu\text{g}/\text{kg}$ and 4.01 to 1439 $\mu\text{g}/\text{kg}$ dry weight (dw) in the road dust samples, 5.1 to 799 $\mu\text{g}/\text{kg}$ and 121 to 3243 $\mu\text{g}/\text{kg}$ lipid weight (lw) in the tree bark samples, respectively. BDE-209 was the predominant congener (contributing to 64.1–99.8% of Σ_8 PBDEs) in all samples. Apart from fugitive emissions from PBDE-containing products, combustion processes and vehicles emissions could also contribute BDE-209 to the road dust and tree bark samples. On average, the PBDEs contamination degree in three cities follow the order of Nantong > Suzhou > Wuxi. Road dust and tree bark proved to be an effective accumulator to reflect the degree of atmospheric PBDEs pollutants in the urban environment.

Keywords: Road dust; Tree bark; Polybrominated diphenyl ethers; Urban area.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are extensively used as flame retardants in various polymers, and especially in electronic equipment such as computers and television sets (de Wit, 2002). Studies have shown certain PBDEs possess the properties of persistent organic pollutants (POPs), i.e., persistent, bioaccumulative, toxic and long-range transportable (de Wit, 2002). Due to various health and environmental threats posed by PBDEs, two major commercial PBDE products (penta-BDE and octa-BDE) were listed as POPs under the Stockholm Convention and have been banned in many countries (Ali *et al.*, 2011).

PBDEs are 'additive' flame retardants and may volatilize into ambient air during production, use and disposal of PBDEs-containing products (de Wit, 2002). Recent studies demonstrated that the lighter brominated PBDEs in urban ambient air mainly come from indoor air, while the highly brominated ones mainly come from combustion sources (Wang *et al.*, 2010, 2011). The studies also demonstrated that PBDEs could form or not be completely destroyed in combustion processes. PBDEs with high concentrations

and amounts from various combustion processes could condense onto the fly ashes or in the flue gases, and then release to the outdoor air. Incinerators, power plants, metallurgical processes and vehicles were recently identified as PBDEs emission sources, which could contribute significant PBDEs to the atmosphere (Wang *et al.*, 2010; Tu *et al.*, 2011; Wang *et al.*, 2011). Many studies have reported that atmospheric PBDEs concentration is higher in industrial areas than in residential areas. However, other studies have reported that the urban environment PBDEs are mainly generated in densely populated locations (Harrad and Hunter, 2006; Mandalakis *et al.*, 2009). Altogether, previous studies have highlighted the occurrence of PBDEs in the urban environment, especially in gases or particles of the urban atmosphere (Chen *et al.*, 2006; Harrad and Hunter, 2006; Deng *et al.*, 2007; Mandalakis *et al.*, 2009).

Road dust is thought as environmental reservoirs for POPs in the urban environment (Offenberg *et al.*, 2003). 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 (Maltby *et al.*, 1995). 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 $\text{PM}_{2.5}$ in the atmosphere of urban environment (Yu *et al.*, 2013). The fugitive dusts can pose serious risks to human health through inhalation (Mandalakis *et al.*, 2009), especially for street sweepers, pedestrians, street vendors and traffic

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policemen. Therefore, POPs pollution in road dust has been a serious concern for the urban environment.

Particulate POPs of the urban atmosphere can be accumulated in road dust via atmospheric deposition (Hassanin *et al.*, 2004). Therefore, road dust can be used as an indicative matrix to reflect the degree of POPs pollutants in the urban atmosphere. Besides road dust, tree bark has been used as a passive sampling medium for monitoring atmospheric POPs for many years (Hermanson and Hites, 1990). Tree bark contains some lipid and its surface is very porous. Hence, it accumulates both gas-phase and particle-phase POPs simultaneously from the surrounding air (Wang *et al.*, 2004). In the present study, urban road dust and camphor tree bark were used as indicators to reflect the level of PBDEs pollutants in the urban atmosphere.

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, traffic congestions, and the large-scale construction activities. As major production center for electronics, textiles and telecommunication equipment in China, the annual production of PBDEs is very high. Therefore, investigating the occurrence and the level of PBDEs pollution in these cities can help us better understand the environmental fate and behaviour of PBDEs in the urbanized areas.

METHODS

Sampling

Three land use classes including the industrial area, the residential/commercial area and the suburb park were chosen as the representative sampling sites. The residential/commercial areas refer to the traditional urban areas with dense population in the present study. The suburb parks are about 5–10 km away from the center of the cities with limited anthropogenic activities.

Fifty-eight road dust samples were collected from the same type of road surface (i.e., pavements with cement brick). Samples were collected by sweeping the street surface with a small brush. Each sample was a composite of five subsamples collected from a rectangular block (2 × 10 m) along the road. Samples were wrapped in aluminum foil, sealed in polyethylene bags and stored in a portable refrigerator, and then transported to the laboratory. The air-dried dust samples were ground and sieved through a 0.15 mm sieve, and kept at –20°C until extraction.

The fragrant camphor tree (*Cinnamomum camphora* L.) belongs to the frequently green arbor. As an urban street or shade tree, the camphor tree is widely planted in the Yangtze River Delta. The bark of the camphor tree is very porous, and the absence of metabolic processes makes it almost inert in the presence of inorganic and organic substances. So it is well suitable for the monitoring of airborne pollutants (Zhao *et al.*, 2008). In the present study, forty bark samples were taken from the camphor trees with their diameter over 20 centimeters. The external surface of the bark, not exceeding 3 mm in depth, was removed by a hard steel knife from different areas of the whole circumference of

each tree at 1–1.5 m height. Each sample was a composite of 3–5 subsamples collected from different trees, which were within 20 meters from each other. Samples were wrapped in aluminum foil, sealed in polyethylene bags and stored in a portable refrigerator, and then transported to the laboratory. The bark sample was cut into pieces of < 1 cm and kept at –20°C until extraction. The lipid concentration was determined gravimetrically. The method was established and described by previous studies (Qiu *et al.*, 2008). The mean percent lipid of the tree bark was 8.74% in present study.

Chemicals and Materials

The mixed standards of eight native PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209) and ¹³C₁₂-PCB209 were obtained from Accustandard Inc. (USA). The mixed standards of eight ¹³C₁₂-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). Anhydrous sodium sulfate (Na₂SO₄), sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were guaranteed reagent (Beijing Chemical Factory, Beijing, China). Sodium sulfate was baked at 450°C and stored in a sealed container. Silica gel was twice washed with n-hexane in a glass flask and activated overnight at 160°C.

Extraction and Analysis

ASE300 (Dionex, USA) was chosen as the sample extraction method for the dust and tree bark samples. Extraction was performed with the same instrumental settings: oven temperature at 100°C, pressure of 1500 psi, static time of 5 minutes, and three repeated extraction cycles using a solvent containing hexane and dichloromethane (1:1, v/v) as the extraction solvent. An aliquot of 5.0 g of sieved fractions of road dust mixed with 5.0 g of acid washed copper powder, or 20.0 g of tree bark mixed with 10.0 g Na₂SO₄ was added to extraction cell of ASE300. 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 H₂SO₄ to each extract. The H₂SO₄ residue was washed with clean water, and water was removed using Na₂SO₄. Then, the extract were condensed and transformed into hexane. 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 Na₂SO₄ (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 Na₂SO₄ (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 ¹³C₁₂-PCB-209, was added to the final extract prior to the instrumental analysis.

Instrument Analysis

Extracts were analyzed for BDE-209 using Shimadzu

model 2010 gas chromatograph (GC) coupled with model QP2010 mass spectrometer (MS) (Shimadzu, Japan) operated negative chemical ionization (NCI) with methane as reagent gas and ZB-5HT MS column (15 m × 0.25 mm × 0.1 μm). The ion source, quadrupole and transfer line temperatures were set at 260, 150 and 300°C respectively. 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 model 7890 Agilent (USA) GC coupled to model 5975 MS operated in electron ionization (EI) and with a DB-5 MS column (30 m × 0.25 mm × 0.25 μm). The ion source, quadrupole and transfer line temperatures were set at 260, 150 and 300°C, respectively. 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.

Quality Assurance/Quality Control (QA/QC)

Concentrations of PBDEs were quantified using isotope dilution method with the addition of ¹³C₁₂- labeled BDEs. The surrogate recoveries in all the samples ranged from 50% to 128%. Concentrations of BDE congeners in all samples were corrected by recoveries of ¹³C₁₂- labeled BDEs. The accuracy and precision of the method was evaluated by analyzing the cleaned samples spiked with known amount PBDEs. The obtained relative standard deviations (SD) were less than 20% (n = 6) when the added PBDEs levels were 10.0 ng. 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 were determined by replicating the analysis of cleaned samples that were spiked with known amount PBDEs (2.0 ng), based on the lowest standard in the calibration curve ,

and taking three folds of the SD as MDLs. The MDLs of BDE-209 was determined by replicating the analysis of procedural blank (n = 6), taking three folds of the SD as MDLs. MDLs for seven BDE congeners of the dust sample ranged from 0.1 to 0.2 μg/kg and 4.0 μg/kg for BDE-209. The concentrations of the tree bark were normalized to the grams of bark lipids to account for the differences in trees. MDLs for seven BDE congeners of the tree bark samples ranged from 0.3 to 0.5 μg/kg (lw) and 22 μg/kg (lw) for BDE-209. Concentrations of BDE-209 in all samples were corrected by subtracting value of blank.

RESULTS AND DISCUSSION

Levels of PBDEs in Road Dust and Tree Bark

Descriptive statistics for the content of PBDEs in the road dust samples (n = 58) and tree bark samples (n = 40) are summarized in Table 1 and 2. The detection frequency for 8 BDE congeners was between 51.7% and 100% in the road dust samples, and 60.0% and 100% in the tree bark samples. The high detection frequency may suggest that these compounds have become ubiquitous in outdoor environments. The detection frequency in the road dust samples followed the order of BDE-209 > 47 > 183 > 28 > 153 > 154 > 99 > 100. Slightly differently, the order was BDE-209 = 47 > 183 > 28 = 99 > 153 > 154 > 100 in the tree bark samples. On average, the individual BDE congener concentrations in two sampling mediums follow the same order of BDE-209 > 183 > 47 > 99 > 153 > 28 > 154 > 100.

The concentrations of Σ₇PBDEs and BDE-209 in the road dust samples ranged from ND to 35.5 μg/kg (8.67 μg/kg as mean, 4.34 μg/kg as geometric mean) and 4.01 to 1439 μg/kg dw (322 μg/kg as mean, 163 μg/kg as geometric mean), respectively. There are relatively few data available on the levels of PBDEs distribution in urban road dust. To

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.

Table 2. Descriptive data of PBDEs in tree bark from Suzhou, Wuxi and Nantong (μg/kg lw).

	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209
Detection (%)	90.0	100	60.0	90.0	75.0	80.0	95.0	100
Mean	2.39	10.5	1.41	6.46	2.40	5.11	20.9	664
Geomean	1.48	4.09	0.76	2.49	0.91	1.26	7.54	406
Median	1.46	5.94	0.435	2.64	0.705	0.850	8.03	386
Maximum	20.9	177	9.13	118	49.7	115	405	3243
Minimum	ND	ND	ND	ND	ND	ND	ND	82.0
St. Dev.	3.40	27.4	2.21	18.4	7.80	18.1	63.4	778

ND: less than the method detection limit.

understand the magnitude of PBDEs contamination in this environmental matrix, the results from this study were compared with Σ_7 PBDEs and BDE-209 observed in urban soils. The concentration of the Σ_7 PBDEs in this study was higher than that reported in Birmingham, UK (0.4–3.8 $\mu\text{g}/\text{kg}$, Harrad and Hunter, 2006), Mainz, Germany (1.0 $\mu\text{g}/\text{kg}$, Thorenz *et al.*, 2010), Shanghai, China (0.02–3.8 $\mu\text{g}/\text{kg}$, Jiang *et al.*, 2010) and in Pujalt, Spain (6.1 $\mu\text{g}/\text{kg}$, Eljarrat *et al.*, 2008). The level of BDE-209 observed in the present study was much higher than that reported in Shanghai, China (0.0029–2.91 $\mu\text{g}/\text{kg}$, Jiang *et al.*, 2010), Mainz, Germany (0.76 $\mu\text{g}/\text{kg}$, Thorenz *et al.*, 2010), Manaus, Brazil (0.5 $\mu\text{g}/\text{kg}$, Thorenz *et al.*, 2010) and Kuwait (3.1–66.6 $\mu\text{g}/\text{kg}$, Gevaio *et al.*, 2010), comparable to that in home dust from Europe (60–467 $\mu\text{g}/\text{kg}$, Frederiksen *et al.* 2009), only lower than that in soil near the PBDEs production area, Laizhou, China (576 $\mu\text{g}/\text{kg}$, Jin *et al.*, 2011). The findings suggested that the road dust is a good environmental matrix which can effectively accumulate particulate PBDEs from the urban environment. Apart from airborne PBDEs, the fraction of construction materials, tire wear and vehicles emissions could also contribute PBDEs to the road dust. It was reported that particulate matters caused by vehicle-based exhaust are an important contributor to road dust (Etyemezian *et al.*, 2003), while other study showed the tailpipe exhausts contain numerous PBDEs (Wang *et al.*, 2010). Anyway, the higher PBDEs contaminant in road dust should be considered in human exposure assessments.

The concentrations of Σ_7 PBDEs and BDE-209 in camphor tree bark ranged from 5.1 to 799 $\mu\text{g}/\text{kg}$ lw (46.0 $\mu\text{g}/\text{kg}$ as mean, 23.1 $\mu\text{g}/\text{kg}$ as geometric mean) and from 121 to 3243 $\mu\text{g}/\text{kg}$ lw (664 $\mu\text{g}/\text{kg}$ as mean, 406 $\mu\text{g}/\text{kg}$ as geometric mean), respectively. The level of Σ_8 PBDEs in the camphor tree bark from Suzhou, Wuxi and Nantong was much higher than that in the pine, camphor, poplar and Chinese fir bark collected at background sites from 68 cities in China (0.02–48.3 $\mu\text{g}/\text{kg}$ lw, Zhao *et al.*, 2008), and much higher than the level of Σ_{17} PBDEs in the pine bark collected at background sites from other countries around the world (Qiu *et al.*, 2008), including Northeastern United States (1.9 $\mu\text{g}/\text{kg}$ lw), Halle, Germany (1.8 $\mu\text{g}/\text{kg}$ lw), Hanam, Korea (8.1 $\mu\text{g}/\text{kg}$ lw) and Trieste, Italy (0.27 $\mu\text{g}/\text{kg}$ lw). The results suggested that the high levels of PBDEs in the tree bark samples might be caused by the large amount of PBDEs emissions from the investigated cities. The finding also showed that camphor tree bark could accumulate PBDEs from the surrounding air in the urban environment effectively, and was a good indicative matrix to reflect the degree of urban atmospheric PBDEs.

PBDEs Congener Profiles

BDE-209 was the major BDE congeners, accounting for 96.7% (89.4–99.8%) and 97.0% (64.1–99.4%) to Σ_8 PBDEs in the road dust and tree bark samples respectively. Levels of individual 7 BDE congeners in all samples were approximately 1–2 orders of magnitude lower than the BDE-209. Recent studies demonstrated that BDE-209 in urban ambient air mainly come from combustion sources (Wang *et al.*, 2010, 2011). During the combustion processes, BDE-

209 could form or not be completely destroyed (Wang *et al.*, 2010, 2011). The abundant BDE-209 congener in the road dust and tree bark samples could come from the large amount of flue gas emission of stationary and mobile combustion sources in this area. In addition, the dominant PBDE mixture production and usage in China is the commercial deca-BDE mixture (Zou *et al.*, 2007), and BDE-209 is the main congener in two Deca-formulations (Saytex 102E and Bromkal 82-0DE with the percentages of 96.8% and 91.6%, respectively (La Guardia *et al.*, 2006). Since BDE-209 has a tendency to strongly attach to particles (Gouin *et al.*, 2006), dry deposition flux of BDE-209 is higher than lighter brominated PBDEs (Lin *et al.*, 2012). Fugitive emissions from PBDE-containing products indoors or from disposal of PBDE-containing products could also contribute BDE-209 to the outdoor environment. The results were consistent with those reported in the a previous study using samples of urban atmosphere and urban soils collected from Yangtze River Delta, China (Jiang *et al.*, 2010; Qiu *et al.*, 2010). Consequently, particulate BDE-209 of urban atmosphere should be of grave concern.

Except for BDE-209, BDE-183 was the main congener among 7 BDE congeners in all samples. BDE-183 contributed 34.2% and 42.5% to Σ_7 PBDEs in the road dust and tree bark samples, respectively. Some researches revealed that BDE-183 could form during the combustion processes, however the amounts were lower than BDE-47 and BDE-99 (Wang *et al.*, 2010, 2011). 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) (La Guardia *et al.*, 2006). 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.

It was reported that BDE-47, 99, 100, 153, 154, and 28 were usually found in the technical penta-BDE mixture (La Guardia *et al.*, 2006). Among these congeners, BDE-47 and 99 dominate the profile of penta-BDE products. In the present study, the mean values of BDE-47 and 99 contributed 29.5% and 29.4% to Σ_6 PBDEs in the road dust samples, and 37.2% and 22.9% to Σ_6 PBDEs in the tree bark samples, respectively. The compositional pattern of 6 BDE congeners found in the road dust and tree bark 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 (La Guardia *et al.*, 2006; Chen *et al.*, 2006; Deng *et al.*, 2007; Jiang *et al.*, 2010; Kang *et al.*, 2011), the results indicated that the compositional pattern of the road dust was similar to the tree barks, but distinct from that of other matrices. Notably, the proportions of BDE-28 of Σ_6 PBDEs in the road dust and tree bark samples 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 (Chen *et al.*, 2006). The results indicated that both road dust and tree bark could accumulate gas-phase and particle-phase PBDEs from the surrounding air. Moreover, relatively higher proportion of

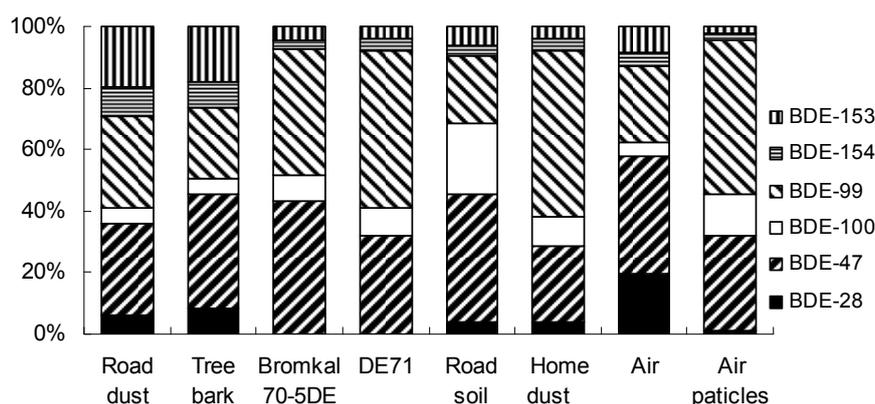


Fig. 1. PBDE congener profile comparison between the penta-BDE technical mixture and other matrix.

BDE-153 was found in the road dust and tree bark samples than in Bromkal 70-5DE, DE-71 (Fig. 1). Previous research reported that BDE-153 could form during the metallurgical processes (Choi *et al.*, 2008), and BDE-153 also could be from Octa-BDE sources, as commercial Octa-BDE mixtures contain BDE-153 (La Guardia *et al.*, 2006). Other BDE-153 might be resulted from debromination of highly brominated congeners (Gerecke *et al.*, 2005). Future investigation of potential PBDEs sources may shed light on this issue in the future.

Comparison of PBDEs Levels in Each City

Fig. 2 and Fig. 3 showed that the levels of dust and tree bark PBDEs in each city. The mean concentration of Σ_8 PBDEs both in the road dust and tree bark samples followed the same order of Nantong > Suzhou > Wuxi. The highest concentration was observed in the industrial area, and the lowest concentration was observed in the suburb park in both the dust and tree bark samples. The same spatial trend of PBDEs contamination among these cities was observed. This suggested that the road dust and tree bark samples could play important roles in identifying PBDEs depositional regions and exploring spatial trends. However, it was found that the tree bark PBDEs levels in Nantong were much higher than in Wuxi and Suzhou, and this phenomenon was not obvious in the road dust samples (Figs. 2 and 3). One explanation is that the tree bark sample could accumulate both gas-phase and particle-phase PBDEs simultaneously from the surrounding air, while the road dust sample could accumulate much more PBDEs in particle-phase than in gas-phase of atmosphere. Another reason is that the tree bark usually stays on the tree for 3 to 5 years, reflecting overall air pollution levels over the time. However, the road dust usually stays on the surface of pavements for a short period of time, reflecting mainly the present air pollution.

The spatial gradient (industrial area > commercial/residential area > suburb park concentrations) observed in the tree bark samples is consistent with the findings in previous studies on ambient air and soils (Qin *et al.*, 2010; Cetin and Odabasi, 2011). The tree bark contamination was the least in the suburb parks that are normally far away from factories and residential areas. This is in line with

previous findings that PBDEs concentrations clearly decrease with increasing distance from the city center (Harrad and Hunter, 2006; Qin *et al.*, 2010). The present study found that the concentrations of tree bark PBDEs from industrial areas were higher than commercial/residential areas, because of the significantly higher PBDEs emissions from plants or other electronic equipment manufacturing facilities located near the sample sites from industrial areas. So the relatively higher Σ_8 PBDEs were found in these samples. For example, the sample from the power plant location (2372 $\mu\text{g}/\text{kg}$ lw, Nantong), from the electrical company location (3287 $\mu\text{g}/\text{kg}$ lw, Nantong), from the resource recycling company location (3457 $\mu\text{g}/\text{kg}$ lw, Suzhou) and from the solid waste incineration power plant location (2600 $\mu\text{g}/\text{kg}$ lw, Wuxi).

The mean concentration of Σ_8 PBDEs in the road dust samples collected from the commercial/residential areas has the same order of magnitude as that from the industrial areas. Consistent with the results in the tree bark samples, 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 (Wang *et al.*, 2010, 2011). 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 (Zhao *et al.*, 2009), because of the higher fine particulates depositional fluxes in the urban areas than in the industrial areas (Zhang *et al.*, 2001). Meanwhile, PBDEs are distributed disproportionately between the fine and coarse fractions (i.e., more PBDEs in the fine fraction than in the bigger coarse particles fraction, Deng *et al.*, 2007). Other study showed that fine particulate matters in urban atmosphere were identified mainly from automobiles and coal combustion sources (Oh *et al.*, 2011),

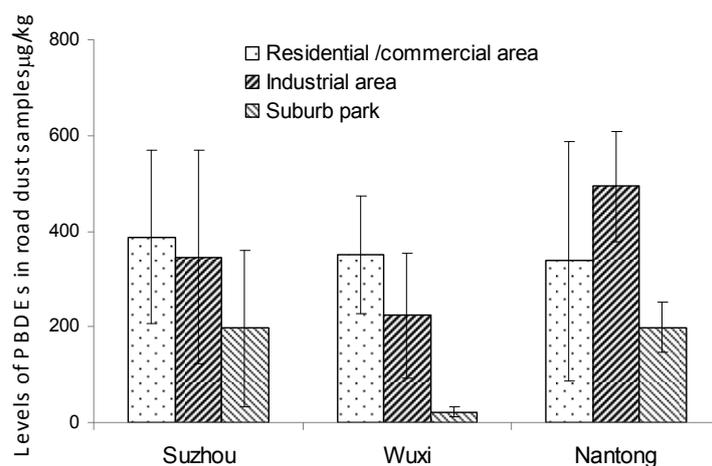


Fig. 2. Levels of Σ_8 PBDEs in road dust samples collected from Suzhou, Wuxi and Nantong. Error bars correspond to one standard deviation.

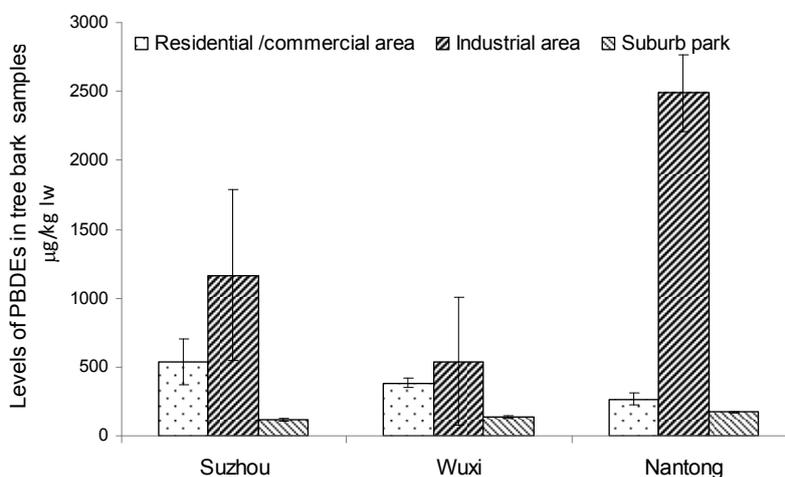


Fig. 3. Levels of Σ_8 PBDEs in tree bark samples collected from Suzhou, Wuxi and Nantong. Error bars correspond to one standard deviation.

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.

CONCLUSIONS

Urban road dust and camphor tree bark were selected as the accumulator to reflect the degree of airborne PBDEs pollutants in the emerging industrial cities in China. Results showed that PBDEs contamination in these cities followed an order of Nantong > Suzhou > Wuxi. Investigation of PBDEs profiles indicated that PBDEs in these cities mainly came from BDE-209. PBDEs contributions from combustion processes and vehicles emissions to the atmosphere should not be ignored. Road dust is an important matrix with high PBDEs contaminant in urban environment that should be considered in human exposure assessments.

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