



Summer atmospheric polybrominated diphenyl ethers in urban and rural areas of northern China

Chen Wang^a, Wei Li^a, Jiwei Chen^a, Hongqijie Wang^a, Tongchao Li^a, Guofeng Shen^a, Huizhong Shen^a, Ye Huang^a, Rong Wang^a, Bin Wang^a, Yanyan Zhang^a, Jianhui Tang^b, Wenxin Liu^a, Xilong Wang^a, Shu Tao^{a,*}

^aLaboratory for Earth Surface Processes, College of Urban and Environmental Science, Peking University, Beijing 100871, China

^bYantai Institute of Coastal Zone Research, CAS, Yantai, Shandong 264003, PR China

ARTICLE INFO

Article history:

Received 22 February 2012

Received in revised form

25 July 2012

Accepted 29 July 2012

Keywords:

PBDEs

Ambient air

Rural areas

North China

ABSTRACT

High levels of polybrominated diphenyl ethers (PBDEs) have been extensively reported in urban areas and at e-waste recycling sites in coastal China. However, data are scarce in northern China and are not available in rural areas at all. In addition, it is often believed that air concentrations in rural areas are lower than those in urban areas without distinguishing rural residential areas and open fields. In this study, air samples were collected at 17 sites covering urban and rural (residential and open field) areas in northern China using active samplers. With BDE-209 dominated in all congeners, the average concentrations of BDE-209 ($41 \pm 72 \text{ pg/m}^3$) and other 13 PBDEs ($16 \pm 12 \text{ pg/m}^3$) were significantly lower than those found in south China, such as in Guangzhou or Hong Kong. On average, the total PBDE concentrations at the urban sites were 2.2 and 2.9 times of those at the rural residential and field sites, respectively.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of additive flame-retardants that have been widely used in commercial and domestic products (de Wit, 2002). The three major commercial PBDE products are penta-BDE (mainly tetra- and penta-BDEs), octa-BDE (mainly hexa- to nona-BDEs), and deca-BDE (consisting mainly of BDE-209) (McDonald, 2002). Release of PBDEs from various products has already caused elevated concentrations in various environmental media including human tissues (Hites, 2004). Being aware of their toxicity, the congeners of the technical penta- and octa-BDE mixtures have been included in the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention on POPs, 2009).

In China, a number of reports published recently suggest high levels of PBDEs in south and east China (Deng et al., 2007; Han et al., 2009), primarily due to the increasing consumption of PBDEs and uncontrolled e-waste recycling activities (Wang et al., 2007). Among various congeners, BDE-209 was often dominant, likely due to the fact that deca-BDE is widely produced and used in China

(Wang et al., 2007). Although in-use emissions are believed to be the dominated sources of PBDEs (Prevedouros et al., 2004; Sakai et al., 2006), some recent studies reported that the combustion sources, like waste incineration and motor vehicle can also emit PBDEs (Wang et al., 2010a–c, 2011).

Atmosphere is a key environmental vector for the transport and redistribution of semi-volatile PBDEs (Tanabe, 2004). In China, the limited number of studies on atmospheric PBDEs were mostly conducted in south and east coastal areas, where numerous manufacturers of electronics, furniture, plastics, textiles, and building materials and majority of e-waste recycling sites are located (Chen et al., 2006; Deng et al., 2007; Han et al., 2009). Among a few studies performed in northern China, Hu et al. reported a mean air concentration of 210 pg/m^3 at a single site in Beijing urban area (Hu et al., 2011). So far, all the studies have been conducted in cities except those at e-waste recycling sites while no data are available for rural China. It is interesting to know whether PBDE concentrations in air of northern China are lower than those in south and whether the PBDE concentrations in air of rural areas are lower than those in cities.

The aim of this study was to investigate PBDEs in atmosphere in urban and rural areas of northern China. Since households can be important sources of PBDEs, rural samples were collected from both villages (rural-residential sites) and open fields (rural-field

* Corresponding author.

E-mail addresses: taos@pku.edu.cn, taos@urban.pku.edu.cn (S. Tao).

sites) to address potential rural residential sources. Differences in abundance and congener profile among different sites and between northern and southern China are discussed.

2. Material and methods

2.1. Sample collection

Air samples were collected at 6 urban, 5 rural-residential, and 6 rural-field sites across northern China (Fig. 1). The urban sites were located in downtown area of big cities. The rural-residential sites were set in rural villages with at least 100 households, and rural-field sites were at least 200 m away from the nearest village (Table S1, Supplementary material). Both PM₁₀ and gaseous phase samples were collected using medium volume (200–400 L/min) cascade impactor (PM10-PUF-300, Guangzhou, China). PM₁₀ were sampled using glass-fiber filters (GFF, 200 × 150 mm², baked under 450 °C for 12 h). Gaseous samples were collected using polyurethane foam plugs (PUF, 45 mm o.d. × 60 mm high, 0.03 g/cm³), which were Soxhlet extracted using acetone, dichloromethane, and hexane in sequence, 8 h each step prior to the sample collection. A 72-h sample was taken each month at each site from July to September, 2010. GFFs were equilibrated in a desiccator (25 °C) for 24 h and weighted both before and after sampling. The meteorological conditions for each site during the sampling days were provided in Table S2, Supplementary material.

2.2. Sample extraction and cleanup

PUFs and GFFs were spiked with ¹³C-PCB 141 (50 ng/sample, Cambridge, USA) as a surrogate and extracted with Soxhlet (150 mL 1:1 hexane/acetone, 8 h) and microwave extractor (CEM, USA, 25 mL 1:1 hexane/acetone, 1200 W, ramp to 110 °C in 10 min and held at 110 °C for another 10 min), respectively. Both PUF and GFF extracts were concentrated to 1 mL and purified on chromatography columns packed with neutral alumina (6 g), neutral silica gel (2 g), basic silica gel (5 g), neutral silica gel (2 g), acid silica gel (6 g), and anhydrous sodium sulfate (1 g) from bottom to top. The silica gel and alumina were baked at 450 °C for 6 h and anhydrous sodium sulfate was baked at 650 °C for 10 h prior to use. The column was eluted with 70 mL of dichloromethane/hexane mixture (1:1). The eluate was concentrated on rotary evaporator at 38 °C to approximate 1 mL and spiked with 50 ng internal standards (¹³C-PCB 208, Cambridge, USA). All samples were condensed again to ~100 μL by gentle stream of purified nitrogen. Analytical grade hexane, acetone (Sinopharm, China) and dichloromethane (Beijing Chemical, China) were purified by distillation. All glassware were cleaned in an ultrasonic cleaner and heated at 400 °C for 6 h.

2.3. Sample analysis

The samples were analyzed on a gas chromatograph (GC, Agilent 7890A) coupled to a mass spectrometer (MS, Agilent 5975C) and a capillary column (HP-5MS, 15 m × 250 μm × 0.1 μm, J&W, USA). Helium was used as the carrier gas (2.0 mL/min) and methane was used as reactant gas. The GC oven temperature was programmed as follows: kept at 110 °C for 5 min, increased to 200 °C at a rate of 20 °C/min, to 280 °C at 10 °C/min, and then to final temperature of 305 °C at 20 °C/min, which was held for 10 min. The MS was operated in negative chemical ionization and the selective ion monitoring mode with an ion source temperature of 230 °C. The samples (1 μL) were injected in splitless mode and the injector temperature was held at 265 °C. The 14 BDE congeners were identified based on retention times and qualitative ions, which were *m/z* 79 and 81 ([Br]⁻) for BDE-17, BDE-28, BDE-71, BDE-47, BDE-66, BDE-100, BDE-99, BDE-85, BDE-154, BDE-153, BDE-138, BDE-183 and BDE-190, and *m/z* 79, 81 and 486 for BDE-209.

2.4. Quality control

Procedural blanks were analyzed for every batch of samples. Only low concentrations of BDE-28 (0.01 ± 0.01 and 0.09 ± 0.16 pg/m³ in PUFs and GFFs), BDE-47 (0.03 ± 0.03 and 0.11 ± 0.20 pg/m³ in PUFs and GFFs), BDE-153 (0.09 ± 0.08 pg/m³ in PUFs) and BDE-209 (0.09 ± 0.16 pg/m³ in GFFs) were detected and were subtracted from those in the sample extracts. Method recoveries determined by spiking the sampling media (five replicates) with a standard mixture of 14 PBDEs (AccuStandard, USA) ranged from 115 to 134% for the PUF plugs and from 101 to 120% for the GFFs. The surrogate recoveries were 86 ± 10 and 89 ± 12% for PUFs and GFFs, respectively. The ratios between native PBDEs and the surrogate in the spiking experiment were provided in Table S3, Supplementary material. Reported concentrations were not recovery corrected. The method detection limits (calculated from instrumental detection limits as three times of signal to noise ratio, sampling volume and the method recoveries) ranged from 0.45 (BDE-66) to 2.29 (BDE-209) pg/m³ for gaseous samples and from 0.51 (BDE-66) to 2.69 (BDE-209) pg/m³ for particulate-bound PBDEs, respectively.

2.5. Statistical analysis

SPSS was used for statistical analysis. For comparison, an one-way analysis of variance was applied at a significant level of 0.05. For principle component analysis (PCA), the measured concentrations were log-transformed and normalized. No factor rotation was applied. The correlation analysis was conducted using the Pearson method.

3. Results and discussion

3.1. PBDE concentrations in ambient air of northern China

The measured concentrations of 14 PBDEs in both gaseous and particulate phases are summarized in Table 1 (see details in Table S4, Supplementary material). Among them, BDE-138 was not detected in all samples. The most abundant congeners were BDE-209, followed by BDE-47, BDE-28, and BDE-66, which were detected in all or most samples at current detection limits. Different from BDE-47 which was detected both in the gaseous and particulate phase, BDE-66 was mainly present in the gaseous phase. Unfortunately, no explanation can be provided for this with rather limited samples and more data should be collected for confirming and interpreting the phenomenon. The total concentration of 13 PBDEs except BDE-209 (Σ₁₃PBDEs) was 16 ± 12 pg/m³ (0.48–52 pg/m³ as range). BDE-209 concentration (gaseous + particulate phase) ranged from 12 to 170 pg/m³ and approximately 90% of BDE-209 was found in particulate phase due to its physicochemical properties (Ter Schure et al., 2004). The measured PBDE concentrations at individual sites were not significantly different among the three months (*p* > 0.05, non-parameter K–S test).

The only data reported for atmospheric PBDEs based on active sampling in northern China were those measured at a single site in Beijing urban area and the annual mean concentration (210 pg/m³) was similar to what we measured at our Beijing site

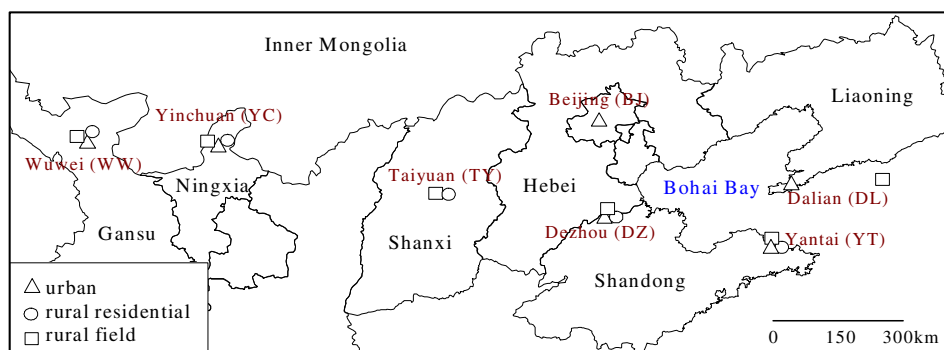


Fig. 1. Map of the sampling sites. The urban, rural-residential, and rural-field sites were represented by triangles, circles and rectangulars, respectively.

Table 1
Gaseous and particulate phase PBDE concentrations (means and standard deviations) in the ambient air of northern China (Unit: pg/m^3).

	Gaseous phase		Particulate phase		Total	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
BDE-17	0.43	1.3	0.056	0.10	0.49	1.4
BDE-28	1.8	1.9	1.4	1.1	3.1	2.0
BDE-71	0.78	2.3	N.D.	N.D.	0.78	2.3
BDE-47	2.1	2.6	6.2	6.6	8.4	7.5
BDE-66	1.4	2.0	0.055	0.17	1.4	2.1
BDE-100	0.23	0.34	0.063	0.18	0.29	0.45
BDE-99	0.36	0.40	0.35	0.72	0.71	0.93
BDE-85	0.036	0.11	0.12	0.34	0.15	0.41
BDE-154	0.067	0.13	0.13	0.30	0.20	0.32
BDE-153	0.082	0.20	0.28	0.60	0.36	0.61
BDE-138	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BDE-183	0.051	0.087	0.41	1.1	0.46	1.1
BDE-190	N.D.	N.D.	0.012	0.060	0.012	0.060
BDE-209	4.0	6.1	37	69	41	72
$\Sigma_{13}\text{PBDEs}$	7.3	6.4	9.1	8.1	16	12
$\Sigma_{14}\text{PBDEs}$	11	9.7	46	69	58	73

$\Sigma_{13}\text{PBDEs}$: the sum of all the target PBDE congeners except BDE-209.

$\Sigma_{14}\text{PBDEs}$: the sum of all 14 PBDE congeners.

N.D.: not detectable.

($202 \pm 213 \text{ pg}/\text{m}^3$) (Hu et al., 2011). With an exception of BDE-209, the measured $\Sigma_{13}\text{PBDEs}$ were generally similar to those reported for many areas in other countries, like 21, 4.5–65, and 3–30 pg/m^3 in Birmingham, Kyoto, and Toronto, respectively (Harner et al., 2006; Harrad and Hunter, 2006; Hayakawa et al., 2004). For BDE-209, the concentrations in our study were similar to those reported for a number of places including Izmir, Turkey, Chicago, U.S. (Cetin and Odabasi, 2008; Hoh and Hites, 2005), but much higher than those measured in a rural site in the Great Lakes, two urban sites in South East Queensland, Australia, an industrial urban site in Lake Maggiore, Italy, and those found in the atmosphere at a research center in northern Italy (Su et al., 2009; Toms et al., 2009; Vives et al., 2007; Mariani et al., 2008). For all the PBDE congeners including BDE-209, the concentrations in northern China were significantly lower than those found in the Pearl River Delta area of southern China (Chen et al., 2006; Deng et al., 2007). For example, it was reported that the particulate phase PBDE concentrations (excluding BDE-209) in air ranged from 204 to 372 pg/m^3 in Guangzhou, and 33.8 to 358 pg/m^3 in Hong Kong, respectively (Deng et al., 2007). And atmospheric BDE-209 concentrations ranged from 263.8 to 4200 pg/m^3 at four sites in Guangzhou (Chen et al., 2006). In the Pearl River Delta area, PBDE concentrations are among the highest in the world because of the extensive use of PBDEs as raw materials by many manufactories for production of furniture, building materials, textiles, plastics, electronics, and many other products (Chen et al., 2006). Moreover,

a number of electronic waste recycling sites without proper emission control facilities in this area added more emissions (Lopez et al., 2011; Wong et al., 2007). Another reason for the higher PBDE concentrations in the air in southern China is that the summer mean temperatures there (26–28 °C) are much higher than those in northern China (19–24 °C), leading to higher rates of volatilization of PBDEs (Ter Schure et al., 2004). On the other hand, compared with 2.2–15 pg/m^3 (average 8.3 pg/m^3) reported for Waliguan Baseline Observatory (WBO) and 0.1–8.3 pg/m^3 for Rawu, Gaerze, and Bomi in Tibet (Cheng et al., 2007; Wang et al., 2010d), the PBDEs concentrations found in the studied areas were much higher.

3.2. PBDE congener profiles

Fig. 2 shows the congener profiles of the 14 PBDEs measured at various sites. Relatively high standard deviations of most homologs (coefficients of variation for half of the congeners were greater than 100%) suggest the significant temporal and spatial variations. Of all the congeners, BDE-209 contributed $64 \pm 14\%$ of the total. Of the 13 PBDEs, BDE-47 and BDE-28 contributed $71 \pm 11\%$ of the total. Octa-BDE (BDE-183 and BDE-138) account for only $0.68 \pm 0.56\%$ of the total 14 PBDEs.

The BDE-209 domination has been reported for other areas in China, especially in southern and eastern China. For example, it was found that BDE-209 accounted for 40–99% of the total PBDEs detected in the air in Guangzhou (Chen et al., 2006). Qiu et al. found that BDE-209 was the most abundant among 33 PBDE congeners analyzed in air samples from Taihu Lake, South China (Qiu et al., 2010). Relatively high percentage of BDE-209 were also found in atmospheric PBDEs in Kyoto, Japan, Izmir, Turkey, South East Queensland, Australia, a sanitary landfill in Ottawa, Canada and an island in the Baltic Sea region (Hayakawa et al., 2004; Cetin and Odabasi, 2008; Toms et al., 2009; St-Amanda et al., 2008; Ter Schure et al., 2004). Besides, the study conducted by Venier and Hites (2008) found that BDE-209 was the most abundant among all congeners in the atmosphere of Cleveland, U.S. BDE-209 was also the dominant congener detected in the outdoor air of an automotive shredding and metal recycling facility and the indoor air of an electronics recycling facility, California (Cahill et al., 2007). On the other hand, some studies revealed relatively small fraction of BDE-209. For instance, the dominant congener found in the atmosphere at a research center in northern Italy and in Lake Maggiore, Italy was BDE-47 (Mariani et al., 2008; Vives et al., 2007). The research conducted in a Mediterranean coastal site, France, found that BDE-47 ($45 \pm 0.5\%$) and BDE-99 ($39 \pm 0.2\%$) predominated in the total PBDEs (Castro-Jiménez et al., 2011). And it was reported that mean BDE-209 and total PBDE concentrations at a site in Davis, California were 11 and 93 pg/m^3 , respectively (Cahill et al.,

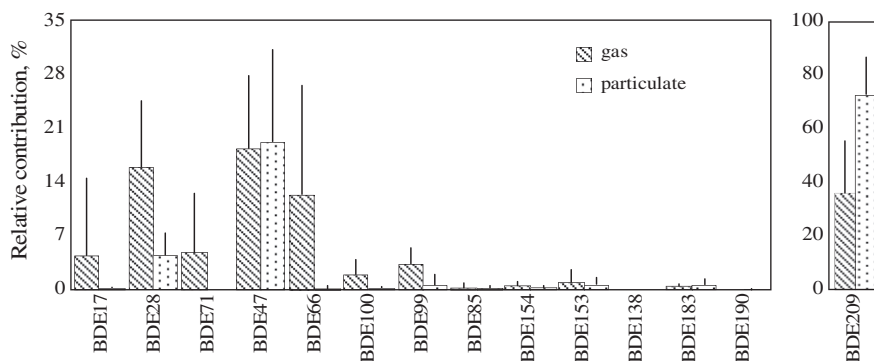


Fig. 2. Congener profiles of gaseous and particulate phase PBDEs. The results are presented as means and standard deviations.

2007). The reason causing such a difference might be related to the distinct source types, including commercial use and potential combustion emissions of PBDEs in different regions (Besis and Samara, 2012; Wang et al, 2010a–c, 2011). The result of this study indicated that the BDE-209 domination occurs not only in southern China, but is also a common phenomenon in a vast region of north China extending from Gansu Corridor (102°E) to the Yellow Sea (123°E), though the total concentrations were much lower than those in southern and eastern China. However, the congener profiles observed in this study were quite different from those found in remote sites of Waliguan Baseline Observatory, where BDE-47 and BDE-99 were dominant, followed by BDE-209 and BDE-100 (Cheng et al., 2007). Without recognizable local sources, PBDEs observed at Waliguan were predominately from long-range transport and BDE-209 has relatively low potential of long-range transport primarily because it is strongly bound to particles (Cheng et al., 2007). Moreover, relatively high photo-degradation rate in comparison with other congeners under solar radiation may also be responsible for the low abundance of BDE-209 in the remote observatory in Waliguan (Söderström et al., 2004).

Table 2 shows the ratios of several PBDE congeners. For all the samples collected in this study, the average ratio of BDE-99 to BDE-47 (total of gaseous and particulate phases) was 0.11, which was far lower than those of the two widely used commercial penta-BDEs (1.3 and 1.0 for DE-71 and Bromkal 70-5DE) (La Guardia et al., 2006). Similar results have been reported previously (Harrad and Hunter, 2006; Hu et al., 2011). Longer half-life and higher volatility of BDE-47 compared to BDE-99 can be an important reason that BDE-99 to BDE-47 ratio in atmosphere was lower than those in commercial products (Eriksson et al., 2004). Relatively high ratios of BDE-17 (0.06), BDE-28 (0.56), and BDE-66 (0.31) to BDE-47 were also found in this study compared to the ratios of DE-71 (0.0018, 0.0065, 0.014) and Bromkal 70-5DE (0.0012, 0.0023, 0.0049) (La Guardia et al., 2006), because higher brominated PBDEs are less volatile (Watanabe and Sakai, 2003). The relative high ratios of BDE-66 to BDE-47 and high proportions of BDE-66 were unusual. This is not a common phenomenon. Unfortunately, no explanation can be provided at present due to limited samples measured. Further study should be conducted before any conclusion can be reached. It was suggested that the ratio of the sum of BDE-47, BDE-99, and BDE-100 to the sum of BDE-153 and BDE-154 ($R_{\text{penta/octa}}$) can be used to assess the relative contributions of penta-BDE and octa-BDE mixtures (Hites, 2004). In the present study, the average ratio was 29 ± 26 , ranged from 6.0 to 94, indicating that penta-BDE is the main contributor in the studied areas. In southern China, the ratio of BDE-99 to BDE-47 was 0.5–1.2, much higher than what we found (0.11), indicating a relatively less BDE-99 domination situation in northern China. On the other hand, average $R_{\text{penta/octa}}$ in southern China is 20 (6.0–60) (Chen et al., 2006), very similar to our observation in the north.

According to the results of a principal component analysis (Table 3) using the log-transformed and normalized data except BDE-138 and BDE-190 which were not detectable in most samples, two major associations (loading > 0.60) identified were PC1{BDE-

Table 2
PBDE congener ratios.

	PBDE congener ratios (gaseous + particulate phase)			
	Mean	S.D.	Min	Max
BDE-99/47	0.11	0.13	0	0.5
BDE-17/47	0.06	0.19	0	1.2
BDE-28/47	0.56	0.33	0.04	1.5
BDE-66/47	0.31	0.52	0	2.4
$R_{\text{penta/octa}}$	29	26	6	94

Table 3
Factor loadings of PCA for different PBDE homologs.

Congener	PC1	PC2	PC3
BDE-17	0.651	−0.729	0.004
BDE-28	0.946	0.275	−0.164
BDE-71	0.449	0.808	−0.354
BDE-47	0.800	0.409	−0.062
BDE-66	−0.723	0.328	0.486
BDE-100	0.295	0.376	−0.872
BDE-99	0.835	−0.094	0.477
BDE-85	0.744	0.061	0.595
BDE-154	0.267	0.963	−0.015
BDE-153	−0.504	0.863	−0.023
BDE-183	−0.446	0.856	0.239
BDE-209	0.389	0.626	0.586
Eigenvalue	4.698	4.485	2.136
%Variance	39.148	37.375	17.796

Note: Factor loadings over 0.60 were highlighted in boldface.

17, BDE-28, BDE-47, BDE-99, and BDE-85} and PC2{BDE-71, BDE-154, BDE-153, BDE-183, and BDE-209}. The influence of penta-BDE can be seen in the PC1 association, in which BDE-47 and BDE-99 are major constituents of penta-BDE (La Guardia et al., 2006). Meantime, most of the congeners in the PC2 association are constituents of commercial deca-BDE and octa-BDE (La Guardia et al., 2006).

3.3. Difference in PBDE concentrations among the sites

The total PBDE concentrations measured at all sites are illustrated in Fig. 3 as means and standard deviations. The sites from left to right are arranged in a general order from west to east. The difference among the three site categories can be seen. In general, the highest average concentrations ($95 \pm 63 \text{ pg/m}^3$) were found at the urban sites, which were significantly higher than those of the other sites based on an one-way analysis of variance ($p < 0.05$). The concentrations at the rural field sites (average $33 \pm 13 \text{ pg/m}^3$) were usually lower than the corresponding rural residential sites (average $43 \pm 14 \text{ pg/m}^3$), while they are not always statistically significant though ($p = 0.05$). By average, the total PBDE concentrations at the urban sites were 2.2 and 2.9 times of those at the rural residential and field sites, respectively. Several previous studies have also demonstrated the elevated urban air PBDE concentrations (Butt et al., 2004; Harner et al., 2006; Harrad and Hunter, 2006). For example, Harner et al. found that the PBDE concentrations in the air in the urban area of Toronto were twice of those in the rural areas (Harner et al., 2006). On a transect across the West Midlands of the UK, the elevated gas phase PBDE concentrations have been detected at urban sites and the difference between the urban and non-urban sites was approximately 2.2 times (Harrad and Hunter, 2006).

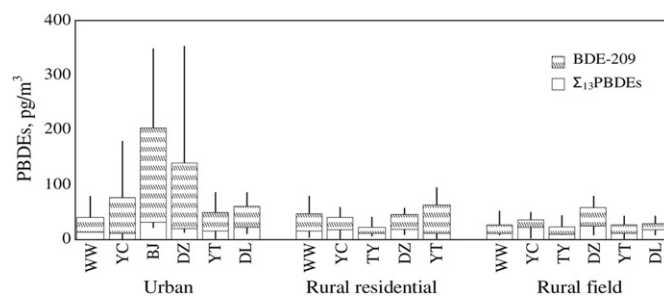


Fig. 3. The measured PBDEs at various sites of the studied area. The results are presented in means and standard deviations. The codes for the sampling sites can be found in Fig. 1. From left to right, the sites are arranged in order from west to east.

The sampling sites were selected following a basic assumption that higher population density, more rapid development, and faster industrialization in east China compared to those in west China may result in heavier contamination. However, the measured PBDE concentrations did not follow an expected decreasing trend from east to west for all the three categories. The highest concentrations among the urban sites occurred in Beijing, and the concentrations at urban site of Yantai (east) were approximately 50% lower than those of Yinchuan (west). One of the most important sources of PBDEs is the usage of household appliances, building materials, textiles, furniture, and others goods containing flame retardants. As a result, higher population density and larger residential area can cause higher air concentrations of PBDEs. Hoh et al. have found that air PBDE concentration in Chicago was 3–6 times higher than those at the other sites in the East-Central United States (Hoh and Hites, 2005). Based on our results, it is suggested that the PBDE concentrations may depend on population density and this hypothesis has been successfully tested in this study. For all the sites, significant correlations ($p < 0.05$, Pearson) were identified between the log-transformed PBDEs (BDE-209 or Σ_{14} PBDEs) in the atmosphere and population density of the sites (Fig. 4, left panel). For all the urban sites, correlation between the log-transformed air PBDE concentrations (penta-BDE, BDE-28, BDE-85, or Σ_{13} PBDEs) and Gross Domestic Production (GDP, GDP data are not available for other sites) were also significant ($p < 0.05$, Pearson) (Fig. 4, right panel). It is interesting to see that BDE-209 correlated only to population, while penta-BDEs were GDP-dependent. The exact reasons causing such relationship cannot be concluded without detailed usage information. The influence of PBDEs emissions from combustion sources cannot be ruled out (Wang et al, 2010a–c, 2011). The relationship based on our data should not be simply generalized. Future study on production and usage of PBDEs at individual sites, influence of combustion emissions and the potential relationship of human population, industrial activities, and PBDEs abundances should be conducted.

The effects of meteorological conditions (mean temperature, pressure, rainfall, and relative humidity during sampling days) on the measured PBDE concentrations and gas-particle partition were investigated. The temperature influence on the gaseous phase behavior of PBDEs was investigated using the Clausius–Clapeyron equation: $\ln P = m/T + b$, where P is the partial pressure of semi-volatile organic compounds in gas phase (atm), T is the ambient temperature (K), and m and b are fitting parameters (Hoff et al., 1998). Since P is related to the air concentration (C), the relationship between $\ln C$ and T is discussed. It was found that T was significantly correlated with $\ln C_{13PBDEs}$ and $\ln C_{14PBDEs}$ ($p < 0.05$), indicating significant influence of ambient temperature on gaseous phase PBDEs. It appears that temperature can explain

approximately 13.2 and 21.3% (R^2) of the variations in $\ln C_{13PBDEs}$ and $\ln C_{14PBDEs}$, respectively. There was no significant correlation between the ambient temperature and gaseous phase concentration of individual PBDE congeners ($p = 0.05$), likely due to the limited sample size collected in this study. It is suggested that more samples should be collected to investigate the influence of temperature on each congener in the future. In addition, the proportions of BDE-28, BDE-47, BDE-100, BDE-85, BDE-154, and BDE-183 in gaseous phase were also significantly correlated with air temperature ($p < 0.05$). Similar influence was also reported in other studies (Qiu et al., 2010; Harner and Shoeib, 2002). There were significantly negative correlations between relative humidity and particulate BDE-209 and Σ_{14} PBDEs ($p < 0.05$). Similar with relative humidity, there were also significantly negative correlations between rainfall and particulate BDE-209 and Σ_{14} PBDEs ($p < 0.05$). Concerning the correlation between relative humidity and rainfall ($p < 0.01$), the wet deposition of particulate PBDEs (especially the higher brominated BDE-209) will increase with increasing rainfall and subsequently higher humidity. No statistical influence was found for other meteorological factors recorded.

3.4. Difference in congener profile among the sites

Although there were significant differences in atmospheric PBDE concentrations among the three site categories, the BDE-209 dominated congener profiles were generally similar among them (Fig. 5). On average, BDE-209 contributed 76 ± 11 , 63 ± 13 and $53 \pm 9.3\%$ of the total at urban, rural residential and rural field sites. Similarity in congener profiles between urban and rural area was also reported for Toronto (Harner et al., 2006). No significant difference in congener profiles was found between east and west.

Average contributions of lighter congeners, including BDE-17, BDE-28, BDE-47 and BDE-66 in the total PBDEs were generally lower at urban sites than those at rural sites (Fig. 4), which was different from BDE-209. This is likely because that these lighter congeners are more mobile in the atmosphere while BDE-209 could be removed from the atmosphere via particle deposition during transport (Raff and Hites, 2007). BDE-47 has similar or higher concentrations at rural sites than urban sites, which might be due to the contributions of both atmospheric transport and local sources. Different from those in YC, DZ, and YT, the ratios of BDE-66 to BDE-47 at rural-field sites were higher than those at urban sites in WW and DL, indicating that additional BDE-66 was formed by degradation of higher PBDEs during atmospheric transport. Further studies about different contributions and concentrations of BDE-47, BDE-66 at rural and urban sites should be conducted.

The average $R_{\text{penta/octa}}$ ratios were 20 ± 17 , 27 ± 29 , and 40 ± 31 for the urban, rural residential, and rural field sites, respectively.

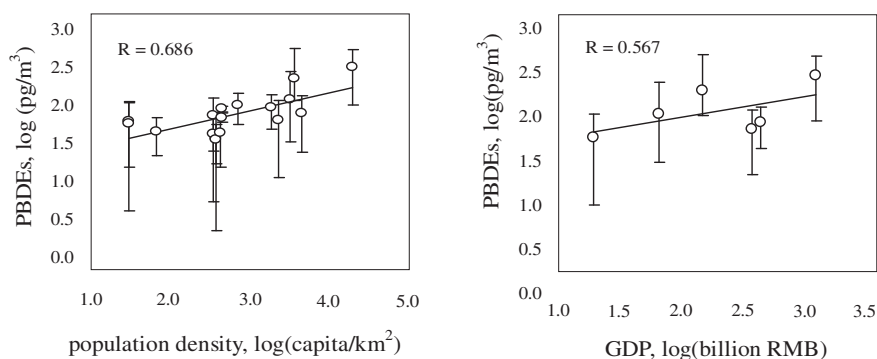


Fig. 4. Correlations between the air concentrations of PBDEs and population density at all sites and between the air concentrations of PBDEs and GDPs at urban sites. The PBDE concentrations, population density, and GDP are log-transformed.

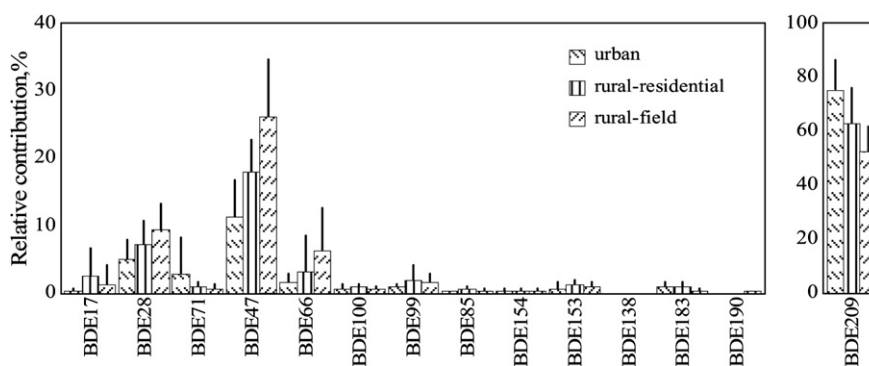


Fig. 5. Relative contributions of various congeners to the total PBDEs in air for the three site categories of urban, rural residential and rural field. Means and standard deviations are shown.

The large standard deviations were resulted from two outliers (urban-Yantai and rural residential-Yantai), which were identified by Grubb's test ($p < 0.05$). At this stage, no explanation can be provided for the outliers. With these outliers excluded, the ratios became 14 ± 6.8 and 14 ± 6.7 for the urban and rural residential sites, respectively, indicating high similarity between them and significant difference from the rural-field sites. The similarity between the urban and rural residential sites is because they are all close to the emission sources, which are believed to be products used in daily life. It appears that the types of products used in rural and urban households were similar and the difference in the total concentrations was caused by the difference in the population density, subsequently product density of these areas. In addition, PBDE emissions from various combustion sources at urban and rural sites could also influence the ratio (Wang et al, 2010a–c, 2011). On the other hand, the rural field sites are relatively far away from the emission sources and hence have higher $R_{\text{penta/octa}}$ ratios, since various BDE congeners behave differently during atmospheric transport. Since the transport potentials of BDE-153 and BDE-154 were lower than that of BDE-47 and low-brominated BDEs like BDE-47 can be formed as the degradation products of higher brominated congeners (Söderström et al., 2004; Zeng et al., 2008), relative accumulation of BDE-47 on the way of air transport can lead to a rise of $R_{\text{penta/octa}}$ ratio from sources to receptors.

4. Conclusions

In this study, air concentrations of polybrominated diphenyl ethers were investigated in rural and urban areas of northern China. In general, air concentrations of PBDEs in our studied region were lower than those in southern China. Similar with those areas, BDE-209 was also the most abundant congener. The ratios of BDE-99 to BDE-47 were 0–0.5, much lower than those in southern China.

Of the three categories of sampling sites, average PBDE concentration in urban sites was 2.2 and 2.9 times of those at rural residential and rural field sites, respectively. For all the sites studied, there was significant correlation between BDE-209 and population density, while for the urban sites, significant correlation was found between penta-BDEs and gross domestic production. The ratios of penta-BDE to octa-BDE at the urban and rural-residential sites were very close to each other and were significantly lower than those at the rural field sites, which are distance away from sources.

Acknowledgment

This research was supported by the grants from the National Natural Science Foundation of China (Grant 41130754, 41001343,

41101490), Beijing Municipal Government (YB20101000101), and the Ministry of Environmental Protection (201209018).

Appendix A. Supplementary material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2012.07.041>.

References

- Besis, A., Samara, C., 2012. Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments – a review on occurrence and human exposure. *Environmental Pollution* 169, 217–229.
- Butt, C.M., Diamond, M.L., Truong, J., Ikononou, M.G., Ter Schure, A.F.H., 2004. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. *Environmental Science and Technology* 38, 724–731.
- Cahill, T.M., Groskova, D., Charles, M.J., Sanborn, J.R., Denison, M.S., Baker, L., 2007. Atmospheric concentrations of polybrominated diphenyl ethers at near-source sites. *Environmental Science and Technology* 41, 6370–6377.
- Castro-Jiménez, J., Mariani, G., Vives, I., Skejo, H., Umlauf, G., Zaldivar, J.M., Dueri, S., Messiaen, G., Laugier, T., 2011. Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). *Environmental Pollution* 159, 1948–1956.
- Cetin, B., Odabasi, M., 2008. Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Chemosphere* 71, 1067–1078.
- Cheng, H.R., Zhang, G., Jiang, X.Y., Li, X.D., Liu, X., Li, J., Zhao, Y.C., 2007. Organochlorine pesticides, polybrominated biphenyl ethers and lead isotopes during the spring time at the Waliguan Baseline Observatory, northwest China: implication for long-range atmospheric transport. *Atmospheric Environment* 41, 4734–4747.
- Chen, L.G., Mai, B.X., Bi, X.H., Chen, S.J., Wang, X.M., Ran, Y., Luo, X.J., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2006. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in south China. *Environmental Science and Technology* 40, 1190–1196.
- Deng, W.J., Zheng, J.S., Bi, X.H., Fu, J.M., Wong, M.H., 2007. Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environmental International* 33, 1063–1069.
- de Wit, C.A., 2002. An overview of brominated flame retardants in the environment. *Chemosphere* 46, 583–624.
- Eriksson, J., Green, N., Marsh, G., Bergman, A., 2004. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. *Environmental Science and Technology* 38, 3119–3125.
- Han, W.L., Feng, J.L., Gu, Z.P., Chen, D.H., Wu, M.H., Fu, J.M., 2009. Polybrominated diphenyl ethers in the atmosphere of Taizhou, a major e-waste dismantling area in China. *Bulletin of Environmental Contamination and Toxicology* 83, 783–788.
- Harner, T., Shoeib, M., 2002. Measurements of Octanol–air partition coefficients (KOA) for polybrominated diphenyl ethers (PBDEs): predicting partitioning in the environment. *Journal of Chemical and Engineering Data* 47, 228–232.
- Harner, T., Shoeib, M., Diamond, M., Ikononou, M., Stern, G., 2006. Passive sampler derived air concentrations of PBDEs along an urban–rural transect: spatial and temporal trends. *Chemosphere* 64, 262–267.
- Harrad, S., Hunter, S., 2006. Concentrations of polybrominated diphenyl ethers in air and soil on a rural–urban transect across a major UK conurbation. *Environmental Science and Technology* 40, 4548–4553.
- Hayakawa, K., Takatsuki, H., Watanabe, I., Sakai, S., 2004. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and

- monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmosphere and bulk deposition in Kyoto, Japan. *Chemosphere* 57, 343–356.
- Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environmental Science and Technology* 38, 945–956.
- Hoff, R.M., Brice, K.A., Halsall, C.J., 1998. Nonlinearity in the slopes of Clausius–Clapeyron plots for SVOCs. *Environmental Science and Technology* 32, 1793–1798.
- Hoh, E., Hites, R.A., 2005. Brominated flame retardants in the atmosphere of the east-central United States. *Environmental Science and Technology* 39, 7794–7802.
- Hu, J.C., Jin, J., Wang, Y., Ma, Z.H., Zheng, W.J., 2011. Levels of polybrominated diphenyl ethers and hexabromocyclododecane in the atmosphere and tree bark from Beijing, China. *Chemosphere* 84, 355–360.
- La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environmental Science and Technology* 40, 6247–6254.
- Lopez, B.N., Man, Y.B., Zhao, Y.G., Zheng, J.S., Leung, A.O.W., Yao, J., Wong, M.H., 2011. Major pollutants in soils of abandoned agricultural land contaminated by e-waste activities in Hong Kong. *Archives of Environmental Contamination and Toxicology* 61, 101–114.
- Mariani, G., Canuti, E., Castro-Jimenez, J., Christoph, E.H., Eisenreich, S.J., Hanke, G., Skejo, H., Umlauf, G., 2008. Atmospheric input of POPs into Lake Maggiore (Northern Italy): PBDE concentrations and profile in air, precipitation, settling material and sediments. *Chemosphere* 73, S114–S121.
- McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. *Chemosphere* 46, 745–755.
- Prevedouros, K., Jones, K.C., Sweetman, A.J., 2004. Estimation of the production, consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe between 1970 and 2000. *Environmental Science and Technology* 38, 3224–3231.
- Qiu, X.H., Zhu, T., Hu, J.X., 2010. Polybrominated diphenyl ethers (PBDEs) and other flame retardants in the atmosphere and water from Taihu Lake, East China. *Chemosphere* 80, 1207–1212.
- Raff, J.D., Hites, R.A., 2007. Deposition versus photochemical removal of PBDEs from Lake Superior air. *Environmental Science and Technology* 41, 6725–6731.
- Sakai, S., Hirai, Y., Aizawa, H., Ota, S., Muroishi, Y., 2006. Emission inventory of decabrominated diphenyl ether (DBDE) in Japan. *Journal of Material Cycles and Waste Management* 8, 56–62.
- Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE209). *Environmental Science and Technology* 38, 127–132.
- Stockholm Convention on POPs, 2009. <http://www.pops.int/> (accessed 13.10.11.).
- St-Amanda, A.D., Mayer, P.M., Blais, J.M., 2008. Seasonal trends in vegetation and atmospheric concentrations of PAHs and PBDEs near a sanitary landfill. *Atmospheric Environment* 42, 2948–2958.
- Su, Y.S., Hung, H., Brice, K.A., Su, K., Alexandrou, N., Blanchard, P., Chan, E., Sverko, E., Fellin, P., 2009. Air concentrations of polybrominated diphenyl ethers (PBDEs) in 2002–2004 at a rural site in the Great Lakes. *Atmospheric Environment* 43, 6230–6237.
- Tanabe, S., 2004. PBDEs, an emerging group of persistent pollutants. *Marine Pollution Bulletin* 49, 369–370.
- Ter Schure, A.F.H., Larsson, P., Agrell, C., Boon, J.P., 2004. Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the Baltic Sea. *Environmental Science and Technology* 38, 1282–1287.
- Toms, L.M.L., Bartkow, M.E., Symons, R., Paepke, O., Mueller, J.F., 2009. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. *Chemosphere* 76, 173–178.
- Venier, M., Hites, R.A., 2008. Flame retardants in the atmosphere near the Great Lakes. *Environmental Science and Technology* 42, 4745–4751.
- Vives, I., Canuti, E., Castro-Jimenez, J., Christoph, E.H., Eisenreich, S.J., Hanke, G., Huber, T., Mariani, G., Mueller, A., Skejo, H., Umlauf, G., Wollgast, J., 2007. Occurrence of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Lake Maggiore (Italy and Switzerland). *Journal of Environmental Monitoring* 9, 589–598.
- Wang, L.C., His, H.C., Wang, Y.F., Lin, S.L., Chang-Chien, G.P., 2010a. Distribution of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in municipal solid waste incinerators. *Environmental Pollution* 158, 1595–1602.
- Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P., 2010b. Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources. *Environmental Pollution* 158, 3108–3115.
- Wang, L.C., Wang, Y.F., Hsi, H.C., Chang-Chien, G.P., 2010c. Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes. *Environmental Science and Technology* 44, 1240–1246.
- Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P., 2011. Polybrominated diphenyl ethers in various atmospheric environments of Taiwan: their levels, source identification and influence of combustion sources. *Chemosphere* 84, 936–942.
- Wang, X.P., Gong, P., Yao, T.D., Jones, K.C., 2010d. Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan Plateau. *Environmental Science and Technology* 44, 2988–2993.
- Wang, Y.W., Jiang, G.B., Lam, P.K.S., 2007. Polybrominated diphenyl ether in the East Asian environment: a critical review. *Environmental International* 33, 963–973.
- Watanabe, I., Sakai, S., 2003. Environmental release and behavior of brominated flame retardants. *Environmental International* 29, 665–682.
- Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007. Export of toxic chemicals – a review of the case of uncontrolled electronic-waste recycling. *Environmental Pollution* 149, 131–140.
- Zeng, X., Simonich, S.L.M., Robrock, K.R., Korytar, P., Alvarez-Cohen, L., Barofsky, D.F., 2008. Development and validation of a congener-specific photodegradation model for polybrominated diphenyl ethers. *Environmental Toxicology and Chemistry* 27, 2427–2435.