



Distribution of polybrominated diphenyl ethers in the atmosphere of the Pearl River Delta region, South China

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Abstract

Air samples were collected from 26 air-monitoring stations located in the Pearl River Delta (PRD) and two in Shaoguan, South China, to investigate the spatial distribution and temporal changes in polybrominated diphenyl ethers (PBDEs) after the production and use of PBDE commercial formulations was restricted in China and the “dual transfer strategy” implemented by Guangdong Province. The spatial distribution of PBDEs was inhomogeneous in the PRD region, with concentrations ranging from 26.3 to 634 pg/m³ and a mean value of 105 pg/m³. The PBDE levels in the five western cities (Guangzhou, Foshan, Zhaoqing, Zhongshan, and Jiangmen) were markedly higher than those in the four eastern cities (Dongguan, Huizhou, Shenzhen, and Zhuhai). BDE-209 was the predominant congener, accounting for 57.3–89.8% of the total measured PBDEs in this study. The proportion of penta- and nona-BDE congeners in the four eastern cities was markedly higher than those in five western cities. Principal component analysis showed that this elevation might be related to the debromination of BDE-209 during the thermal treatment process of products when PBDEs are used as flame retardants. Although the PBDE levels found in this study were markedly lower than those reported in previous studies, further efforts are still needed to clarify if there was a decreasing trend for PBDEs in the atmosphere of the PRD, in view of the increasing trends of PBDEs found by other researchers in mangrove sediments from Hong Kong and the Pearl River estuary in 2014 and 2015.

Keywords Polybrominated diphenyl ethers · Distribution · Atmosphere · Pearl River Delta

Introduction

As one category of brominated flame retardants, polybrominated diphenyl ethers (PBDEs) have been widely used in a variety of commercial and industrial products including electronic equipment, the transportation sector, textiles, and furniture to slow the rate of ignition and retard the propagation of combustion (Chen et al. 2012; Venier et al. 2015; Pozo et al. 2017). Since they were

first developed in the 1970s, PBDEs were produced in three major commercial formulations in the global market: penta-BDE, octa-BDE, and deca-BDE (Li et al. 2017). By 2001, nearly 70,000 t of PBDEs per year were sold worldwide (Venier et al. 2015). However, in 2004, the production and use of commercial penta-BDE and octa-BDE were banned in the European Union (EU), China, and several states in the USA (Li et al. 2017). Moreover, PBDEs were added to the Stockholm Convention's list of restricted substances in 2009 because of their persistence in the environment, tendency for bioaccumulation, and potential toxicity to the ecosystem and humans (Guo et al. 2015). Additionally, use of deca-BDEs was restricted by the EU in 2008, while the USA stopped its production in 2013 (Yang et al. 2013; Venier et al. 2015). However, deca-BDEs are still being produced and used in large quantities in China to meet high demand (Mai et al. 2005; Yu et al. 2016).

Polybrominated diphenyl ethers may easily enter the environment during manufacturing processes, usage, and disposal of PBDE-containing products because they are additives that are not chemically bound to the flame-retarded materials (Venier et al. 2015). Once in the environment, PBDEs tend

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to persist in sediment, accumulate in biota, and undergo long-range atmospheric transport (de Wit 2002; Chen et al. 2007; Chen et al. 2012; Guo et al. 2015; Li et al. 2017; Chakraborty et al. 2017). Moreover, PBDEs with different bromination levels have exhibited very different distribution patterns in the environment depending on their volatilization/sorption properties. For example, higher brominated PBDEs are less mobile and tend to accumulate in high levels in sediments near their emission sources because of their low volatility, water solubility, bioaccumulation, and strong adsorption to sediments. Conversely, lower brominated PBDEs are predicted to be transported to remote areas far from pollution sources (Gouin and Harner 2003; Breivik et al. 2006), or to accumulate in marine organisms or humans because they are more volatile, water soluble, and bioaccumulative than higher brominated PBDEs.

As one of the most developed areas in China, the Pearl River Delta (PRD) has undergone rapid industrialization and urbanization during recent decades, and this area is currently the largest manufacturing base for electronic/electrical products in the world. The PRD is also famous for its large number of factories for producing textiles and garments, plastic automobile products, and building and decorating materials. Several studies have shown that this rapid industrialization and urbanization has led to severe PBDE pollution in soil (Zou et al. 2007; Luo et al. 2009; Gao et al. 2011), sediments (Mai et al. 2005; Chen et al. 2007; Guan et al. 2009), air samples (Chen et al. 2006; Tian et al. 2012), biota, and humans (He et al. 2012). However, since 2004, the Chinese government has started to prohibit the use of commercial formulations of PBDEs (penta-BDEs and octa-BDEs) in all flame-retardant products nationwide. Moreover, the production of deca-BDEs has been restricted, and its annual production capability decreased from 25,000 metric tonnes in 2009 to 10,000 metric tonnes in 2011 (Chen et al. 2012; Dong et al. 2015; Zhu et al. 2017). These restrictions on PBDEs should have led to reductions in their levels in the PRD. Furthermore, the government of Guangdong Province has enforced the “dual transfer strategy” since 2008 to transfer labor-intensive industries and outdated industries that lead to more environmental pollution and energy consumption to circumjacent areas of the PRD (Liu 2016). This was also intended to reduce PBDE contamination from the PRD to a certain extent. However, to the best of our knowledge, only one study has reported a decreasing trend for PBDEs in sediment cores collected from the South China Sea (Zhang et al. 2009a), while investigations of mangrove sediments from Hong Kong and the Pearl River estuary showed increasing trends (Zhu et al. 2014; Zhang et al. 2015). As PBDEs can enter the air and eventually pose potential risks to humans via inhalation/or ingestion exposure, it is still necessary to reconfirm the

concentration and sources of PBDEs in the PRD region and assess the spatial distribution and temporal changes in air PBDE levels. Such information may provide the government with insight into the effectiveness of these regulations.

To achieve this goal, air samples were collected from 26 sampling sites in nine cities in the PRD region in the present study and compared to samples obtained from two sites in Shaoguan. The PBDE concentrations and the congener profiles in air samples were assessed, and principal component analyses were performed to explore the potential sources of PBDEs in the PRD.

Materials and methods

Sample collection

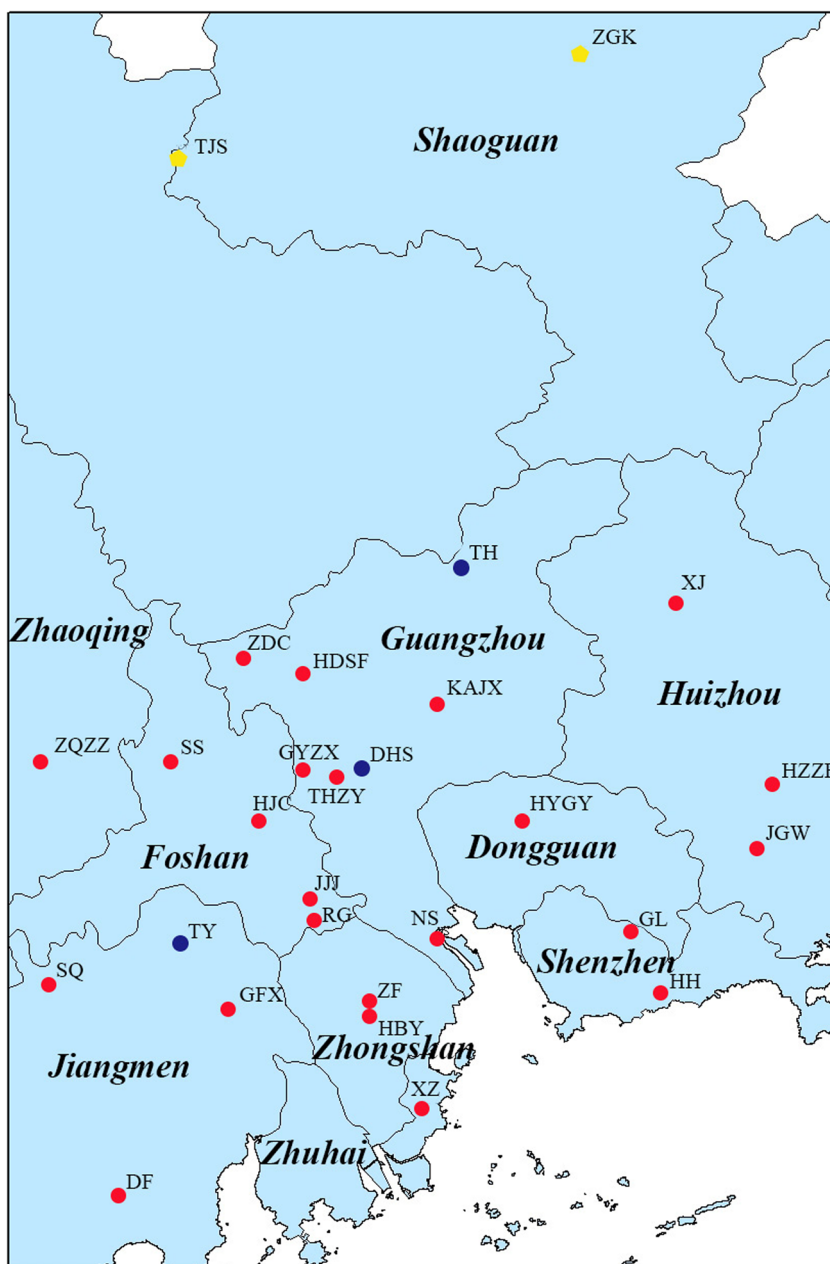
The 26 air-monitoring stations in the PRD region and two background control stations are shown in Fig. 1. The PRD region consisted of nine cities, Guangzhou (GZ), Shenzhen (SZ), Foshan (FS), Dongguan (DG), Zhuhai (ZH), Zhaoqing (ZQ), Huizhou (HZ), Jiangmen (JM), and Zhongshan (ZS). Shaoguan (SG), which lies in the northern Guangdong Province, far from densely inhabited regions, was selected as the background control sites. A total of 28 air samples were collected by passive samplers at these sampling sites from February to April of 2015. Three active samplers were simultaneously placed at three air-monitoring stations (DHS, TH, and TY) to facilitate calculation of the sampling rate of the passive samplers.

Passive atmosphere samplers were assembled on the spot using steel-sheltered chambers and polyurethane foam (PUF) disks (see Jaward et al. 2004 for details). Active air samples were obtained using a high-volume sampler (model TH-1000C, Tianhong Instruments (China) Co. Ltd., Wuhan, China) every 7 days with a constant flow rate of 300 L/min during the same sampling period. For the passive atmospheric samplers, both particulate and gaseous contaminants were trapped by PUF disks, whereas for the active atmosphere samplers, particles were retained on Teflon® filters and gaseous contaminants were collected on PUF plugs. Finally, all samples, including PUF disks, PUF plugs, and Teflon® filters, were stored at $-20\text{ }^{\circ}\text{C}$ until further analysis.

Chemicals and materials

The mixed PBDEs standards, including BDE-47, -66, -99, -100, -153, -183, -196, -197, -201, -202, -206, -207, -208, and -209, were obtained from AccuStandard, Inc. (New Haven, CT, USA). Surrogate standards, BDE-128 and BDE-181, were also acquired from AccuStandard, Inc. ^{13}C -PCB-208,

Fig. 1 The location of sampling sites in the PRD region and background sites. (1) Ten cities were marked with bold italic styles and abbreviations of 28 sampling stations were marked with Times New Roman font. (2) Two background stations and three active sampling stations were marked with yellow solid circles and dark blue solid circles, respectively



which was used as the internal standard, was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). All solvents and reagents used were pesticide grade. Envi-Florisil® SPE columns (1 g/6 mL) were acquired from Supelco (Bellefonte, PA, USA). Teflon® filters (203 × 254 mm, Munktell, Sweden) were ultrasonically cleaned in acetone/*n*-hexane (1:1 *v/v*) solvent for more than 30 min. The PUF disks (14-mm diameter, 1.35-cm thickness) and PUF plugs (63-mm diameter, 80-mm length) were pre-cleaned with dichloromethane (DCM), then Soxhlet extracted for 48 h. All filter and PUF materials were dried under vacuum and stored at -20 °C prior to use.

Sample extraction and chemical analysis

Prior to extraction, each sample was spiked with BDE-128 and BDE-181, then Soxhlet extracted with 250 mL DCM for 72 h. The extracts were then reduced to about 2 mL by rotary evaporation and exchanged into *n*-hexane, after which they were again concentrated to 1 mL. Next, the extracts were subjected to the Envi-Florisil® SPE cartridge separation. The cartridges were conditioned continuously with 5 mL ethyl acetate, 5 mL *n*-hexane/dichloromethane (8:2 *v/v*), and 8 mL *n*-hexane, and the analytes were eluted with 10 mL *n*-hexane/dichloromethane (8:2 *v/v*). The collected

fraction was subsequently concentrated and passed through a silica cartridge (2 g silica gel containing 44% [w/w] concentrated sulfuric acid) for further purification. The cartridge was conditioned with 12 mL *n*-hexane, and the analytes were eluted with 12 mL *n*-hexane/dichloromethane (8:2 v/v). Finally, the eluate was concentrated to 100 μ L under a gentle stream of nitrogen gas. Prior to instrumental analysis, a specific amount of ^{13}C -PCB-208 was added to the samples as an internal standard.

All of the target compounds were analyzed with an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrograph (Agilent Technologies, Palo Alto, CA, USA) in negative chemical ionization and selected ion monitoring mode. The injection mode was splitless and the injection volume was 1 μ L. The detailed gas chromatography-mass spectrometry parameters for PBDEs can be found in our previous study (Gao et al. 2011). Briefly, high-brominated PBDEs (BDE-196, -197, -201, -202, -206, -207, -208, and -209) were applied to a DB-5HT column (15 m \times 0.25 mm \times 0.1 μ m, J&W Scientific) and subjected to 110 $^{\circ}\text{C}$ for 5 min; then ramped to 200 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C}/\text{min}$, where they were held for 4.5 min; and finally increased to 300 $^{\circ}\text{C}$ at a rate of 7.5 $^{\circ}\text{C}/\text{min}$, where they were held for 10 min.

Low-brominated PBDEs (BDE-47, -66, -99, -100, -153, and -183) were applied to a DB-5MS column (30 m \times 0.25 mm \times 0.25 μ m, J&W Scientific) and then subjected to 110 $^{\circ}\text{C}$ for 1 min; after which, they were ramped to 180 $^{\circ}\text{C}$ at a rate of 8 $^{\circ}\text{C}/\text{min}$, where they were held for 1 min; then further increased to 240 $^{\circ}\text{C}$ at a rate of 2 $^{\circ}\text{C}/\text{min}$, where they were held for 5 min; then heated to 280 $^{\circ}\text{C}$ at a rate of 2 $^{\circ}\text{C}/\text{min}$ and held for 15 min; and then finally ramped to 300 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ and held for 12 min.

Quality assurance/quality control

Seven PUF disks, six Teflon® filters, and six PUF plugs sealed in aluminum foil envelopes without exposure to air were taken to sampling sites and set as field blanks. All field blanks together with six solvent blanks were analyzed to identify any background contamination. Special attention was paid to the analysis of BDE-209 because of its tendency to degrade under high temperature in the gas chromatograph system. No target compounds were found at levels above the limit of detection in any field blanks or solvent blanks, and the LOD values were from 0.01 to 0.13 and 0.08 to 0.42 pg/m^3 for low-brominated PBDE congeners and high-brominated PBDEs, respectively. BDE-128 and BDE-181 were added into the samples as surrogates to monitor the procedural performance and matrix effects. The surrogate recoveries for all actual samples were $90.1 \pm 14.4\%$ for BDE-128 and $87.3 \pm 14.4\%$ for BDE-181. The reported concentrations of target compounds in air samples were not corrected by blanks and recovery.

Calibration of air volume of passive air sampling

According to previous studies (He and Balasubramanian 2010; Jaward et al. 2004), the equivalent air volumes (V_{eq}) sampled by PUF disks could be calculated by Eq. (1):

$$V_{\text{eq}} = R_{\text{PUF}} \times D_s \quad (1)$$

where R_{PUF} is the sampling rate of individual PBDEs and D_s is the sampling duration (days) of each PUF disk.

As previous studies reported, passive air samplers can capture both particulate phase and gas phase (Chaemfa et al. 2009; Jaward et al. 2004; Tao et al. 2007). Therefore, the corresponding R_{PUF} values in our study could be calculated using the following Eq. (2) with both gaseous and particulate concentrations determined by active sampling.

$$R_{\text{PUF}} = M_{\text{PUF}} / (t \times C_{\text{air}}) \quad (2)$$

where M_{PUF} is the mass (pg) sequestered by the PUF disks after time t (days) and C_{air} is the concentration of individual PBDEs in the air (pg/m^3) determined by active sampling.

Results and discussion

Concentrations and distribution of PBDEs

Fourteen congeners of PBDEs, including BDE-47, -66, -99, -100, -153, -183, -196, -197, -201, -202, -206, -207, -208, and BDE-209, were identified and quantified in the present study. Table 1 summarizes the concentration of PBDEs in 26 air samples collected from nine cities in the PRD region, as well as data from two air samples collected from SG as the background control (see Table S1 for details). The concentration of total PBDEs (excluding BDE-209) ranged from 11.1 to 161 pg/m^3 with a mean value of 31.0 pg/m^3 , while the concentration of BDE-209 ranged from 15.2 to 570 pg/m^3 with a mean value of 73.6 pg/m^3 (Table 1). In general, the PBDE levels in the western half of the PRD (GZ, FS, ZQ, ZS, and JM) were markedly higher than those in the other four cities in the eastern half of the PRD. Specifically, the PBDE levels in samples from GZ, FS, and ZQ were nearly four times greater than those in the eastern four cities, with mean values of 160, 148, and 143 pg/m^3 , respectively. Unexpectedly, the concentrations of PBDEs in the eastern four cities (DG, HZ, SZ, and ZH) were comparable to those in air samples from the background sites. The highest PBDE level (634 pg/m^3) was detected at the site of DHS, which was located near an urban expressway in GZ. In comparison, the concentration of PBDEs in the present study was higher than that in northern China (mean value 58 pg/m^3) (Wang et al. 2012), central China (mean value 59.4 pg/m^3) (He et al. 2014), and urban areas of Shanghai (mean value 33.1 pg/m^3) in eastern China (Zhu et al.

Table 1 Polybrominated diphenyl ether (PBDE) concentrations (in pg/m^3) in air samples from ten cities in South China

Sampling city	LBr-PBDE ^a			HBr-PBDE ^b			BDE-209		
	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
GZ (<i>n</i> = 8)	3.81–20.1	12.5	11.8	8.92–142	32.4	13.3	24.2–570	115	54.1
ZQ (<i>n</i> = 1)		13.1			12.7			117	
FS (<i>n</i> = 4)	12.4–26.4	18.6	17.8	16.9–45.8	26.4	21.4	84.3–119	103	105
ZS (<i>n</i> = 2)	5.79–10.8	8.31	8.31	10.8–14.1	12.5	12.5	22.3–94.1	58.2	58.2
JM (<i>n</i> = 4)	5.95–11.6	7.62	6.45	10.9–21.2	13.8	11.6	32.5–60.0	42.6	39.0
DG (<i>n</i> = 1)		8.30			9.23			27.8	
HZ (<i>n</i> = 3)	2.91–13.3	6.41	3.00	8.18–10.0	9.15	9.23	15.2–32.9	21.6	16.8
SZ (<i>n</i> = 2)	3.16–9.53	6.35	6.35	8.92–9.80	9.36	9.36	21.4–33.9	27.7	27.7
ZH (<i>n</i> = 1)		4.54			10.2			26.2	
SG (<i>n</i> = 2)	1.69–19.0	10.3	10.3	5.94–10.1	8.00	8.00	10.3–16.8	13.5	13.5

GZ Guangzhou, SZ Shenzhen, FS Foshan, DG Dongguan, ZH Zhuhai, ZS Zhongshan, HZ Huizhou, JM Jiangmen, ZQ Zhaoqing, SG Shaoguan

^a LBr-PBDE = sum of BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, and BDE-183

^b HBr-PBDE = sum of BDE-196, BDE-197, BDE-201, BDE-202, BDE-206, BDE-207, and BDE-208

2017). Moreover, the PBDE levels observed in the present study were also higher than those found in Chile ($0.4\text{--}55 \text{ pg}/\text{m}^3$) (Poza et al. 2017), South Korea ($7.05 \text{ pg}/\text{m}^3$), Japan ($16.4 \text{ pg}/\text{m}^3$) (Nguyen Thanh et al. 2016), and the USA ($56 \text{ pg}/\text{m}^3$) (Ma et al. 2013).

Previous studies have shown that the PBDE concentrations in Guangzhou were $235\text{--}7873 \text{ pg}/\text{m}^3$ in 2004 (Chen et al. 2006), $838 \pm 126 \text{ pg}/\text{m}^3$ in 2009 (Yang et al. 2013), $77\text{--}372 \text{ pg}/\text{m}^3$ in Dongguan, and $195\text{--}1450 \text{ pg}/\text{m}^3$ in Shunde (a district of Foshan) in 2007 (Zhang et al. 2009b), all of which were higher than the PBDEs detected in the present study. The prohibition of PBDE commercial formulations or the implementation of the dual transfer strategy adopted by the Guangdong Province is expected to have reduced the level of PBDEs in the studied areas. The temporal changes in PBDE concentrations in air samples from the PRD areas appeared to decrease from 2004 to 2015. However, two studies

performed in mangrove sediments from Hong Kong and the Pearl River estuary revealed increasing levels of PBDEs (Zhu et al. 2014; Zhang et al. 2015). Accordingly, further efforts are still needed to clarify whether the decline in PBDE concentrations observed in the present study are linked to regulations on PBDE production and use in China after 2004, to the industrial transfer from 2008, or to both of these reasons.

PBDE congener profiles and potential source analysis

When compared with the background control samples collected from SG, the PBDE congener profile in most air samples from the PRD was dominated by BDE-209 (except for the sample from ZDC in GZ, with a proportion of 27.7% for BDE-209), which accounted for 57.3–89.8% of the total measured PBDEs. These findings were consistent with those of several previous studies conducted in China (Yang et al. 2013;

Fig. 2 PBDE congener profiles in air samples collected from ten cities

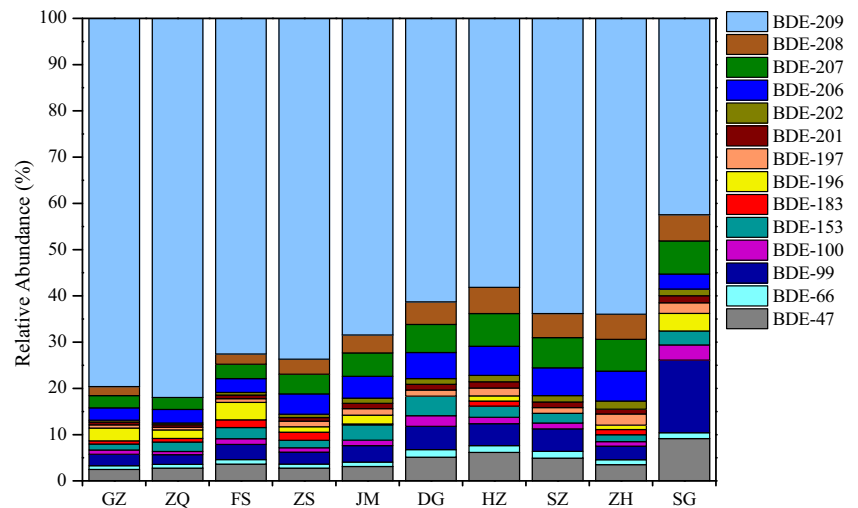
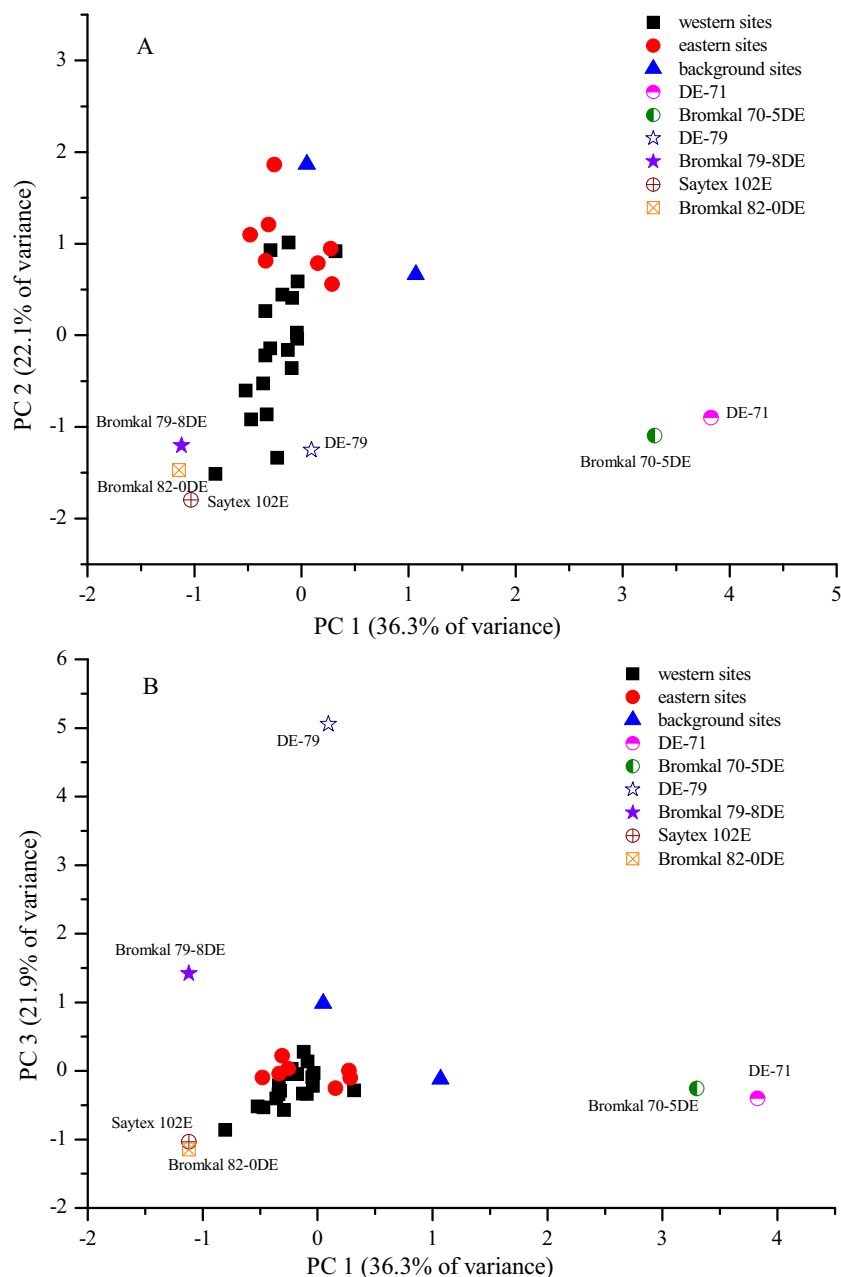


Fig. 3 Scatter diagram of principal component analysis (PCA) scores for samples collected from ten cities and available commercial formulations. Western sites include the samples collected from Guangzhou, Foshan, Zhongshan, Jiangmen, and Zhaoqing. Eastern sites include the samples collected from Dongguan, Huizhou, Shenzhen, and Zhuhai. Background sites include the samples collected from Shaoguan



Li et al. 2015; Xu et al. 2015; Li et al. 2016), which was also expected because deca-BDEs are the predominant commercial PBDEs used in China (Li et al. 2016). The congener profiles appeared to differ significantly ($p < 0.05$) among samples from the nine cities in the PRD (Fig. 2). Specifically, the average proportion of BDE-209 in the five western cities ranged from 68.9 to 81.9%, while it ranged from 58.2 to 64.0% in the four eastern cities. Moreover, the average proportion of other PBDE congeners in the five western cities, whether it was higher brominated PBDEs or lower brominated PBDEs, was apparently lower than those in the eastern four cities. Obviously, the congener profiles in the four eastern cities were more similar to those of the background control

sites (SG). In this study, the background control samples were collected from northern SG, which was far from developed PRD regions and has very few industrial activities. Accordingly, the occurrence of PBDEs in these control regions was considered a result of long-range atmospheric transportation from emission sources.

There is no doubt that regulations on PBDE production and use in China since 2004, and implementation of the dual transfer strategy in Guangdong province could reduce the concentration, or influence the distribution of PBDEs in the PRD region. However, as DG, HZ, and SZ are still the largest manufacturing base for electronic/electrical products in the world, the occurrence of PBDEs in the four eastern cities of

the PRD was clearly not a result of migration from other vicinities. Nevertheless, its PBDE concentrations were comparable to those in SG, as was its congener profile. Additionally, several factors including air transport, air deposition, and photodegradation could also change the levels and congener profiles in the research areas (Gouin and Harner 2003; Schenker et al. 2008). Therefore, further principal component analysis was required to discuss the outcome responsible for the variable PBDE congener profiles.

Principal component analysis of PBDE congener profiles

In this study, we conducted principal component analysis to differentiate the similarities or differences among congeners of samples collected from various locations in the PRD areas. The residual values in samples below the detection limits were treated as zero, and all data were normalized to a percentage of the total PBDEs. Additionally, six available commercial formulations (La Guardia et al. 2006), including penta-, octa-, and deca-BDE mixtures, were employed to explore the potential sources and changes in trends of the PBDEs in the present study. Three principal components (PC1, PC2, and PC3) that explained 80.3% of the total variance among samples were extracted (Fig. 3). PC1, which explained 36.3% of the total variance, was mainly associated with high loading of BDE-209, BDE-208, BDE-207, and BDE-206. PC2 explained 22.1% of the total variance and was associated with a high loading of BDE-196 and BDE-183. When compared to air samples collected from the four eastern cities and background control sites, most air samples from the five western cities were more closely related to the two deca-BDEs (Saytex 102E and Bromkal 82-0DE) (Fig. 3a), indicating a more extensive use of deca-BDEs as a flame retardant in these cities. These findings were also confirmed by the higher PBDE concentrations (Table 1) and BDE-209 contribution (Fig. 2) found in air samples from these five cities. Conversely, the air samples from the five western cities were also similar to the two octa-BDE mixtures (DE-79 and Bromkal 79-8DE), but this might have occurred because of debromination of BDE-209 during the thermal treatment process of products when PBDEs are used as flame retardants (Artha et al. 2011; Ortuño et al. 2015) because the production and use of octa-BDE mixtures have never been permitted in China (Zhu et al. 2014). In addition, although PC3 explained 21.9% of the total variance and there was high loading of BDE-47, BDE-99, BDE-100, and BDE-153, nearly all samples tended to cluster together, closer to the two deca-BDE mixtures than the two penta-BDE mixtures (DE-71 and Bromkal 70-5DE) (Fig. 3b). These findings suggest that the lower brominated PBDE congeners found in the present study might be associated with the photodegradation of deca-BDE mixtures employed in the region.

Conclusions

The concentrations and distribution of PBDEs were investigated in air samples collected from various cities in the PRD, South China. The results were as follows: (1) the concentrations of PBDEs ranged from 26.3 to 634 pg/m^3 , with a mean value of 105 pg/m^3 . The distribution of PBDEs was inhomogeneous in the PRD region, and the PBDE levels in the western half of the PRD were markedly higher than those in the eastern half. (2) BDE-209 was the predominant congener among the 13 congeners detected and quantified in this study. The proportions of lower brominated PBDEs in the four eastern cities were apparently higher than those in the five western cities. (3) The PBDE levels found in the present study were markedly lower than those reported by previous studies, which may indicate a decreasing trend in the atmosphere in the PRD region. However, further efforts are needed to clarify these findings regarding the increasing trends of PBDEs found in mangrove sediments from Hong Kong and the Pearl River estuary.

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