Particle-bound Dechlorane Plus and polybrominated diphenyl ethers in ambient air around Shanghai, China

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ABSTRACT

In present study, atmospheric particles from Shanghai, the biggest city and the most important industrial base in China, were analyzed for polybrominated diphenyl ethers (PBDEs) and Dechlorane Plus (DP). Concentrations of $\sum_{20}$PBDEs and DP both exhibited the changing trend of industrial area > urban areas. Jiading District had the highest levels of particulate PBDEs and DP with values of 744 ± 152 pg/m^3 and 5.48 ± 1.28 pg/m^3, respectively. Compared with similar data in other areas of the world, PBDEs in Shanghai were at medium pollution level, while DP was at lower level, which reflected their different production and use in Shanghai. The results from multiple linear regression analysis suggested that deca-BDE mixture was the most important contributor of particulate PBDEs in Shanghai. The fractions of anti-DP showed no significant differences to those of the technical mixtures ($p > 0.05$), which suggested that no obviously stereoselective process occurred in ambient air around Shanghai.

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1. Introduction

Recent research has shown that some halogenated flame retardants are potentially toxic, bio-accumulative, ubiquitous and persistent in the environment (Ismail et al., 2009; Muir and Howard, 2006), especially polybrominated diphenyl ethers (PBDEs) (de Wit, 2002; Law et al., 2003, 2006, 2008; Talsness, 2008). Penta- and octa-BDEs were regulated in Europe and the Unites States (Hites, 2004) and were added as new persistent organic pollutants (POPs) to the Stockholm Convention at the 4th Conference of the Parties (COP-4) held in May 2009 (www.pops.int). Deca-BDE, however, is still produced and used in many countries in the world. Due to its susceptibility to degradation in the environment via debromination and its potential to form lower brominated BDE congeners, which are found in banned penta- and octa-BDEs commercial mixtures, several agencies conducted in-depth risk assessments to determine its environmental behavior and degradation potential (Stapleton et al., 2006). The Europe Union (EU) restricted its use in 2008. The United States also voluntarily plan to restrict its production, import and sale in the country at the end of 2013. But there is still no regulation on deca-BDE in China until now. In China, PBDE studies in the environmental media started in 2003. Since then, many studies

have been conducted and the results indicated that concentrations of BDE-209 of China were higher than the worldwide levels, whereas $\sum$PBDEs concentrations (except BDE-209) of China were within the range of worldwide levels (Mai et al., 2005; Wang et al., 2010a).

Dechlorane Plus (DP) is a high-chlorinated flame retardant mainly used in coating electrical wires and cables, connectors used in computers, and plastic decoration materials (Qiu et al., 2007). It was only recently detected in the environment (Hoh et al., 2006) even though it has been produced for almost fifty years. Most published research on DP has focused on the Great Lakes area (Hoh et al., 2006; Qiu et al., 2007; Qiu and Hites, 2008; Sverko et al., 2008, 2010; Tomy et al., 2007), which results suggest that DP is bio-available and bio-accumulative (Gauthier and Letcher, 2009; Ismail et al., 2009). As for Asia, Qiu and Hites (2008) analyzed the tree barks from China and Korea and suggested that there might be Asia-specific sources of DP to the environment. E-waste recycling activities, urban activities and manufacturing industry have been proved as important DP sources of China (Ren et al., 2008, 2009; Wang et al., 2010a,b). It is necessary to pay attention to the environmental fate and risk assessment of these "new" emerging contaminants in China.

Air plays an important role in the transportation and transformation of organic pollutants and air particle inhalation is one of the most important PBDE exposure ways according to the assessment data of U.S. EPA (U.S. EPA, 2010). In China, atmospheric PBDEs levels in some industrial areas, typical urban areas (Chen et al., 2006; Zhang et al., 2009) and e-waste recycling areas (Chen et al.,

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2009; Deng et al., 2007; Han et al., 2009) were significantly higher than those in other countries (Wang et al., 2010a). As for DP, Ren et al. (2008) reported the atmospheric levels of DP in 97 urban and rural sites of China and the concentrations of urban sites (15.6 ± 15.1 pg/m^3) were about 5 times greater than those of rural areas, which were comparable to those of some urban sites in the Great Lakes area (Hoh et al., 2006; Venier and Hites, 2008). The highest atmospheric levels of DP so far (7737–26734 pg/m^3) were found near the DP manufacturing factory (Anpon) in Jiangsu Province, China (Wang et al., 2010), which began to produce DP several years ago with the annual output of about 300 tons and affected the surrounding area (Wang et al., 2010a,b).

To our knowledge, few studies focused on the halogenated flame retardants in Shanghai, an important commercial and industrial base and a typical metropolitan city of China, especially for air samples. In our previous work, we found that the atmospheric polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) of Shanghai were at higher levels compared with data from other countries (Li et al., 2008). As PBDEs were considered as PBDD/Fs' most important precursor (WHO, 1998), it is very important to conduct the PBDEs study in Shanghai. Furthermore, Ren et al. (2008) analyzed one air sample for DP from Minhang District of Shanghai with the value being comparable to some urban cities of U.S. (Hoh et al., 2006; Venier and Hites, 2008). And actually, Shanghai is about 400 km from the DP manufacturing plant-Anpon, it is necessary to investigate whether DP's production in Jiangsu Province could affect Shanghai city via air transport. With this background, we conducted this study with aims to investigate the levels, congener profiles and the possible sources of PBDEs and DP in the air particles of Shanghai.

2. Materials and methods

2.1. Sample collection

The industrial Jiading District (JD) and three urban districts Huangpu (HP), Zhabei (ZB), and Pudong (PD), which represent a prosperous commercial and traveling center, an old residential and traffic center, and a new developing area, respectively, were selected to evaluate the atmospheric pollution of particle-bound DP and PBDEs in Shanghai. Fig. 1 shows maps of China and Shanghai with the sampling sites being marked, respectively.

Short-term sampling (about one week) without rain or snow was scheduled at each site using intelligent high-volume air samplers with the flow rate of 1.05 m^3/min during February 23–March 10, 2006. Total suspended particles were collected on Whatman glass fiber filters (GFFs, 20.3 cm × 25.4 cm), which were heated at 450 °C for 4 h in air to remove possible background organic contaminants and then sealed in aluminum foil until to use. Time for each sample was 24 h with the sampling volume >1000 m^3. The interval between sampling was about 1 h and calibration of flow rate was conducted during the air sampling interval with an air sampler calibrator (Tianhong Intelligent Instrument Plant in Wuhan, China). A total

of 5, 6, 7 and 7 samples were obtained for HP, PD, ZB and JD, respectively. After sampling, the filters were packaged with aluminum foil and stored at <−10 °C until analyzed. The detailed sampling parameters and information can be obtained from our previous study (Li et al., 2008).

2.2. Analysis

2.2.1. Reference standards and chemicals

14 PBDE mixture standards solution (BDE-COC, 5 μg/mL for BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190 and 25 μg/mL for BDE-209, in isoctane) and individual high-brominated BDE standard solutions (BDE-196, -197, -203, -206, -207, -208, -209, 50 μg/mL, in isoctane) were obtained from Accustandards Inc. (New Haven, CT, USA). Polychlorodiphenyl (PCB)-209, ^{13}C-labeled PCB-141 and ^{13}C-labeled PCB-208 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Individual solutions of the syn- and anti-DP isomers (50 μg/mL, in toluene, purity >95%) were bought from Wellington Laboratories (Guelph, ON, Canada).

The solvents and reagents used during the whole procedure were all analytical or pesticide grade. The silica gel (70–230 mesh, Aldrich, USA) and the alumina (60–100 mesh, Merck, Germany) were activated at 180 °C and 250 °C for 24 h and deactivated with 5% (w/w) distilled water before use, respectively. Sodium sulfate was baked at 450 °C and stored in sealed desiccator.

2.2.2. Sample extraction and clean-up

The methods used for sample extraction and clean-up have been described previously (Chen et al., 2009; Ren et al., 2009). Briefly, samples were Soxhlet-extracted with 1:1 (v:v) n-hexane: acetone for 48 h after being spiked with ^{13}C-PCB-141 and PCB-209. The extracts were rotary evaporated and cleaned on the multi-layer silica/alumina columns (1 cm i.d.) which were wet-loaded sequentially with 6 cm aluminum, 2 cm silica gel, 5 cm basic silica gel (1 M NaOH, w/w, 33%), 2 cm silica gel, 8 cm acid silica gel (silica gel: sulfuric acid = 2:1, w:w) and 2 cm anhydrous Na$_2$SO$_4$ from the bottom to the top. The column was eluted with 10 mL n-hexane and 70 mL 1:1 (v:v) n-hexane: DCM. The second elution was concentrated to 100 μL in n-hexane under a gentle nitrogen stream and spiked with the internal standard ^{13}C-PCB-208 with a target concentration of 20 pg/μL before injection.

2.2.3. Instrumental analysis

The determination of PBDEs and DP were both performed with an Agilent 7890A gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC-MS) in negative chemical ionization (NCI) and selected ion monitoring (SIM) mode. The carrier gas was helium. 1 μL of sample or calibration solution was injected in splitless mode. The detailed GC–MS parameters for PBDEs and DP can be seen in Chen et al. (2009) and Ren et al. (2009), and are listed briefly as follows:

2.2.3.1. High-brominated PBDEs (octa- through deca-) and DP. 15-m DB-5-HT MS column (250 μm i.d., 0.10-μm film thickness; J&W Scientific, Folsom, CA, USA). GC oven temperature program: 110 °C (5 min) to 200 °C (4.5 min) at the rate of 20 °C/min, then to 300 °C (16 min) at 7.5 °C/min. The temperatures of the injection port, the transfer line, ion source, and the quadrupole rods were 260 °C, 280 °C, 250 °C and 150 °C, respectively. Ions monitored: m/z 79 and 81 for PBDEs; m/z 486.7 and 488.7 for BDE-209; m/z 473.7 and 475.7 for ^{13}C-PCB-208; m/z 498 and 500 for PCB-209; m/z 651.7 and 653.7 for DP.

2.2.3.2. Low-brominated PBDEs (tri- through hepta-). 30-m HP-5 MS column (250 μm i.d., 0.25-μm film thickness; J&W Scientific, Folsom, CA, USA). The temperature program of GC: 110 °C (1.0 min) to 180 °C (1.0 min) at 8 °C/min, then to 240 °C (5.0 min) at 2 °C/min, and to 280 °C (15 min) at 2 °C/min, and finally to 300 °C
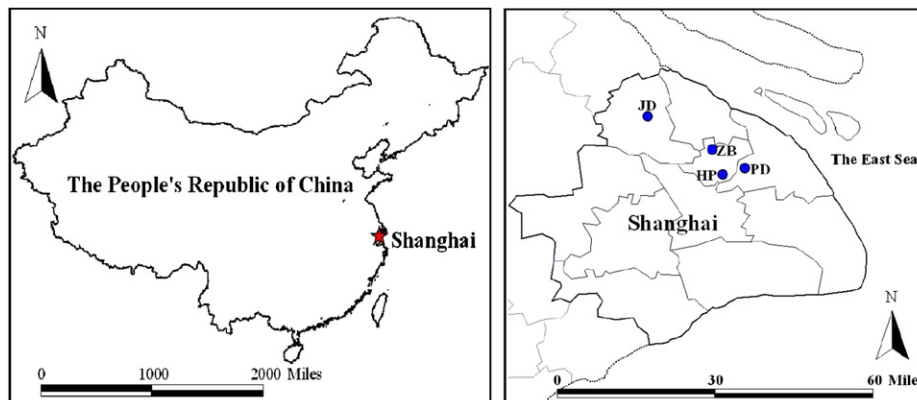

Fig. 1. The detailed sampling sites of the four districts in Shanghai, China (JD-Jiading District, ZB-Zhabei District, HP-Huangpu District, PD-Pudong District).

Table 1
Concentrations (pg/m^3) and percentages (%) or fractions of PBDEs and DP in the atmospheric particle samples from the four districts of Shanghai, China.

Comp.	JD		ZB		HP		PD	
	Conc.	Percentage	Conc.	Percentage	Conc.	Percentage	Conc.	Percentage
BDE-17	0.0481 ± 0.0158	0.01 ± 0.00	0.0454 ± 0.0292	0.01 ± 0.00	0.0341 ± 0.0079	0.04 ± 0.01	0.0296 ± 0.0161	0.01 ± 0.00
BDE-28	1.51 ± 1.04	0.18 ± 0.11	0.358 ± 0.231	0.07 ± 0.03	0.0966 ± 0.0297	0.11 ± 0.03	0.123 ± 0.053	0.06 ± 0.01
BDE-47	1.63 ± 0.634	0.20 ± 0.06	0.850 ± 0.382	0.18 ± 0.04	0.343 ± 0.107	0.39 ± 0.11	0.293 ± 0.127	0.14 ± 0.03
BDE-66	0.554 ± 0.308	0.07 ± 0.03	0.362 ± 0.186	0.07 ± 0.02	0.122 ± 0.048	0.12 ± 0.04	0.134 ± 0.063	0.05 ± 0.01
BDE-71	0.477 ± 0.168	0.07 ± 0.02	0.212 ± 0.082	0.05 ± 0.01	0.179 ± 0.044	0.21 ± 0.05	0.175 ± 0.085	0.05 ± 0.01
BDE-85	0.970 ± 0.764	0.11 ± 0.08	0.207 ± 0.137	0.04 ± 0.02	0.0980 ± 0.0377	0.12 ± 0.05	0.0384 ± 0.0155	0.05 ± 0.02
BDE-99	4.31 ± 2.61	0.50 ± 0.26	0.503 ± 0.095	0.14 ± 0.02	0.216 ± 0.081	0.37 ± 0.16	0.389 ± 0.185	0.16 ± 0.02
BDE-100	4.02 ± 3.22	0.44 ± 0.34	0.577 ± 0.414	0.10 ± 0.05	0.0986 ± 0.0341	0.12 ± 0.04	0.140 ± 0.068	0.04 ± 0.01
BDE-138	0.926 ± 0.731	0.10 ± 0.08	0.162 ± 0.098	0.03 ± 0.01	0.106 ± 0.054	0.11 ± 0.07	0.119 ± 0.067	0.02 ± 0.01
BDE-153	0.388 ± 0.264	0.05 ± 0.03	0.401 ± 0.221	0.08 ± 0.02	0.127 ± 0.049	0.13 ± 0.05	0.246 ± 0.134	0.06 ± 0.01
BDE-154	1.31 ± 1.02	0.14 ± 0.11	0.218 ± 0.050	0.06 ± 0.01	0.222 ± 0.094	0.22 ± 0.09	0.352 ± 0.178	0.09 ± 0.02
BDE-183	1.16 ± 0.58	0.17 ± 0.06	0.762 ± 0.214	0.20 ± 0.04	0.856 ± 0.398	0.90 ± 0.51	0.715 ± 0.349	0.19 ± 0.02
BDE-190	0.678 ± 0.558	0.08 ± 0.06	0.124 ± 0.063	0.03 ± 0.01	0.250 ± 0.133	0.20 ± 0.08	0.0457 ± 0.0386	0.01 ± 0.00
BDE-196	14.1 ± 9.1	1.68 ± 0.92	3.22 ± 1.25	0.75 ± 0.12	5.52 ± 2.73	4.48 ± 1.58	3.66 ± 1.71	1.21 ± 0.11
BDE-197	28.9 ± 21.9	3.33 ± 2.25	6.09 ± 3.45	1.21 ± 0.37	10.6 ± 5.1	9.06 ± 4.20	3.01 ± 1.36	1.03 ± 0.11
BDE-203	7.23 ± 3.21	0.94 ± 0.31	2.82 ± 0.90	0.70 ± 0.08	4.33 ± 2.00	3.71 ± 1.40	3.78 ± 1.78	1.23 ± 0.13
BDE-206	18.7 ± 6.7	2.47 ± 0.61	9.07 ± 2.56	2.38 ± 0.31	6.36 ± 2.84	5.42 ± 0.85	7.69 ± 3.57	2.73 ± 0.28
BDE-207	12.0 ± 2.2	1.73 ± 0.15	6.95 ± 1.53	1.84 ± 0.08	12.1 ± 7.1	8.77 ± 2.33	8.46 ± 3.94	3.16 ± 0.39
BDE-208	9.45 ± 2.71	1.30 ± 0.23	4.74 ± 1.26	1.23 ± 0.07	7.71 ± 3.19	6.82 ± 1.86	4.98 ± 2.30	1.96 ± 0.25
$\sum_{19}$PBDEs[a]	104 ± 54		37.2 ± 12.9		49.2 ± 23.0		34.0 ± 15.7	
BDE-209	640 ± 143	86.93 ± 5.28	330 ± 58	90.97 ± 1.06	59.2 ± 15.5	59.08 ± 10.76	283 ± 140	87.92 ± 1.21
$\sum_{20}$PBDEs	744 ± 152		367 ± 71		108 ± 34		317 ± 153	

Comp.	JD	ZB	HP	PD
syn-DP	1.58 ± 0.26	1.31 ± 0.19	0.651 ± 0.159	1.30 ± 0.44
anti-DP	3.90 ± 1.04	3.77 ± 0.67	1.67 ± 0.37	2.77 ± 1.27
$\sum$DP	5.48 ± 1.28	5.08 ± 0.84	2.32 ± 0.50	4.07 ± 1.71
f_{anti}[b]	0.69 ± 0.02	0.74 ± 0.02	0.72 ± 0.03	0.64 ± 0.02

[a] BDE-209 was not included in the concentrations of $\sum_{19}$PBDEs.
[b] f_{anti} = Concentration of anti-DP/concentration of the total DP.

(12 min) at 10 °C/min. Injection port: 280 °C. Transfer line: 300 °C. Ion source: 200 °C. Quadrupole rods: 150 °C. Ions monitored: m/z 79 and 81 for PBDEs; m/z 372.0 and 374.0 for ^{13}C-PCB-141, m/z 473.7 and 475.7 for ^{13}C-PCB-208.

2.3. Quality assurance and quality control (QA/QC)

One field GFF blank sample, one laboratory blank sample, one standard spiked blank sample and one standard spiked matrix sample were performed for each batch of twelve samples for quality control. The compounds were identified and quantified when the deviation of the GC retention times from those of the standards were within ±0.1 min, the signal-to-noise ratio (S/N) was ≥10 and the isotope ratios for the monitored ion-pairs matched the theoretical value within 15% deviation. Concentrations were calculated with an eight-point calibration standard curve. All samples were spiked with ^{13}C-PCB-141 and PCB-209 to assess the extraction efficiency and clean-up procedures. The recoveries of ^{13}C-PCB-141 and PCB-209 were in the range of 73–127% and 85–110%, respectively. The recoveries of the spiked standards were 102 ± 4% for DP isomers and 90 ± 11% for PBDEs congeners, respectively.

2.4. Calculations

All analyzed PBDE congeners and DP isomers were not detected (n.d., S/N < 3) or un-quantified (n.q., 3 ≤ S/N < 10) in the laboratory blank samples except BDE-209. The concentrations of BDE-209 in the blank samples (2–5 pg/μL) were much lower than that of particle samples (<2%). Therefore all the concentrations were not blank or recovery corrected and concentrations below the quantification limits were regarded as nil. The mean value plus–minus one standard error was adopted as the representative concentration of each set of samples. Statistical analysis was performed using SPSS 13.0 software and the statistical significance was defined as $p < 0.05$.

The three commercial PBDE products, penta-, octa- and deca-BDEs, are all mixtures of many congeners, of which congener composition ratios were analyzed by La Guardia et al. (2006). Similar to the principle component analysis, multiple linear regression analysis is also used to investigate the most important contributor in several known factors with the formula of $y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots \beta_n x_n$. In this study, we presumed the three PBDE mixtures as the possible sources of particulate PBDEs in Shanghai, the composition ratios of penta-BDEs, octa-BDEs and deca-BDEs as three known independent variables x_1, x_2 and x_3, respectively, and the average percentages of PBDE congeners of the four districts in Shanghai as variables y, and analyzed the most important contributor of the three technical mixtures to particulate PBDEs of Shanghai according to their respective composition fingerprints through multiple linear regression analysis. The analysis was performed with SPSS

13.0 and the significance was defined as $a = 0.005$. The formula is $y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3$ (β is the coefficient, $n = 20$, $m = 3$). The test values used to evaluate the analytical results were obtained from the F and t distribution tables or were calculated with the following equations:

$$F_a = F_{0.005(m,n-m-1)} = F_{0.005(3,16)} = 6.30$$

$$R_a = \sqrt{\frac{mF_a}{(n-m-1)+mF_a}} = \sqrt{\frac{3 \times 6.30}{16 + 3 \times 6.30}} = 0.7359$$

$$t_a = t_{0.005(n-m-1)} = t_{0.005(16)} = 2.921$$

3. Results and discussion

3.1. Atmospheric concentrations of PBDEs and DP

All twenty PBDE congeners including BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190, -196, -197, -203, -206, -207, -208, and -209 were detected in the atmospheric particulate samples, their concentrations and relative abundances are listed in Table 1. The concentrations of individual DP isomers and the anti-isomer fractions in the total DP are also summarized in Table 1. As shown in Table 1, the concentrations of $\sum_{20}$PBDEs and DP were 744 ± 152 and 5.48 ± 1.28, 367 ± 71 and 5.08 ± 0.84, 108 ± 34 and 2.32 ± 0.50, 317 ± 153 and 4.07 ± 1.71 pg/m^3 for JD, ZB, HP and PD districts, respectively. Both $\sum_{20}$PBDEs and DP exhibited the following trends: industrial area (JD) > urban areas (ZB ≈ PD > HP), which implied that industry had a significant influence on the environmental levels of these halogenated flame retardants. This trend was also reported for PBDEs in ambient air around Guangzhou (Chen et al., 2006).

Although some studies in other countries have reported atmospheric PBDE concentrations, a comparison of these studies is difficult due to inconsistencies in the congeners analyzed, small data sets and samples collected only after specific events or for only

a limited time during the year (Venier and Hites, 2008). Table 2 summarizes the reported atmospheric PBDE levels in different areas of the world. A simple comparison based on average concentrations was made between our data and the data from these studies.

As Table 2 indicates, ambient air around e-waste recycling areas, e.g. Guiyu (Chen et al., 2009; Deng et al., 2007) and Fengjiang (Han et al., 2009), had the highest ever-reported atmospheric levels of PBDEs, followed by the industrial areas of Guangzhou (Chen et al., 2006), Chicago (Hoh and Hites, 2005) and Osaka (Ohta et al.,

2002), where the levels were significantly higher than those in general urban, semi-urban and rural areas of China (Deng et al., 2007; Zhang et al., 2009), Canada (Su et al., 2009) and the UK (Lee et al., 2004). Comparatively, the particulate atmospheric PBDEs in this study ($\sum_{19}$PBDEs, 34.4–108 pg/m^3, BDE-209 was not included) were at medium levels, similar to those of some urban areas and a little higher than those of some semi-rural/rural areas in the world. These levels might be underestimated as only the particle phase was calculated in this study, while some low-brominated PBDEs were

Table 2
Comparison between the concentrations of PBDEs and DP in ambient air around different areas in the world[c].

Sampling Site	Sampling year	Description	BDE-47	BDE-99	$\sum$PBDEs[a]	BDE-209	DP[b]	References
Guangzhou, China	2004	10 congeners	P:3.48–27.74	P:7.26–42.55	P:25.04–108.9	P:263.8–4200		Chen et al., 2006
Hongkong, China	2004	22 congeners	3.52–79.7	2.58–129	33.8–358			Deng et al., 2007
Guangzhou, China		Only particle	71.1–122	61.0–122	204-372			
Guiyu, China			6456 ± 1942	5519 ± 2751	21474 ± 7241			
Waliguan, China	2005	8 congeners Gas + particle	0.6–5.9	0.2–5.5	8.3 ± 4.0c	0.1–4.2		Cheng et al., 2007
Guiyu, China	2005	11 congeners	848-4105	487-2491	3182-9579	1649-2164		Chen et al., 2009
Chendian, China		Gas + particle	75.2–115	28.2–45	170-244	66.2–132		
Fengjiang, Taizhou, China	2006–2007	13 congeners	38-72	30-75	135.1–678.5	137.7–2087.3		Han et al., 2009
Luqiao, Taizhou, China		Gas + particle	5-26	5-15	17.4–165.1	85.8–438.8		
The Pearl River Delta, China	2006–2007	15 congeners	P:0.3–5.1	P:0.6–7.9	P: 61-1383c	P:49-1158		Zhang et al., 2009
		Only particle						
Osaka, Japan	2001	31 congeners			104-347c	100-340		Ohta et al., 2002
Chicago, USA	1997–1999	7 congeners	21-48	11-25	33-77c	0.20–0.35		Strandberg et al., 2001
Chicago, USA	2002–2003	19 congeners	3.9–42	2.4–15	13-980c	1.5–878		Hoh and Hites, 2005
Hazelrigg, UK	2000–2001	21 congeners	0.78–15	0.53–11	2.8–37			Lee et al., 2004
Chilton, UK			0.72–7.2	0.82–15	3.4–33			
Mace Head, UK			0.16–1.9	0.28–1.9	0.22–5.0			
Point Petre, Canada	2002–2004	15 congeners	0.10–32	0.14–27	0.78–75	0.14–6.4		Su et al., 2009
Jiading, Shanghai, China	2006	20 congeners	0.29–1.63	0.22–4.31	34.4–108	59–640	5.48 ± 1.28	In this study
Zhabei, Shanghai, China		Only particle					5.08 ± 0.84	
Huangpu, Shanghai, China							2.32 ± 0.50	
Pudong, Shanghai, China							4.07 ± 1.71	
Sturgeon point, NY, USA	2004						34 ± 24	Hoh et al., 2006
Cleveland, OH, USA							23 ± 9.8	
Chicago, IL, USA							3.19 ± 0.88	
Point Petre, ON, USA							3.40 ± 1.71	
Sleeping Bear Dunes, MI, USA							0.30 ± 0.07	
Eagle Harbor, MI, USA							0.15 ± 0.05	
Sturgeon point, NY, USA	2005–2006						20 ± 6	Venier and Hites, 2008
Cleveland, OH, USA							7.2 ± 1.2	
Chicago, IL, USA							2.4 ± 0.3	
Sleeping Bear Dunes, MI, USA							0.8 ± 0.3	
Eagle Harbor, MI, USA							0.8 ± 0.6	
26 Urban areas, China	2005						15.6 ± 15.1	Ren et al., 2008
71 Rural areas, China							3.5 ± 5.6	
Minhang, Shanghai, China							21	
Harbin, China	2008						0.35 ± 0.21	Ma et al., 2009
Anpon, Huai'an, China	2009						7737-26734	Wang et al., 2010

[a] BDE-209 was not included in the concentrations of $\sum$PBDEs.
[b] DP concentrations in pg/m^3 are showed in mean ± one standard error mode.
[c] High volume samplers were used for air sampling in all mentioned references except Ren et al., 2008, in which passive air sampler was used.

partly partitioned in the gas phase. The concentrations of BDE-209 in this study (59–640 pg/m³), however, are comparable to or significantly higher than those reported in other countries such as Japan, USA, and Canada (Hoh and Hites, 2005; Strandberg et al., 2001; Su et al., 2009; Venier and Hites, 2008), which is consistent with the fact that deca-BDE has always been the primary PBDE formulation used in China (Chen et al., 2007; Venier and Hites, 2008). However, these concentrations of BDE-209 are lower than those in the industrial areas of Guangzhou (Chen et al., 2006) and the e-waste recycling areas in China (Chen et al., 2009; Han et al., 2009), which suggests that atmospheric BDE-209 in Shanghai is at the medium level in China.

As for DP, the mean concentrations of total particulate DP (2.32 ± 0.50–5.48 ± 1.28 pg/m³) showed a similar trend to those of PBDEs in different districts, however, there were no statistically significant differences between the values for JD, ZB, HP and PD using the t-test ($p > 0.05$), which indicated that there were no significant point emission sources in these four districts. The published atmospheric levels of DP in different areas of the world are presented in Table 2. According to these data, DP was mainly produced and used in North America and therefore was found at higher environmental levels in these areas. Hoh et al. (2006) first reported atmospheric levels of DP in the Great Lakes area and the highest mean value of 34 ± 24 pg/m³ was found at the station nearest to the DP manufacturing plant, and the total DP decreased from east to west (Hoh et al., 2006). Similar results were also found in another study (Venier and Hites, 2008). Recently, atmospheric DP concentrations around the DP manufacturing factory (Anpon) in Jiangsu Province, China were also investigated and the levels were 7737–26734 pg/m³, the greatest atmospheric levels of DP so far (Wang et al., 2010). Even though, China was still found to have comparatively lower environmental levels of DP due to limited production and usage (Ma et al., 2009; Ren et al., 2008). Ren et al. (2008) measured the ambient air across 97 Chinese urban and rural sites using passive air samplers and the total DP concentrations were 15.6 ± 15.1 pg/m³ and 3.5 ± 5.6 pg/m³ for urban and rural sites, respectively. Ma et al. (2009) analyzed samples collected using a high-volume sampler in 2008 and calculated that the average air concentration of DP at Harbin, China was 0.35 ± 0.21 pg/m³. Obviously, the DP levels in this study were considerably lower than those at the areas near the DP manufacturing plant in North America (Sturgeon Point and Cleveland) (Hoh et al., 2006) and China (Wang et al., 2010), and some urban areas of China (Ren et al., 2008). Comparatively, the levels at Shanghai were similar to those at rural sites in China (Ren et al., 2008) and some rural sites in the Great Lakes area (Hoh et al., 2006; Venier and Hites, 2008), which were all at lower levels.

3.2. Compositional patterns of PBDEs and the isomer ratios of DP

As shown in Table 1, high-brominated BDEs including deca- and nona-BDEs were the major homologs in this study. BDE-209 was the dominant individual congener in all four districts with the relative percentages ranging from 51.2% to 91.2%, especially at JD, ZB and PD (84.6–91.2%). The major congeners were sequentially BDE-207 (1.62–11.2%), BDE-197 (0.95–9.83%), BDE-206 (2.42–5.87%) and BDE-208 (1.27–7.12%). These results are consistent with those reported in soil samples from Shanghai city (Jiang et al., 2010). However, they are obviously different from those reported in North America and Europe (de Wit, 2002; Hites, 2004; Law et al., 2006, 2008), where penta- and octa-BDEs were the mainly-used brominated flame retardants (BFRs) and BDE-47 and -99 were the dominant congeners in the environment. One reason for the relatively low percentages of penta- and octa-BDEs in this study is that technical deca-BDE (mixture of deca- and nona-BDEs) is the most widely used BFR in China (Chen et al., 2007). Studies in sediments, air, and

biota also verify that BDE-209 is the predominant congener in China (Chen et al., 2006, 2007; Wang et al., 2010a). Another possible reason is that only particulate samples were analyzed in this study, while low-brominated BDEs exist both in gas and particle phases.

Multiple linear regression analysis, which determines the most important factors among several variables, was performed in this study to further discuss the compositional pattern of PBDEs. We assumed the congener composition in the different districts of Shanghai as the dependent variable (y) and those of the three common technical mixtures of PBDE as three independent variables (x_1, x_2, x_3), which were measured by La Guardia et al. (2006). The averaged values were selected as the final results. These results showed that significant linear relationships were found between y and x_1, x_2, x_3 ($a = 0.005$) and the regression coefficients R were 0.971–1.000 (Table 3). The unstandardized coefficients of x proved that deca-BDE was the most important factor for all four districts of Shanghai, while the contributions from penta- and octa-BDEs were minor and negligible.

Generally, the fraction of *anti*-DP or *syn*-DP in total DP has always been used to discuss the environmental transportation and fate of the two structural isomers. In this study, f_{anti} was calculated (Table 1) with the concentration of *anti*-DP being divided by the sum of the concentrations of *anti*-DP and *syn*-DP for air samples from the four districts in Shanghai. The mean f_{anti} values $\pm$ one standard error for JD, ZB, HP and PD were 0.69 ± 0.02, 0.73 ± 0.02, 0.72 ± 0.03, and 0.64 ± 0.02, respectively. Although the mean f_{anti} values of the four sampling sites exhibited small variations, there were no statistically differences among them (t-test, $p > 0.05$).

The f_{anti} value of commercial DP products were reported to be 0.75–0.80 (Hoh et al., 2006; Qiu et al., 2007) and 0.65 (Tomy et al., 2007), respectively. The mean f_{anti} values in this study were very close to that of the commercial product, and were similar to the results of ambient air samples from other urban and rural areas in China (0.67 ± 0.10, Ren et al., 2008) and some sampling sites near Niagara Falls (Hoh et al., 2006), but were higher than those at Sleeping Bear Dunes and Eagle Harbor (<0.50), which are far from the presumed source of DP in the Great Lakes and long-range transport may change the *anti*-DP fractions (Hoh et al., 2006).

The previous result that the f_{anti} values in air and sediment samples collected from sites furthest from the Niagara production source were smaller than those from sites which were closer suggested the enrichment of *syn*-DP (Gauthier and Letcher, 2009; Hoh et al., 2006). Other data from sediment samples have conversely indicated that the

Table 3
The multiple linear regression analysis results of the atmospheric PBDEs congeners compositions in the four districts of Shanghai, China.

Sampling region	F[a]	R[a]	Factors	Unstandardized coefficients		t[b]
JD	2209.886	0.999	Constant	β_0	0.288	0.911
			Penta-BDEs	β_1	0.002	0.130
			Octa-BDEs	β_2	0.045	1.306
			Deca-BDEs	β_3	0.892	66.424
ZB	7531.993	1.000	Constant	β_0	0.161	0.896
			Penta-BDEs	β_1	$-4.9E-06$	0.000
			Octa-BDEs	β_2	0.020	0.997
			Deca-BDEs	β_3	0.945	123.442
HP	82.292	0.971	Constant	β_0	1.840	1.807
			Penta-BDEs	β_1	-0.046	-0.789
			Octa-BDEs	β_2	0.179	1.613
			Deca-BDEs	β_3	0.512	11.843
PD	7214.683	1.000	Constant	β_0	0.232	1.266
			Penta-BDEs	β_1	-0.004	-0.364
			Octa-BDEs	β_2	0.017	0.842
			Deca-BDEs	β_3	0.939	120.858

[a] $F > Fa$ and $R > Ra$ mean the regression relationship is significant.
[b] $t > ta$ means the independent factor x is important for y and should not be excluded.

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anti-isomer is more environmentally persistent than the *syn*-isomer (Qiu et al., 2007; Tomy et al., 2007). However, the two isomers showed no obvious *syn*- or *anti*-stereoselective enrichment in 97 air samples from China (Ren et al., 2008). Furthermore, the two isomers showed the same atmospheric persistence according to results of tree bark samples from the Great Lakes area (Qiu and Hites, 2008). Data from the present study showed that *anti*-DP had a good linear relationship with *syn*-DP in the four districts of Shanghai ($R = 0.9294$), which also suggested that no obvious stereoselective process occurred in ambient air around Shanghai.

3.3. Preliminary analysis of local source

Three typical DP emission sources have been reported in the published literature: DP manufacturing plant (Hoh et al., 2006; Qiu et al., 2007; Sverko et al., 2010; Tomy et al., 2007), DP-containing e-waste recycling activities (Ren et al., 2008, 2009) and the use of DP-containing products (Zhu et al., 2007). Furthermore, DP could affect source-nearby areas *via* air transportation (Qiu et al., 2007). In China, there is only one factory which began to produce DP several years ago with an annual output of about 300 tons (Wang et al., 2010a,b). Our analytical results have suggested that no obvious emission point sources were found in the four districts of Shanghai. Therefore, air transportation from other areas and release from DP-containing products are the most likely sources of particulate atmospheric DP in the four districts. DP is mainly used for coating electrical wires and cables, connectors in computers, and plastic decoration materials (Qiu et al., 2007), which are widely used in urban areas. Therefore, urban areas could be significant source of DP, which was also suggested by Kang et al. (2010).

As for PBDEs, the production, usage and waste disposal of PBDEs and PBDEs-containing products are all possible emission sources (Alcock et al., 2003). PBDEs are used widely in the furniture industry, in electrical/computer components and housing, e.g. high-impact polystyrene, flexible polyurethane foam, textile coatings (not clothing), wire and cable insulation, electrical/electronic connectors and other interior parts (WHO, 1994). In this study, atmospheric concentrations of PBDEs showed the following trend: industrial area (JD) > urban areas. Industries in JD include automobile production, electron and electric equipment manufacture, and refined chemical synthesis (Li et al., 2008), all of which possibly use PBDEs and may act as potential emission sources (WHO, 1994). Moreover, this district has the biggest municipal solid waste incineration in Shanghai and many small waste disposal centers. Consequently, it had the highest atmospheric levels of PBDEs in the four districts of Shanghai, China. HP is a famous commercial area and travel center in Shanghai with the Bund, the Pearl Tower and other attractions along both sides of the Huangpu River. There are few local industrial pollution sources in this area. Therefore, the possible PBDE sources in this region are air transportation from other places and release from office equipment and household appliances. In addition, the open space and flowing air above the Huangpu River would dilute the air contamination to a certain degree. All of these factors may result in HP having the lowest level of PBDEs of the three urban areas of Shanghai, China.

Furthermore, PBDEs are reported to be the main source of PBDD/Fs (WHO, 1994, 1998). In this study, Pearson correlation analysis was performed between particulate PBDEs and the corresponding PBDD/Fs concentrations which were reported in our previous study (Li et al., 2008). Significant positive correlations were observed between these two types of pollutants with a coefficient of 0.702 at the 0.01 level (2-tailed). These results clearly indicate that PBDEs are a potential major source of atmospheric PBDD/Fs. Our previous study reported that atmospheric PBDD/Fs in Shanghai had similar or even higher toxic equivalent levels than chlorinated dioxins and

were at comparatively high levels (Li et al., 2008). Therefore, it is strongly recommended that more attention should be paid to PBDEs contamination in Shanghai.

4. Conclusion

Compared with other areas in the world, the four districts of Shanghai evaluated in this study had moderate PBDEs levels and comparatively low DP levels. Deca-BDE was the most important contributor to the total concentration of PBDEs using multiple linear regression analysis of the congener profiles of PBDEs. Due to BDE-209's significant use in China, frequent detection in various environmental compartments, recently proved toxicity, and its potential in the formation of PBDD/Fs, it is strongly suggested that more attention should be paid to BDE-209 and more detailed and in-depth studies should be carried out in the future.

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