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Polybrominated Diphenyl Ethers in the Atmosphere of Taizhou, a Major E-Waste Dismantling Area in China

Wenliang Han · Jialiang Feng · Zeping Gu ·
Duohong Chen · Minghong Wu · Jiamo Fu

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Abstract Concentrations, congener profiles, gas-particle partitioning and size distributions of polybrominated diphenyl ethers (PBDEs) in the atmosphere of Taizhou were studied to evaluate the impact of e-waste recycling on the environment. Total concentration of 13 PBDEs near the e-waste dismantling area was 506 pg m^{-3} in summer and 1,662 pg m^{-3} in winter, about 7 times higher than that of the reference urban site, but much lower than that of Guiyu, another major e-waste dismantling area in China. This should be attributable to the centralized management measures taken in recent years in Taizhou. BDE-209 was the major congener and mainly in coarse particles.

Keywords PBDEs · E-waste · Atmosphere · China

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in plastics, polymers, textiles, foams packing and insulating materials. Because of their weak bonding to the materials, PBDEs can be easily released and are ubiquitous in the environment. PBDEs are persistent, bioaccumulative and biomagnifiable as other POPs (Wit 2002). Every year, 20–50 million tons of electrical and electronic wastes (e-waste) are generated world-wide, and a large part of them is exported to China for recycling (UNEP 2005). Taizhou of Zhejiang province and Guiyu of Guangdong province are two major e-waste dismantling areas in China. More than two million tons of e-wastes were dismantled in Taizhou every year to recycle metals such as copper, aluminum etc. E-wastes are regarded as misplaced resources in China, many e-waste dismantling factories have been set up in recent years and e-waste recycling industry is expected to last for a long time in China. Researches had found very high PBDEs levels in the atmosphere of Guiyu (Deng et al. 2007; Chen et al. 2009). It is thus important and interesting to know if PBDEs pollution is also a big problem in Taizhou because the types of wastes dismantled in Taizhou are somehow different from that in Guiyu and thus the dismantling manner. Centralized management on the e-waste dismantling activities is adopted by the local government of Taizhou in recent years and would be model for the e-waste dismantling in other areas of China. Air is the main transport pathway of PBDEs and inhalation was found to be an important exposure route to PBDEs of human being (Meng et al. 2007). Study on the airborne PBDEs in/near the e-waste dismantling area is thus important to understand the impact of the e-waste dismantling activities on the environment. There have been a few studies on the concentrations of PBDEs in soil, leaves and human hair in Taizhou (Wen et al. 2008; Yang et al. 2008), but only one brief study on the atmospheric PBDEs based on only two days of samples (Li et al. 2008).

This study reports the PBDEs concentrations, seasonal variations, congener profiles, gas-particle partitioning, size distributions and the correlations between OC, EC and PBDEs in the atmosphere of Taizhou to evaluate if PBDEs from the e-waste dismantling activities have great impact on the environment.

W. Han · J. Feng (✉) · Z. Gu · M. Wu · J. Fu
Institute of Environmental Pollution and Health, Shanghai University, Shanghai 200072, China
e-mail: fengjialiang@shu.edu.cn

D. Chen · J. Fu
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

Materials and Methods

Standard mixture of 13 PBDEs (BDE-17, -28, -71, -47, -66, -100, -99, -85, -154, -153, -138 and -183) at 5 μg mL^{-1} and BDE-209 at 25 μg mL^{-1} was purchased from Accu-Standards (New Haven, CT, USA). $^{13}C_{12}$-labeled internal standard ($^{13}C_{12}$-CB-208) and surrogates ($^{13}C_{12}$-CB-141, $^{13}C_{12}$-CB-209) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

$PM_{2.5}$, TSP and gas phase samples were collected 5–12 July 2006 and 6–14 January 2007 on the roof-top of a three-story building about 400 m downwind of the e-waste dismantling industrial park at Fengjiang (FJ) of Taizhou, and the reference samples were collected on the roof-top of a six-story building in the urban area (LQ). LQ is about 6 km northwest of FJ. Two sets of samples with four size cuts of <0.5, 0.5–0.9, 0.9–1.3 and 1.3–2.5 μm were also collected using cascade impactors in the high-volume $PM_{2.5}$ sampler at FJ on 6 and 14 January 2007.

$PM_{2.5}$ samples were collected on quartz fiber filters (QFF, Whatman, 20.3 × 25.4 cm) using two high-volume $PM_{2.5}$ sampler (1.13 m^3 min^{-1}, Model GUV 16HBL, Thermo, USA). TSP and gas phase samples were collected on similar quartz fiber filters and polyurethane foam (PUF) plugs (6.5 cm in diameter × 7.5 cm in length with a density of 0.030 g cm^{-3}) by a modified high-volume air sampler (THC1000, Tianhong Intelligent Instrument Co. China). Prior to sampling, the QFFs were baked at 450°C for at least 4 h to remove any organic contaminants, and PUF plugs were Soxhlet extracted with methanol and acetone/hexane mixture (1:1) for 48 h each sequentially.

The extraction protocol used was a modified version of that reported by Chen et al. (2006). In brief, the samples were spiked with $^{13}C_{12}$-CB-141 and $^{13}C_{12}$-CB-209 and Soxhlet extracted with a mixture of acetone/hexane (1:1) for 48 h. The concentrated extracts were cleaned and fractionated through acidic/basic multilayer silica/alumina columns, and the fraction containing PBDEs was eluted with 70 mL hexane/methylene chloride (1:1). The final extracts were concentrated under gentle N_2 stream to 100 μL, and a known amount of internal standard ($^{13}C_{12}$-CB-208) was added prior to instrumental analysis. PBDEs concentrations were measured by GC-MS (Agilent 6890N GC coupled with Agilent 5975 Mass Selective Detector) with negative chemical ionization (NCI) in selected ion monitoring (SIM) mode. PBDEs congeners except BDE-209 were determined with a DB-5 ms capillary column (30 m length × 0.25 mm i.d × 0.25 μm thick). The column temperature was initiated at 110°C (held for 1 min), increased to 180°C at 20°C min^{-1} (held for 1 min), then to 280°C at 2°C min^{-1} (held for 1 min), and finally to 305°C at 5°C min^{-1} (held for 15 min). For BDE-209, a short DB-5 ms capillary column (9 m × 0.25 mm i.d × 0.1 μm thick) was used to reduce degradation in the column. The oven temperature was programmed from 110°C (held for 1 min) to 300°C at a rate of 10°C min^{-1} (held for 6 min). The ion source, inlet and interface temperatures were set to 250, 290 and 285°C respectively.

Based on the average sampling volume of about 1,500 m^3 for $PM_{2.5}$ and 500 m^3 for TSP plus PUF samples, the method detection limit of 12 PBDEs and BDE-209 were 0.02–0.09 and 0.13 pg m^{-3}. Field blanks were analyzed and only low concentrations of BDE-28, -47 and -209 were detected. The field blank levels were less than 5% of the concentrations in the samples. The mean recovery of the measured 13 PBDEs was 94 ± 15% in the spiked blank samples, and 104 ± 18% in the matrix spiked samples. Duplicate samples showed deviations less than 11% for $\sum_{12}$PBDEs (BDE-17, -28, -71, -47, -66, -100, -99, -85, -154, -153, -138 and -183) and 20% for BDE-209. Surrogate recoveries were 71.5–121.9% for $^{13}C_{12}$-CB-141 and 92.0–123.6% for $^{13}C_{12}$-CB-209 in all the samples. Concentrations reported were not recovery corrected.

A Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory, Forest Grove, OR) was used to measure the concentrations of organic carbon (OC) and elemental carbon (EC) based on thermal-optical transmittance using the National Institute for Occupational Safety and Health (NIOSH) Method 5040 protocol.

Results and Discussion

The concentrations of PBDEs are summarized in Table 1. The total PBDEs (TSP plus gas phase) concentration in the ambient air of FJ was 1,662 pg m^{-3} in winter, which was about 7 times of that at the urban reference site LQ, showing the impact of the e-waste dismantling activities on the airborne PBDEs level. The winter PBDEs level was about 3 times of that in summer, which should be mainly due to the seasonal variation in meteorological conditions because we did not found obvious seasonal difference in the amount of e-wastes dismantled during our sampling periods. The atmospheric mixing heights in winter were usually low due to lower ambient temperatures, making dispersion less favorable.

Compared with Guiyu of Guangdong, another major e-waste dismantling area in south China, the concentrations of PBDEs at FJ were much lower (concentrations of PBDEs at Guiyu were 16.6 ng m^{-3} in $PM_{2.5}$ and 21.5 ng m^{-3} in TSP, Deng et al. 2007). The first reason for this should be the differences in the types of e-wastes dismantled between the two sites. E-wastes in Taizhou are mainly cables and electric equipments, while electronic products such as personal computers and TVs are dominant in Guiyu. The amounts of PBDEs contained in the e-wastes

Table 1 Summary of PBDEs concentrations in the atmosphere of Taizhou (pg m^{-3})

Site (period)		PM$_{2.5}$		TSP		Gas phase		Air concentration (TSP + Gas)	
		$\sum_{12}$PBDEs[a]	BDE-209	$\sum_{12}$PBDEs	BDE-209	$\sum_{12}$PBDEs	BDE-209	$\sum_{12}$PBDEs	BDE-209
FJ	Mean	58.0	185.5	113.9	290.4	102.1	ND[b]	216.0	290.4
(06–07)	Min	6.1	47.0	31.5	137.7	79.4	ND	135.1	137.7
	Max	170.2	418.2	252.4	425.7	117.2	ND	362.0	304.0
	SD	55.0	154.4	79.5	109.8	20.0	ND	115.0	85.3
LQ	Mean	26.7	56.6	53.6	216.6	60.4	ND	114.0	216.6
(06–07)	Min	8.1	30.5	15.2	84.4	32.4	ND	64.2	107.8
	Max	58.7	100.9	91.9	438.8	89.2	ND	165.1	438.8
	SD	17.8	26.6	31.3	153.3	28.4	ND	54.7	167.0
FJ	Mean	335.9	601.7	412.9	1,205.5	34.3	9.4	447.2	1,214.9
(07–01)	Min	91.5	226.3	147.8	727.7	13.7	0.5	161.5	730.7
	Max	546.0	1,306.4	622.3	2,061.3	68.2	26.0	678.5	2,087.3
	SD	189.3	424.0	185.7	574.1	21.4	10.1	205.4	577.7
LQ	Mean	36.6	60.3	37.4	196.8	7.5	7.7	44.8	204.4
(07–01)	Min	12.3	23.4	14.2	81.6	3.2	0.3	17.4	85.8
	Max	77.4	94.9	71.0	277.8	10.8	19.1	79.5	278.4
	SD	27.0	26.6	21.9	77.1	3.0	8.5	24.0	76.7

[a] $\sum_{12}$PBDEs: Sum of the concentrations of 12 PBDEs including BDE-17, -28, -71, -47, -66, -100, -99, -85, -154, -153, -138 and -183

ND, Not detected

at the two sites and the dismantling manner are thus different. Centralized management on the dismantling activities by the local government of Taizhou in recent years should also be a reason of the lower PBDEs concentrations. To regulate the e-waste dismantling activities and reduce the pollutants emissions, an e-waste dismantling industrial park of about one square kilometer was set up at FJ by the local government, and the qualified factories were moved to the park. Open burning of plastic containing e-wastes such as wires and cables is prohibited and many of the plastics are recycled, though illegal uncontrolled burning can still be found from time to time. Our results of the concentrations of PBDEs at FJ were comparable to that of an automotive shredding and metal recycling facility in California (810 pg m^{-3}, Cahill et al. 2007).

By comparing the concentrations of PBDEs at FJ and the reference urban site LQ, transportation of pollutants from FJ to LQ was found in summer. The PBDEs concentration at FJ was only 1.6 times of that at the reference urban site LQ in summer, while about 7 times in winter. LQ was in the northwest of FJ and the prevailing wind direction was southeast during the summer sampling period, so LQ was in the downwind direction of FJ in summer. While in winter, the prevailing wind was from the northwest direction thus LQ became upwind of FJ and the pollutants from FJ would not reach LQ. Consequently, the PBDEs concentration at LQ in summer was comparable to that in winter (Table 1).

The concentration of PBDEs at the reference site LQ (about 330 pg m^{-3} in summer and 250 pg m^{-3} in winter) was comparable to or slightly higher than the reported concentrations in other cities such as Hong Kong and Guangzhou of China (Chen et al. 2006; Deng et al. 2007), Izmir of Turkey (Cetin and Odabasi 2007), Kyoto of Japan (Hayakawa et al. 2004), Chicago of USA (Hoh and Hites 2005), confirming that the PBDEs emissions from the e-waste dismantling at FJ did not severely damage the air quality of the reference urban area.

Among the 13 PBDEs measured, BDE-209 was the major component in all samples (33.4–93.7%, mean = 70.7%), indicating that the decabromodiphenyl ethers (deca-BDE) was the major commercial PBDEs contained in the e-wastes dismantled at FJ. As deca-BDE is the most widely used brominated flame retardants around the world (Wit 2002), the high percentage of BDE-209 found in Taizhou was expectable.

Besides BDE-209, BDE-47, -99 and -183 were other three dominant congeners in all the samples (Fig. 1). BDE-47 and -99 are the major components of the commercial penta-BDE, and BDE-183 is the major component of octa-BDE (Alaee et al. 2003), it can thus be known that the commercial penta- and octa-BDE products were also widely used in the e-wastes dismantled at FJ. It's known that more than 97% of the penta-BDE products were used in North America (Alaee et al. 2003), the distribution pattern of PBDEs confirmed that some of the e-wastes at FJ were from North America. Congener profile of PBDEs at FJ was obviously different from that found in Guiyu, where commercial penta-BDE (mainly BDE-47, -99) was dominant and deca-BDE (BDE-209) only took 20%–30% of the atmospheric PBDEs concentration (Chen et al. 2009), confirming that the e-wastes dismantled at the two sites are different.

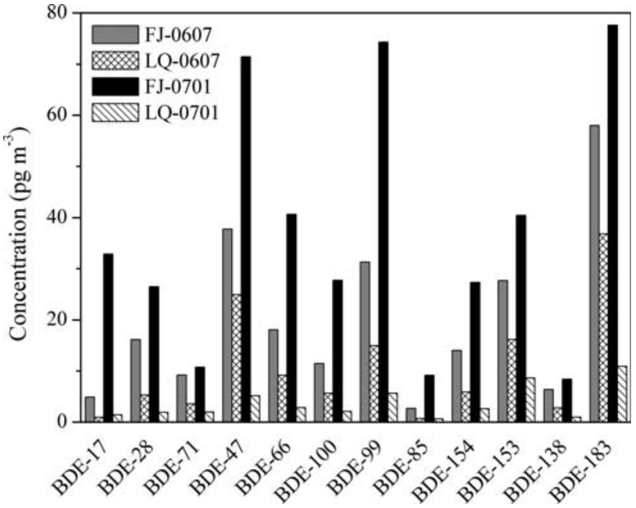
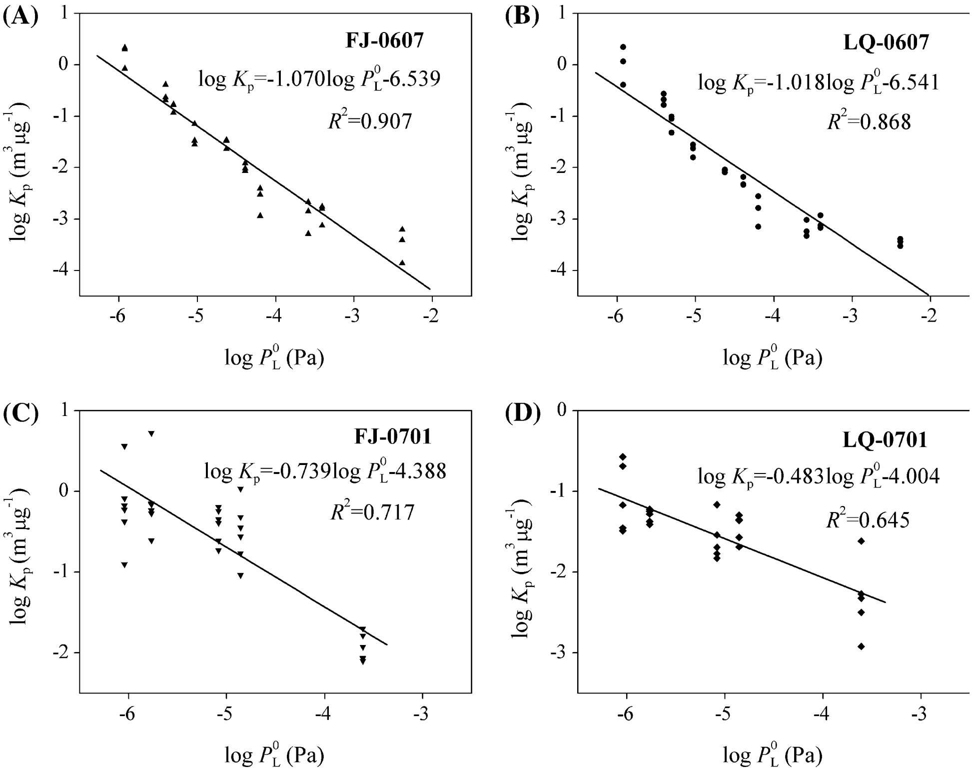


Fig. 1 Congener profiles of 12 PBDEs in the atmosphere of Taizhou (TSP plus gas phase)

BDE-209 in the atmosphere of Taizhou was almost exclusively in the particle phase in summer (≥99% at both sites) and winter (≥99% at FJ, ≥96% at LQ). The other 12 PBDEs existed in both particulate and gaseous phases. The particle phase $\sum_{12}$PBDEs accounted for 53% of the total $\sum_{12}$PBDEs (TSP plus gas phase) at FJ and 47% at LQ in summer, while 92% at FJ and 83% at LQ in winter. Higher percentage of particulate phase at FJ is expectable since the FJ sampling site is near the source and less semi-volatile PBDEs loss was experienced for the particles.

Gas-particle partitioning of the semi-volatile PBDE species was examined by checking the relationship between the particle-gas partition coefficient, log K_p (m^3 µg^{-1}), and the vapor pressure of the analyte's subcooled liquid, log P_L^0 (Pa) (Pankow 1994). P_L^0 of the PBDEs congeners were calculated after the method of Tittlemier et al. (2002) using the average ambient temperatures of the sampling periods (30.8°C in summer and 5.9°C in winter). Figure 2a, b shows the log K_p versus log P_L^0 plots for the 10 PBDEs (BDE-17, -71 were excluded due to the lack of P_L^0 data) in the summer samples. The slopes (m_r) were -1.07 and -1.02 for the summer samples of FJ and LQ, respectively, indicating that the partitioning was near equilibrium (Pankow 1994). Goss and Schwarzenbach

Fig. 2 Plots of log K_p versus log P_L^0 for PBDEs in summer and winter samples



(1998) reported that m_r could be an indication of the partitioning mechanism: 1) $m_r < -1$, surface adsorption, 2) $m_r > -0.6$, absorption by the organic matter, and 3) $-1 < m_r < -0.6$ for coexistence of both mechanisms. So the dominant mechanism of gas-particle partitioning in Taizhou in summer might be adsorption onto the particle surfaces. Figure 2c, d showed the gas-particle partitioning in winter. As the concentrations of the gas phase PBDEs were much lower in winter, only five of the lower brominated BDEs with higher gas phase concentrations (BDE-28, -47, -66, -100, -99) were included to avoid the propagation of analytical errors. The m_r values were -0.74 and -0.48 for FJ and LQ respectively, suggesting that absorption by the organic matter was also the partitioning mechanism (Goss and Schwarzenbach 1998). In general, the gas-particle portioning of PBDEs in Taizhou was similar to that found in Guangzhou (Chen et al. 2006) and Kyoto of Japan (Hayakawa et al. 2004).

The average $PM_{2.5}$/TSP ratio of $\sum_{12}$PBDEs concentrations was 84% (59%–103%) in winter, and 55% (22%–79%) in summer at both sites, indicating that BDEs with 3–7 bromine atoms existed mainly in fine particles especially in winter. The lower summer ratio was reasonable as most of the 3–7 BDEs were semi-volatile and are biased to the gas phase in summer due to high ambient temperatures, and the gas phase species probably adsorbed to the surface of the coarse particles. Meanwhile, the average $PM_{2.5}$/TSP ratio of BDE-209 concentration was 41% (20%–80%) in winter, and 45% (20%–92%) in summer, indicating that BDE-209 existed mainly in coarse particles and it is thus not expected to be transported too far. Wilford et al. (2008) also found that BDE-209 was associated with the 3–10 μm particles.

Closer investigation of the size distribution of PBDEs in fine particles was achieved by collecting two sets of samples with <0.5 μm, 0.5–0.9 μm, 0.9–1.3 μm and 1.3–2.5 μm cuts using cascade impactors in the high-volume $PM_{2.5}$ sampler at FJ on 6 and 14 January 2007. The results showed that the PBDEs were mainly in the <0.5 μm cut, accounting for 52% of the total PBDEs in the fine particles, and the size distribution pattern of PBDEs was very similar to that of the mass concentration, indicating that no size effect existed.

Table 2 Correlation (r^2) of PBDEs with OC, EC and TC

Season	Site	OC	EC	TC
Summer	FJ	0.57	0.38	0.55
	LQ	0.24	0.03	0.17
Winter	FJ	0.79	0.19	0.81
	LQ	0.94	0.54	0.93

The relationship between particulate PBDEs concentrations and OC, EC and TC (OC + EC) were investigated and listed in Table 2. Generally speaking, PBDEs correlated better with OC than EC, suggesting that the sources of PBDEs and EC were different. The main source of EC presumably is from fossil fuel combustion (Park et al. 2003), while burning/melting of polymers for PBDEs. Stronger correlation with OC also suggested that part of the PBDEs was absorbed into the organic matter. No significant correlations between PBDEs and OC, EC were found at LQ in summer, confirming that much of the PBDEs at LQ might be transported from the e-waste dismantling area and had different sources with the local OC/EC. However, in winter, they correlated well with OC and EC at LQ, suggesting that PBDEs at LQ were from combustion sources.

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