Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China

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Abstract

Air samples of total suspended particles (TSP, particles less than 30–60 μm), and particles with aerodynamic diameter smaller than 2.5 μm (PM$_{2.5}$) were collected simultaneously at Guiyu (an electronic waste recycling site), three urban sites in Hong Kong and two urban sites in Guangzhou, South China from 16 August to 17 September 2004. Twenty-two PBDE congeners (BDE-3, -7, -15, -17, -28, -49, -71, -47, -66, -77, -100, -119, -99, -85, -126, -154, -153, -138, -156, -184, -183, -191) in TSP and PM$_{2.5}$ were measured. The results showed that the overall average concentrations of TSP and PM$_{2.5}$ collected at Guiyu were 124 and 62.1 μg m^{-3}, respectively. The monthly concentrations of the sum of 22 BDE congeners contained in TSP and PM$_{2.5}$ at Guiyu were 21.5 and 16.6 ng m^{-3}, with 74.5 and 84.3%, contributed by nine congeners (BDE-28, -47, -66, -100, -99, -154, -153, -183 and -191 respectively). This pattern was similar to Tsuen Wan site of Hong Kong. Two urban sites of Guangzhou had the same congener pattern, but were different from Yuen Long and Hok Tsui sites of Hong Kong. The results also showed that the amount of mono to penta brominated congeners, which are more toxic, accounted for 79.4–95.6% of Σ_{22}PBDEs from all sites. All congeners tested in Guiyu were up to 58–691 times higher than the other urban sites and more than 100 times higher than other studies reported elsewhere. The higher concentration in the air was due to heating or opening burning of electronic waste since PBDEs are formed when plastics containing brominated flame retardants are heated.
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Keywords: Polybrominated diphenyl ethers (PBDEs); Total suspended particles (TSP); PM$_{2.5}$; Electronic waste

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame-retardant additives in plastics (such as high-impact polystyrene) electrical appliances, television sets, computer circuit boards and casings (Rahman et al., 2001). The Bromine Science Environmental Forum (BSEF) estimated the worldwide production of PBDEs in 2001 was about 67,000 t (BSEF, 2003). In addition to the initial twelve chemical compounds which have been identified as persistent organic pollutants (POPs) under the Stockholm Convention, commercial pentabromodiphenyl ether (Penta-BDE) and octabromodiphenyl ether (Octa-BDE) are chemicals under consideration for inclusion in the Convention due to their new and

emerging concern over environmental levels and the health effects of exposure to PBDEs (UNEP, 2006).

PBDEs are additives mixed into polymers and are not chemically bound to plastic or textiles and therefore may separate or leach from the surface of their product applications into the environment (www.bsef.com). The toxicological endpoints of concern for environmental levels of PBDEs are likely to be thyroid hormone disruption, neurodevelopmental deficits and cancer (McDonald, 2002). PBDEs can be easily volatilized into atmosphere from the products in which they reside (Tanabe, 2004). The atmosphere is considered to be the key environmental vector for the transport of these semi-volatile chemicals.

PBDEs are bioaccumulative and possess potential endocrine disrupting properties. They are lipophilic compounds so are easily removed from the aqueous environment and sorb onto particulate matter or to fatty tissue, aiding their distribution throughout the environment. Various PBDEs have been detected with significant

levels in environment, mostly in sediment, soil, and biota samples (Wurl and Obbard, 2005; Liu et al., 2005). Increasing PBDE levels have been observed in human milk from Sweden and Germany (Meironyté et al., 2001; Sjödin et al., 2003); and in human adipose tissue samples from Spain, Israel, Finland and Canada (McDonald, 2002). PBDEs were found to be manifested in food webs even in remote regions such as Baltic Sea and northern Atlantic Sea (Burreau et al., 2006). However, there are limited data on PBDEs concentration in air, especially South China (Julander et al., 2005; Gevao et al., 2006).

Illegal and unsafe recycling operations of electronic waste (e-waste) have been conducted in Guiyu Town in Guangdong Province, China (Texas Campaign for the Environment, 2002). Guiyu is located in an upwind position and the prevailing wind would contribute to regional fine PM pollution in the Pearl River Delta Region of South China, which has a population of about 45 million people. The town is located about 250 km northeast of Hong Kong and comprises of a cluster of small villages that have become a booming recycling centre for e-waste arriving from various regions of the world since 1995. Villagers and migrant workers use primitive and environmentally unacceptable techniques, such as open burning to separate and recover metals from printed circuit boards, polyvinyl chloride-coated wires and cables. This unsafe e-waste recycling practice causes severe environmental pollution from heavy metals, fire retardants, and via the secondary formation of polyhalogenated dibenzo-p-dioxins and dibenzofurans (Wang et al., 2005). The levels of BDE-209 in rice field of Guiyu was found to be 79-3973 times greater than the background soil value of southern Sweden. The high PBDEs level in the soils and sediments in Guiyu should be derived from the combusted residue and ash of plastic cables and plastic chips, in which PBDEs are often used as fire retardants (Leung et al., 2007; Wong et al., in press). However, there is a lack of information on the PBDE congener profiles and concentrations around the e-waste recycling site. It is expected that PBDEs will be dispersed into the air, which may eventually impose adverse human health effects.

Since detailed source inventories for environmental releases of PBDEs are not available, this work was undertaken to measure ambient air concentrations of PBDEs in TSP and $PM_{2.5}$ at Guiyu, comparing with other urban sites in South China, and to identify the congener patterns of PBDEs produced by e-waste recycling activities. It is hoped that the results obtained will serve as valuable references for future risk assessment and environmental management measures in Guiyu and South China.

2. Methods

2.1. Sampling sites

2.1.1. Guiyu, the e-waste recycling site

The locations of the six sampling sites are shown in Fig. 1. Guiyu (23°327′ N, 116°342′E) is characterized by residential and commercial buildings involved in e-waste recycling. Guiyu town is located in Chaoyang District, Shantou City, Guangdong Province, southeast China, with a total area of 52 km² and a population of 150,000 (Wong et al., in press). Air samples were taken on the roof of a 3-story building located on a street where there are open burning and other e-waste recycling operations.

2.1.2. Hong Kong urban sites

Hong Kong is located at the southern end of the China coastline and faces the South China Sea. There are three sampling sites in Hong Kong: Yuen Long

Fig. 1. Sampling sites. Guiyu (GY, 23°327′N, 116°342′E), Li Wan (LW, 23°07.756′N 113°14.331′E), Tian He (TH, 23°08.914′N 113°21.519′E) in Guangzhou, Yuen Long (YL, 22°26.699′N 114°01.376′E), Tsuen Wan (TW, 22°22.302′N 114°06.881′E), Hok Tsui (HT, 22°12.572′N 114°15.477′E) in Hong Kong.

(YL, 22°26.699′N 114°01.376′E) site is adjacent to the border of mainland China and has undergone rapid development within these few years; Tsuen Wan (TW, 22°22.302′N 114°06.881′E) site is set back from heavily traveled roads in a highly populated residential area with many stores, offices, and light industry; and Hok Tsui (HT, 22°12.572′N 114°15.477′E) is a rural background site located at the southeast end of Hong Kong Island, with strong wind blowing from the sea which provides good air dispersion (Louie et al., 2005). Air sampling was performed on top of a 6- and 5-story building, which was about 8 m away from the main traffic road in YL and TW, respectively, and on a concrete platform located on a hillside ∼60 m above mean sea level in HT.

2.1.3. Guangzhou urban sites

Guangzhou is the capital of Guangdong Province, South China. Two sampling sites in Guangzhou are: Li Wan (LW, 23°07.756′N 113°14.331′E) and Tian He (TH, 23°08.914′N 113°21.519′E). LW, in the western downtown area, has a population of 440,000 and an area of 11.8 km^2. It is surrounded by residences, schools, restaurants, shops, and heavy traffic, which would create a complex mix of pollutants. TH is located in the eastern part of the downtown area with extensive highway connection. Most of TH area is schools, residences, office buildings, and highways (Duan et al., 2005). Air sampling was performed on top of 9- and 8-story buildings, 25 m and 20 m, respectively, above ground level.

2.2. Sample collection

Air samples were collected from August 16 to September 17 2004 using a high volume air sampler (Graseby Anderson) to collect PM$_{2.5}$ at a flow rate of 1–1.2 m^3/min, and a compatible high-volume air sampler (Tianhong Intelligent Instrument Plant, Wuhan, China) to collect TSP at the flow rates 1–1.2 m^3/min. The ambient air samples were taken from the atmosphere with inlet heights between 1.8 and 2 m above ground. Particulate-associated contaminants were isolated from the atmosphere by drawing air through a Whatman quartz fiber filter (QFF, 8 in. × 10 in.) for approximately 24 h. After sampling, the filters were wrapped in aluminum foil and stored in Ziplock® bags at −20 °C. The concentrations of TSP and PM$_{2.5}$ were determined by weighing the filters before and after exposure. The filters were then cut into seven strips and archived in cold storage (−20 °C). All treatments were carefully handled using a pair of stainless steel scissors.

2.3. Extraction, clean-up and GC/MS analysis

The filters with a certain size particle were extracted using Soxhlet apparatus for 16 h in 200 ml of solvent mixture (acetone:DCM:hexane, 1:2:3). The extract was then evaporated to around 1 ml by a rotary evaporator (Büchi Rotavapor R-124), added to pre-cleaned silica gel column (silica gel was active by heating to 450 °C for 5 h), and eluted with 20 ml of solvent mixture (hexane:DCM, 4:1). The eluted solution was reduced to 80 μl for GC-MS determination. Analytical procedures followed those of Zheng et al. (2004).

The sample extracts were analyzed by Agilent Technologies 6890 N Network GC system and Agilent Technologies 5973 inert Mass Selective Detector (GC-MS) EI with 30 m DB-1 fused silica capillary column (0.25 mm diameter and 0.25 um film thickness; 100% dimethyl-polysiloxane), with helium at a rate of 1 ml/min as the carrier gas. The 1 μl injection of the combined sample and C^{13} calibration standard solutions were made in the splitless mode. The injector temperature was 280 °C. GC oven temperature was programmed as follows: 90 °C for 2 min, increasing 20 °C/min to 230 °C, followed by 2 °C/min to 247 °C, then 20 °C/min to final temperature of 280 °C, which was held for 25 min. Total run time was 46.15 min. The mass spectrometer was operated in

electron impact with selected ion monitoring (EI/SIM) mode. The following quantifying ions (M/Z) were used to monitor BDE compounds in the EI/SIM mode: mono-Br 248–260, di-Br 328–340, tri-Br 406–418, tetra-Br 486–498, penta-Br 564–576, hexa-Br 644–656, hepta-Br 721–733. The BDE congeners were quantified using isotope dilution method with addition of C^{13} labeled BDEs. Concentrations of BDEs were measured by using a C^{13} labeled BDE internal standard mixture. In the case where no internal standards were added, the BDE concentrations were measured with the "nearest neighbor" C^{13} labeled BDE internal standard. All BDEs were identified based on the relative retention time of external standards and computer library of mass spectra fragmentation patterns on the MS detector in EI/SIM mode.

The 22 BDE congeners investigated in this study were: BDE-3, -7, -15, -17, -28, -49, -71, -47, -66, -77, -100, -119, -99, -85, -126, -154, -153, -138, -156, -184, -183, -191 in order of retention times, with no measurement of −209 due to instrument limitations. Absolute recoveries of PBDEs ranged between 76 and 110%. This paper mainly focused on 9 predominant congeners: BDE-28, -47, -66, -100, -99, -154, -153, -183, and -191. QA/QC was conducted by performing field and laboratory blanks, standard spiked recoveries and GC/MS detection limits. Filter blanks were less than 10% of the sample amount. The relative standard deviation was below 10% for BDE congeners.

3. Results and discussion

3.1. 24-h average concentrations of TSP and PM$_{2.5}$ in Guiyu, Hong Kong and Guangzhou

Mass concentrations of TSP and PM$_{2.5}$ particles were simultaneously collected onto quartz filters using high-volume Anderson samplers over the summer period. Twenty-four hour average concentrations of TSP and PM$_{2.5}$ collected from Guiyu and urban sites in Hong Kong and Guangzhou are shown in Table 1.

The 24-h overall average of TSP concentration collected at the e-waste site in Guiyu was 124 μg m^{-3}, which was almost twice the average of urban sites in Hong Kong (57.8–99.0 μg m^{-3}), but similar to urban sites in Guangzhou (133–138 μg m^{-3}). The 24-h overall average PM$_{2.5}$ concentration at Guiyu (62.1 μg m^{-3}) was also higher than Hong Kong sites which include a residential site YL (54.8 μg m^{-3}), an urban site TW (50.0 μg m^{-3}), and a rural site HT (31.9 μg m^{-3}). Twenty-eight out of thirty days at Guiyu site exceeded the USEPA 24-hr PM$_{2.5}$ ambient air quality standard (35 μg m^{-3}, NAAQS, 2006) and was much higher than the PM$_{2.5}$ mass concentrations in Shanghai, China during the summer (36.8 μg m^{-3}) (Ye et al., 2003).

The ratio of PM$_{2.5}$ to TSP mass concentrations, for the same sampling day, was calculated in order to investigate the size of aerosols collected at Guiyu. The average ratio was 0.53 (with a standard deviation of 0.12), implying that a greater number of fine particles exist in the atmosphere of Guiyu (Deng et al., 2006). As shown in Fig. 2, PBDEs distributed disproportionally between the fine and coarse fractions (i.e., more PDDEs in the fine fraction than the bigger coarse particles fraction). This is consistent with other investigations that combustion processes produce more fine particles and contributed to PM pollution (Vallius et al., 2003; McDonald, 2002). The ratio of PM$_{2.5}$ to TSP mass concentrations was higher than 0.5, which indicated the potential for the fine PM$_{2.5}$ with high levels of PBDEs. Being finer in particle size and its potential transport in a regional scale, this kind of

Table 1
24-h average concentrations of TSP and PM$_{2.5}$ of Guiyu and urban sites in Hong Kong and Guangzhou (μg m^{-3})

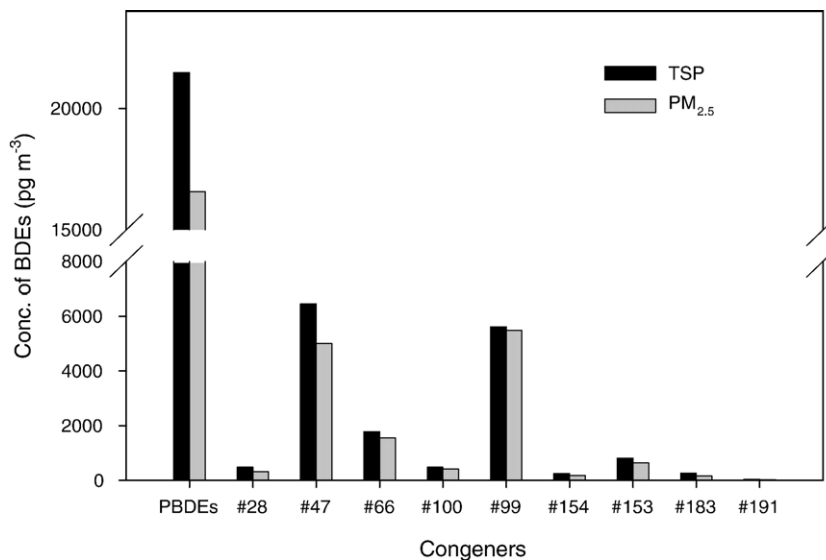| Sites	Guiyu	Hong Kong			Guangzhou	
		YL	TW	HT	LW	TH
TPS	124±44.1	99.0±66.4	80.1±52.4	57.8±36.3	138±59.5	133±59.5
PM$_{2.5}$	62.1±20.5	54.8±38.5	50.0±33.1	31.9±26.0	112±54.0	105±35.7
PM$_{2.5}$ /TSP	0.53	0.55	0.62	0.55	0.79	0.88

Fig. 2. Predominant PBDEs congeners detected in TSP and PM$_{2.5}$ from Guiyu during August 18 to September 17 2004.

PBDEs loaded particles may contribute to regional PM$_{2.5}$ pollution and its negative impact to human health.

In this study, this ratio was similar to Hong Kong sites (0.55–0.62), but lower than Guangzhou sites (0.79–0.88). Compared with other studies, this average value was similar to that obtained at Tokchok Island, Yellow Sea (0.59±0.19) (Lee et al., 2002), but higher than that throughout the US (0.31±0.11) between 1972 to 2000 (Lall et al., 2004). Based on the above comparison, the ambient air of Guiyu, as well as the urban sites in Hong Kong and Guangzhou were more dominated by fine particles, which seemed to be related to the increasing number of residents at Guiyu suffering from respiratory and cardiovascular ailments (Qiu et al., 2004). It is commonly known that TSP is more related to respiratory diseases, while PM$_{2.5}$ to cardiovascular diseases (Wyzga, 2002).

3.2. Concentrations of PBDEs in the air of Guiyu, Hong Kong and Guangzhou

Concentrations of Σ_{22}PBDEs in TSP and PM$_{2.5}$ from Guiyu, Hong Kong and Guangzhou are shown in Table 2. The total concentrations of Σ_{22}PBDEs contained in TSP at Guiyu ranged between 13.2 and 45.4 ng m^{-3} with a median value of 21.5 ng m^{-3} ($n=30$). For PM$_{2.5}$, Σ_{22}PBDEs ranged between 5.45 and 36.9 ng m^{-3} with a median value of 16.6 ng m^{-3} ($n=30$).

The concentration of Σ_{22}PBDEs in TSP from urban sites of Hong Kong and Guangzhou, i.e., YL, TW, HT, LW and TH was 69.0, 358, 33.8, 204 and 272 pg m^{-3}, while the concentrations in PM$_{2.5}$ from YL, TW, HT, LW and TH were 45.0, 196, 24.0, 118 and 200 pg m^{-3}, respectively. The descending order of Σ_{22}PBDEs concentrations in TSP and PM$_{2.5}$ from Guiyu and the other five urban sites was: Guiyu>TH, TW>LW>YL>HT. Σ_{22}PBDEs concentrations in TSP from Guiyu were 311, 60, 635, 105 and 58 times of YL, TW, HT, LW and TH, respectively. For Σ_{22}PBDEs concentrations in PM$_{2.5}$, Guiyu were 238, 85, 691, 140 and 83 times of YL, TW, HT, LW and TH, respectively.

There were significantly higher concentrations of Σ_{22}PBDEs at Guiyu compared to other urban sites in Hong Kong and Guangzhou. This may be due to uncontrolled recycling activities at Guiyu, such as the heating of printed circuit boards inside recycling workshops or open burning of e-waste containing PBDEs (Leung et al., 2006). It may also be due to discharge of exhaust fumes from the electronic

recycling factories situated beside our sampling building. High levels of PBDEs (63.7 ng m^{-3}) have also been detected in indoor air in dismantling halls at electronic recycling stations in southern Sweden (Sjödin et al., 2001). In addition, the higher concentrations found in this study were also due to the high ambient temperature (32.5 °C) during the sampling period (August-September), resulting in higher rates of volatilization of PBDEs. High temperatures have been shown to increase atmospheric concentrations of persistent organic pollutants (POPs) due to high volatilization from contaminated surfaces (Ter Schure et al., 2004).

The present results showed that among the three urban sites in Hong Kong, TW had the highest concentrations of average Σ_{22}PBDEs (358 and 196 pg m^{-3} in TSP and PM$_{2.5}$, respectively), due to the high traffic flows and industrial emissions. The lowest mass concentration was found at the background site, HT, (33.8 and 24.0 pg m^{-3} in TSP and PM$_{2.5}$, respectively), as it is located upwind of anthropogenic emission sources. TW is characterized by urban surroundings mixed with light industrial establishments such as metal degreasing, dry cleaning, and building material manufacturing located within 0.5 to 1 km NW and SE of the TW site. In addition, a hospital with large heating units and a medical incinerator are located 0.1 to 0.2 km N and NNW of the TW site. On the contrary, HT site is situated at the southeastern tip of Hong Kong and should be subjected to the least amount of aerosol transport from the continent. YL is situated northwest of Hong Kong, adjacent to the economically fast growing city of Shenzhen in south China.

During the past two decades, the explosive increase in industrial and agricultural productivity and the growing population in Guangzhou have led to a serious environmental problem. The atmospheric environment in Guangzhou City has become seriously polluted, mainly from vehicle exhaust (Chan et al., 2002; Bi et al., 2003). Li Wan is a well-established commercial/industrial district, with a population of approximately 0.55 million. The area is influenced by a typical mixture of emissions from vehicles, residences, commerce and industries such as power plants, chemical plants and plastic manufacturers. Natural gas and coal are utilized for domestic use and power generation. In addition, the large-scale construction and building activities within the whole territory are believed to significantly contribute to air pollution (Bi et al., 2002). Tian He is a rapidly developed commercial/residential district located in the middle of

Table 2
Concentrations and congener patterns of PBDEs (pg m^{-3}) in air particles from Guiyu, Hong Kong and Guangzhou sampled during Aug 16 to Sept 17 2004 (n = sample size)

	BDE congener	Guiyu (n=30)	Hong Kong			Guangzhou	
			YL(n=30)	TW(n=30)	HT(n=30)	LW(n=30)	TH(n=30)
TSP	BDE-28	486±289	1.79±0.62	2.99±1.18	0.97±0.40	5.75±1.14	4.60±3.15
	BDE-47	6456±1942	4.76±3.12	79.7±37.4	3.52±0.81	71.1±58.4	122±95.2
	BDE-66	1782±528	1.61±0.70	5.55±2.82	0.54±0.42	6.32±2.65	11.7±6.28
	BDE-100	481±181	1.73±0.82	33.6±21.9	0.70±0.33	14.8±10.9	34.8±22.8
	BDE-99	5519±2751	7.30±5.27	129±64.7	2.58±0.80	61.0±40.8	122±110
	BDE-154	247±79.9	0.82±0.34	5.52±3.07	0.37±0.27	2.61±1.16	4.15±3.42
	BDE-153	811±333	1.36±0.94	5.40±3.35	0.47±0.36	3.00±0.83	2.96±1.75
	BDE-183	267±130	2.49±1.80	2.40±1.66	1.05±0.62	3.44±1.41	3.74±3.29
	BDE-191	37.2±21.6	2.62±2.06	3.20±1.56	2.85±1.65	3.98±0.76	3.29±1.47
	Σ_{22}PBDEs	21474±7241	69.0±27.8	358±286	33.8±11.6	204±113	372±213
	Σ_{9}BDE/Σ_{22}PBDEs(%)	74.5	35.5	74.8	32.8	84.3	83.1
PM$_{2.5}$	BDE-28	316±225	1.64±0.82	2.48±1.47	0.86±0.41	4.40±2.38	2.97±1.63
	BDE-47	5004±4466	3.80±2.35	49.5±36.1	3.15±1.30	26.8±16.4	52.9±39.2
	BDE-66	1552±1398	0.86±0.69	1.66±1.18	10.29±0.19	4.60±2.34	3.94±1.98
	BDE-100	411±261	0.66±0.42	18.5±10.5	0.50±0.24	5.58±3.10	16.8±8.86
	BDE-99	5489±4304	3.58±3.44	93.3±46.5	2.10±1.54	25.2±23.9	66.1±51.5
	BDE-154	181±107	0.28±0.25	4.15±2.15	0.15±0.13	1.94±1.58	2.16±1.26
	BDE-153	639±501	0.50±0.32	2.67±1.51	0.36±0.31	2.40±1.69	2.57±1.67
	BDE-183	156±90.8	0.97±0.69	1.17±0.63	1.96±0.70	2.09±1.60	3.07±2.07
	BDE-191	23.2±20.8	1.64±1.12	6.14±4.56	9.79±3.52	2.46±1.11	2.24±1.38
	Σ_{22}PBDEs	16575±13286	45.0±35.3	196±159	24.0±5.43	118±74.0	200±144
	Σ_{9}BDE/Σ_{22}PBDEs(%)	84.3	31.0	89.1	42.0	63.9	76.4

several major highways. Over the past several years, vehicle emission leading to street-level air pollution has been receiving much public concern.

3.3. Congener distribution patterns of PBDEs in air of Guiyu, Hong Kong and Guangzhou

Table 2 shows that there were 22 PBDE congeners in the air samples of TSP and PM$_{2.5}$ commonly found in samples from Guiyu and other urban sites. Fig. 2 further shows the distribution of predominant PBDEs congeners (BDE-28, -47, -66, -99, -100, -154, -153, -183, -191) detected in TSP and PM$_{2.5}$ collected from Guiyu. In the Guiyu atmosphere, the sum of 9 predominant congeners accounted for 74.5 and 84.3% of Σ_{22}PBDEs in TSP and PM$_{2.5}$, respectively. The same trend was observed in TW, with 74.8 and 89.1% in TSP and PM$_{2.5}$, respectively, compared with LW and TH which had higher percentages of Σ_{9}PBDE in TSP than PM$_{2.5}$. The health hazard would be more severe if PM$_{2.5}$ contained higher concentrations of PBDEs as they could be easily inhaled by human beings. However, low percentages of Σ_{9}PBDE were observed in YL and HT, with only 32.8–35.5% and 31.0–42.0% in TSP and PM$_{2.5}$, respectively. The sum of BDE-3, -7, -15, -17, -28 (mono-tri brominated congeners) accounted for more than 70% of the total PBDEs.

In the atmosphere of Guiyu, the most abundant PBDEs were 2,2′,4,4′-tetraBDE (BDE-47) and 2,2′,4,4′,5-pentaBDE (BDE-99). The median values of BDE-47 and BDE-99 were 6.46 and 5.52 ng m^{-3} in TSP, and 5.00 and 5.49 ng m^{-3} in PM$_{2.5}$, respectively. The commercial penta mixtures generally contain 40–60% penta-BDEs (WHO, 1995). Because of its high persistent and bioaccumulative propensity, penta-BDE was banned in Europe as of August 2004 (BSEF, 2003). BDE-99 and BDE-47 account for approximately 75% of the total mass of penta. As these compounds persist in the environment and bioaccumulate up the food chain, the patterns of congeners evolve (Alaee et al., 2001). While the ratio of BDE-99 to BDE-47 is nearly double in the commercial penta product, the levels of BDE-99 are almost the same as

those of BDE-47, which was also observed by another study conducted in the air of South China (Birnbaum and Cohen Hubal, 2006).

The lower brominated congeners are persistent and more toxic to humans. Mono- to penta-brominated congeners are more carcinogenic and mutagenic due to the smaller atomic size of bromine (Rahman et al., 2001; McDonald, 2002). The total amount of mono- to penta-brominated congeners contributed to the majority of Σ_{22}PBDEs, accounting for 92.5 and 92.8% in TSP and PM$_{2.5}$, respectively. The percentages of low brominated diphenyl ethers to Σ_{22}PBDEs in PM$_{2.5}$ and TSP at urban sites of Hong Kong and Guangzhou were 79.4–95.6%.

3.4. Comparison of congener distribution patterns and concentrations of PBDEs in TSP and PM$_{2.5}$ between Guiyu and other studies

Table 3 compares PBDE congeners, as well as total PBDEs concentrations in the air with other studies. The concentrations of Σ_{22}PBDEs of the respirable fraction, PM$_{2.5}$ (16.6 ng m^{-3}), and the total fraction, TSP (21.5 ng m^{-3}), at Guiyu were much higher than other urban sites all over the world. Mean Σ_{22}PBDEs concentration in air was 16.6 ng m^{-3}. Using an inhalation rate of 8 and 20 m^3 day^{-1} for children and adults, exposure via inhalation is estimated to be 132.8 and 332 ng day^{-1} respectively.

Σ_{24}PBDEs including BDE-209 in the respirable and total dust fractions detected in air inside an electronics recycling facility in Örebro, Sweden were 6.2 (±0.8) and 33.5 (±3.4) ng m^{-3} (±SD), respectively (Julander et al., 2005). The concentration of Σ_{22}PBDEs respirable particles from outside the electronics recycling factories in our study were relatively higher (16.6 ng m^{-3}), indicating potential high exposure to the workers.

Σ_{22}PBDEs in the total air from other urban sites in Guangzhou and Hong Kong were in the range of 33.8–372 pg m^{-3}, which were higher than other urban and rural sites all over the world. The concentration of Σ_{21}PBDEs in air samples from a rural area in Ontario (Canada) ranged between 6 and 85 pg m^{-3} (Gouin et al., 2005). Concentrations of Σ_{7}PBDEs in air from three sampling sites around the Great Lakes varied between 5.5 and 15 pg m^{-3}, which were close to Chicago levels

Table 3
Comparison of PBDE concentrations in TSP and $PM_{2.5}$ from Guiyu with other studies

Sites	Description	PBDEs conc. (pg m^{-3})	References
e-waste sites			
Outside area in Guiyu, China	22 congeners (particulate)	$21{,}474 \pm 7241$	This study
Inside an e-waste recycling factory in Örebro, Sweden	24 congeners (dust respirable particles)	6200 ± 800	Julander et al. (2005)
	24 congeners (dust total particles)	$33{,}500 \pm 3400$	
Urban and rural sites			
Guangzhou	22 congeners (particulate)	204–372	This study
Hong Kong	22 congeners (particulate)	33.8–358	This study
Ontario, Canada	21 congeners (particulate)	Below determine limit-34	Gouin et al. (2005)
	21 congeners (gaseous+particulate)	6–85	
Great Lakes, USA	7 congeners (gaseous+particulate)	5.5–15	Strandberg et al. (2001)
Chicago, USA	7 congeners (gaseous+particulate)	52	Strandberg et al. (2001)
Island Gotska Sandö, Sweden	10 congeners (gaseous+particulate)	8.6	Ter Schure et al. (2004)
Urban ambient UK air	6 congeners, excluding BDE209 (particulate)	1.3–6.7	Harrad and Hunter, (2004)
Over the continent of Europe		250	Wurl et al. (2006)
Over the continent of Asia		340	Wurl et al. (2006)
Background sites			
Over the Indian Ocean	8 congeners (gaseous)	2.5	Wurl et al. (2006)
Mace Head, Ireland, European background site	8 congeners (gaseous+particulate)	2.6	Lee et al. (2004)
Canadian Arctic and Siberia, Russia	BDE-47 and-99 (gaseous+particulate)	1–7	Alaee et al. (2001)

of 52 pg m^{-3} (Strandberg et al., 2001). Ter Schure et al. (2004) reported mean Σ_{10}PBDEs concentration of 8.6 pg m^{-3} on the Gotska Sandö island in Sweden. Urban ambient UK air was found to contain median PBDE (6 congeners, excluding BDE-209) concentrations ranging from 1.3-6.7 pg m^{-3} (Harrad and Hunter, 2004). Atmospheric PBDE concentrations obtained (using a passive air sampler) over the continent of Europe and Asia were up to 250 and 340 pg m^{-3}, respectively, but a lower range of up to 8 pg m^{-3} was detected at several rural sites (Wurl et al., 2006). The concentration of Σ_8PBDE in Mace Head, Ireland (a European background site) was 2.6 pg m^{-3} (Lee et al., 2004). PBDEs (reported as the sum of BDE-47 and BDE-99) were detected in air from the Canadian Arctic and Siberia, Russia in the range of 1–7 pg m^{-3} (Alaee et al., 2001).

This suggests that the air in Guiyu contained PBDEs 100 times higher than other sites in the world. Higher concentrations in the air of Guiyu were due to e-waste burning since PBDEs are released when plastics containing brominated flame retardants are heated (welding of mats, melting of polymers) (de Wit, 2002).

4. Conclusion

The present results indicated that levels of Σ_{22}PBDEs (especially penta-BDE) in TSP and $PM_{2.5}$ from Guiyu were higher than those from Guangzhou, Hong Kong, and other locations in the world. This is due to uncontrolled dismantling, open burning, and dumping of e-waste. The presence of relatively high concentrations of PBDEs in the atmosphere of the e-waste recycling site suggests that atmospheric PBDEs are now industrially ubiquitous and have the potential to adversely affect environmental and human health.

Acknowledgements

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