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On-site and off-site atmospheric PBDEs in an electronic dismantling workshop in south China: Gas-particle partitioning and human exposure assessment

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ABSTRACT

Gas samples and total suspended particle during work and off work time were investigated on-site and off-site electronic waste dismantling workshop (I- and O-EWDW), then compared with plastic recycling workshop (PRW) and waste incineration plant (WIP). TSP concentrations and total PBDE were 0.36–2.21 mg/m^3 and 27–2975 ng/m^3 at different workshops, respectively. BDE-47, -99, and -209 were major ∑PBDE congeners at I-EWDW and WIP, while BDE-209 was only dominant congener in PRW and control sites during work time and all sites during off work time. The gas-particle partitioning result was well correlated with the subcooled liquid vapor pressure for all samples, except for WIP and I-EDWD, at park during work time, and residential area during off work time. The predicted urban curve fitted well with measured φ values at O-DEWD during work time, whereas it was slightly overestimated or underestimated for others. Exposure assessment revealed the highest exposure site was I-EDWD.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame-retardant additives in plastic electrical appliances, television sets, computer circuit boards, and casings (Rahman et al., 2001). Emission of PBDEs into the environment mainly occurs during the production and from products impregnated with brominated flame retardants (BFRs) (Strandberg et al., 2001). The electronics industry is one of the world's largest and fastest growing industry; electronics are produced in large quantities around the world. Disposal of electronic waste (e-waste) is a potential pollution source of PBDEs to the atmosphere, which may ultimately deposit at remote areas due to semi-volatility and persistence. For higher profit, the dismantling and recycling of e-waste are growing rapidly in many developing countries. Approximately 80% of the total e-waste is exported into Asia, and nearly 90% of which is sent to China legally or illegally (Hileman, 2002).

Since 1995, Guiyu, a small town in South China, has been known worldwide as an e-waste recycling site. Fumes and ashes not only pollute the water, air, and soil, but also endanger the workers and residents due to flourished waste from many unorganized backyard workshops. PBDEs are prone to adsorption onto particulate matter, bioaccumulation, and biomagnification in the food chain due to their high affinity for lipids (Burreau et al., 1997). The toxicological endpoints of concern for environmental levels of PBDEs are likely to be thyroid hormone disruption, neuro-developmental deficit, and cancer (Burreau et al., 1997; McDonald, 2002). PBDE pollution has been confirmed from recent studies that have observed PBDEs in a variety of environmental matrices, including water (Xu et al., 2009), soil (Wong et al., 2007; Yang et al., 2008), sediment (Leung et al., 2006; Wong et al., 2007), air (Deng et al., 2007; Li et al., 2008), fish (Luo et al., 2007),and human blood (Bi et al., 2007; Qu et al., 2007; Roosens et al., 2010).

Recently, occupational exposure to BFRs has been investigated in several studies (Pettersson-Julander et al., 2004; Qu et al., 2007), which have shown that electronic recycling facilities strongly enhance gas concentrations of PBDEs compared with other occupational settings (Pettersson-Julander et al., 2004; Wilford et al., 2005). Nevertheless, Guiyu is one of the most PBDE-polluted places around the world. Monthly ∑$_{20}$PBDE concentration in PM2.5 was over 100 times more than in Hong Kong and Guangzhou (Deng et al., 2007). The highest BDE-209 concentration yet reported in humans is 3.1 μg/g lipid in Guiyu (Bi et al., 2007), which is 50–200 times higher than those reported in occupational populations (Qu et al., 2007; Sjodin et al., 1999). Inhalation and dust ingestion make an important contribution to overall PBDE exposure (Harrad

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et al., 2006). The atmosphere is considered to be a key environmental vector for the transport of these semi-volatile chemicals. Insight into mechanisms that influence gas-particle partitioning of PBDEs would provide better understanding of environmental behavior (i.e., deposition, degradation, and atmospheric transportation) and fate (Chen et al., 2006). However, to date, in a strong contrast to off-site PBDE concentrations and distributions, little is known regarding on-site characteristics from inside a representative e-waste dismantling workshop.

This work aims to determine PBDE concentrations both in the gas phase and in TSP on- and off-site the e-waste dismantling workshop in Guiyu in order to identify the congener patterns of PBDEs produced by dismantling activities, and to analyze PBDE partition between gas and particulate phases during work and off work time, respectively. For comparison, a neighborhood residential area (RA) and a park were simultaneously investigated as control areas. Furthermore, PBDE concentrations from these sites were also used to estimate human exposure and to evaluate potential hazards to human health. The findings of this study may serve as a valuable reference for future risk assessment and environmental management in Guiyu, South China.

2. Materials and methods

2.1. Study location

The study was conducted in Guiyu (23°327′N, 116°342′E), which is located in Chaoyang District, Guangdong Province, in Southeast China. Guiyu has a total area of 52 km^2 and a population of 150 000. Six sampling sites were chosen to encompass a range of aerosol types and potential PBDE sources (Fig. S1). Briefly, inside (on-site) and outside (off-site) an electronic waste dismantling workshop (I-EWDW and O-EWDW), a plastic recycling workshop (PRW) and a waste incineration plant (WIP) in Guiyu were selected as representative e-waste recycling center sampling sites. One residential area (RA) and one park were investigated as control sites. A detailed description of the sampling sites is given in the Supporting information.

2.2. Sample collection

Air samples of TSP and gas phase were collected according to previous study (Cetin and Odabasi, 2008). Air samples were collected simultaneously from six sites in October, 2007. Air volumes of 108–180 m^3 were drawn at 0.15–0.25 m^3/min for 12 h through 20.3 cm × 25.4 cm glass fiber filters (GFF) (Whatman, Maidstone, England), and subsequently through 6.5 cm in diameter × 7.5 cm in thickness (a density of 0.030 g/cm^3) polyurethane foam (PUF) plugs using a high-volume air sampler (Tianhong, China). Prior to sampling, GFFs were baked at 450 °C for 12 h to remove any organic contaminant, and PUF plugs were Soxhlet extracted for 48 h with methanol and for another 48 h with an acetone and hexane mixture (1:1). Gas samples and total suspended particle (TSP) were sampled during work (day) and off work (night) time, more information were provided in support materials.

After sampling, loaded GFFs were wrapped with pre-baked Al foils and sealed with double-layer polyethylene bags. PUF plugs were stored in solvent-cleaned glass jars with Al foil-lined lids. The samples were transported to the laboratory and stored at −20 °C until extraction. Concentrations of TSP were determined by weighing filters before and after exposure/sampling.

2.3. Extraction, clean-up, and analysis

PUF plugs and GFF were spiked with ^{13}C-PCB 209, ^{13}C-PCB 141, and Soxhlet-extracted with a 200 ml mixture of acetone:hexane (1:1) for 72 h. The extract was evaporated to approximately 2 ml by a rotary evaporator, and then solvent-exchanged to n-hexane. Concentrated extracts were cleaned and fractionated on acid/basic/neutral multilayer silica gel/alumina columns according to Reference (Mai et al., 2005), then eluted with 70 ml solvent mixture (hexane:dichloromethane of 1:1). The final extracts were solvent-exchanged into hexane and concentrated to 200 μl under a gentle N_2 stream.

Sample analysis was performed with a Shimadzu model 2010 gas chromatograph (GC) coupled with a model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization in the selective ion monitoring mode with external standard and seven-point calibration curves. Quantification of BDE-197, -203, -196, -208, -207, -206, and -209 was performed on GC/MS-QP2010 equipped with a DB-5HT column (15 m × 0.25 mm, 0.10 μm) with helium as the carrier gas. A 1 μl sample was injected automatically in splitless mode. The initial oven temperature was maintained at 110 °C for 5 min, programmed at a rate of 20 °C/min to 200 °C, held for another 4.5 min, then 10 °C/min to 310 °C, and then held for

another 15 min. The determination of BDE-17, -28, -47, -99, -71, -66, -85, -138, -183, -190, -100, -153, and -154 was performed by GC/MS-QP2010 equipped with a DB-XLB column (30 m × 0.25 mm, 0.25 μm). The ion m/z monitored for target compounds, surrogate standards, internal standards, and details of instrument temperature programs were described in a previous report (Mai et al., 2005).

2.4. QA/QC

Recoveries from eight spiking experiments (eight PBDE standards spiked into three clean GFF and three PUF plugs) ranged from 73.5% to 86.7%. Two individual samples were subsampled (for four samples) from GFFs, then analyzed. Differences between duplicate samples were typically less than 20%. As for method blanks ($n = 3$) for PUF and GFF analysis procedures, though a very small amount of PBDE such as BDE-47, -99, -190 and -209 was detected in PUF, their amount were less than 5% of the concentrations in control site samples, thus the data were not blank-corrected. The surrogate recoveries in 81 field- and laboratory-prepared samples ranged from 69% to 118% for ^{13}C-PCB 141 and from 78% to 104% for ^{13}C-PCB 209. Reported concentrations were not corrected with surrogate recovery. The limit of quantification (LOQ) was set to be the lowest concentration of the calibration standard (5 μg/L equal to 0.01 ng/m^3 for tri- and hexa-BDEs, 10 μg/L equal to 0.02 ng/m^3 for hepta-, octa-, nona-, and deca-BDEs). The data reported in this research was not corrected by the recoveries.

3. Results and discussion

3.1. TSP concentrations

TSP concentrations from different functional workshops are illustrated in Fig. 1. All workshops, such as I-EWDW, WIP, and PRW, were seriously contaminated by TSP, especially during work time, according to the Chinese Ambient Air Quality Standard (GB3095-1996). TSP concentrations in different workshops varied greatly between work and off work time. During work time, TSP concentrations were 1.78, 1.94, and 2.21 mg/m^3 in PRW, WIP, and I-EWDW, respectively. These values are 2.4–3.3 times higher than those during off work time in the workshops, 3.6–4.4 times higher than the third-grade standard of GB3095-1996, and 12–15 times higher than samples taken during work time on the roof of a three-storey building located near the region (Deng et al., 2007). The values are only slightly lower than those in a dismantling hall (3.3 mg/m^3) in an e-waste recycling plant in Sweden (Sjodin et al., 2001). However, all of these results are far below the maximum allowed occupational level in Sweden, which is 10 mg/m^3 for total particles.

Comparing TSP concentrations at O-EWDW and I-EWDW, approximately 56% TSP can be instantly deposited on areas near the source and re-distributed on a local scale, while the rest portion is subject to long-range transportation towards the neighborhood during work time and off work time; This may be the reason TSP
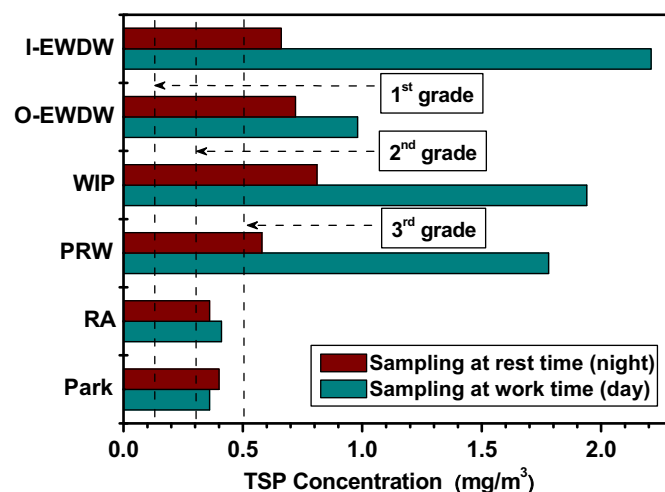

Fig. 1. TSP concentration for different sampling sites during work and off work time.

concentration increases during off work time in nearby RA and park. Of course, it might be also due to the temperature inversions and the low boundary layer in the night. It is because that the average concentrations of TSP were generally higher after the boundary layer collapsed at night.

3.2. TSP-associated PBDE concentrations

Generally, TSP concentrations in the air increase continuously during work time, indicating TSP emission at all workshops. The concentration of PBDE per gram TSP by weight was used to describe PBDEs in TSP. The total concentrations of PBDE and BDE-209 associated with TSP are listed in Table S1. During work time, the highest $\sum_{20}$PBDE concentration was obtained at I-EWDW (1042 μg/g), which is approximately 6.1, 3.5, and 4.0 times higher than that of PRW, WIP, and O-EWDW, respectively. There was hardly any difference in $\sum_{20}$PBDE concentration from the control and other sites such as PRW, WIP, and O-EWDW. The $\sum_{20}$PBDE concentrations decreased dramatically at all sites, except at PRW during off work time. The decrease of $\sum_{20}$PBDE concentrations is probably due to the deposition of partial TSP. While in the PRW, many large plastic particles are produced during the work time. Nevertheless, these large particles did not contain so much PBDE (Julander et al., 2005); thus the deposition of coarse particles during off work time might lead to the decrease of TSP total mass but not so much of the $\sum_{20}$PBDE contents, resulting in the increase of PBDE concentration in TSP at PRW.

The ratio of BDE-209 to $\sum_{20}$PBDE is also presented in Table S1. From work time to off work time, the ratios decreased in PRW, O-EWDW, RA, and the park, whereas they increased in WIP and I-EWDW. PBE-209 was apparently the dominant congener in all sampling sites associated with TSP, except with I-EWDW during work time. This might be because a higher temperature is employed only in WIP and I-EWDW during work time. However, one research work (Gouin et al., 2006) reported that the temperature dependence for BDE-209 is not as significant as low-bromine compounds. The other work (Julander et al., 2005) reported that smaller particle sizes adsorb more PDE-209. Consequently, the decisive condition may not be temperature, but the particulate size and physico-chemical characters, for PDE-209. Particle-associated BDE-209 can therefore adhere more stably on the fine particles, whereas some low-bromine congeners easily volatilize into the air (Hale et al., 2006). Many higher molecular compounds are able to absorb onto the coarse particles and deposit. This is confirmed by results from Fig. S2. During work time, nearly all PBDE congeners are associated with particles, except for BDE-17 and -28. During off work time, part of the TSP would deposit and led to decrease of the $\sum_{20}$PBDE content. Nevertheless, the temperature was decreased at night and the low-brominated congeners would redistribute onto the particles. Therefore the percentages of lower molecular congeners were much higher onto TSP during off work time than work time due to the temperature decrease. The highest BDE-209 concentration was in the park (216 μg/g) during off work time, which is far lower than the highest ever recorded in the car dust of 210 000 μg/g from U.S (Batterman et al., 2009).

3.3. PBDE concentrations and congener composition in air

PBDE concentrations in gas are listed in Table S2. The highest concentration obtained was 320 ng/m³ at I-EWDW during work time and 95 ng/m³ at O-EWDW during off work time. In the particulate phase, the highest concentration of 2656 ng/m³ was also obtained at I-EWDW during work time. In the control sites, PBDE concentrations both in gas and particulate were much lower than those in PRW, WIP, I-EWDW, and O-EWDW during work and

off work time. The concentrations in gas increased in PRW and O-EWDW, but decreased significantly in WIP and I-EWDW during off work time. The possible reason is that the heating or burning leads to higher concentrations of low-brominated congeners associated with gas during work time due to a temperature increase in the workshops.

Total PBDE concentration-integrated gas with particulates varies significantly between work and off work time (Fig. 2), as summarized in Table S2. They were higher during work time than off work time, especially in I-EWDW (25 times higher). The highest concentrations were detected in I-EWDW (2975 ng/m³) during work time, with the lowest in WIP during off work time (107 ng/m³), except in the control sites. BDE-99, -47, and -209 were the most abundant congeners in the air from I-EWDW; their concentrations account for 19.85%, 18.97%, and 14.01% of the total PBDE during work time, whereas dominant congeners become BDE-209 and -47 during off work time (Fig. 3). As described, the dismantled e-wastes in this workshop were all TV set circuit boards produced decades ago, and tetra- and penta-bromodiphenyl ether prevailed at that time. Thus, BDE-99 and -47 were the dominant congeners in this workshop, which are different from those in the ambient air of Sweden (Cahill et al., 2007), where BDE-209 was shown to be the only dominant congener in EWDW. Compared with other studies, PBDE concentrations in this study were relatively higher. Although BDE-209 was not the only dominant congener in I-EWDW during work time, BDE-209 was 417 ng/m³ (Fig. 3, Table S2). BDE-209 was the dominant congener and was still higher than those (Julander et al., 2005; Pettersson-Julander et al., 2004; Sjodin et al., 2001) ranging from 12 to 70 ng/m³ at the dismantling hall, 150 to 200 ng/m³ near the shredder (Sjodin et al., 2001), and 157.6 to 208.6 ng/m³ in dust (Julander et al., 2005).

Control sites also have the same trend as workshops. Total PBDE concentrations in RA and the park (97 and 68 ng/m³) during the work time were approximately 3.5 and 1.6 times higher than those
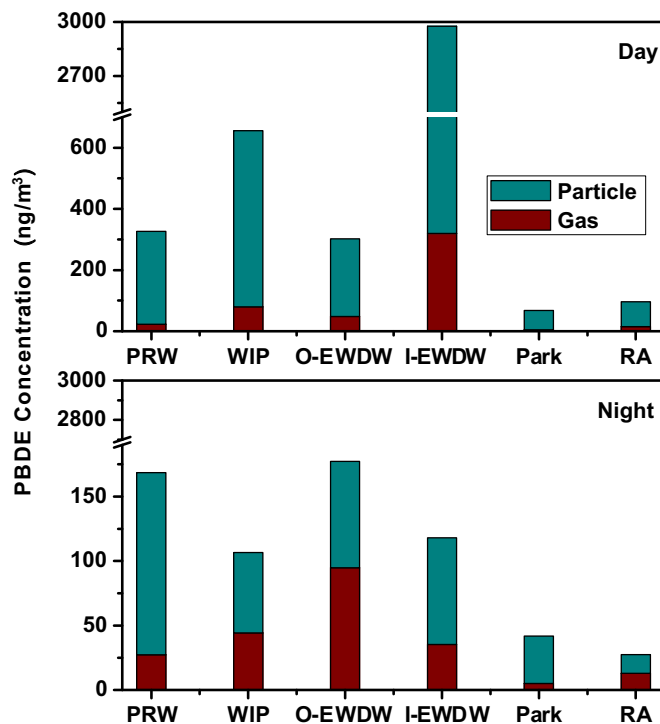

Fig. 2. PBDE concentrations in gas and particulate phase for different sampling sites during work and off work time.
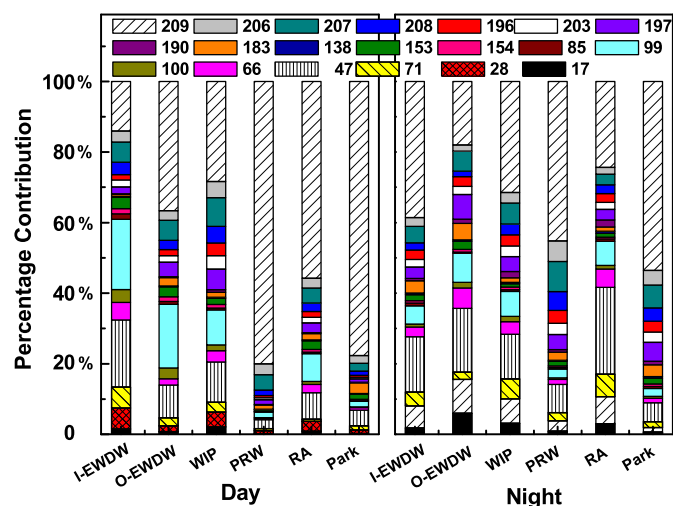
Fig. 3. Percentage contributions of individual congeners to $\sum_{20}$PBDE concentrations for different sampling sites during work and off work time.

at off work time (Table S2). This may be due to the spread of these workshops during work time, in which most PBDEs and other compounds were produced and subsequently diffused toward the neighborhood in the form of ashes, particles or the release from PBDE-containing products. As observed, PBDE concentrations at the control sites were far lower than those in workshops. However, they were still higher than those from other sources. Hoh and Hites (2005) reported average concentrations of $\sum_{26}$PBDEs to be 100 ± 35 pg/m³ in Chicago, and Agrell et al. (2004) found average concentrations of $\sum_{7}$PBDE and BDE-209 to be only 6.3 and 10.4 pg/m³, respectively, near WIP.

The deposition pattern of particles, temperature change, BDE-209 degradation, and redistribution between gas and particulates may be influenced by the ratio of congeners to total PBDEs. The percentages of individual PBDE congeners at all sites during work and off work time are given in Fig. 3. The proportion of lower molecular congeners rose in all sites during night. BDE-209 was the dominant congener during work time in all sites, and it was changed to BDE-47 and -209 during off work time. BDE-99 and -209 were dominant congeners in O-EWDW during work time, and it was changed to BDE-47 and -209 during off work time. BDE-47, -99, and -209 were the dominant congeners during work time in I-EWDW, which changed to BDE-47 and -209 during off work time. The levels of PBDE, such as penta- to deca-BDE present in gas were several orders of magnitude higher at I-EWDW than in any other workshops. Thus, more PBDEs are expected to be produced at I-EWDW than at PRW and WIP, which may impose more harm on the environment and on health.

3.4. Gas-particle partitioning

The relative abundances of PBDE in all sampling sites are shown in Fig. S2. In the park, RA, PRW, and O-EWDW, tri-BDEs (BDE-17, -28) were dominantly in the gas phase (96%–98%) during work and off work time. More than half of tetra-BDEs (BDE-71, -47) were also found in the gas phase, except in RA during work time. Almost all octa-BDEs (BDE-197, -203, and -196), nona-BDEs (BDE-208, -207, -206) and deca-BDEs (BDE-209) were detected in particulates during work time in all sampling sites. Heavier PBDE congeners were more associated with particles, whereas lighter congeners tended to distribute in the gas phase. These results are consistent with the study in Taizhou, another e-waste dismantling area in

China (Li et al., 2008). The cause for this is higher molecular PBDEs tended to absorb onto the coarse particles and deposit during off work time, whereas lower molecular PBDEs remain in the gas phase. In contrast, in WIP and I-EWDW, where the heating is employed during work time, nearly all congeners were detected in particles, and more than 20% and 40% BDE-17 presented.

The gas-particle partition coefficient (K_p) is commonly used to describe gas-particle partitioning of semi-volatile organic compounds (SVOCs) through the equation $K_p = (F/A)/\text{TSP}$, where F and A are particulate and gas-phase concentrations, respectively (Pankow, 1994). Two different mechanisms exist for the partitioning process (i.e., adsorption onto the surface of aerosols and absorption into the aerosol organic matter). Both mechanisms lead to a linear relationship between $\log K_p$ and $\log P_L^0$ (i.e., $\log K_p = m_{r-}\log P_L^0 + b_r$), where P_L^0 is the organics' subcooled liquid vapor pressure. The slope should be close to -1 for either adsorption or absorption mechanism in true equilibrium state (Pankow, 1994). The intercept is mainly dependent on the type and properties of the aerosols.

Fig. S3 shows the plots of $\log K_p$ *vs.* $\log P_L^0$ for the PBDEs measured in this study. Only PBDE congeners with detectable concentrations in a given sample were included; some was not included due to the lack of P_L^0 values. Temperature-dependent P_L^0 was calculated for all PBDE congeners based on a published method (Tittlemier et al., 2002) at the average ambient temperature of 28.3 °C in all sampling sites, except at 36.0 °C for WIP and I-EWDW during work time. Good linear correlations between $\log K_p$ and $\log P_L^0$ were obtained with R^2 values in the range 0.8013–0.8506 for samples at all sites, except for WIP and I-EDWD during work time, and in the range 0.5881–0.7716 for samples at all sites, except for the park and RA during off work time. All m_r values were significantly greater than -1 (from -0.2971 to -0.9299). Nevertheless, such a deviation does not sufficiently suggest disequilibrium between the gas and particle phases. Samples from the park, RA, PRW, and O-EWDW during work time with higher correlation coefficients than those during off work time agreed with the linear isotherm model for gas-particle partitioning of airborne pollutants (Pankow and Bidleman, 1992), indicating that PBDEs appeared to be closer to the equilibrium between gas and particle phases during work than off work time at these sites. As mentioned, higher temperatures were applied in WIP and I-EWDW during work time, PBDE concentrations increased in the gas phase and decreased in particulates compared with other sampling sites. The overall result is an increase in measured values of $\log K_p$ (Pankow and Bidleman, 1992). This makes measured values of m_r and b_r shallower and larger, respectively, than those during off work time at the same sites (Fig. S3). For control sites, the situation is exactly opposite to that of WIP and I-EWDW. The measured values of m_r are steeper, and those of b_r are lower, than their counterparts during off work time. In contrast, both lower correlation coefficient (0.4470 and 0.3467 for the park and RA, respectively) and a lower m_r value (-0.3896 and -0.2971) during off work time were not entirely anticipated. However, the deviation of slope m_r from -1 does not necessarily indicate non-equilibrium effect (Goss and Schwarzenbach, 1998). Slopes significantly steeper than -1 indicate the adsorption, while the slopes shallower than -0.6 point to absorption. Slopes in the range between -0.6 and -1 can occur for the situation of both the absorption and the adsorption (Goss and Schwarzenbach, 1998).

3.5. Adsorption model

The Junge–Pankow adsorption model (J–P model) is the most common method for describing the atmospheric gas-particle partitioning of SVOCs associated with aerosols (Bidleman, 1988). The

model predicts that the fraction (φ) of SVOCs adsorbed onto particles is related to the subcooled liquid vapor pressure (P_L^0) of the compound and the particle surface area per unit volume of air (θ) by $\varphi = c\theta/(P_L^0 + c\theta)$. The constant c (Pa cm) is related to the heat of condensation and chemical surface properties. An empirical value of 17.2 Pa cm is often used, although it might vary with compounds. Values for surface area θ are often assumed to be 1.1×10^{-5} and 4.2×10^{-7} cm^2/cm^3 for urban and rural air, respectively (Bidleman, 1988).

Fig. 4 compares the percentage ($\varphi \times 100\%$) of PBDEs predicted by the J–P model with average measured values. Each measured φ was calculated as the amount of compounds in the particle phase (F) divided by the total amount of compound ($F + A$). The predicted urban curve fitted well with the measured φ values at O-DEWD during work time, whereas particulate sorption was slightly over-estimated in the park and I-DEWD during off work time (Fig. 4a). Overestimated φ values by the J–P model were also reported for PBDEs (Chen et al., 2006; Li et al., 2008) and other SVOCs (Helm and Bidleman, 2005; Lee and Jones, 1999). However, the J–P model tends to underestimate the sorption of most PBDE congeners in WIP and I-EDWD during work time (Fig. 4b) with higher temperature. This occurs because the gas-particle partitioning of SVOCs is mainly controlled by parameters such as the temperature and vapor pressure. The deviation between the model and the field measured values is due to the different c and φ values with respect

to different compounds and aerosol types (Lee and Jones, 1999). Of course, the complete understanding to the point needs to wait for further more specific researches.

3.6. Exposure assessment

As mentioned, inhalation and dust ingestion play important roles in the overall human exposure to PBDEs (Harrad et al., 2006). Ingestion of dust can lead to almost 100-fold higher exposure than "average" for a toddler in a house where PBDE concentrations are elevated (Jones-Otazo et al., 2005). The average daily human intake of PBDEs via inhalation (assuming 100% absorption of intake) can be calculated using the following equations:

$$\sum \text{exposure} = [(C_w T_w) + (C_r T_r) + (C_p T_p)]*R_R/BW \quad (1)$$

$$\text{Hazard Index} = \sum \text{PBDE Congener Hazard Quotients}$$
$$= \sum (\text{Daily Intake})/(R_f D) \quad (2)$$

where $\sum$exposure is the daily adult human exposure via inhalation (ng of $\sum$PBDE person^{-1} day^{-1}); $C_{w/r/p}$ is the $\sum$PBDE concentration (ng/m^3) in the workshop/RA/park, respectively; R_R is the adult respiration rate (20 m^3/d); and $T_{w/r/p}$ is the respective fraction of day spent at the workshop/RA/park. Body weight (BW) was assumed to be 70 kg. The activity areas within a day are hypothesized to be limited to the workplace, RA, and park.

Given that employees work in workshops approximately 10 h/d, and spent 10 h (off work time) at RA with 4 rest hours in the park (calculated data used during off work time), concentrations of workshop during work time and concentrations during off work time in other two places were used to evaluate exposure to the three workshops investigated in this study. The highest exposure site is at I-EWDW (603,915.6 ng/d), followed by WIP (140,063.6 ng/d). The lowest is up to 74,105.6 ng/d at PRW. This has been proven by the result of Qu et al. (2007), which stated that the highest PBDE concentrations is obtained in the serum of EWDW workers. A comparison of BDE-congener exposure via the inhalation for different workshop workers is given in Fig. S4. BDE-47, -99, and -209 are the dominant congeners for the inhalation exposure, no matter what site. The hazard quotients for BDE-47, -99, -153, and -209 were calculated using the reference dose (RfD), as reported by USEPA IRIS Toxicological Evaluations (U.S. EPA, 2008). The draft RfD value was 0.1 μg/kg/d for BDE-47, -99, 0.2 μg/kg/d for -153, and 7 μg/kg/d for -209. Accordingly, the hazard indices of 36.41, 5.28, and 1.83 for all congeners were obtained at I-EWDW, WIP, and PRW, respectively (Table 1). All these reveal that the e-waste recycling would discharge higher PBDEs, which would be more harmful to worker health than other workshops. Notably, the risk values presented here are based on the model estimations of PBDE intake for the workers; these may not represent the intake for highly exposed individuals and do not consider the risk related to sensitive subpopulations (e.g., children) via other chemicals aside from PBDEs. Overall, these results provide a reasonable set data
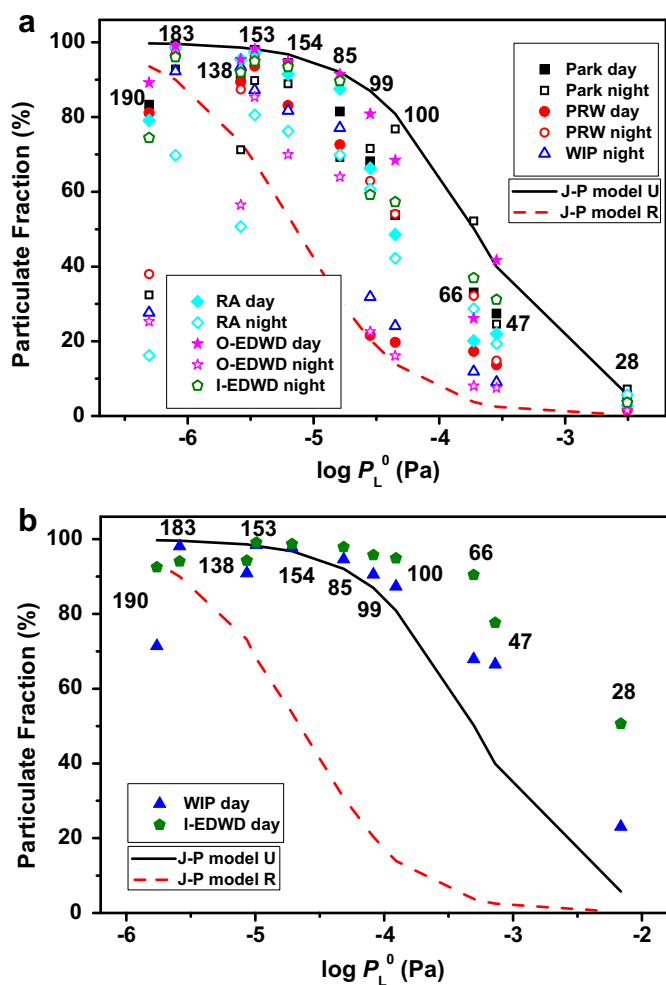

Fig. 4. Measured particulate fractions ($\varphi \times 100\%$) of PBDEs with theoretical predictions with the Junge–Pankow adsorption model.

Table 1
Evaluation of hazard indices for PBDE congeners -47, -99, -153, and -209.

	DRAFT RfDa (μg/kg/day)	Hazard quotient		
		PRW	WIP	I-EWDW
BDE-47	0.1	0.46	2.36	16.34
BDE-99	0.1	0.21	1.93	16.94
BDE-153	0.2	0.03	0.17	1.36
BDE-209	7	1.13	0.82	1.77
Hazard index		1.83	5.28	36.41

describing on-site PBDE levels in the representative e-waste recycling region of South China. These values allow for an accurate determination of PBDEs intake from the inhalation of region-specific consumption data.

In addition, lower brominated congeners are more persistent and toxic to humans. Mono- to penta-brominated congeners are more carcinogenic and mutagenic due to the smaller number of bromine (McDonald, 2002; Rahman et al., 2001). However, these congeners are prone to association with the gas phase, which plays an important role in the exposure of workers and RA people. As exposure mainly accounts for the particles, the intake risk for local people may be ignored (Julander et al., 2005; Wilford et al., 2005); then, high exposure in the workshops is overestimated because almost all PBDEs are associated with particles, whereas some of the larger particles may not be inhaled into the lungs.

4. Conclusions

Gas samples and TSP were investigated at different functional workshops and control sites at an e-waste recycling center in South China. Research found that average TSP and total PBDEs concentrations at O-EWDW (off-site) were much lower than those at I-EWDW (on-site) during work time, but the opposite trend was found during off work time. BDE-209 was the only dominant PBDE congener in PRW and control sites during work time and all sites during off work time. Comparatively, BDE-47, -99, and -209 were main congeners at I-EWDW and WIP. Partitioning of PBDEs between the gas and particle phases (K_p) was well correlated with the subcooled liquid vapor pressure (P_L^0) for all of the samples, except for WIP and I-EDWD, at the park during the work time, and the residential area during off work time. The predicted urban curve by the J–P model fitted well with the measured φ values at O-DEWD during work time. Exposure assessment revealed that workers in I-EDWD were the highest exposure population among all workshop employees.

Acknowledgments

Appendix. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.envpol.2011.08.014.

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