POLYBROMINATED DIPHENYL ETHER CONCENTRATIONS IN INDOOR AND OUTDOOR AIR FROM VEHICLUAR DISMANTLER PLANTS, SOUTHERN TAIWAN

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Introduction

Brominated fire retardants (BFRs) including polybrominated diphenyl ethers (PBDEs) are globally emerged persistent organic pollutants (POPs) in the recent years. The organobromines of PBDEs with resistance to chemical, physical, and biological degradation are ubiquitously existed in the environment to be easily bioaccumulated at the biota[1]. PBDEs are widely used in a number of commercially consumer products, such as upholstered furniture, textiles, and household electronic equipment to improve their fire resistance[1]. At first, PBDEs and polychlorinated biphenyls (PCBs) are recognized as the similar organohalogen compounds because they have similar structure; but in contrast to point sources of PCB contamination, PBDEs are widespread and released into the environment from more sources[2]. The commercial products of pentaBDEs and octaBDEs have been banned to manufacture in Europe and voluntarily phased out in the world since 2004[3], but decaBDE is still produced and widely used in most countries except for Europe and several states in USA since 2012. Tetra-, penta-, hexa-, and heptaBDEs have been added on the list of persistent organic pollutants (POPs) of the Stockholm Convention- Annex A[4]. Despite the bans of PBDE use in a lot of industrialized countries including European countries and the United States, there will be the continuous release of PBDEs from exiting products for many years to come[5].

Several recent studies have shown that PBDE concentrations are detected in indoor dust and indoor air samples[6-9]. Thuresson *et al.* (2012) indicated that PBDEs were detected in indoor air and dust from houses, apartments, day care centers, offices, and cars from Sweden[6]. BDE-209 was found to be an extremely predominant compound among PBDE and HBCD congeners in indoor dust and air from most published articles[6-8]. In comparison with PBDEs in indoor air and outdoor air, Björklund et al. (2012) indicated that concentrations of BDE-28, 47, 99, 153, and 209 emitted from indoor air to be roughly estimated for consisting 90% of total emissions to outdoor air, indicating that PBDE contaminated air in indoor environment is an important source of PBDE contamination to the ambient air in outdoor environment[10]. Levels of PBDEs in atmospheric air from northern China were 11 pg/m^3 in gaseous phase and 46 pg/m^3 in particulate phase, respectively, and BDE-209 was predominant to contribute 36.4-80.4 % of the total ΣPBDEs[11]. Levels of PBDEs in Toronto air were ranged from 047 to 110 pg/m^3 between October 2007 and October 2008[12]. A recent study was assessed to investigate PBDEs in the air from various sampling districts to show that ΣPBDE concentrations were decreased as the following order: industrial zone site> historical e-waste site> e-waste site> suburban site> residential site> background site in summer and winter[13]. Hearn et al. (2012)[14] indicated that air PBDE concentrations in the vicinity of an automotive shredding and metal recycling plant were between 230 and 699 pg/m^3 with the mean of 444 pg/m^3. In the previous Taiwanese study[15], atmospheric PBDE concentrations were 165 ± 65.0 (mean± SD) pg/Nm^3 in the heavy steel area, 93.9 ± 24.5 pg/Nm^3 in the metals complex areas, and 35.5 ± 15.5 pg/Nm^3 in the urban areas, respectively. To our knowledge, few studies reported PBDE concentrations in indoor and outdoor air in the vehicular dismantler factories.

Materials and methods

Thirty PBDE standards (BDE-7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156, 183, 184, 191, 196, 197, 203, 206, 207, 208, and 209) from Cambridge Isotope Laboratories and 9 ^{13}Clabeled PBDEs (BDE-15, 28, 47, 99, 153, 183, 197, 207, and 209) used as standards from Wellington Laboratories. Sodium sulfate, alumina oxide, potassium oxalate, and silica gel of the highest grade were obtained from Merck (Darmstadt, Germany).

Indoor and outdoor ambient air samples were collected from three vehicular dismantler factories located at Kaohsiung city and Pingtung County in southern Taiwan between November 2012 and February 2013 (Figure 1). Each factory including indoor and outdoor air was simultaneously sampled lasting for 4-5 days within the duty hours to obtain good representative samples in the duration of a week exposure. Each air sample was approximately collected for 40 hours at ~0.225 m^3/min with a PS-1 sampler (Graseby Andersen, GA) following US EPA Reference Method TO9A. A quartz fiber filter followed by PUF gathered PBDEs with particle and gas phase. After the collection, the quartz fiber filter and PUF of each air sample were combined for analysis for thirty PBDEs. The analytical method for PBDEs was according to US EPA Method 1614 as described previously[15]. In brief, PBDE internal standards were spiked to the samples before Soxhlte extraction with toluene. The concentrated extract was treated with concentrated H_2SO_4 after the extraction. The elute was followed by a series of sample cleanup and multi-column fractionation procedures, including a multi-layered silica column, alumina column, and activated carbon column. The multi-column systems were sequentially eluted with 25 mL dicloromethane/hexane (40/60, v/v) to be concentrated to approximately 1 mL and transferred to a vial before PBDEs analysis. Thirty PBDE congeners were BDE-7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156, 183, 184, 191, 196, 197, 203, 206, 207, 208, and 209. The final elute was analyzed by a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) (Hewlett-packard 6970 Series GC/Micromass Autospec Ultima) equipped with a DB-5HT capillary column (L=60, i.d.=0.25 mm, film thickness= 0.1 μm)(J&W Scientific, CA). The HRMS was equipped with a positive electron impact (EI^+) source. The quality assurance and quality control (QA/QC) in this study was met to the criteria of US EPA Method 1614.

Results and discussion

ΣPBDE concentrations in the indoor air from three vehicular dismantler factories were ranged from 69.3 to 756 pg/Nm^3 and ΣPBDEs were between 39.8 and 417 pg/Nm^3 in outdoor air from these three factories. The mean and standard deviations of Σ_{30}PBDEs was 305 ± 241 pg/Nm^3 in indoor air and 205 ± 149 pg/Nm^3 in outdoor air, respectively (Figure 1). The predominant BDE among 30 PBDE congeners was BDE-209 in indoor air as well as in outdoor air. BDE-209 was consisted 83.0 % in indoor air and 77.6% in outdoor air, respectively, of Σ_{30}PBDEs. There were no significant differences in concentrations of PBDE congeners and ΣPBDEs between indoor air and outdoor air (p<0.05) by examining Mann-Whitney *U* tests, although PBDE concentrations in indoor air have higher magnitudes than those in outdoor from these three vehicular dismantler factories. Compared with Σ_{30}PBDE levels with the high-volume samplers in the heavy steel complex area (165 pg/Nm^3), the metal complex area (93.9 pg/Nm^3), and the urban area (35.3 pg/Nm^3) from Taiwan[15], elevated PBDE levels in indoor and outdoor air from the vehicular dismantler factories were performed in the present study. Our values including Σ_{30}PBDEs in indoor air and outdoor air were still higher than Σ_{10}PBDE concentrations (839-1250 pg/m^3) in atmospheric air using high-volume samplers from the Yangtze River Delta[16], which is one of China's most developed, dynamic, and densely populated and concentrated industrial areas, Σ_{10}PBDEs (230-669 pg/m^3) in the automotive shredding and metal recycling facility from Australia[14] , and Σ_{40}PBDEs (620-720 pg/m^3) using air passive samplers in indoor air from Vietnamese e-waste recycling sites[17].

Significant correlation coefficients for diBDEs and triBDEs (r=0.829, p=0.045), tetraBDEs and pentaBDEs (r=0.829, p=0.045), and PBDEs from octa to deca (r=0.886-0.943, p=0.39 -<0.001) were found in indoor air (Table 1). In Table 2, significant correlations were found among certain PBDE congeners especially for the highest brominated PBDEs from octa to deca. Highly correlation coefficients were performed among the highest brominated PBDEs from octa to deca in indoor air as well as in outdoor air indicating that octaBDEs, nonaBDEs, and decaBDE may be emitted from the indoor environment to the outdoor environment. Swedish scientists indicated PBDEs in indoor air may be an important source of PBDEs to be contributed in outdoor air[10]

In Table3, the workers who were exposed by PBDEs in the work place of the vehicular dismantler factory were evaluated as the equation of daily intake via inhalation=(C×IR×IEF)/(b.w.) followed by Hearn's study[14]. We assumed Σ_{30}PBDE concentrations (C) in indoor air from the present study, inhalation rate (IR) of adults as 130 m^3/day, indoor exposure fraction (IEF) of 0.33 for 8hr/24hr, and adults' body weights (b.w.) of 70 kg and 50 kg for man and women, respectively. Estimated PBDEs daily intake through inhalation for the male and female workers was 17.0 and 23.8 pg/b.w./day, respectively. The estimated PBDEs daily intake from inhalation of air was 27 pg/b.w./day for Australian workers (b.w.=70 kg) and 14 pg/b.w./day for the adults (b.w.=70 kg, IEF=0.53) at home based on the similar assumption with our study. Recently, PBDE levels in 108 food samples were measured to estimate daily intake of PBDEs through 9 types of typical consumed food for Taiwanese[18], indicating that estimated PBDEs dietary daily intake for Taiwanese adults was 68 ng/day (971 pg/b.w./day if the body weight was assumed as 70 kg). In our previous study, estimated PBDEs daily intake from house dust was 171 pg/b.w./day (159 pg/b.w./day for 70 kg adults) for the 65-kg Taiwanese adults[19]. For the internal dose of Taiwanese, PBDEs exposure rout through inhalation based on the present finding was minor in comparison of PBDEs ingestion from the dietary based on the Chen's study[18] and those from house dust in our previous study[19]. Hearn et al. (2013) indicated the majority of PBDEs exposure routs were dietary ingestion and dust ingestion for the Australian adults[20].

In conclusion, PBDE concentrations in indoor air were higher than those in outdoor air from vehicular dismantler factories, but there were no significant differences in PBDEs and Σ_{30}PBDEs between indoor air and outdoor air. PBDEs daily intake for the workers in the vehicular dismantler factory via inhalation was 17.0 and 23.8 pg/b.w./day for men and women. The vehicular dismantler workers exposure to PBDEs through inhalation from indoor air was minor compared with the PBDEs exposure routs from dietary and house dust.

Acknowledgements

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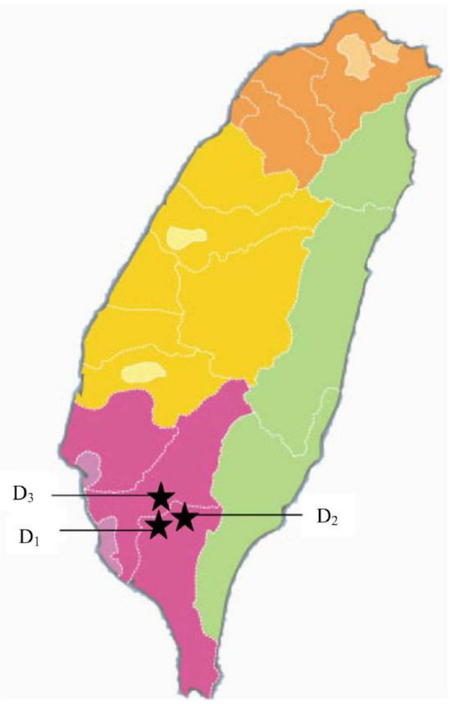

Figure 1. The location of three vehicular dismantler factories in sourthern Taiwan

Table 1. Correlations of PBDE homologues in indoor air from the vehicular dismantler factory

	i2Br	i3Br	i4Br	i5Br	i6Br	i7Br	i8Br	i9Br
i3Br	0.829*							
i4Br	0.086	0.371						
i5Br	-0.086	0.086	0.829*					
i6Br	0.086	-0.086	0.6	0.714				
i7Br	0.086	-0.429	-0.714	-0.657	-0.029			
i8Br	-0.429	-0.771	-0.257	-0.2	0.371	0.714		
i9Br	-0.543	-0.771	0.086	0.257	0.657	0.371	0.886*	
i10Br	-0.371	-0.657	-0.029	0.029	0.6	0.543	0.943**	0.943**

$^*p<0.05$, $^{**}p<0.01$

Table 3. Estimated daily PBDEs intake through inhalation for male and female employers in the vehicular dismantler factories with 8 duty hours (pg/kg body weight (b.w.) /day)^a

	Male employers	Female employers
Employers in D$_1$	28.66	40.12
Employers in D$_2$	4.29	6.01
Employers in D$_3$	18.1	25.34

^{a} Estimated daily PBDEs intake via inhalation =(C×IR×IEF)/(b.w.); C=ΣPBDE concentrations in indoor air of work place; IR=inhalation rate (m^3/day), IR was assumed as 130 m^3/day; IEF= indoor exposure fraction (hours spent per day in the work environment), IEF was assumed as 0.33 (8 hr/24 hr); b.w.=body weight for adults, we assumed body weights for man and women as 70 kg and 50 kg, respectively.

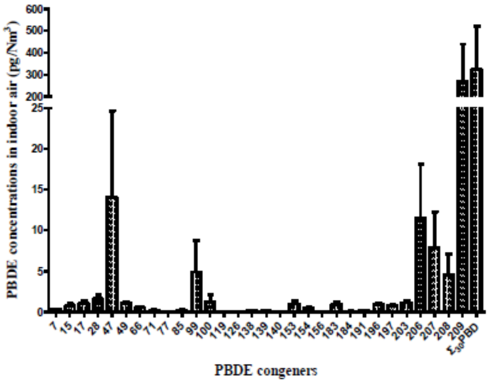

Figure2. Characteristics of PBDE congeners in indoor air from three vehicular dismantler factories

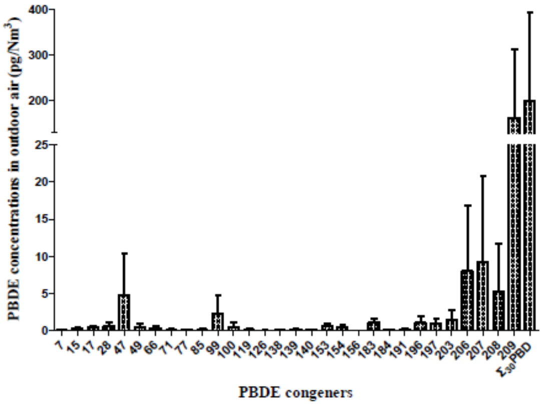

Figure 3. Characteristics of PBDE congeners in outdoor air from three vehicular dismantler factories

Table 2. Correlations of PBDE homologues in outdoor air from the vehicular dismantler factory

	O2Br	O3Br	O4Br	O5Br	O6Br	O7Br	O8Br	O9Br
O3Br	1**							
O4Br	0.771	0.771						
O5Br	0.714	0.714	0.943**					
O6Br	0.943**	0.943**	0.829*	0.771				
O7Br	0.829*	0.829*	0.714	0.6	0.943**			
O8Br	0.771	0.771	0.829*	0.943**	0.829*	0.657		
O9Br	0.543	0.543	0.829*	0.943**	0.6	0.371	0.886*	
O10Br	0.6	0.6	0.771	0.886*	0.543	0.257	0.829*	0.943**

$^*p<0.05$, $^{**}p<0.01$