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Pollution Characteristics and Diurnal Variations in Polybrominated Diphenyl Ethers in Indoor and Outdoor Air from Vehicle Dismantler Factories in Southern Taiwan

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are a class of the emerging persistent organic pollutants that have shown potential harmful effects in *in-vivo* and human studies. Our goal was to investigate 30 airborne PBDEs in day-to-night or indoor-to-outdoor in three vehicle dismantling factories located in southern Taiwan to assess worker risks. Thirty PBDEs including 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 were analyzed using high-resolution-gas chromatography/high-resolution-mass-spectrometer. Levels of airborne Σ_{30}PBDEs were 275, 336, 200 and 494 p gm^{-3} in indoor daytime, indoor nighttime, outdoor daytime, and outdoor nighttime, respectively, and their differences were not significant. BDE-209 was the predominant congener among the 30 PBDEs consisting of 82.5–97.9% of Σ_{30}PBDEs in both indoor and outdoor air. Pollution characterizations of the PBDE patterns were similar in air samples except for the outdoor air in the nighttime. Diurnal variations in PBDEs in both indoor and outdoor air were not observed. A principal component analysis was used to test for possible sources of PBDE contamination. BDE-209 in outdoor air was possibly contributed from PBDEs in indoor air, particularly from BDE-209. Characteristics of diurnal PBDE contamination in indoor and outdoor air in vehicle dismantling factories were linked to commercial technical OctaBDE (Bromkal 79-8DE) and DecaBDEs (Bromkal 82-0D and Saytex 102E) mixtures. The highest PBDE intakes of workers via inhalation were assessed as 41.8 and 32.7 pg kg^{-1} bw day^{-1} for male and female adults, respectively. It was hypothesized that airborne PBDEs in indoor factories are released from the surface of DecaBDE or OctaBDE technical formulations and influence outdoor air through ventilation or natural dispersion. However, occupational exposure through inhalation might be an important PBDE contamination pathway, but it is minor compared to PBDE dietary intake.

Keywords: Polybrominated diphenylethers (PBDEs); Diurnal variation; Indoor and outdoor air; Vehicle dismantling factory; Occupational inhalation exposure.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs), which are only used in brominated fire retardants (BFRs) to reduce fire accidents, have emerged as a class of persistent organic pollutants in the global environment (Alaee *et al*., 2003). These organobromines, including the commercial formulations such as PentaBDEs, OctaBDEs, and DecaBDE, have been banned for use in Europe or voluntarily discontinued in some parts of the USA due to their high resistance to chemical, physical, and biological degradation and because

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they are ubiquitous in the environment. At the present, DecaBDE technical mixtures are still sold and widely used in most countries, including Taiwan (Chao *et al*., 2014a). PBDEs with high lipophilicity are easily bioaccumulated in the biota, including terrestrial and aquatic living organisms (de Wit *et al.*, 2010). To raise both official and public concern, the toxicological endpoints of human exposure to PBDEs in current scientific reports, particularly for young children include disruption of thyroid hormone secretion (Lin *et al*., 2011; Shy *et al.*, 2012), neurodevelopment or neurobehavioral development (Chao *et al*., 2011; Shy *et al*., 2011), and male or female reproductive functions (Chao *et al*., 2007; Wang *et al*., 2008; Chao *et al*., 2010; Abdelouahab *et al*., 2011).

Humans spend more than 90% time in the indoor environment. Diverse contaminants, such as polycyclic aromatic hydrocarbons, BFRs, polybrominated dibenzo-*p*-dioxins/furans, cations, anions, heavy metals, dioxin-like compounds, in the indoor environment were the important source of human exposure (Chao *et al.*, 2014a; Chou *et al.*, 2015; Cheruiyot *et al.*, 2015; Saraga *et al.*, 2015; Shy *et al*., 2015; Gou *et al.*, 2016). PBDEs are easily released from the surface of consumer products such as household electronic equipment, building materials, upholstered furniture, carpets, computers, textiles, and automobiles (de Wit, 2002). Owing to the extensive use by a wide variety of household consumers and people preferring to stay indoors most of the time (more than 90%), indoor environments or microenvironments present a significant contribution of human exposure to PBDEs (de Wit, 2002; Chao *et al*., 2014a). Indoor air and dust are the possible exposure routes for human exposure to PBDEs in the indoor environment (Chao *et al*., 2014b; Hsu *et al*., 2014; Shy *et al*., 2015; Chou *et al*., 2016). Compared with PBDE concentrations in outdoor air, elevated levels of PBDEs in indoor air have been presented in most literature (Harrad *et al*., 2010; Bjorklund *et al*., 2012; Newton *et al*., 2015). PBDE levels have not been found to differ in regard to the matched indoor air and outgoing air in ventilation systems (Bjorklund *et al*., 2012; Newton *et al*., 2015) and Björklund *et al* (2012) indicated indoor air as a significant source of PBDEs from the outdoor environment though ventilation facilities. The inverse result was reported in a recent Chinese study, which revealed that PBDE concentrations in outdoor air in a community in Gungzhou in the Pearl River Delta (PRD) were notably higher than those in indoor air (Ding *et al*., 2016). Extremely high levels of PBDEs in the indoor and outdoor air have also been found in e-waste workplaces steelmaking plants and dismantling areas (Hearn *et al*., 2012; Tue *et al*., 2013; Ren *et al*., 2014; Li *et al.*, 2015; Xu *et al*., 2015). Workers near an automotive shredding and metal recycling plants were assessed to be two times higher to be likely to be exposed to PBDEs compared with Australians in their home environments (Hearn *et al*., 2012).

Most studies on this topic have been conducted based on diurnal variations in PBDEs in the atmospheric air including remote regions and the heavily contaminated areas like e-waste dismantling locations (Chen *et al*., 2009; Iacovidou *et al*., 2009; Gevao *et al*., 2010; Chen *et al*., 2011; Zhang *et al*., 2012). Very few studies have considered airborne PBDE variations under both day-to-night and indoor-to-outdoor situations. In the present study, diurnal and indoor-to-outdoor variations on PBDE characteristics in vehicle dismantling factories were examined to further assess the associated factors and workers' risk of exposure.

METHODS

Sample Location and Collection

Indoor and outdoor air samples were collected in three vehicle dismantler factories located in Pingtung County (V1 and V2) and Kaohsiung City (V3) in southern Taiwan between November, 2012 and February, 2013. Four types of air samples, including day time indoor air, day time outdoor air, night time indoor air and night time outdoor air, were collected for the present study. Following the US EPA Reference Method TO9A, each air sample was collected for approximately 40 hours at ~0.225 m^3 min^{-1} with a PS-1 sampler (Graseby Andersen, GA) equipped with a quartz fiber filter and a glass cartridge containing polyurethane foam (PUF) to capture the particulates and gas samples. Before air sampling, the PUFs were spiked with surrogate standards to obtain their recovery rates.

The V1 vehicle dismantler factory is a two-story building near an agricultural area. Two PS-1 samplers were set on the first floor and second floor of a machine component zone close to the major dismantler zone in the factory. One PS-1 sampler was set outside of the V1 factory at a distance of approximately 150 meters. The V2 vehicle dismantler factory is a flat building located near a crossroad and areca plantation. Two PS-1 samplers were set in the same position at that of the machine component zone for indoor air while the outdoor air site was set near a crossroad approximately 200 meters away from the indoor site. Notably, the major dismantler zone in the V2 area was located outside far away from the indoor air site. The V3 vehicle dismantler factory is a semi-open space architectural building located behind the main road between Pingtung County and Kaohsiung City in the middle of a recycling processing plant and iron factory. One PS-1 sampler was set near the main major dismantler zone, and two PS-1 samplers were set approximately 30–50 meters behind the factory.

Sample Pretreatment Procedure

After sample collection, Soxhlet extraction and cleanup procedures were done in the present study. The details of the sample pretreatment procedure were provided in our previous studies. Prior to Soxhlet extraction, the quartz fiber filter and PUF were combined as one air sample (the particle pool and gas phase), and the internal standards including $^{13}C_{12}$-labeled BDE-15, 28, 47, 99, 153, 154, 183, 197, 207, and 209 were spiked in each air sample. Each air sample was extracted with 300 mL toluene for 24 h in the Soxhlet extractor, and then concentrated to 10 mL by using a rotary evaporator for the next step of the cleanup procedure. After the sample was concentrated, the extract was passed through acid silica gel and multiple silica gel including alumina and activated carbon columns, and then further eluted with 15 mL hexane, 25 mL dichloromethane/hexane (1/24, v/v) and 5 mL toluene/methanol/ethyl acetate/hexane

(1/1/2/16,v/v/v/v) to collect PBDEs. The eluate was evaporated to near dryness using a gentle stream of gaseous nitrogen. The final eluate prior to injection was 0.2 mL.

Chemical Analysis

Thirty PBDE congeners including 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 were analyzed by a high-resolution gas chromatograph equipped with a high-resolution mass spectrometer (HRGC/HRMS, Hewlett-Packard 6970 Series gas/Micromass Autospec Ultima). A DB-5HT column (15 m × 0.25 mm, 0.1 μm particle size) (J&W Scientific, Folsom, CA) was used for the HRGC analysis. The HRMS spectrometer was equipped with a positive electron (EI+) source in selected ion monitoring (SIM) mode, and the electron energy was specified at 70 eV. The detailed analysis conditions were described in our previous study (Shy *et al*., 2015).

The quality assurance and quality control (QA/QC) including the recovery rate of the surrogate standards and internal standards, blank test, and limits of detection (LOD) followed the US EPA Method 1614A. The acceptable recovery rates of the di-BDE, tri to octa-BDE and nona to deca-BDE surrogate standards and internal standards ranged from 20–200%, 60–140% and 50–150%, respectively. The LOD value was defined based on a 3 times signal-to-noise (S/N) ratio which ranged from 0.262–46.0 pg g^{-1} for twenty-nine PBDE congeners, and 333 pg g^{-1} for BDE-209.

Statistical Analysis

The concentrations of PBDEs below LOD (limits of detection) were set to zero for further statistical analysis. A paired-T test (examined with 1000 bootstrap tests) was used to reveal significant differences between daytime and nighttime and indoor and outdoor air PBDEs levels, and the association between homologues of PBDEs in different type air samples, and six available commercial flame retardant mixture products were tested by principal components analysis. All statistical analyses were performed using Statistical Product and Service Solutions version 12.0.

RESULTS AND DISCUSSION

As shown in Table 1, the mean concentration of Σ_{30}PBDEs in the vehicle dismantling plants was observed to be 275 pg m^{-3} in daytime indoor air, 336 pg m^{-3} in nighttime indoor air, 200 pg m^{-3} in daytime outdoor air, and 494 pg m^{-3} in nighttime outdoor air. The highest levels of PBDEs occurred at V3 during the nighttime (1134 and 756 pg m^{-3}) in both outdoor and indoor air, respectively (data not shown). The V3 factory is located near a recycling processing plant and an iron factory, which might be the reason for the occurrence of the extremely high PBDE levels at V3. Besis*et al*. (2016) investigated three areas (urban-industrial, urban-traffic and urban-background) in Thessaloniki, Greece and reported that the PBDE concentration in industrial air (28.7 pg m^{-3}) was 7.45 times higher than that in the background air (3.87 pg m^{-3}), suggesting an association between corresponding PBDE levels and localization of sources like industrial and traffic areas. In the present study, there were no significant differences found in airborne PBDE levels between indoor and outdoor or daytime and nighttime except for the significant diurnal variation of BDE-28 in the indoor air (1.60 pg m^{-3} in the daytime vs. 2.05 pg m^{-3} in the nighttime, $p = 0.022$) and the significant indoor-to-outdoor variation of BDE-66 in the nighttime (0.657 pg m^{-3} in indoor air vs. 0.251 pg m^{-3} in outdoor air, $p = 0.030$). The most predominant congener in both the indoor and outdoor air samples was BDE-209 among all of the 81.0–92.5% of Σ_{30}PBDEs detected. Sequentially, BDE-47 (5.10 and 4.85% in daytime and nighttime, respectively) and BDE-206 (3.06 and 2.20% in daytime and nighttime, respectively) were followed by BDE-209 in both the daytime and nighttime indoor air. The outdoor air mass distribution was dominated by BDE-47, 206, 207, 208, and 209, which contributed 94.5% of Σ_{30}PBDEs in the daytime and 97.9% in the nighttime, respectively. Both indoor and outdoor levels of PBDEs in the present study were higher than those in Taiwanese home environments (Σ_{14}PBDEs: 81.1 and 13.1 pg m^{-3} in indoor and outdoor air, respectively) (Shy *et al*., 2015) and ambient air in the rural area of Pingtung (Σ_{14}PBDEs: 15.9 pg m^{-3}) (Chao *et al*., 2014c). As compared with other studies published from 2004 to 2016 and shown in Table 2, the mean level of PBDEs in the indoor air in the present study was lower than those in the vehicle parking areas in southern China (Li *et al*., 2016) and e-waste storage facilities in Thailand (Muenhor *et al*., 2010), but levels were still higher than those in the domestic environment (Wilford *et al*., 2004; Takigami *et al*., 2009; Shy *et al*., 2015; Ding *et al*., 2016). Our value in the outdoor air was only lower than those collected from vehicle parking areas (Li *et al*., 2016), and in the e-waste storage facilities (Muenhor *et al*., 2010), and a PRD community (Ding *et al*., 2016). In comparison with various indoor environments (Bjorklund *et al*., 2012; de Wit *et al*., 2012; Thuresson *et al*., 2012; Newton *et al*., 2015; Shy *et al*., 2015), indoor air levels of PBDEs in the present study were lower than those in offices, day care centers, and cars, but higher than those in homes and apartments.

PBDE homologues (di-BDE, tri-BDE, tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, octa-BDE, nona-BDE, and deca-BDE) from indoor and outdoor air samples are presented in Fig. 1(a); while airborne concentrations of PBDE homologues in daytime and nighttime are illustrated in Fig. 1(b). Only di-BDE homologue levels showed significant differences between both the indoor and outdoor air ($p = 0.009$) and between daytime and nighttime air ($p = 0.047$). The mean level of tri-BDEs in the indoor air was significantly higher than that in the outdoor air ($p = 0.045$). The PBDE compositions of indoor and outdoor air in the daytime and nighttime are shown in Fig. 2. Few published literatures were focused on the differences in airborne levels of di-BDEs and tri-BDEs between indoor and outdoor environment. Our results presented higher levels of di-BDEs and tri-BDEs indoors than outdoors in the car dismantling factories to indicate that there were still di-BDEs and tri-BDEs release from the surface of the recycled consumer products. Very similar patterns of PBDEs were found in the indoor air during both daytime and nighttime. The PBDE homologue

Table1. Mean concentrations of thirty PBDE congeners in the indoor and outdoor air in three vehicle dismantler factories (pg m^{-3}).

	Indoor air			Outdoor air			*p*-value	
	Daytime (n = 3)	Nighttime (n = 3)	*p*-value [a]	Daytime (n = 3)	Night time (n = 3)	*p*-value [b]	Day time [c]	Night time [d]
BDE-7	0.264	0.428	0.371	0.0823	0.174	0.083	0.199	0.068
BDE-15	0.702	0.821	0.349	0.240	0.298	0.136	0.209	0.070
BDE-17	1.00	1.58	0.156	0.362	0.436	0.068	0.235	0.141
BDE-28	1.60	2.05	0.022*	0.539	0.645	0.193	0.215	0.175
BDE-47	14.0	16.3	0.080	4.67	4.56	0.753	0.380	0.310
BDE-49	1.03	1.38	0.146	0.480	0.626	0.117	0.248	0.095
BDE-66	0.536	0.657	0.332	0.282	0.251	0.741	0.398	0.030*
BDE-71	0.154	0.169	0.471	0.0780	0.0757	0.946	0.317	0.177
BDE-77	0.0390	0.0633	0.371	0.0217	0.0523	0.159	0.210	0.349
BDE-85	0.178	0.131	0.408	0.0833	0.0460	0.551	0.449	0.440
BDE-99	4.79	5.20	0.527	2.22	1.52	0.597	0.521	0.283
BDE-100	1.16	1.28	0.404	0.470	0.365	0.574	0.472	0.301
BDE-119	0.014	0.0883	0.228	0.0820	0.0453	0.423	0.423	0.191
BDE-126	< LOD	< LOD	-	0.00433	0.00367	0.423	0.423	0.423
BDE-138	0.120	0.197	0.456	0.0903	0.122	0.205	0.504	0.128
BDE-139	0.102	0.224	0.412	0.107	0.101	0.903	0.919	0.414
BDE-140	0.0540	0.157	0.382	0.0670	0.0650	0.919	0.703	0.377
BDE-153	0.937	1.33	0.448	0.630	0.625	0.970	0.543	0.163
BDE-154	0.493	0.784	0.461	0.407	0.396	0.923	0.769	0.208
BDE-156	< LOD	< LOD	-	< LOD	< LOD	-	-	-
BDE-183	0.891	1.27	0.422	1.04	0.908	0.591	0.447	0.519
BDE-184	0.0723	0.212	0.365	0.0380	0.0943	0.246	0.508	0.423
BDE-191	0.126	0.182	0.463	0.154	0.146	0.890	0.698	0.525
BDE-196	0.816	1.05	0.477	1.02	0.821	0.610	0.653	0.398
BDE-197	0.706	1.03	0.364	0.895	0.777	0.782	0.618	0.541
BDE-203	1.05	1.20	0.661	1.44	1.02	0.598	0.631	0.578
BDE-206	8.41	7.40	0.887	8.01	12.0	0.401	0.958	0.304
BDE-207	5.64	6.13	0.910	9.15	6.77	0.654	0.689	0.575
BDE-208	3.27	3.41	0.956	5.19	3.51	0.582	0.707	0.819
BDE-209	227	281	0.829	162	457	0.341	0.687	0.320
Σ_{30}PBDEs	275	336	0.820	200	494	0.337	0.703	0.373

[a] Comparison between indoor daytime and indoor nighttime using a Paired T-test with 1000 bootstrap tests.
[b] Comparison between outdoor daytime and outdoor nighttime using a Paired T-test with 1000 bootstrap tests.
[c] Comparison between indoor daytime and outdoor daytime using a Paired T-test with 1000 bootstrap tests.
[d] Comparison between indoor nighttime and outdoor nighttime using a Paired T-test with 1000 bootstrap tests.
* $p < 0.05$.

distribution in the daytime outdoor air was also related to those in indoor air, but the PBDE distribution in nighttime outdoor air was different from those in both daytime and nighttime indoor air and daytime outdoor air. Furthermore, possible PBDE contaminated sources, including indoor and outdoor air in the daytime and nighttime, were investigated in the vehicle dismantling factories. PCA tests with varimax rotation were used to determine correlations in PBDE homologues in indoor and outdoor air (Fig. 3(a)) or the possible similarity with PBDE technical commercial formulations (Fig. 3(b)). For consideration of indoor and outdoor air (Fig. 3(a)), the two principal components (PCs) determined 56.3% and 23.6%, respectively, of the total variance in our data. PC1 is composed of higher PBDE homologues from hexa to deca in indoor air and decaBDE in outdoor air. The concentrations of BDE-209 in the ambient air in the vicinity of the vehicle dismantling factories were affected by PBDEs from hexa to deca in the indoor air, particularly in the case of BDE-209. According to our results, BDE-209 concentrations contributed 82.5% and 83.6% of the Σ_{30}PBDEs in indoor air, including both daytime and nighttime. BDE-209 was also the most predominant component in outdoor daytime and nighttime air among the 30 BDE congeners, consisting of 81.0% and 92.6% of the Σ_{30}PBDEs, respectively. Indoor BDE-209 was the major source of outdoor BDE-209. In our previous studies, BDE-209 concentrations were 59.7% and 70.0% of Σ_{14}PBDEs in the ambient air including daytime and nighttime air collected in the rural university (Chao *et al.*, 2014c) and the rural residence (Shy *et al.*, 2015), respectively. The ambient air level of BDE-209 in PRD areas was over 88.4% of the total PBDEs (Ding *et al.*, 2016). PBDEs in nighttime outdoor

Table 2. Summary of the current data on PBDE levels in indoor and outdoor air (pg m^{-3}).

Reference	Location	Style	Range (mean)		PBDE congeners
			Indoor air	Outdoor air	
This study	Southern Taiwan, Taiwan	Vehicular dismantle factory	69.3–756 (305)	39.8–1133 (347)	Σ_{30}PBDEs: 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
Ding *et al.*, 2016	Guangzhou, China	House	1.43–57 (68.5)[a]	1.21–1522 (404)[a]	Σ_{12}PBDEs: BDE-28, 47, 66, 99, 100, 138, 153, 154, 206, 207, 208 and 209
Li *et al.*, 2016	Guangzhou, China	Vehicle parking areas	363–16102 (3590)	2165–24792 (7724)	Σ_{20}PBDEs: BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 196, 197, 203, 206, 207, 208 and 209
Shy *et al.*, 2015	Southern Taiwan, Taiwan	House	13.1–156 (81.1)	19.3–72.0 (42.7)	Σ_{14}PBDEs: BDE-28, 47, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 208 and 209
Muenhor *et al.*, 2010	Thailand	E-waste storage facility	46–350 (127)	8–150 (55.3)	Σ_{10}PBDEs: BDE-17, 28, 47, 49, 66, 85, 99, 100, 153 and 154
Takigami *et al.*, 2009	Hokkaido, Japan	House	17.0–55.0 (36.0)	19.0–25.0 (22.0)	Σ_{8}PBDEs: BDE-28, 47, 66, 99, 100, 153, 154 and 209
Wilford *et al.*, 2004	Ottawa, Canada	House and apartment	2.00–3600[b] (260)	< LOD–4.40[c] (2.20)	Σ_{10}PBDEs: BDE-17, 28, 47, 66, 71, 85, 99, 100, 153 and 154 Σ_{5}PBDEs: BDE-17, 28, 47, 99 and 100.

[a] Median.
[b] Expressed as mean of Σ_{10}PBDEs.
[c] Expressed as mean of Σ_{5}PBDEs.

air is dominated by BDE-209 probably due to PBDEs from indoor air to outdoor air in the vehicle dismantling factories and occurrence of photodegradation. Photodegradation is possibly a debromination pathway for conversion of deca-BDE to nona-BDEs or the other low brominated PBDEs. Davis and Stapleton, (2009) indicated that rapid photodegration from decaBDE to nonaBDEs (i.e., BDE-206, 207 and 208) was consisted under natural sunlight. PC2 is composed of PBDEs from di to nona in the outdoor air, accounting for 23.6% of the total variances, indicating that the indoor PBDE contamination sources were not one of the main factors affecting outdoor PBDEs from di to nona. The possible sources existed in the outdoor environment itself, like traffic emissions and long-range transportation. In Fig. 3(b), PC1 was explained to be 80.9% of the total variations, expressing that the composition of PBDE homologues in the air samples was associated with two DecaBDEs (Saytex 102E and Bromkal 82-0D) and an OctaBDE (Bromkal 79-8DE) commercial technical formulation. The other three commercial technical mixtures, such as DE-71 and Bromkal 70-5DE, which are PentaBDEs products, and DE-79, which is an OctaBDE product, were not included in PC1. The indoor air in the vehicle dismantling factories probably contained PBDE contamination released from OctaBDE and DecaBDEs technical mixtures or from debromination of commercial DecaBDEs. Wu *et al*. (2015) revealed that BDE-209 consists of 98.0% (64.6 ng g^{-1}) and 61.5% (20.3 ng g^{-1}) of Σ_{14} PBDEs in the outdoor soil and dust, respectively, near the automobile manufacturing area (Wu *et al*., 2015). The dominant contributor of BDE-209 to ΣPBDE concentrations in the vehicle dust was found to be associated with the extensive usage of DecaBDE formulation in the automobiles (Lagalante *et al*., 2009; Kalachova *et al*., 2012).

Although Σ_{30}PBDE concentrations in the nighttime air were slightly higher than those in the daytime in either indoor or outdoor air, their differences were not significant. Few reports have considered on diurnal variations or day-to-night changes in airborne PBDEs in indoor environments. PBDE concentrations in indoor air are possibly governed by both ventilation and temperature. Macleod *et al*. (2007) indicated that day-to-night changes or diurnal variations in persistent organic pollutants, including PBDEs, are probably influenced by temperature, source characterization, hydroxyl radical concentrations, and atmospheric mixing layer height and stability in the atmosphere. For the outdoor air in the present study, our result was consistent with that found in previous studies except for the most highly contaminated region (e.g., e-waste region), which indicated that the weak diurnal variation in atmospheric PBDE levels was probably due to short distance to indoor contaminated sources, long-distance transport, and low fluctuations of temperature and atmospheric mixing layer height (Chen *et al*., 2009; Iacovidou *et al*., 2009; Chen *et al*., 2011). The unique pollution characterizations and violent diurnal fluctuations in ambient PBDEs usually occur in special events like severe dust storms (Gevao *et al*., 2010) or because of heavily contaminated regions like e-waste dismantling areas (Chen *et al*., 2009). Several studies have reported that ambient PBDE concentrations are positively correlated with e-waste industries (Chen *et al*., 2009; Chen *et al*., 2011; Ding *et al*., 2016). Chen *et al*. (2009, 2011) indicated that average airborne PBDEs in the daytime were two-fold higher than that in nighttime in e-waste recycling and dismantling sites mainly due to temperature and severe emission of PBDEs from these

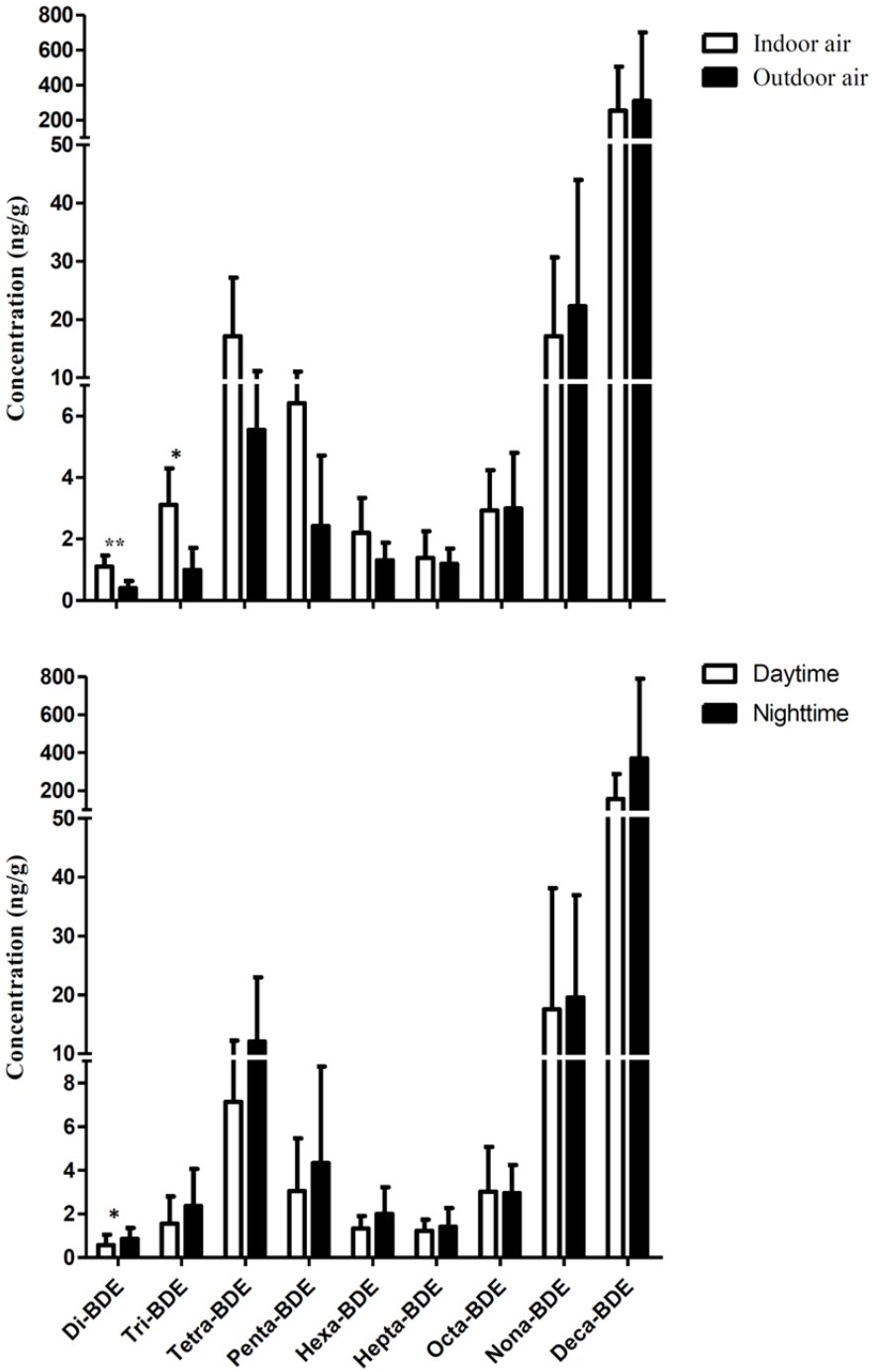

Fig. 1. Concentration of PBDE homologues between (a) in indoor air and outdoor air (b) in daytime and nighttime (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$).

disposal and storage sites. Inversely, atmospheric levels of PBDEs in the nighttime were shown to be significantly and almost three-fold higher than those in the daytime during a severe dust storm (Gevao *et al*., 2010). Violent diurnal fluctuations of PBDEs are possibly associated with pollution characterization in a dust storm event or heavily contaminated regions based on the current data (Chen *et al*., 2009; Gevao *et al*., 2010; Chen *et al*., 2011). In the present study, although variant pollution characterization was observed between indoor and outdoor air, diurnal changes did not seem to affect the distribution of PBDEs in the indoor and outdoor environments. Day-to-night changes did not affect PBDE distribution indoors and outdoors mainly base on the different pollution characterizations. In the indoor air of the vehicle dismantling factories, PBDE dispersion was limited by the semi-open space, and ventilation might be the major route of PBDEs from indoor air to outdoor air if the ventilation systems are working. Indoor air PBDEs are probably associated with the release of PBDE technical formulations on the consumer products used in vehicles in

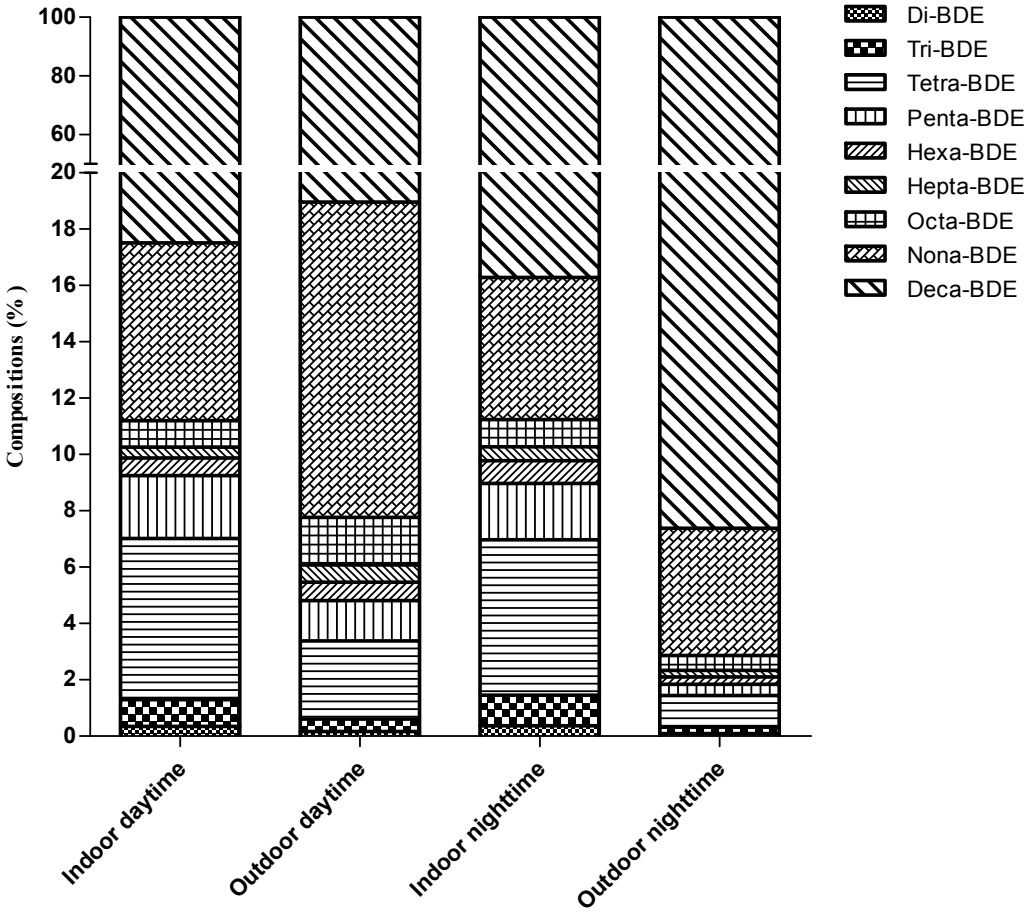

Fig. 2. Compositions of PBDE homologues in indoor and outdoor air in the vehicle dismantler factory air.

the vehicle dismantling factories. Unlike the indoor air, outdoor air PBDEs are largely affected by pollution sources including indoor air, transportation emissions, and long-range transport.

According to previous Australian and Taiwanese studies (Hearn *et al*., 2012; Shy *et al*., 2015), the equation was estimated using the PBDE daily intake via inhalation as $DI_{\text{indoor air inhalation}} = C_{\text{indoor air}} \times IR_{\text{inhalation rate}} \times 0.95_{\text{absorption rate}} \times IEF_{\text{indoor exposure fraction}}/BW_{\text{body weight}}$. C is the concentration of BDE-209 and Σ_{30}PBDEs in indoor air; IR is the inhalation rates of an adult which were assumed to be 19.7 and 12.6 $m^3\,day^{-1}$ for males and females, respectively (USEPA, 2008). The absorption rate of PBDEs in the human intestinal tract was set at 0.95, and IEF was the working time in the vehicle dismantler factory, which was defined as 8 hours per day (0.333). According to the Nutrition and Health Survey in Taiwan (NAHSIT), the mean body weight (BW) was 69.0 and 56.6 kg for male and female adults between 2004 and 2008 (NAHSIT, 2008). The daily PBDE intake (pg kg^{-1} bw day^{-1}) for workers with occupational exposure via inhalation in the three vehicle dismantling factories is listed in Table 3. BDE-209 and Σ_{30}PBDEs ranged from 3.78 to 34.5 pg kg^{-1} bw day^{-1} and from 6.26 to 41.8 pg kg^{-1} bw day^{-1}, respectively for male adults and from 2.95 to 27.0 pg kg^{-1} bw day^{-1} and from 4.90 to 32.7 pg kg^{-1} bw day^{-1}, respectively, for female adults. The highest PBDE daily intake was estimated in the V1 vehicle dismantler factory, which was approximately 4 times higher than those estimated in Taiwanese residential houses (Shy *et al*., 2015). Although workplaces with heavy PBDE contamination is an important source of occupational exposure to PBDEs via inhalation, according to Chen's study (Chen *et al*., 2012), the daily PBDE intake from foodstuff was estimated as 68.0 ng day^{-1} in Taiwanese adults, so the median inhaled PBDEs intakes in this study (1.56 and 1.00 ng day^{-1} for male and female adults, respectively) were still minor compared with the dietary PBDE intake in Taiwan.

CONCLUSIONS

Diurnal and indoor-to-outdoor variations of airborne PBDEs were not obviously changed in the vehicle dismantling factories. The findings of the present study were that indoor airborne PBDEs possibly come from DecaBDE or OctaBDE technical formulations on the skin surface of vehicular consumers. For the PBDEs in the outdoor air near the vehicle dismantling factories, the PBDE sources might be from indoor sources, traffic emissions, and long-range transport. The amount of airborne PBDEs inhaled by workers in the vehicle dismantling factories was still minor as compared with uptakes of PBDEs via dietary sources for Taiwanese adults.

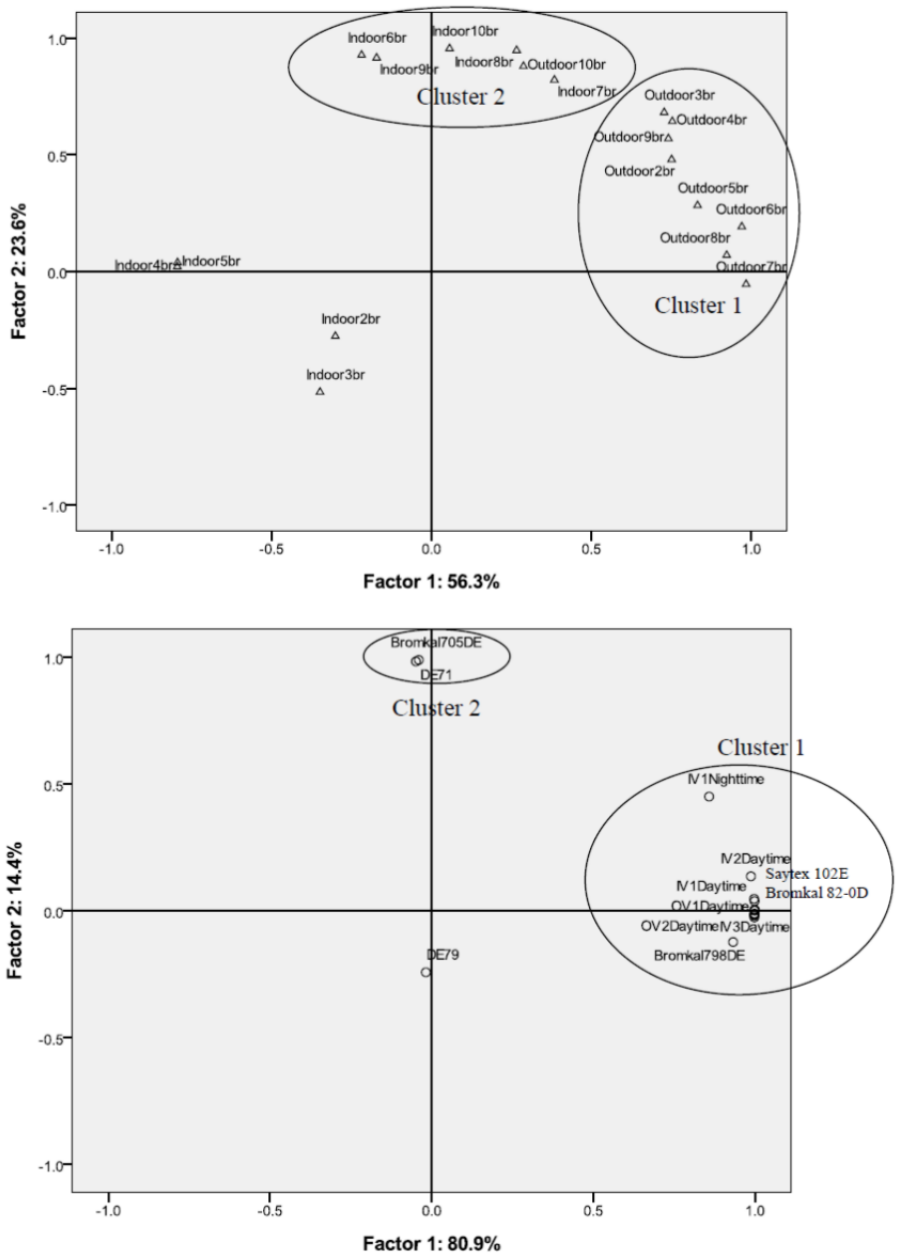

Fig. 3. Principal component analysis of (a) PBDE homologues in indoor air and outdoor air (b) association between PBDE homologues in the air of three vehicle dismantler factories, including V1, V2 and V3 indoor daytime, V1, V2 and V3 indoor nighttime, V1, V2 and V3 outdoor daytime, V1, V2 and V3 outdoor nighttime and commercial Penta, Octa and Deca-BDEs flame retardant mixtures, including DE-71, Bromkal 70-5DE, DE-79, Bromkal 79-8DE, Saytex 102E and Bromkal 82-0D formulation.

Table 3. Daily intake of vehicle dismantler factory workers via inhalation from daytime indoor air.

	Males (pg kg^{-1} bw day^{-1})	Females (pg kg^{-1} bw day^{-1})
V_1		
BDE-209	34.5	27.0
ΣPBDEs	41.8	32.7
V_2		
BDE-209	3.78	2.95
ΣPBDEs	6.26	4.90
V_3		
BDE-209	23.1	18.1
ΣPBDEs	26.4	20.6

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DISCLAIMER

The authors declare no conflict of interest with regard to this study.

REFERENCES

Abdelouahab, N., Ainmelk, Y. and Takser, L. (2011). Polybrominated diphenyl ethers and sperm quality. *Reprod. Toxicol.* 31: 546–550.

Alaee, M., Arias, P., Sjodin, A. and Bergman, A. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* 29: 683–689.

Besis, A., Voutsa, D. and Samara, C. (2016). Atmospheric occurrence and gas-particle partitioning of PBDEs at industrial, urban and suburban sites of Thessaloniki, northern Greece: Implications for human health. *Environ. Pollut.* 215: 113–124.

Bjorklund, J.A., Thuresson, K., Palm Cousins, A., Sellstrom, U., Emenius, G. and de Wit, C.A. (2012). Indoor air is a significant source of tri-decabrominated diphenyl ethers to outdoor air via ventilation systems. *Environ. Sci. Technol.* 46: 5876–5884.

Chao, H.R., Wang, S.L., Lee, W.J., Wang, Y.F. and Papke, O. (2007). Levels of polybrominated diphenyl ethers (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects. *Environ. Int.* 33: 239–245.

Chao, H.R., Shy, C.G., Wang, S.L., Chen, S.C., Koh, T.W., Chen, F.A., Chang-Chien, G.P. and Tsou, T.C. (2010). Impact of non-occupational exposure to polybrominated diphenyl ethers on menstruation characteristics of reproductive-age females. *Environ. Int.* 36: 728–735.

Chao, H.R., Huang, H.L., Hsu, Y.C., Lin, C.W., Lin, D.Y., Gou, Y.Y. and Chen, K.C. (2014a). Impact of brominated pops on the neurodevelopment and thyroid hormones of young children in an indoor environment—A review. *Aerosol Air Qual. Res.* 14: 1320–1332.

Chao, H.R., Shy, C.G., Huang, H.L., Koh, T.W., Tok, T.S., Chen, S.C.C., Chiang, B.A., Kuo, Y.M., Chen, K.C. and Chang-Chien, G.P. (2014b). Particle-size dust concentrations of polybrominated diphenyl ethers (PBDEs) in southern Taiwanese houses and assessment of the pbde daily intakes in toddlers and adults. *Aerosol Air Qual. Res.* 14: 1299–1309.

Chao, H.R., Lin, D.Y., Chen, K.Y., Gou, Y.Y., Chiou, T.H., Lee, W.J., Chen, S.J. and Wang, L.C. (2014c). A mospheric concentrations of persistent organic pollutants over the Pacific Ocean near southern Taiwan and the northern Philippines. *Sci. Total Environ.* 491–492: 51–59.

Chao, H.R., Tsou, T.C., Huang, H.L. and Chang-Chien, G.P. (2011). Levels of breast milk PBDEs from southern Taiwan and their potential impact on neurodevelopment. *Pediatr. Res.* 70: 596–600.

Chen, D., Bi, X., Zhao, J., Chen, L., Tan, J., Mai, B., Sheng, G., Fu, J. and Wong, M. (2009). Pollution characterization and diurnal variation of PBDEs in the atmosphere of an e-waste dismantling region. *Environ. Pollut.* 157: 1051–1057.

Chen, D., Bi, X., Liu, M., Huang, B., Sheng, G. and Fu, J. (2011). Phase partitioning, concentration variation and risk assessment of polybrominated diphenyl ethers (PBDEs) in the atmosphere of an e-waste recycling site. *Chemosphere* 82: 1246–1252.

Chen, M.L., Wang, L., Chi, Y.K., Mao, C.C., Lung, S.C., Mao, I.F. (2012). Polybrominated diphenyl ethers in foodstuffs from Taiwan: level and human dietary exposure assessment. *Sci. Total Environt*. 431: 183–187.

Cheruiyot, N.K., Lee, W.J., Mwangi, J.K. Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J., Zhang, R. and Chang-Chien, G.P. (2015) An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient Air. *Aerosol Air Qual. Res.* 15: 2730–2762.

Chou, H.M., Kao, C.C., Chuang, K.P., Lin, C., Shy, C.G., Chen, R.F., Tsai, C.C., Chuang, C.Y., Cheng, Y.C. and Chen, C.C. (2016). Levels of polybrominated diphenyl ethers in air-conditioner filter dust used to assess health risks in clinic and electronic plant employees. *Aerosol Air Qual. Res.* 16: 184–194.

Chou, P.H., Lee, C.H., Ko, F.C., Lin, Y.J., Kawanishi, M., Yagi, T., and Li, I.C. (2015) Detection of hormone-like and genotoxic activities in indoor dust from Taiwan using a battery of in vitro bioassays. *Aerosol Air Qual. Res*. 15: 1412–1421.

Davis, E.F. and Stapleton H.M. (2009). Photodegradation pathways of nonabrominated diphenyl ethers, 2-ethylhexyltetrabromobenzoate and di(2-ethylhexyl) tetrabromophthalate: Identifying potential markers of photodegradation. *Environ. Sci. Technol.* 15: 5739–5746.

de Wit, C.A. (2002). An overview of brominated flame retardants in the environment. *Chemosphere* 46: 583–624.

de Wit, C.A., Herzke, D. and Vorkamp, K. (2010). Brominated flame retardants in the arctic environment--Trends and new candidates. *Sci. Total Environ.* 408: 2885–2918.

de Wit, C.A., Bjorklund, J.A. and Thuresson, K. (2012). Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from stockholm microenvironments 2: Indoor sources and human exposure. *Environ. Int.* 39: 141–147.

Ding, N., Wang, T., Chen, S.J., Yu, M., Zhu, Z.C., Tian, M., Luo, X.J. and Mai, B.X. (2016). Brominated flame retardants (BFRs) in indoor and outdoor air in a community in Guangzhou, a megacity of southern China. *Environ. Pollut.* 212: 457–463.

Gevao, B., Jaward, F.M., MacLeod, M. and Jones, K.C. (2010). Diurnal fluctuations in polybrominated diphenyl ether concentrations during and after a severe dust storm

episode in Kuwait City, Kuwait. *Environ. Sci. Technol.* 44: 8114–8120.

Gou, Y.Y., Que, D.E., Chung, C.Y., Chao, H.R., Shy, C.G., Hsu, Y.C., Lin, C.W., Chuang, K.P., Tsai, C.C. and Tayo, L.L. (2016) Dust levels of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) in the Taiwanese elementary school classrooms: assessment of the risk to school-age children. *Sci. Total Environ*. doi: 10.1016/j.scitotenv.2016.07.044.

Harrad, S., de Wit, C.A., Abdallah, M.A., Bergh, C., Bjorklund, J.A., Covaci, A., Darnerud, P.O., de Boer, J., Diamond, M., Huber, S., Leonards, P., Mandalakis, M., Ostman, C., Haug, L.S., Thomsen, C. and Webster, T.F. (2010). Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: An important exposure pathway for people? *Environ. Sci. Technol.* 44: 3221–3231.

Hearn, L.K., Hawker, D.W. and Mueller, J.F. (2012). Dispersal patterns of polybrominated diphenyl ethers (PBDEs) in the vicinity of an automotive shredding and metal recycling facility. *Atmos. Pollut. Res.* 3: 317–324.

Hsu, P.C., Guo, Y.L., Smith, D.R., Lin, Y.S., Tseng, L.H., Lee, C.W. and Chen, J.R. (2014). Airborne persistent organic pollutants and male reproductive health. *Aerosol Air Qual. Res.* 14: 1292–1298.

Iacovidou, E., Mandalakis, M. and Stephanou, E.G. (2009). Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean. *Chemosphere* 77: 1161–1167.

Kalachova, K., Hradkova, P., Lankova, D., Hajslova, J. and Pulkrabova, J. (2012). Occurrence of brominated flame retardants in household and car dust from the Czech Republic. *Sci. Total Environ.* 441: 182–193.

Lagalante, A.F., Oswald, T.D. and Calvosa, F.C. (2009). Polybrominated diphenyl ether (PBDE) levels in dust from previously owned automobiles at United States dealerships. *Environ. Int.* 35: 539–544.

Li, H., Liu, H., Mo, L., Sheng, G., Fu, J. and Peng, P. (2016). Airborne polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs), and dechlorane plus (DP) in concentrated vehicle parking areas. *Environ. Sci. Pollut. Res. Int.* 23: 10702–10713.

Li, S., Liu, W., Liu, G.L., Wang, M., Li, C. and Zheng, M. (2015) Atmospheric emission of polybrominated dibenzo-*p*-dioxins and dibenzofurans from converter steelmaking processes. *Aerosol Air Qual. Res.* 15: 1118–1124.

Lin, S.M., Chen, F.A., Huang, Y.F., Hsing, L.L., Chen, L.L., Wu, L.S., Liu, T.S., Chang-Chien, G.P., Chen, K.C. and Chao, H.R. (2011). Negative associations between PBDE levels and thyroid hormones in cord blood. *Int. J. Hyg. Environ. Health* 214: 115–120.

MacLeod, M., Scheringer, M., Podey, H., Jones, K.C. and Hungerbuhler, K. (2007). The origin and significance of short-term variability of semivolatile contaminants in air. *Environ. Sci. Technol.* 41: 3249–3253.

Muenhor, D., Harrad, S., Ali, N. and Covaci, A. (2010). Brominated flame retardants (BFRs) in air and dust from electronic waste storage facilities in Thailand. *Environ. Int.* 36: 690–698.

NAHSIT (2008). NAHSIT 2004-2008 Nutrition and Health Survey in Taiwan, https://srda.sinica.edu.tw/search/scidown/4749, Last Access: June 2016.

Newton, S., Sellstrom, U. and de Wit, C.A. (2015). Emerging flame retardants, PBDEs, and HBCDDs in indoor and outdoor media in Stockholm, Sweden. *Environ. Sci. Technol.* 49: 2912–2920.

Ren, Z., Xiao, X., Chen, D., Bi, X., Huang, B., Liu, M., Hu, J., Peng, P., Sheng, G. and Fu, J. (2014). Halogenated organic pollutants in particulate matters emitted during recycling of waste printed circuit boards in a typical e-waste workshop of southern China. *Chemosphere* 94: 143–150.

Saraga D.E., Markrogkika A., Karavoltsos S., Sakellari A., Diapouli E., Eleftheriadis K., Vasilakos C., Helmis, C. and Maggos T. (2015) A pilot investigation of PM indoor/outdoor mass concentration and chemical analysis during a period of extensive fireplace use in Athens. *Aerosol Air Qual. Res.* 15: 2485–2495.

Shy, C.G., Huang, H.L., Chang-Chien, G.P., Chao, H.R. and Tsou, T.C. (2011). Neurodevelopment of infants with prenatal exposure to polybrominated diphenyl ethers. *Bull. Environ. Contam. Toxicol.* 87: 643–648.

Shy, C.G., Huang, H.L., Chao, H.R. and Chang-Chien, G.P. (2012). Cord blood levels of thyroid hormones and IGF-1 weakly correlate with breast milk levels of PBDEs in Taiwan. *Int. J. Hyg. Environ. Health* 215: 345–351.

Shy, C.G., Hsu, Y.C., Shih, S.I., Chuang, K.P., Lin, C.W., Wu, C.W., Chuang, C.Y. and Chao, H.R. (2015). Indoor level of polybrominated diphenyl ethers in the home environment and assessment of human health risks. *Aerosol Air Qual. Res.* 15: 1494–1505.

Takigami, H., Suzuki, G., Hirai, Y. and Sakai, S. (2009). Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. *Chemosphere* 76: 270–277.

Thuresson, K., Bjorklund, J.A. and de Wit, C.A. (2012). Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from stockholm microenvironments 1: Levels and profiles. *Sci. Total Environ.* 414: 713–721.

Tue, N.M., Takahashi, S., Suzuki, G., Isobe, T., Viet, P.H., Kobara, Y., Seike, N., Zhang, G., Sudaryanto, A. and Tanabe, S. (2013). Contamination of indoor dust and air by polychlorinated biphenyls and brominated flame retardants and relevance of non-dietary exposure in vietnamese informal e-waste recycling sites. *Environ. Int.* 51: 160–167.

USEPA (2008) Child-specific Exposure Factors Handbook, EPA/600/R-06/096F.https://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=484738, Last Access: June 2016.

Wang, Y.F., Wang, S.L., Chen, F.A., Chao, H.A., Tsou, T.C., Shy, C.G., Papke, O., Kuo, Y.M. and Chao, H.R. (2008). Associations of polybrominated diphenyl ethers (PBDEs) in breast milk and dietary habits and demographic

factors in Taiwan. *Food Chem. Toxicol.* 46: 1925–1932.

Wilford, B.H., Harner, T., Zhu, J., Shoeib, M. and Jones, K.C. (2004). Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* 38: 5312–5318.

Wu, M.H., Pei, J.C., Zheng, M., Tang, L., Bao, Y.Y., Xu, B.T., Sun, R., Sun, Y.F., Xu, G. and Lei, J.Q. (2015). Polybrominated diphenyl ethers (PBDEs) in soil and outdoor dust from a multi-functional area of Shanghai: Levels, compositional profiles and interrelationships. *Chemosphere* 118: 87–95.

Xu, F., Zhang, G., Wang, J., Zhang, W., Liu, L. and Lin, K. (2015). Polybrominated diphenyl ethers in air and fallouts from an e-waste polluted region in southeast China: Insight into levels, compositional profiles, and seasonal variation. *Environ. Sci. Pollut. Res. Int.* 22: 19676–19686.

Zhang, B.Z., Zhang, K., Li, S.M., Wong, C.S. and Zeng, E.Y. (2012). Size-dependent dry deposition of airborne polybrominated diphenyl ethers in urban Guangzhou, China. *Environ. Sci. Technol.* 46: 7207–7214.

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