FRACTIONATED CONCENTRATIONS OF POLYBROMINATED DIPHENYL ETHERS IN HOUSE DUST FROM SOUTERN TAIWAN

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated fire retardants that are used to reduce the flammability of consumer products[1]. PBDEs contamination has been raising the global concern due to their lipophilicity, persistence, and bioaccumulation. PBDEs are ubiquitously existed in indoor environment due to their persistence and the widespread use in consumer products. Therefore, PBDEs have been recognized as the significant persistent pollutants of the indoor environment in recent years. Various studies reported PBDE concentrations in in-house dust several fold higher than in out-house dust[2,3]. A Chinese study examined PBDEs in central air conditioner filter from a new office building to reveal that human exposure to PBDEs through inhalation and ingestion of indoor dust in the new building was less than the old ones[4]. Several epidemiological studies were reported that human exposure to PBDEs caused the adverse health effects including lower birth outcomes[5], disruption of thyroid hormones[6], interference with reproduction[7], and influence on neurodevelopment[8]. In the indoor environment, PBDEs in maternal and umbilical cord blood was associated with that in house dust[9]. Toddlers were estimated to have higher body burden of PBDEs from dust ingestion compared with adults[10]. Although previous PBDEs studies have concentrated on residential exposures, little is known about fractionated dust exposure in home environment. For toddlers and infants, the indoor environment can be an essential exposure route through dust ingestion with hand-to-mouth behavior and respiration inhalation to accumulate PBDEs in their bodies. In Taiwan, this is the first report to perform PBDE concentrations in in-house dust. To our knowledge, there are also the first data to show three fractionated concentrations of PBDEs in house dust.

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}C-labeled 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).

The paired samples of indoor dust, floor and electronic dust, were collected from 9 different homes selected from our previous PBDEs cohort. This PBDEs cohort was 138 healthy mother-infant paired participants to be randomly selected from four hospitals in southern Taiwan between April 2007 and April 2010[6]. Paired samples of in-house dust, including floor and electronic dust, were collected by our researchers using a vacuum cleaner (Nilfisk Advance Euroclean UZ934 HEPA canister vacuum cleaner) with a strictly specific protocol. This HEPA filter vacuum is recommended by HUD and OSHA for capturing and controlling lead paint dust, and is the consummate vacuum for cleaning hospitals, hotel/motels, office, and homes. Four stages filtration of the vacuum cleaner included a dust bag and washable pre-filter which collect regular to fine particulates before the HEPA filter, and an exhaust filter. Samples were taken from ground floors, including living rooms, studies room, and bedroom, and consumer products, including the surface and filter of electronics. The collecting instruments were cleaned thoroughly by washing deionized distilled water and soapy water and using an n-hexane-impregnated disposable wipe[11]. Each dust sample was sieved through 100 (<0.149 mm) and 200 meshes (<0.074mm) by

shaking 10 minutes, homogenized and stored in a glass bottle with a Teflon cap at -20^{o}C prior to analysis. Three fractionated samples including >100 mesh (first fraction, coarse), 100-200 mesh (second fraction, medium), and <200 mesh (third fraction, fine) dust were separated in floor and electronic dust. Fractionated dust samples were packaged in chemically clean containers and transported to Cheng Shiu University in southern Taiwan for analytical PBDE levels.

A fractionated dust sample (1-3 grams) in a cellulose tube was extracted by a Soxhlet extractor with 200 ml of toluene for 16 hours; these were then concentrated to dryness by a rotary evaporator. $^{13}C_{12}$-labeled PBDE congeners of BDE-15, 28, 47, and 99 (100 ng/mL), and 153, 183, 197, 207, and 209 (200 ng/mL) were added into the samples before the extraction. The extract was cleaned up as follows. The first cleanup involved treatment with concentrated sulfuric acid. The next cleanup procedure involved a multi-layered silica column. The final cleanup procedure involved an acid alumina column. The eluate was collected, concentrated to near dryness by using a nitrogen stream, and then transferred to a vial. A total of 50 µl of ^{13}C-labeled BDE-139 was added to a vial containing the eluate as an internal standard after the clean-up prior to injection. The final extract was reduced in volume to 0.2 mL under a stream of nitrogen. PBDE levels were analyzed using high resolution gas chromatography (Hewlett-Packard 6970) and high resolution mass spectrometry (Micromass Autospec Ultima) with a DB-5HT column (L= 15 m, i.d.= 0.25 mm, film thickness = 0.1 µm) (J&W Scientific, Folsom, CA) in splitless mode at 280°C with constant helium flow of 1 ml/min. The GC oven temperature was programmed to be held at 100°C for 4 min, to increase from 100°C to 200°C at a rate of 40°C/min, to stay 3.5 min at 200°C, to change to 325°C by 10°C/min, and to maintain 325°C for 2.5 min. The two most abundant isotope masses were measured for each component. Quantification was performed using internal/external standard mixtures via the isotope-dilution method. Limits of detection (LODs) in 29 PBDE congeners from BDE-7 to 208 are ranged from 0.262 to 46.0 pg/g. LOD of BDE-209 is 333 pg/g.

Concentrations of PBDEs were not normally distributed using the Kolmogorov-Smirnov method. Spearmen's rank correlation coefficients were initially tested to examine the relations of PBDEs in paired samples of floor and electronic dust or series samples of fractionated dust. The differences in PBDEs between floor and electronic dust or among three fractionated samples were examined by paired-samples T tests with 2000 bootstrap samples. We also used factor analysis to determine the associated characteristics of PBDE homologues from diBDEs to decaBDE. Analyses were carried out using the Statistical Package for Social Science (SPSS) version 12 (SPSS Inc, Chicago, IL, USA).

Results and discussion

Table 1 shows descriptive analysis of 30 PBDE congeners in floor and electronic dust from 9 selected families. The predominant congener in house dust including floor and electronic dust is BDE-209. This finding in this study is consistent with the reports from the several studies[2,3,12]. There are no significant differences in the whole dust levels of 30 PBDEs and Σ_{30}PBDEs between floor and electronic dust in the present study (p<0.05). A pair of house dust (floor and electronic dust) from a family shows the extremely higher levels of ΣPBDEs and 30 PBDE congeners compared to those in the remainder of 8 families particularly for BDE-209. Compared with indoor dust PBDE levels in different countries listed in the review article by two Greek authors[13], a median of PBDE levels in floor and electronic dust from our study is lower than those reported in the studies from USA, Canada, UK, Sweden, China, and Australia, but higher than the reports from Kuwait, Thailand, Belgium, and Portugal. Extremely high PBDE levels were found in dust from inside television sets to suggest that PBDEs is possibly transferred from television components to indoor dust[14]. Chinese researchers also found the significant higher levels of ΣPBDEs in television and computer dust in comparison to house dust, PBDEs-containing products used in the indoor environment were potentially important emission source for PBDEs in indoor dusts[2].

Distribution of PBDEs in fractionated dust samples including floor and electronic dust is shown in Figure 1 and 2. The levels of ΣPBDEs and higher brominated PBDEs (from heptaBDEs to decaBDE) in the 2nd fraction of floor and electronic dust are higher than those in the 1st and 3rd fraction, but no statistically significant differences in PBDEs are found among these fractionated dust samples (p<0.05). BDE-209 concentrations are also found to be the predominated among 30 PBDE congeners in all fractionated dust samples. It is not surprising to obtain that BDE-209 is extremely higher than the other PBDE congeners based on continuously imported decaBDE in Taiwan in recent years, but pentaBDEs and octaBDEs has been phased out in Taiwan since 2005. To our knowledge, few studies focused on fractionated indoor dust samples to explore the associations with human health especially for the infants and toddlers who are highly exposed to PBDEs

compared with the adults. In the previous report from China, a significantly good correlation of PBDE concentrations between air conditioner dust and computer dust was found and BDE-209 was predominated in electronic dust[4]. The distributed PBDE profiles of fractionated floor and electronic dust in the present study and those in air-conditioning filter and computer dust from a Chinese study are similar to the distribution of PBDEs in commercial decaBDEs[4]. According to our results showing no significant differences in PBDEs among three fractionated dust samples, it is concluded that PBDEs is heterogeneously distributed in house dust even though 3rd fraction dust (<0.074 μm) weights 50-76% of the whole dust and the levels of PBDEs in the 3rd fraction dust is not the highest concentration among three fractionated dust. In this study, PBDE exposure through dust ingestion is evaluated based on following the equation described as[15]: $Intake_{dust}$ (ng/day) = $Conc_{dust}$ (ng/g) × R_d; where R_d is the dust ingestion rate (g/day). The mean R_d values are 0.00416 g/day for adults and 0.055 g/day for toddlers, respectively. The in-house floor dust median PBDE daily intake was estimated to be 2.68 and 35.5 ng/day for adults and toddlers. The median PBDE daily intake of in-house electronic dust was calculated as 13.2 and 175 ng/day for adults and toddlers. Our value of PBDE daily intake via in-house floor dust is lower than the value (adults: 7.5 ng/day; toddlers: 99 ng/day) reported by Wilford et al. (2005).

The characteristics of 30 PBDE congeners are examined by factor analysis to show their exposure patterns in the whole floor and electronic dust in Figure 3 and 4. In floor dust, component 1 consists of lower and higher brominated PBDEs from di to hepta and component 2 is composed of highest brominated PBDEs including octaBDEs, NonaBDEs, and decaBDE (Figure 3). In electronic dust, component 1 and 2 comprise PBDEs from BDE-15 to 154 and from 196 to 209, respectively (Figure 4). The PBDE patterns of the fractionated dust are similar to those in the whole dust (data not shown). High Spearman's rho correlation coefficients of low brominated PBDEs from di to tetra in three fractionated dust are found in dust samples of floor and electronic (r=0.667-0.933, p<0.05) (Figure 5). In the homologues of pentaBDEs (r=0.683, p=0.042) and hexaBDEs (r=0.867, p=0.002), the significant associations were only observed in the 2nd fraction. In the homologues of the highest brominated PBDEs from octa to deca, the significant associations are appeared in the 1st fraction of the dust samples (r=0.733-0.967, p<0.05). The inconsistent variations of octaBDEs, nonaBDEs, and decaBDE are found in the dust from 9 families, these three highest brominated PBDE homologues accounts for 70-95% of the total. Based on the results from the correlations of PBDEs between floor and electronic dust in the present study, it is probable that the frequency of cleaning house dust and numbers of consumer products in house may be the important factors to determine PBDE levels in house dust.

Acknowledgements

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Table1. Descriptive analysis of PBDE levels in house dust (ng/g d.w.)

Congeners	Ground dust		Electronic dust		p-value
	Mean ± SD	Median	Mean ± SD	Median	
28	8.00±22.7	0.386	4.12±7.17	0.500	0.863
47	178±474	6.24	161±407	22.3	0.605
49	15.8±44.3	0.633	10.4±19.0	1.23	0.931
71	2.84±8.70	0.100	1.29±2.19	0.200	0.666
85	31.4±88.1	0.420	29.8±82.8	1.56	0.546
99	445±1276	9.95	370±993	34.6	0.730
100	141±392	1.66	91.0±252	6.09	0.605
139	12.4±35.1	0.267	12.3±32.3	0.920	0.436
140	2.97±8.28	0.113	3.31±8.01	0.160	0.340
153	93.2±257	2.662	110±234	30.2	0.387
154	76.3±221	1.26	80.0± 205	7.45	0.436
183	16.0±22.5	6.26	46.0±60.9	65.4	0.161
184	1.07±1.99	0.323	1.59±1.93	1.27	0.297
196	14.2±18.010	8.98	24.9±24.3	29.9	0.258
203	15.5±17.8	8.24	28.6±34.0	20.9	0.258
206	236±491	57.7	349±466	204	0.340
207	138±271	33.7	196±252	127	0.387
209	1075±2051	426	2835±3804	1687	0.190
Total	2625±3816	645	4530±4553	3178	0.387
Total [a]	1551±2903	315	1695±2272	776	0.489

[a] ΣPBDEs excluding BDE-209

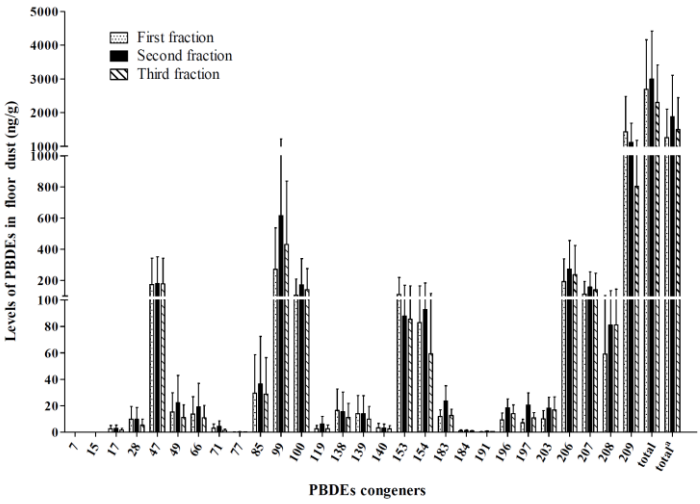

Figure 1. PBDE distributed in fractionated floor dust

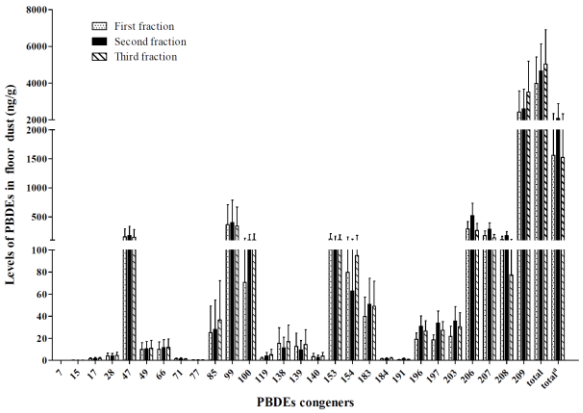

Figure 2. PBDE distributed in fractionated electronic dust

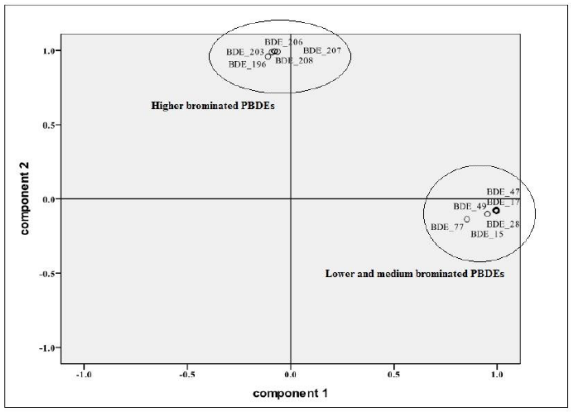

Figure 3. factor analysis of 30 PBDE congeners in floor dust

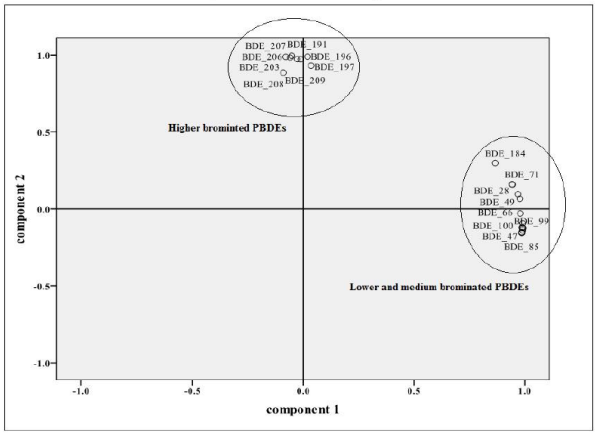

Figure 4. Factor analysis of 30 PBDE congeners in the fractionated electronic dust

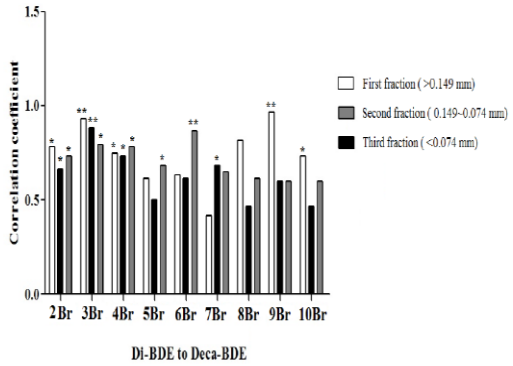

Figure 5. Spearman correlation coefficient of PBDE homologues between floor and electronic dust