

Distribution of polybrominated diphenyl ethers and dust particle size fractions adherent to skin in indoor dust, Pretoria, South Africa

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Abstract In order to determine human exposure to the indoor toxicant, selection of dust fraction and understanding dust particle size distribution in settled indoor dust are very important. This study examined the influence of dust particle size on the concentration of polybrominated diphenyl ethers (PBDEs) congeners, assessed the distribution of dust particle size and characterized the main indoor emission sources of PBDEs. Accordingly, the concentrations of PBDE congeners determined in different indoor dust fractions were found to be relatively higher in the order of dust particle size: 45–106 μm > (<45 μm) > 106–150 μm . The finding shows arbitrary selection of dust fractions for exposure determination may result in wrong conclusions. Statistically significant moderate correlation between the concentration of Σ_9 PBDEs and organic matter content calculated with respect to the total dust mass was also observed ($r=0.55$, $p=0.001$). On average, of total dust particle size <250 μm , 93.4 % ($m/m\%$) of dust fractions was associated with less than 150 μm . Furthermore, of skin adherent dust fractions considered (<150 μm), 86 % ($v/v\%$) is in the range of particle size 9.25–104.7 μm . Electronic materials treated with PBDEs were found the main emission sources of PBDE congeners in indoor environment. Based on concentrations of PBDEs determined and mass of indoor dust observed, 150 μm metallic sieve is adequate for human exposure risk assessment.

However, research in this area is very limited and more research is required to generalize the fact.

Keywords PBDE · Particle size · Settled indoor dust · Organic matter content · PBDE emission source · Adherent fraction

Introduction

Polybrominated diphenyl ethers (PBDEs) have been used for more than three decades as flame retardants in consumer products in order to increase fire resistance of the materials in which they are applied. There are three categories of commercial PBDEs flame retardant mixtures: Penta-, Octa- and Deca- mixture formulations. Commercial PentaBDE composed of six major congeners: BDE-47, 99, 85, 100, 153 and 154 with the first two as major component. OctaBDE mixture is composed of BDE-153, 154, 183, 196, 197, 203, 206 and 207 with BDE-183 as a major component. This shows that BDE-153 and BDE-154 are found in both Penta- and Octa-mixture. DecaBDE mixture essentially composed of BDE-209 (La Guardia et al. 2006). As they are additive flame retardants, they can easily migrate from the product materials into the environment and then contaminating indoor air and dust (Harrad et al. 2006). Furthermore, due to their wide use in different consumer products, their detection in various environmental samples has been increased. The widespread production and use of PBDEs and strong evidence of increasing contamination of the environment by these chemicals have attracted worldwide scientific attention. Thus, many researchers have shown their presence in indoor dust (Batterman et al. 2009, 2010; D'Hollander et al. 2010; Harrad et al. 2006, 2008 a, b; Kefeni et al. 2011a, b; Suzuki et al. 2006; Webster et al. 2009), landfill leachates (Odusanya et al. 2009) and human tissue samples such as blood serum (Anderson et al. 2008; Fromme

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et al. 2009; Johnson et al. 2010; Roosens et al. 2009; Toms et al. 2008) breast milk (Asante et al. 2011; Li et al. 2008) and liver and adipose tissue (Covaci et al. 2008).

According to Johnson-Restrepo and Kannan (2009), ingestion and dermal absorption of house dust are the major pathways of PBDE exposure in toddlers, children, teenagers and adults, on average, accounting for 56–77 % of the total PBDE intake in the USA. Researchers hypothesized that the efficiency of absorption from ingested dust is very high for the fine dust particles. The adherence of dust on hand or skin and hence ingestion and dermal absorption may vary with particle sizes (Cao et al. 2012; Duggan et al. 1985; Lewis et al. 1999; Maertens et al. 2004; Mercier et al. 2011; Roberts et al. 2009). For example, dust particles less than 100–200 μm in diameter were retained most efficiently by skin (Lewis et al. 1999; Maertens et al. 2004). Duggan et al. (1985) concluded that most of the particles (90–98 %) found on the hands of schoolchildren were less than 10 μm in diameter (the maximum varied between 80 and 100 μm). Furthermore, previous studies demonstrated that increment of contaminant with decrease of dust particle size. For instance, Lewis et al. (1999) reported the increased concentration of polycyclic aromatic hydrocarbons with decreased particle size. To our knowledge, there is only one study that compared concentrations of total PBDEs present in three dust sample fractionations collected from two homes and one car (Wei et al. 2009). According to Wei et al. (2009), over 80 % of the Σ_{13} PBDEs was associated with particle size less than 150 μm in diameter. In spite of the differences in concentrations of PBDEs in different dust fractionations, there is no recommended standard metallic sieve in literature. For instance, different sizes of metallic sieves have been used; 75 μm (Katrin et al. 2008; Martínez et al. 2010), 100 μm (Hwang et al. 2008; Kang et al. 2011), 150 μm (Huang et al. 2010; Johnson et al. 2010; Meeker et al. 2009; Wilford et al. 2005), 250 μm (Kefeni et al. 2011a; Wei et al. 2009), 500 μm (Roosens et al. 2009; Watkins et al. 2011; Webster et al. 2009), 1.0 mm (Dirtu et al. 2008; Suzuki et al. 2009) and 2.0 mm (Schechter et al. 2005).

PBDEs are in much higher concentration indoor than outdoor. The main sources are thought to be consumer products treated with flame retardants. As a result, the links between products and PBDEs in indoor dust and air remain as an emergent field of investigation (Webster et al. 2009). Recently, X-ray fluorescence has been used for identification of bromine-containing furniture and electronic materials (Allen et al. 2008; Webster et al. 2009). Some researchers also used comparison of concentrations of PBDEs detected in house dust with that detected from dust collected inside electronic materials for identification of the source. For example, similar congener type of PBDEs was detected in the dust taken from home and television (TV) compartments, with the higher concentrations of PBDEs in TV (48,000 $\mu\text{g g}^{-1}$) than home dust (300 $\mu\text{g g}^{-1}$). The result showed that TV component parts

are the source of brominated flame retardants (BFRs; Takigami et al. 2008). Similarly, by comparing PBDEs congeners detected in indoor air and outdoor air, Wang et al. (2011) demonstrated that combustion as one of a major emission source of highly BFRs to outdoor air.

Currently, very little information concerning pollutant distribution as a function of particle size of dust in homes and offices is available. Consequently, the area requires more research since dust ingestion is one of the major routes via which contaminants can enter into the human body. Thus, the main objectives of this study were (a) to investigate the distribution of PBDEs congeners and dust particle size in different particle size ranges and (b) to estimate the most probable sources of PBDEs in indoor dust.

Materials and methods

Chemicals

House dust standard reference material-2585 was purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA). 1.2 ml of 50 mg l^{-1} of each certified standard solutions of sixteen PBDE congeners (BDE-3, 15, 17, 28, 47, 66, 77, 85, 99, 100, 126, 138, 153, 154, 183 and 209) was purchased from Wellington Laboratories (Guelph, Ontario, Canada). 1.2 ml of 50 mg l^{-1} isotopic labelled internal standards $^{13}\text{BDE-139}$ and $^{13}\text{BDE-209}$ was purchased from Cambridge isotope laboratories (CIL, Andover, MA, USA). Copper powder (purity 99.98 % from Saarchem (Pty) Ltd., Muldersdrift, South Africa), silica gel (100–200 mesh), sodium sulphate (purity 99.9 %), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane (products of Sigma Aldrich (Chemie GmbH, Steinheim, Germany), 50 ml of nonane (Purity 99.8 %, Sigma Aldrich, product of Switzerland) were purchased from Industrial Analytical Pty. Ltd.

Sample collection

Sample collection was carried out in between April 2011 to June 2011. During collection time, the number and type of electronic materials and furniture were recorded (Table S1). Dust samples were collected using portable hose less standard vacuum cleaner 1,000 watts (Model: 601SA, shark) equipped with a dust collection paper bag. The paper bags were used to prevent dust coming into contact with the inner surface part of vacuum cleaner. To avoid cross contamination, new paper bags and exchangeable tip parts of the vacuum cleaners were used for each home and office. Before use, the vacuum cleaner tip parts were pre-washed with mixture of ethanol and ultra-pure water (1:1 v/v) and dried between collections.

All dust samples were collected from floor of offices and living room of homes, except for tracing sources of PBDEs where collection was done from inside electronic materials. The numbers of corresponding samples used for analysis were 4, 9, 16 and 12 for determination of PBDEs in different dust particle size fractions and organic matter content (OMC), tracing source of PBDEs, comparison of dust particle size distribution observed using metallic sieves with that of particle size analyser and characterization of dust size fractions adherent to skin, respectively. In addition, for the latter case, one composite sample of dust previously collected from 81 offices and 31 homes also analysed. The details of sampling are as follows:

To investigate the relationship between concentrations of PBDE congeners and OMC in different dust particle size fractions, two offices and homes were systematically identified from 31 home and 16 composite office dust samples based on concentration and number of PBDE congeners detected in our previous study of office dust (Kefeni and Okonkwo, 2012) and home dust analysis results (Table S2). Relatively, in these offices and homes, BDE-47 and BDE-99 were detected in higher concentrations next to BDE-209. To get sufficient dust samples from each offices and homes, samples were collected once per a week for 1 month. For PBDEs source characterization, similar identification method was used. It should be noted that due to the non-detection of PBDEs or detection of less number of congeners which vary in between 1 to 3 with low concentrations, most of the offices and homes were not considered for the study. Accordingly, five homes and four offices were identified. From offices, dust was collected from the inside of computer monitors and printers. From homes, dust was sucked by vacuum cleaner from the inner part of TV and surface parts of digital compact disc players. In addition, polyurethane foam (PUF), which has been almost changed into fine particles, was collected from inside old cushioning and chairs (O4). Carpet was also collected from one home (H5) and office (O4). The exact origin of the PUF and carpet were not known. Most of computer monitors available in the offices where dust samples collected were manufactured in between September 2000 and October 2001. For comparison of dust particle size distribution with that of metallic sieves and particle size analyser, 16 dust samples were collected from the same offices and homes listed in Table S1. In order to characterize dust size fractions adherent to skin, 12 dust samples were collected from offices (O3–O8) and homes (H3–H8) using the same equipment.

Sample preparation, extraction and clean-up

For tracing source of PBDEs, all dust samples were sieved using 150 μm metallic sieves and kept in brown glass jar until extraction. The carpet was cleaned with ultra-pure water to remove any other contaminants on the surface and dried under

fume hood, and then cut into very small pieces using a pair of pre-cleaned scissors and ready for extraction.

For determination of PBDEs and OMC in dust fractions; initially, all dust samples were sieved using 250 μm , then three different size sets of metallic sieves placed over each other in the order of lower to higher sizes from bottom to top (45, 106 and 150 μm). After introducing weighed dust samples, metallic plates were placed at the bottom and top for dust collection and covering, respectively. The sieves were shaken by hand for 5–6 min. Fibres and cotton-like debris were left on the surface of 150 μm sieves, based on 16 dust sample investigated, on average, these accounted for the dust fraction of 6.6 %. These dust samples may contain PBDEs, however, after the fibres and cotton-like debris were discarded, the fine dust leftover was found insufficient for both PBDEs and OMC. Furthermore, these dust are likely less adherent to the skin; consequently, these samples were not considered for analysis. All sieved dust were collected on aluminium foil and weighed to determine the dust fraction recovered for each sample based on total dust sieved. Small portion of each dust fractions were taken for OMC determination. The OMC in dust was determined by measuring the loss on ignition of each weighed dust fraction in a muffle furnace for about 5 h at a temperature of 550 $^{\circ}\text{C}$ (Wei et al. 2009).

For comparison of dust particle size distribution (metallic sieve versus particle size analyser) similar method of sieving used for PBDEs and OMC in dust fractions was applied. Furthermore, all dust samples used for the study of dust size distribution and characterization of dust size adherent to skin were sieved using 150 μm sieves and kept until analysis in clean glass jar.

For extraction, dust samples of about 0.5 g for tracing sources of PBDEs and 2.5–3.5 g for PBDEs determination in each dust fractions, and 0.5 g of each foam and carpet were weighed. Pre-prepared activated copper powder (0.3 g) was added (to remove elemental sulphur), and then transferred to a cellulose extraction thimble (19 mm ID and 90 mm in length), spiked with internal standards BDE-77 (20 ng), $^{13}\text{C}_{12}$ -BDE-139 (50 ng) and $^{13}\text{C}_{12}$ -BDE-209 (50 ng) and homogenised. Thereafter, the sample was covered with glass wool, placed inside Soxhlet apparatus and extracted with 250 ml of *n*-hexane/acetone (2:1, *v/v*) for 8 h. Thimbles containing activated copper powder and glass wool that represented the method blank samples were also extracted under the same condition. The extract was reduced to 2 ml in a rotary evaporator (RotaVapor R-210, BÜCHI Labortechnik AG, Switzerland) under a fume cupboard. For clean-up, a Pasteur pipette column of 5 mm inner diameter (Hirschmann Laborgerate, GmbH & Co. KG, Germany) was plugged with glass wool at the bottom and packed with pre-prepared silica gel and sodium sulphate from bottom to top in the following order (glass wool, sodium sulphate and silica gel pre-baked at 450 $^{\circ}\text{C}$ for 12 h): neutral silica gel (0.2 g), basic silica gel

(0.2 g), neutral silica gel (0.2 g), acidic silica gel (0.2 g) and sodium sulphate (0.2 g) at the top. To enhance cleaning, glass wool was used for partitioning in between each packed chemicals. Each of the packed disposable Pasteur pipette columns was first eluted with *n*-hexane/dichloromethane (5:1, *v/v*) mixture after which the extract was transferred onto it. Subsequently, it was eluted with 2×10 ml of *n*-hexane/dichloromethane (5:1, *v/v*) mixture. The extract was further concentrated under a gentle flow of nitrogen to about 10 and 50 µl for tracing sources and PBDEs distribution in dust fractions, respectively. Finally, the concentrated extract was topped up to 50 and 200 µl by a mixture containing *n*-nonane/toluene (9:1, *v/v*) in the same order and ready for analysis.

PBDEs analysis

The analysis was carried out using an Agilent Technologies 7890A GC system. One microlitre solution of the extracted sample was injected by Agilent Technologies 7693 Autosampler into split/splitless injection port on HP-5MS GC column (30 m, 0.25 mm ID, 0.25 µm d_f). Helium was used at a flow rate of 1.5 ml min⁻¹ as a carrier gas, splitless time of 1 min, injection temperature of 290 °C and oven programme of 90 °C for 1 min, ramped by 30 °C min⁻¹ to 300 °C for 5 min and 10 °C min⁻¹ to 310 °C for 1 min. The GC was coupled to an Agilent 5975C inert MSD with triple axis detector, operated in EI mode, with ion source of 250 °C, and transfer line of 300 °C. Identifications were carried out using selected ion monitoring (SIM) mode (Table S3, supplementary material). Each congener was quantified against five level external standard calibration curves and internal standards (BDE-77, ¹³C₁₂-BDE-139) based on the relative response factor established. The analysis of BDE-209 were done under similar conditions but using ZB-5 GC column (15 m, 0.25 mm I.D., 0.1 µm d_f) and quantified by internal standard ¹³C₁₂-BDE-209. The recoveries of the internal standard added were determined based on external standard method. Furthermore, before and after triplicate analysis of each sample, solution containing spiked internal standard of the same concentration with the spiked sample was injected to control any instrumental variation that occurs during analysis.

Particle size distribution

Small portions of each sieved dust fraction were taken and analysed on Microtrac S3500 particle size analyser to determine particle size distribution. Compressed nitrogen of purity 99.9 % in the presence of strong vacuum pump was used to disperse the dust particles. The instrument provides information on the percentage of particle size in different ranges, information on each peak, particle size distribution curve and detailed statistical data.

Quality control and quality assurance

Several quality control methods were assessed in order to obtain reliable data as described below. Quantitative analyses were done by using five level calibration curve and internal standards. For each congener, good linearity was achieved with r^2 value of greater than 0.989. After injections of three samples, solvent blank and standard were run to ensure that the samples and the analysis process were free of contamination as well as to control deviation of the retention time. The recovery of the spiked internal standards BDE-77, ¹³C₁₂-BDE-139 and ¹³C₁₂-BDE-209 varied in between 84–112 %, 76–96 % and 72–84 %, respectively, and correspond to the average recovery of 95 %, 86 % and 78 % in the same order. The validation of the method was done through analysis of SRM-2585 in triplicate. Good recoveries which is >89 % were achieved for the lower than the higher congeners such as BDE-183 (85 %) and BDE-209 (78 %; Table S4, supplementary material). No target BFRs were detected in method and solvent blanks, therefore, the LOD was calculated by extrapolating the concentration that would give a signal-to-noise ratio of 3 (S/N=3) by injecting extracted spiked sample of the lowest concentration. The LOD values ranged from 0.04 to 0.7 ng g⁻¹ for all congeners except for BDE-209 which was 1.8 ng g⁻¹. For determination of particle size distribution, the initial and final dust fractions were weighed to find any mass loss during sieving. Consequently, there was a loss of 2–5 % due to adherence of dust particles on the surface of metallic sieve for which we could not determine the particle size categories, but assumed similar ratio has been lost.

Statistical analysis

All descriptive statistics were computed using Microsoft Excel 2010. Pearson correlation coefficient and two-tailed Student's *t* tests were used to evaluate the relationship between concentrations of Σ_9 PBDEs and corresponding percentage of total OMC of each dust fraction. For all PBDEs congeners, values below LOD were treated as zero during all statistical analysis and $p < 0.05$ was considered statistical significant in this study.

Results and discussion

Dust size fraction versus concentration of Σ_9 PBDE

In both offices and homes, the following PBDE congeners were found with detection frequency of 100 %: BDE-47, 66, 99, 100 and 153, 75 % for BDE-209, 50 % for BDE-154 and 25 % for BDE-15 and BDE-183 (Table S5). The total concentration of Σ_9 PBDE ranged from 30.9 to 205 ng g⁻¹ in home dust samples and 73.8–625 ng g⁻¹ in office dust

samples, with the overall mean concentrations of 20.6, 29.5 and 10.4 ng g⁻¹ corresponding to the dust fraction of <45, 45–106 and 106–150 μm, respectively. Summary of corresponding mean percentage concentration of PBDEs for each dust fraction of offices and homes is given in Fig. 1a. Analytical results vary significantly with the material and particle size fractions after sieving (Cao et al. 2012; Lewis et al. 1999). According to some studies, for most of the pollutants, the concentrations in dust increased as particle size decreased (Lee and Dong, 2011; Lewis et al. 1999). Research conducted in urban areas of Greece atmosphere also showed that more enrichment of ΣPBDEs in smaller particle size (Mandalakis et al. 2009).

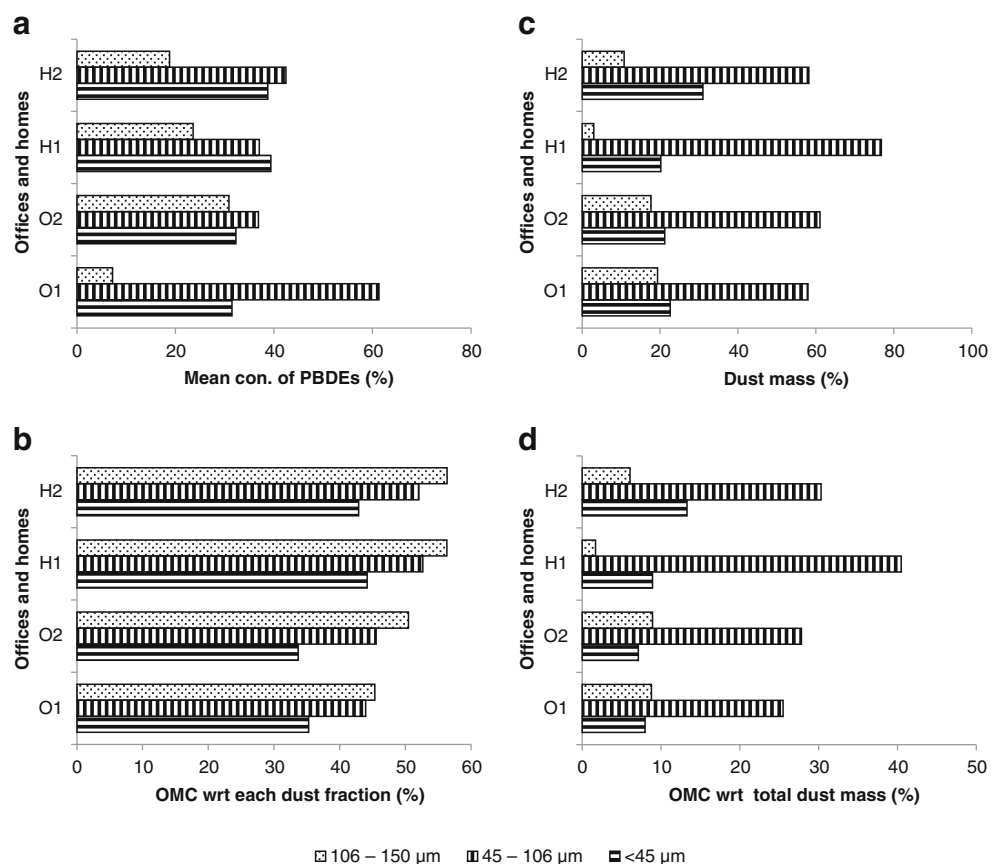
However, in this study, the highest concentration corresponds to the middle dust size fractions. This may be attributed to the lower number of sample size used for which we are unable to increase for the reasons mentioned earlier. In spite of low sample size used, the differences in mean concentration of PBDEs in different dust fractions observed in this study warranted additional similar work. The analysis result also clearly showed more contamination of the office than home dust. Higher contamination of offices than homes by PBDEs was reported by many researchers (Chen et al. 2008; D'Hollander et al. 2010; Harrad et al. 2008a; Huang et al.

2010; Suzuki et al. 2006; Toms et al. 2009). The difference in concentrations of PBDEs was attributed to the presence of more electronic materials and their usage time in office than home.

Dust size fraction versus OMC

Percentage of OMC within each dust fraction correlated with dust size (Fig. 1b). On the other hand, the OMC for each dust fraction based on the total dust sieved was by far higher in dust size between 45 and 106 μm and it was similar with dust mass fraction. The results are presented in Fig. 1c, d. In homes and offices considered, on average 22.2 %, 59.6 %, 11.6 % and 6.6 % of dust fractions were associated with dust particle size fractions less than 45, 45–106, 106–150 and 150–250 μm, respectively, excluding 2–5 % of mass lost on sieving (Table S6). Hence, the percentage of dust fraction less than 150 μm was about 93.4 % while less than 106 μm was about 82 %. Wei et al. (2009), reported over 80 % of the dust fraction that was associated with particle size <150 μm (four dust particle sizes were considered; <75, 75–150, 150–250 and 250–420 μm). The differences may be attributed to the additional range of dust particle sizes considered (250–420 μm) or more probably due to the differences of particle size

Fig. 1 a Summary of mean concentrations of PBDEs in different dust fractions, b OMC with respect to each dust fraction, c dust mass distribution, and d OMC calculated with respect to total mass sieved



distribution of settled dust, which may vary among different countries/regions and types of indoor environment (Cao et al. 2012; Liou et al. 2002; Wensing et al. 2005).

Using Pearson correlation test and *t* test distribution, the relationship between concentrations of Σ_9 PBDEs and corresponding percentage of total OMC of each dust fraction was evaluated. Accordingly, a moderate positive correlation with statistically significant value was observed between the two ($r=0.55, p=0.001$). High concentration of Σ_9 PBDEs, mass of dust fraction and fraction of OMC calculated with respect to the total dust mass are in the order of dust particle size 45–106 μm > (<45 μm) > 106–150 μm (Fig. 1 a, c, d). Similar to this study, Yu et al. (2012) also observed statistical significant strong correlation between the concentrations of PBDEs and OMC in eight dust samples.

Measurement of dust size distribution using particle size analyser

The dust size distribution obtained from particle size analyser showed that the average maximum dust sizes for 16 samples that correspond to 95 percentile were 44, 95 and 132 μm which correspond to the dust particles sieved using metallic sieve size of <45, 45–106 and 106–150 μm , respectively. As an example, Fig. 2 summarizes the analysis result of dust samples collected from one of the offices (O1), the average maximum dust sizes that correspond to 95 percentile for A, B and C were 44.95, 97.30 and 147.10 μm , respectively. According to the metallic sieve size used for Fig. 2b, c, no less than 45 and 106 μm dust particle sizes were expected. However, the analysis result showed about 58.7 % and 65.7 % below 45 and 106 μm , respectively. The repeatability of the analysis results was also checked by analysis of triplicate samples. The standard deviations corresponding to 95 percentile for Fig. 2a, b, c were 1.10, 1.96 and 2.13, respectively. Generally, similar results were obtained for the other 15 samples. Therefore, reports of dust particle size using metallic sieve do not show clearly the distribution of dust particle size. As observed in this study, the main reason is that during sieving, weak van der Waals attractive forces or London dispersion forces can affect dust particles. As a result, some of the dust particles can adhere to one another and do not pass through the metallic sieves. Consequently, the volume or mass percentage of dust samples left on the surface of sieves is increased. However, in the case of Microtrac S3500 particle size analyser, due to the use of inert gas and strong vacuum system, any adhered dust to one another can be easily separated. This shows the advantage of particle size analyser over metallic sieves in characterizing dust size fractions, particularly for exposure determination or risk assessment.

On the other hand, it is also possible to see very small deviations that correspond to dust particle size above the size of the metallic sieves used (Fig. 2). From the data, 3 %, 4 %

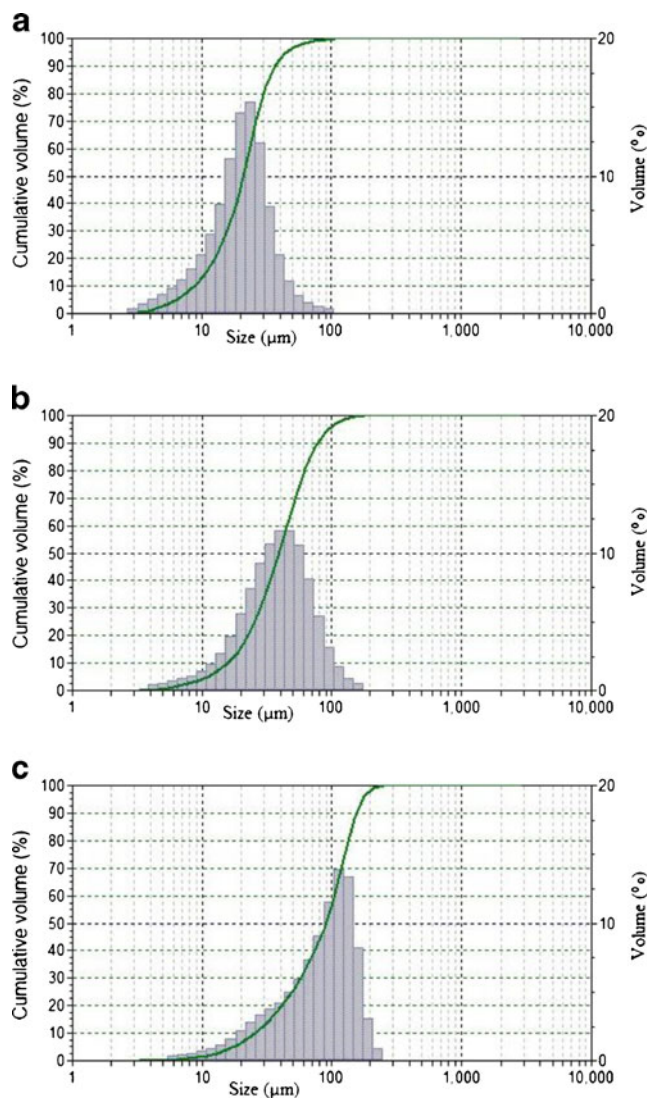


Fig. 2 Office dust particle volume and cumulative volume distribution analysed by Microtrac S3500, sizes corresponding to: **a** <45, **b** 45–106, and **c** 106–150 μm

and 8 % dust particles analysed were above 45, 106 and 150 μm , respectively. Such deviation may be attributed to both metallic sieve and particle size analyser error or the presence of fibre and cotton-like debris which are not fine dust particles present in the sample.

Characterization of dust size fractions adherent to skin

In literature, there were no consistent ranges of dust size fractions adherent to skin; however, there is a consent that the finest particles adhered better to skins than coarse dust particles. It has been suggested to pay more attention to dust particle size less than 100 μm and that larger than 250 μm is neither adherent nor proper for human exposure risk assessment (Cao et al. 2012). It should be known that nobody is

selectively exposed to the ranges of different adherent dust particle sizes; however, in reality, it is expected that higher proportion of the adherent percentage ranges of the dust fractions may imply the higher the tendency of adherence to the skin. In this study, the indoor dust samples were sieved to obtain fine fraction most likely to adhere to human skin ($<150\ \mu\text{m}$; Roberts et al. 2009). The corresponding percentages of different ranges based on total amount of dust sieved are presented in Fig. 3a, b, c. The polynomial function of order two ($Y=0.006X^2+0.36X+10.3$, $r^2=0.87$) is well described the distribution of settled dust in home while exponential function ($Y=5.07e^{0.031X}$, $r^2=0.94$) is best fit to describe office dust particle distribution. On the other hand, both functions equally describe the composite dust samples ($r^2=0.85$) collected from homes and offices. Looking at peaks of dust particle size versus volume percentage ($v/v\%$) given in Fig. 4a, b, c, four groups of skin adherent categories were identified such as 104.7–150, 44–104.7, 9.25–44 and $<9.25\ \mu\text{m}$. On average, each four skin adherent categories correspond to the volume percentage of 5.1 %, 42.5 %, 43.6 % and 8.8 %, respectively. This shows, the $v/v\%$ of dust particles 9.25–104.7 accounts for 86.1 % of indoor dust of particle size $<150\ \mu\text{m}$. Therefore, for exposure study, at least, the latter dust particle size ranges must be included. Furthermore, since the adherent dust fractions may vary with the type of sources in different indoor environments, countries or regions; the particle size distribution of settled dust or mathematical equations that describe the distribution of dust particles will be expected to vary in similar manner.

Of the total dust less than $150\ \mu\text{m}$ dust particle size, on average, dust particle size of less than $5.5\ \mu\text{m}$ is 6.5 % and 2.3 % in office and home, respectively. One reason for the lower percentage may be the settling capacity of lower sized particles is negligible. Smaller particles have lower deposition velocities compared to course particles, hence, can remain in the air for a longer time (Latif et al. 2009; Matson 2005). In addition, the data showed the presence of more fine dust particles in office than home (Table 1). The reason for the differences, probably, related to the frequent usage of ventilation systems in home than office. The ventilation systems can easily remove the suspended fine dust particles before they settle (Takigami et al. 2009). Liroy et al. (1999) also reported that frequent use of efficient vacuum cleaners reduces fine dust particles, which is usually common in homes than offices. In addition, the presence and usage of more electronic materials in the office than home can also attribute to the difference in releasing more fine particulates to indoor dust.

Generally, based on the (a) higher percentage of dust mass fractions observed in less than $150\ \mu\text{m}$ (93.4 %), (b) ease of skin adherent characteristics of fine dust particles combined with its high efficiency of absorption after ingestion than course ones and (c) more enrichment of PBDEs concentrations in a fine dust particles than a course ones, it is possible to

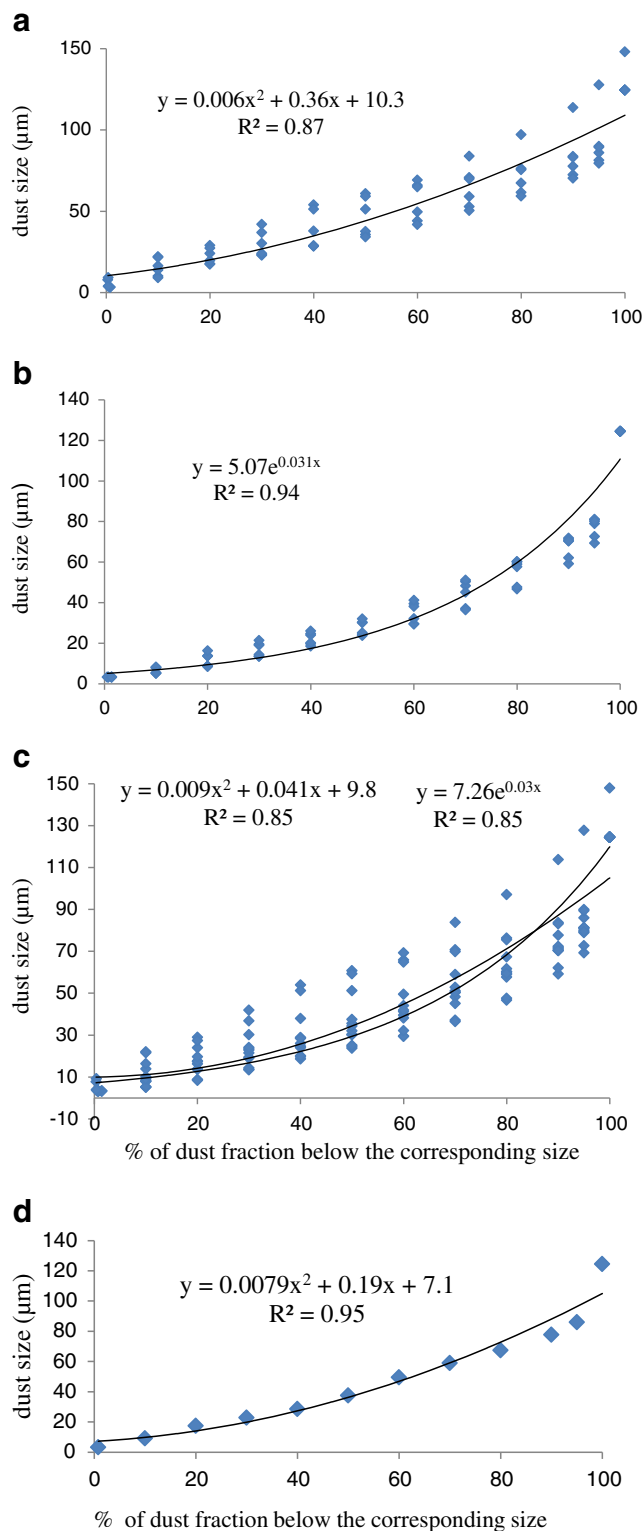


Fig 3 Summary of indoor dust particle size distributions for: **a** home, $n=6$; **b** office, $n=6$; **c** combination of office and home dust, $n=12$; and **d** composite dust sample, $n=112$

recommend that for total toxicant determination $250\ \mu\text{m}$ sieve looks promising while for exposure determination $150\ \mu\text{m}$ metallic sieves is important. It should be noted that including

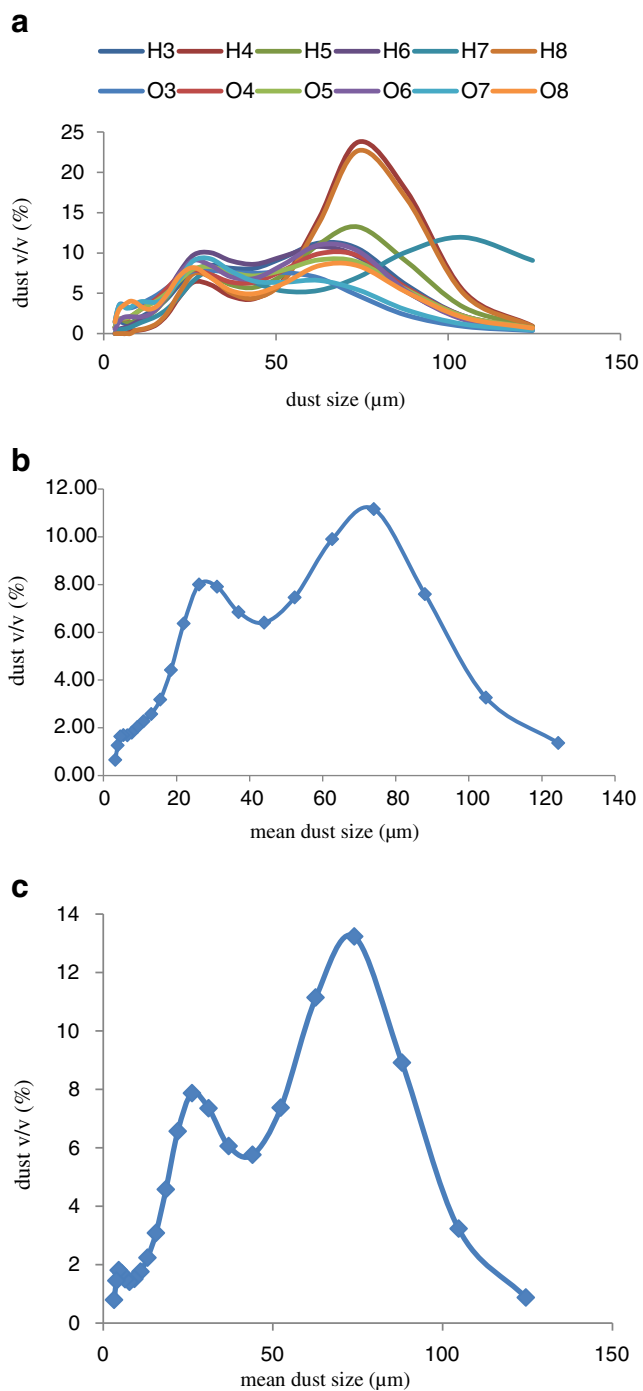


Fig 4 Summary of dust size fraction versus percentage volume distribution for: **a** home and office, **b** mean dust size distribution for both office and home, and **c** mean dust size distribution for composite dust sample, $n = 112$

large sized particles in which less or none PBDEs exist may underestimate human exposure.

Tracing sources of PBDEs

Out of 15 PBDEs congeners considered for identification, only 9 congeners were detected (BDE-15, 47, 66, 85, 99,

100, 153, 154 and 209) with a detection frequency of almost 100 % for all these congeners in electronic materials. However, the average detection frequency of BDE-15, 66, 85, 100, 153 and 154 in floor dust vary in between non-detection (BDE-15 and 154) to 70 % (BDE100 and 153). In all these samples analysed, none of the major congener of Octa-BDE (BDE-183) was detected. The highest concentration detected was 571 and 932 ng g^{-1} corresponding to the concentration of BDE-209 in the dust collected from office of floor dust and electronic materials, respectively. In these selected offices and homes, the patterns of congeners detected are more similar with Penta- and Deca-commercial mixtures. The three congeners (BDE-47, 99 and 209) constituted a total concentration of 94.4 % and 89.3 % for the dust collected from the floor while 91 % and 51 % for the dust collected from the inside electronic materials for office and home, respectively. High difference in percentage of the three major congeners in office and home electronic materials may be attributed to the differences in usage of Penta- and Deca-mixtures for computer and printed circuit boards versus TV and digital compact disc players. Relative percentage concentrations of each PBDEs congeners detected from both environments to the total concentration of PBDEs detected in dust collected from floor and inside electronic materials is given in supplementary material (Fig. S1). For comparison purpose, percentage of \sum_9 PBDE congener detected from the same indoor relative to the total concentrations (\sum_9 PBDE congener's detected of dust collected from floor plus inside electronic materials) for both environments is given in Fig. 5. From Fig. 5, the ratio of total concentrations of PBDEs detected from dust collected inside the electronic materials to that of the settled dust were: 1.7(O3), 0.33(O4), 4.8 (O5), 12.1(H3), 1.5(H4) and 0.67(H5). Overall, the finding shows that electronic materials are one of the major emission sources of PBDEs to the indoor environments. On the other hand, the opposite result was obtained for O4 and H5. During the settled dust collection from O4, there were six computers, two lap tops, two printers and one refrigerator often used in the office. However, during dust collection from electronic materials, only two computers and printers were available in the office from which dust samples were collected. The other computers were removed from the office to electronic store room while refrigerator was taken to other offices. Partially, this probably attributes to the lower concentration of PBDEs observed or those old computers and refrigerator removed are the main emission sources than from which the dust was collected. This argument is supported by the previous research findings that older electronic materials are being identified as a major emission source of PBDEs than the newer ones (Chen et al. 2008; Hazrati and Harrad 2006). For H5, the total concentration of PBDEs found in settled dust was (102 ng g^{-1}) slightly higher than dust collected from inside TV and digital compact disc players (68 ng g^{-1}). Since dust was

Table 1 Particle size distribution of settled dust in office and home after sieving using 150 μm

Dust sample	10%tile (μm)	mean (μm)	Median (μm)	95%tile μm	%<105 μm	%<11 μm	%<5.5 μm
O3 ^a	5.41	32.73	25.07	80.10	99.33	25.27	10.33
O4	5.14	28.60	23.74	69.32	99.60	25.04	11.40
O5	21.30	41.83	41.45	69.22	100.0	2.09	0.35
O6	8.00	36.59	30.15	81.16	99.30	15.20	5.69
O7	7.84	36.18	30.37	80.94	99.30	15.48	5.84
O8	8.22	37.45	32.00	79.00	99.50	13.49	5.14
H3 ^b	22.07	56.05	60.80	89.98	100.0	1.15	0.00
H4	13.84	39.16	34.27	79.44	99.42	6.68	1.70
H5	21.61	54.60	59.24	89.39	99.13	0.92	0.00
H6	10.09	39.50	35.55	81.33	99.34	11.10	4.80
H7	9.13	41.97	37.52	85.98	99.13	11.87	5.73
H8	16.38	60.16	51.27	127.80	85.07	5.25	1.37

^a Office 3^b Home 3

collected in other homes from similar electronic materials, there was no good reason for the differences. However, it is possible that the electronic materials from which dust samples were collected may not have been the main sources of PBDEs, which means, there may be other sources. No PBDEs congeners were detected in the part of carpet samples and PUF, showing that these materials may not have been treated with PBDEs. Furthermore, in one home (H6), where previously PBDE congeners were absent in the settled dust, no PBDE congeners were also detected from the dust collected inside TV and digital compact disc players, confirming that these electronic materials were not treated with PBDEs.

Conclusions

This study mainly emphasised on the characterization of PBDEs as a function of dust particle size, distribution of dust

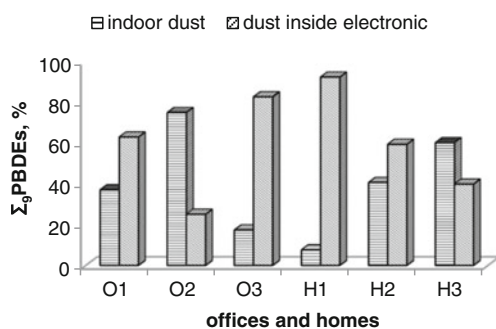


Fig. 5 Comparison of total concentrations of PBDEs obtained from dust collected inside the electronic materials and settled indoor dust of the same office or home. O3, O4, and O5 and H3, H4, and H5 represent office and home, respectively

particle size in the range of dust particle size adherent to human skin and tracing source of PBDEs to indoor dust. Generally, dependence of PBDEs concentrations on dust particle size and organic matter content has been observed. The observed variation of concentration of PBDEs in different skin adherent dust fractions in this study reveals that improper selection of metallic sieve will lead to large deviation from the near reality concentrations of contaminants that human is being exposed. Especially, including non-skin adherent dust fractions or large particle size in which less or none PBDEs exist may underestimate human exposure estimation. Based on the concentration of PBDEs detected in different dust particle size fractions and distribution of dust particle sizes observed, 150 μm metallic sieves is more appropriate than 250 μm for determination of human exposure. Use of 150 μm metallic sieves for future studies may help for comparing results across similar studies. Furthermore, this study also clearly showed that characterization of dust particle size distribution is best done by using particle size analyser than metallic sieves.

By comparing total concentration of PBDEs detected in dust collected from the floor and electronic materials of the same indoor environment, major sources of PBDEs were identified. As observed in this study, exact identification of all possible emission sources of PBDEs to indoor dust is quite complex, however, the result shows imported electronic materials are the major source of PBDEs to the indoor dust. Moreover, due to limited sample of carpet and PUF used in this study, it is very difficult to draw precise conclusion whether these materials are treated with PBDEs or not. Therefore, more research with large sample size is required to sort out those PBDEs treated or/and untreated carpet and PUF products along with their country of origin.

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