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Differences in the seasonal variation of brominated and phosphorus flame retardants in office dust

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ABSTRACT

This study documents the temporal variability in concentrations of flame retardants (FRs) in floor dust from three offices in Beijing, China. Dust from Office A (OAD) was collected weekly from March to August, 2012, and sampling of dust from Office B and C (OBD and OCD) was conducted fortnightly (each two weeks) from March to December 2012. With intensive and continuous sampling, we report for the first time on clear and coherent temporal trends of polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs) and phosphorus flame retardants (PFRs) in indoor dust. The observed mean concentrations of $\sum$9PBDEs, $\sum$4NBFRs and $\sum$9PFRs, were 554, 11,100 and 128,000 ng g^{-1} in OAD; 7560, 5000 and 17,300 ng g^{-1} in OBD; and 4750, 3550 and 17,200 ng g^{-1} in OCD, respectively. With exception of PBDEs, concentrations of FRs were elevated in OAD than in OBD and OCD. Two to ten-fold variations were observed between the minimum and maximum concentrations of FRs in the same office, indicating that the sampling moment exerts a substantial influence on the level of FR contamination. Different seasonality was distinctively found between BFRs and PFRs. Except for a few occasional abnormal values, BFR levels in office dust were generally constant among different seasons. The abundance rank order for PFRs was: winter > autumn > summer, with peak values occurring in late winter and early spring. This pattern may be attributable to the fact that PFRs are more sensitive to temperature changes compared to PBDEs and NBFRs owning to their higher volatilities. The absence of significant seasonal variation for BFR concentrations in indoor dust compared to outdoor air and dust concentrations is also discussed.

1. Introduction

Flame retardants (FRs) are ubiquitously used in polymers since the 1960s. The total consumption of FRs in Europe in 2006 was 465,000 tons, of which 10% were brominated flame retardants (BFRs), while phosphorus flame retardants (PFRs), proposed as alternatives for BFRs, were responsible for 20% (van der Veen and de Boer, 2012). Recently, worldwide restrictions and bans on polybrominated diphenyl ether (PBDE) formulations have significantly simulated the market demand of novel brominated flame retardants (NBFRs) (Covaci et al., 2011) and PFRs (van der Veen and de Boer, 2012) as alternatives. BFRs and some PFRs are additives and can be easily released into environment by volatilization or abrasion process (Cao et al., 2013). The interest in the occurrence of FRs in different compartments of the indoor environment has systematically increased in the last decade. Recently, a new method was optimized for the comprehensive and simultaneous determination of legacy and current-use FRs, such as PBDEs, NBFRs, and PFRs (Van den Eede et al., 2012).

Temporal variation is an important factor in environmental monitoring. However, for indoor exposure assessment of FRs, it has not been adequately considered. Temporal variability of FR contamination in indoor dust may significantly influence the reliability of human exposure assessments that are based on single point sampling in time. Several studies have involved the investigation of temporal variation of PBDE occurrence in indoor dust (Allen et al., 2008; Batterman et al., 2009; Harrad et al., 2008a; Vorkamp et al., 2011; Yu et al., 2012), of which only one study was specifically devoted to this topic (Muenhor and Harrad, 2012). Yet, these investigations were subjected to considerable uncertainty, because most of their conclusions were based on limited and discontinuous sampling sizes. To our knowledge, no systematical information about temporal variations in the concentrations of BFRs and PFRs in indoor dust is available in the literature.

In China, contamination of PBDEs in environmental, biological and human samples (He et al., 2012), and in e-waste recycling area (Labunsk et al., 2013; Leung et al., 2011; Ma et al., 2009; Wang et al., 2010; Yang et al., 2013; Zheng et al., 2010) has been of concern for years. However, studies about the FR occurrence in indoor dust are still limited considering the size of the country and its population (Chen et al., 2011; Huang et al., 2010; Ni et al., 2011, 2012; Yu et al., 2012). Moreover, there are practically no substantial data for NBFRs and PFRs up to now. Consequently, there is an urgent need to investigate the occurrence characteristics of BFRs and PFRs in indoor dust from China.

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Consequently, we conducted a comprehensive investigation on the seasonal variation patterns in the concentrations of selected PBDEs, NBFRs and PFRs in office dust. This would help to understand how concentrations of FRs change in indoor dust over months and seasons.

2. Materials and methods

2.1. Sampling strategy and methods

For this study, three offices were selected in one building located in Beijing, China to evaluate if the concentrations of FRs in indoor dust and the corresponding human exposure vary with seasonal changes. Office A is located in a foreign company with crew size of 25 and area of about 140 m^2. Office B and C both belong to domestic corporations with the same area of about 550 m^2. The crew size of Offices B and C is 110 and 90, respectively. Based on cleaning routines of each site, sampling of dust from Office A (OAD) was conducted at weekly intervals between 4th March 2012 and 5th August 2012 (about 5 consecutive months), while dust from Office B and C (OBD and OCD) were sampled fortnightly (each two weeks) between 25th March 2012 and 23rd December 2012 (about 9 consecutive months). During the whole sampling period, there was no apparent addition or removal of FR containing products. In total, 56 samples of floor dust from the carpet were taken from these three offices, with 23 samples from Office A, 17 samples from Office B and 16 samples from Office C. Samples were directly collected from their office-hold vacuum bags, and around 20, 120, and 100 gram dust were sampled each time from Offices A, B and C, respectively. After sampling, the vacuum bags were cleaned with water and dried under the sunlight. All samples were homogenized and sieved through a stainless mesh to collect particles <2 mm in size, from which approximately 10 g each was further packed with aluminum foil and sealed in clean polyethylene zip bags. Samples were stored in the dark at −20 °C until analysis was performed.

2.2. Analytical methods

Dust analysis was performed in the Toxicological Centre of University of Antwerp. A multi-residue analysis method for the simultaneous determination of PBDEs, NBFRs and PFRs was used in this study (Van den Eede et al., 2012). Nine PBDEs (BDE 28, 47, 100, 99, 85, 154, 153, 183 and 209), eighteen NBFRs (BATE, TBP-AE, TBX, TBCT, PBT, PBEB, TBP-DBPE, EH-TBB, HBB, PBB-Acr, BEH-TEBP, BTBPE, OBTMPI, DBDPE, PBBs, DBE-DBCH, TBCO, DBHCTD), and ten PFRs (TPP, TNBP, TBOEP, TEHP, TCEP, TCIPP, TDCPP, TPHP, TMPP, EHDPP) were analyzed based on previously reported method. The full names of the compounds and the detailed method are presented in Table SI-1 and the Supporting information.

2.3. QA/QC

Dust samples ($n = 56$) were analyzed in 4 batches. Each batch included 3 laboratorial blanks and one certified dust sample (SRM 2585, NIST, Gaithersburg, MD, US), thus in total 12 laboratorial blanks and 4 replicates of SRM 2585. In blanks, only BDE 85, BDE 209, DBDPE and TNBP were commonly detected at much lower levels (less than 5%) than that in the samples (Table SI-3). Their mean values of blanks were, then, subtracted from measured values from samples. The results of all analyses of SRM 2585 demonstrated both good repeatability (RSD (relative standard deviations) for individual congeners ranging between 3.8 and 29.4%) and good agreement with the certified values or literatures (Van den Eede et al., 2012). More information is included in Table SI-4.

3. Results and discussion

Table 1 summarizes the concentrations of PBDEs, NBFRs and PFRs measured in the three offices. During the ten-month monitoring, the ranges of ΣPBDEs, ΣNBFRs and ΣPFRs varied substantially. The concentrations of ΣPBDEs in OAD, OBD and OCD ranged from 135 to 949 ng g^{-1}, 3060 to 30,200 ng g^{-1} and 2380 to 13,300 ng g^{-1}, respectively. The concentrations of ΣNBFRs in OAD, OBD and OCD ranged from 4180 to 14,600 ng g^{-1}, 2240 to 16,400 ng g^{-1} and 2440 to 6730 ng g^{-1}, respectively. The concentrations of ΣPFRs in OAD, OBD and OCD ranged from 41,000 to 212,000 ng g^{-1}, 11,100 to 25,900 ng g^{-1} and 12,200 to 25,500 ng g^{-1}, respectively. These two to ten-fold variations (between maximum and minimum values) (Table 1) in the concentrations of FRs indicate that the time of dust sample collection plays a very important role in the human exposure assessment, and occasionally abnormal values might be obtained through single sampling in time.

3.1. Concentrations and profiles of FRs in the three offices

Fig. 1 illustrates the differences in the mean ΣPBDEs, ΣNBFRs and ΣPFRs concentrations among the three offices of the present study, showing that concentrations of FRs substantially displayed spatial variability within the building. In agreement with the literature (Ali et al., 2012a; Besis and Samara, 2012), the results of the present study show that the levels of PFRs in the indoor environment are usually higher than those of BFRs. The total consumption of PFRs in Europe in 2006 was twice as much as that of BFRs (van der Veen and de Boer, 2012). However, PFR levels in indoor dust were always around one order of magnitude higher than BFRs (Ali et al., 2012a; Besis and Samara, 2012). This might be attributable to the higher volatilities of PFRs than BFRs (Covaci et al., 2011; van der Veen and de Boer, 2012; Yue and Li, 2013), which lead to the easier migration of PFRs from consumer products to indoor dust.

The mean Σ9PBDEs concentrations of OAD, OBD and OCD of this study are 554, 7560, and 4750 ng g^{-1} (Table 1), respectively, which fall within the range reported previously for offices (from median = 581 ng g^{-1} of Σ10PBDE including BDE 209 in Belgium (lowest) (D'Hollander et al., 2010) to median = 8750 ng g^{-1} of Σ21PBDEs including BDE 209 in US (highest) (Batterman et al., 2010)). The concentrations in OAD are to our knowledge the lowest reported value in office dust to date, and OBD was highly contaminated. In the present study, mean Σ4NBFRs concentrations in OAD, OBD and OCD were 11,100, 5000, and 3550 ng g^{-1}, respectively (Table 1). From the limited data available, it appears that the contamination with NBFRs in these three Chinese offices was higher than that of New Zealand (Ali et al., 2012a), Pakistan (Ali et al., 2012b), Belgium, UK (Ali et al., 2011) and US (Stapleton et al., 2008). Mean Σ9PFRs concentrations in OAD, OBD and OCD were 128,000, 17,300, and 17,200 ng g^{-1}, respectively (Table 1). Similarly, PFRs in OBD and OCD are comparable to house dust levels from New Zealand (Ali et al., 2012a), Belgium (van den Eede et al., 2011), US (Stapleton et al., 2009) and Spain (Garcia et al., 2007), and that in OAD are about an order of magnitude higher.

Regarding the profiles, PFRs were the dominant components of all three groups of FRs, especially for Office A, the foreign company. Concentrations and profiles of PBDEs, NBFRs and PFRs in settled dust were similar in two domestic corporations, Office B and C, where PBDEs still accounted for important proportions (Fig. 1). It might be possible that PBDEs have been phased out and substituted by NBFRs and PFRs in Office A, while old commercial products containing high loads of PBDEs were still present in Offices B and C. This coincides with the fact that Office A is relatively small, but decorations seem newer and of higher quality, while Offices B and C are large, but with relative simpler and older furnishings. Within the same building, as PBDEs in OAD exhibit extremely low levels compared to that in OBD and OCD, it can