Environment International 135 (2020) 105348

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Polybrominated diphenyl ethers and organophosphate esters flame retardants in play mats from China and the exposure risks for children

Bo Peng, Zi-Min Yu, Chen-Chou Wu, Liang-Ying Liu*, Lixi Zeng, Eddy Y. Zeng

Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou 511443, China

ARTICLE INFO

Handling Editor: Heather Stapleton

ABSTRACT

A total of 41 play mats made from different raw materials, such as polyethylene (PE), ethylene–vinyl acetate copolymer (EVA), chemical crosslinked polyethylene (XPE), and polyvinyl chloride (PVC), were obtained from Chinese markets and analyzed for flame retardants. Polybrominated diphenyl ethers (PBDEs) and their replacements, organophosphate esters (OPEs), were measured and the associated exposure risks for children were evaluated. The levels (range; median) of OPEs (6.6–7400; 200 ng g^{-1}) were generally 1–2 orders of magnitude higher than those of PBDEs (0.13–72; 13 ng g^{-1}), consistent with the production and usage trends of flame retardants. The concentrations of both PBDEs and OPEs were the lowest in XPE mats (0.13–5.6; 3.3 ng g^{-1} for PBDEs and 6.6–320; 47 ng g^{-1} for OPEs) compared to the other three types. Concentration comparison and compositional analysis suggested that PBDEs and OPEs in play mats were most probably from leaching of raw materials, during production, storage, and/or transport. Children's exposure to PBDEs and OPEs from play mats was estimated for three pathways, i.e., dermal contact, inhalation, and hand-to-mouth ingestion. The combined exposure was 5–6 orders of magnitude lower than the established reference dose values, suggesting no obvious health concern regarding the occurrence of PBDEs and OPEs in play mats. Nevertheless, selection of less contaminated, i.e., XPE mats among those under investigation, by consumers is strongly recommended to minimize any potential exposure risk.

1. Introduction

Flame retardants are a group of chemicals applied to various commercial and household products, including baby products or toys, to meet flammability standards and regulations. Polybrominated diphenyl ethers (PBDEs) were the most extensively used flame retardants, and have been gradually phased out due to their environmental ubiquity, persistence, and bioaccumulation (Covaci et al., 2011). Organophosphate esters (OPEs) have re-emerged as replacements of PBDEs since 2004 (He et al., 2018). They have been ubiquitously detected in the environment and humans (Kim et al., 2014; Liu et al., 2016; van der Veen and de Boer, 2012; Wei et al., 2015). Recent studies demonstrated that concentrations of OPEs in environments and human were 1–3 orders of magnitude higher than those of PBDEs (Cristale et al., 2016; Giulivo et al., 2017; Liu et al., 2016; Salamova et al., 2014). Increasing studies have also confirmed the toxic effects of OPEs (Andresen et al., 2004; Liu et al., 2019; Ren et al., 2008). For example, tris(2-chloroethyl)phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and tris(2-butoxyethyl) phosphate (TBEP) were suggested to be carcinogenic (Andresen et al., 2004; Ni et al., 2007; WHO, 1998). TCEP, TDCIPP, and triphenylphosphate (TPhP) were suggested to be neurotoxic (Andresen et al., 2004; Dishaw et al., 2011; Tilson et al., 1990). Because PBDEs and OPEs may co-occur in environmental media and/or household products, simultaneous measurement of these two classes of flame retardants could lead to better understanding of the effects of the revolution of flame retardants industry. Furthermore, the determination of both the phased-out and emerging flame retardants in environments and/or household products is essential in assessing potential exposure risks.

Numerous studies reported the occurrences of PBDEs in indoor environments (Cristale et al., 2016; Harrad et al., 2010; He et al., 2018; Sun et al., 2016). Efforts have been made to identify and quantify OPEs in a variety of children's products, including toys (Guzzonato et al., 2017; Ionas et al., 2014), mattresses (Boor et al., 2015), car seats (Stapleton et al., 2011), and strollers (Stapleton et al., 2011) among others. As additive flame retardants, OPEs can be easily released into the environment (Salamova et al., 2014), resulting in their widespread

* Corresponding author at: Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou 511443, China.

E-mail address: liuliangying3@126.com (L.-Y. Liu).

https://doi.org/10.1016/j.envint.2019.105348
Received 4 September 2019; Received in revised form 13 November 2019; Accepted 18 November 2019
Available online 26 December 2019

occurrence in indoor environments around the globe (Araki et al., 2014; Carlsson et al., 1997; Cristale et al., 2016; Hartmann et al., 2004). Household products are therefore important exposure sources of PBDEs and OPEs for children, as children spend most of their time in indoor environments. Exposure to PBDEs and OPEs embedded in household products is particularly a health concern for children because they are physiologically and developmentally vulnerable (Harrad et al., 2010; Hoffman et al., 2015; Langer et al., 2016; Zhou et al., 2017).

As one of the common house products, play mats are frequently used in homes and kindergartens around the world. Children are in close contact with play mats when they play and crawl on the mats. Therefore, play mats are expected to be a potential exposure source of flame retardants to children. However, this potential source and the associated health risk have not been adequately investigated. Only a few recent studies investigated concentration levels and compositional profiles of PBDEs and OPEs in mat samples (Chen et al., 2009; Stubbings et al., 2018), which were principally composed of polyurethane foam (PUF). It was demonstrated that PUF nap mats were an important source of PBDEs and OPEs in childcare environments (Stubbings et al., 2018). Despite PUF nap mats, there are a variety of other types of play mats on the markets, including polyethylene (PE), ethylene–vinyl acetate copolymer (EVA), chemical crosslinked polyethylene (XPE), and polyvinyl chloride (PVC) among others. Plastics were recycled as raw materials for new products, resulting in PBDEs contamination in children's toys and food-contact articles (Guzzonato et al., 2017). Apparently some play mats on the markets may be made from recycled plastics due to cost control. However, no study has systematically investigated the sources and concentrations of flame retardants and the exposure risks associated with play mats.

To fill this knowledge gap, the present study was conducted to measure and compare the concentrations and compositional profiles of PBDEs and OPEs in selected different types of play mats, which are best-sellers in China's markets. The objectives were to illustrate the state of flame retardant contamination in play mats, to test if there is any difference among different types of play mats, and to assess children's exposure to PBDEs and OPEs via dermal contact, inhalation, and hand-to-mouth ingestion.

2. Materials and methods

2.1. Materials

A standard solution, BDE-MXE, consisting 27 individual BDE congeners (BDE-3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209) was purchased from Wellington Laboratories (Guelph, ON, Canada). Nine individual OPE solution, TCEP, TCIPP, TDCIPP, tributyl phosphate (TBP), TBEP, tris(2-ethylhexyl) phosphate (TEHP), 2-ethylhexyl diphenyl phosphate (EHDPP), TPhP, and tri-*m*-tolyl phosphate (TMTP) were obtained from AccuStandard (New Haven, CT, USA). BDE-51 and BDE-115 from AccuStandard, as well as ^{13}C-BDE-209 from Wellington Laboratories were used as surrogate standards for PBDEs. TDCIPP-d_{15}, TPhP-d_{15}, TBP-d_{27}, and tris(2-butoxy[$^{13}C_2$]-ethyl) phosphate (M_6-TBEP) from Wellington Laboratories were used as surrogate standards for OPEs. BDE-69, BDE-118, and BDE-181 from AccuStandard were used as internal standards for PBDEs. Coumaphos-d_{10} from Toronto Research Chemicals (Toronto, Canada) was used as internal standard for OPEs.

2.2. Sample collection

A total of 41 play mat samples from 20 best-selling brands were purchased from Jingdong Online Mall of China in 2017–2019. The samples were grouped into four categories based on their raw materials described by the producers, i.e., polyethylene (PE), ethylene–vinyl acetate copolymer (EVA), chemical crosslinked polyethylene (XPE), and polyvinyl chloride (PVC). These samples were sealed and maintained at room temperature until further analysis.

2.3. Sample preparation and instrumental analysis

Approximately 25 cm^2 of play mat sample was weighed and cut into pieces prior to pretreatment. Upon addition of known amounts of surrogate standards, samples were Soxhlet extracted with 200 mL of *n*-hexane:acetone mixture (1:1 by volume) for 48 h. The sample extract was purified following our previously published method (Liu et al., 2015). Briefly, the extract was evaporated, solvent changed to *n*-hexane, and reduced to approximately 1 mL under a gentle nitrogen flow with a TurboVap II (Biotage, Sweden). The extract was fractionated on a column packed with 6 g of 2.5% (by weight) water deactivated Florisil (Sigma-Aldrich; St. Louis, MO, USA). The column was consecutively eluted with 35 mL of *n*-hexane and 35 mL of 1:1*n*-hexane: dichloromethane (PBDEs fraction), and 25 mL of 1:1 dichloromethane: acetone (OPEs fraction). The PBDEs fraction was further cleaned with a 5 cm acidic silica gel column (0.23 cm i.d.), concentrated to 50 µL and spiked with internal standards. The OPEs fraction was reduced to near dryness under a gentle nitrogen flow, reconstituted in 1 mL of methanol, and spiked with internal standard.

Concentrations of PBDEs were determined with a Shimadzu Model 2010 gas chromatograph coupled with a QP2010 mass spectrometer (Shimadzu, Japan) in the electron capture negative ionization mode and DB-5HT capillary column (15 m × 0.25 mm i.d. × 0.25 µm film thickness). Detailed information on the instrumental analysis was adopted by previous study (Liu et al., 2015). OPEs levels were measured with an ultra-performance liquid chromatograph (Nexera X2, Shimadzu Japan) coupled to a tandem mass spectrometer (Triple Quad 5500 System, AB SCIEX). Detailed information on the instrumental analysis could be found in the previous study (Fu et al., 2017).

2.4. Quality assurance and quality control

One procedural bank, one matrix spike sample, and one blank spike sample were analyzed along with each batch of 8–10 samples. The recoveries (average ± standard deviation) of matrix spike samples ranged from 69 ± 5% for BDE-209 to 103 ± 7% for BDE-47, and from 64 ± 7% for TCEP to 138 ± 14% for TCIPP. The recoveries of surrogate recovery standards in play mat samples were 67 ± 20%, 63 ± 18%, 54 ± 26%, 64 ± 14%, 84 ± 14%, 85 ± 30%, and 76 ± 2% for BDE-51, BDE-115, ^{13}C-BDE-209, TDCIPP-d_{15}, TPhP-d_{15}, TnBP-d_{27}, and M_6-TBEP, respectively. Average levels in procedural blanks ranged from 0.01 ng g^{-1} for BDE-17 to 0.59 ng g^{-1} for BDE-209 (Table S1). Average procedural blank level plus two times its standard deviation were normalized to an average sample weight of 1.88 g and defined as the limit of quantification (LOQ). The LOQs for the target compounds ranged from 0.02 ng g^{-1} for BDE-17 to 12 ng g^{-1} for TCIPP (Table S1).

2.5. Data analysis

Concentrations were corrected for blanks but not for surrogate recoveries. All concentrations were normalized to sample weight unless specially specified. Concentrations below the LOQ were treated as non-detects. Logarithmically transformed concentrations of each compound were subject to analyses of variance (ANOVA) to see if there is any differences in concentrations of PBDEs and OPEs among different types of play mats.

2.6. Exposure and risk assessment

The average daily exposure (ADD; pg (kg b.w.)$^{-1}$ day^{-1}) of children at four age levels (0.5–1, 1–2, 2–3, and 3–5 years) was assessed for three pathways, dermal contact (ADD_{derm}), inhalation (ADD_{inh}), and hand-to-mouth ingestion (ADD_{ing}). Average, median, and 95th percentile concentrations of all play mats were used for the calculation of exposure. Dermal exposure was estimated by Eq. (1) which was modified from published literatures (Chen et al., 2009; Xue et al., 2017).

$$ADD_{derm} = C_{area} \times F_{mig} \times BSA \times F_{contact} \times F_{pen} \times t_1 \times N/BW \tag{1}$$

where C_{area} is the concentrations of flame retardants in play mats normalized to sample area (pg cm^{-2}), F_{mig} is the migration rate of flame retardants to the skin (0.005 d^{-1}) (BfR), BSA is the body surface area in contact with play mats (cm^2) (U.S. EPA, 2011), $F_{contact}$ is the fraction of contact area for skin (assumed to be 0.5, unitless), F_{pen} is the penetration rate of chemicals into body (0.01, unitless) (BfR), t_1 is the contact duration time of each play event (assumed to be 2 h), N is the number of playing events (assumed to be 2 day^{-1}), and BW is body weight of children (kg) (U.S. EPA, 2011).

The average daily exposure via inhalation was estimated by

$$ADD_{inh} = C_{air} \times InhR \times t_2/BW \tag{2}$$

where C_{air} (pg m^{-3}) is the indoor air concentrations of PBDEs and OPEs due to emission from the play mats (detailed in Supplementary Data), $InhR$ is the inhalation rate (m^3 h^{-1}) (U.S. EPA, 2011), and t_2 is the daily exposure duration time (h day^{-1}) (Chen et al., 2009).

A certain portion of PBDEs and OPEs loaded on hands can be orally ingested due to children's hand-to-mouth ingestion. Ingestion exposure was estimated by

$$ADD_{ing} = C_{area} \times F_{mig} \times CA \times TE \times EF \times t_2 \times N/BW \tag{3}$$

where CA is the contact area within each hand-to-mouth event (cm^2), TE is transfer efficiency at each contact (0.05) (Washburn et al., 2005), and EF is the frequency of contact (h^{-1}) (Xue et al., 2007). Detailed input parameters for exposure assessment are summarized in Table S2.

3. Results and discussion

3.1. Occurrence of PBDEs and OPEs

Summarized information on the detection frequencies and concentrations (ranges, medians, and geometric means) for PBDE and OPE compounds are given in Table S3. BDE-3, 49, 66, 71, 77, 85, and 126 were not detected in all samples thus not included in the following discussion. Significantly positive correlation ($p < 0.05$) was observed between the concentrations of PBDEs and OPEs, suggesting that PBDEs and OPEs in play mats might share a similar source. In general, Σ_{20}PBDE (sum of BDE-7, 15, 17, 28, 47, 99, 100, 119, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209) levels (median ± standard errors) (13 ± 3.3 ng g^{-1}) were 2 orders of magnitude lower ($p < 0.05$) than those of OPEs (200 ± 210 ng g^{-1}) (Table S3). This is also true for each of the four types of play mats. This pattern agrees well with the production and usage history of flame retardants. PBDEs have been gradually phased out since 2003 while OPEs have been used as a replacement (van der Veen and de Boer, 2012). Similar patterns have been widely observed in environmental media and biota, including atmosphere (Salamova et al., 2014), indoor dust (Cristale et al., 2016), sediment (Giulivo et al., 2017), consumer products (Kajiwara et al., 2011), as well as human hair and nails (Liu et al., 2016).

To the best of our knowledge, this is the first study to comprehensively investigate legacy and emerging flame retardants in different types of children's play mats. Only a few datasets of PBDEs in play mats are available in the literature (Chen et al., 2009; Stubbings et al., 2018); thus any comparison between the present and previous studies can only be made for different household products from China and other countries. In general, PBDE levels (0.13–72 ng g^{-1}; median: 13 ng g^{-1}; Table S3) in play mats investigated in the present study were slightly higher than those in curtain (7.4–9.1 ng g^{-1}) and wallpaper (3.1–14 ng g^{-1}) collected from Japan (Kajiwara et al., 2011), much lower than those in crib mattresses (2,200,000–14,700,000 ng g^{-1}) from the U.S. (Boor et al., 2015), hard plastic toys (162–5,340,000 ng g^{-1}; median 53,000 ng g^{-1}), foam toys (240–72,400 ng g^{-1}; median: 960 ng g^{-1}), and stuffed toys (112–1300 ng g^{-1}; median: 150 ng g^{-1}) obtained in Chinese markets (Chen et al., 2009). Obviously, the content of PBDEs in play mats were far below those in polymers treated with flame retardants (5–16%) (Alaee et al., 2003).

The concentrations of OPEs in all samples ranged from 6.6 to 7400 ng g^{-1} with a median of 200 ng g^{-1} (Table S3). Concentrations of individual and the sum of all OPE compound in play mats were far lower than those in commercial household products. For example, concentrations of OPE compounds (Table S3) in play mats were 6–7 orders of magnitude lower than those of TPhP (4,100,000–9,900,000 ng g^{-1}) and TMTP (300,000–1,900,000 ng g^{-1}) in children's PUF nap mats used in the U.S. childcare centers (Stubbings et al., 2018), and 2–4 orders of magnitude lower than those in foam and textile toys (85,000 ng g^{-1}) and hard plastic toys (1,100,000 ng g^{-1}) from a recycling park in Antwerp, Belgium (Ionas et al., 2014). Concentrations of individual and the sum of all OPE compounds (Table S3) in play mats (6.6–7400; median: 200 ng g^{-1}) were several orders of magnitude lower than those of TCEP (1,080,000–5,940,000 ng g^{-1}), TCIPP (1,110,000–14,400,000 ng g^{-1}), and TDCIPP (2,400,000–124,000,000 ng g^{-1}) in PUF samples from commonly used baby products obtained in the U.S. (Stapleton et al., 2011), and those of TDCIPP (10,000,000–50,000,000 ng g^{-1}) in PUF samples from furniture collected in the U.S. (Stapleton et al., 2009). OPEs typically account for an average of 5–15% of polymeric materials if used as additive flame retardants (Hartmann et al., 2004). Concentrations of OPEs in play mats are obviously far lower than this level.

These comparisons suggested that PBDEs and OPEs levels in play mats were substantially lower than those in toys, baby products, and furniture, most of which were treated with flame retardants. Above discussion suggested that play mats analyzed in the present study contained insufficient amounts of PBDEs and OPEs to impart flame retardancy. However, this result does not necessarily mean that there is no health concern with the frequent use of play mats. It is also speculated that play mats investigated in the present study were not intentionally treated with flame retardants during the manufacturing processes. Other sources such as raw materials may have introduced flame retardants into play mats.

3.2. Source assessment and implications for recycled plastics

ANOVA test suggested that the concentrations of PBDEs and OPEs were different among the four types of play mats (Fig. 1). For example, the concentrations (median ± standard errors) of Σ_{20}PBDE (sum of BDE-7, 15, 17, 28, 47, 99, 100, 119, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209) in PE (30 ± 7.1 ng g^{-1}) and EVA (28 ± 4.6 ng g^{-1}) mats were significantly higher ($p < 0.05$) than those in XPE (3.3 ± 0.83 ng g^{-1}) and PVC (2.5 ± 4.3 ng g^{-1}) mats. The concentrations of OPEs in PE (110 ± 27 ng g^{-1}), EVA (320 ± 55 ng g^{-1}), and PVC (210 ± 870 ng g^{-1}) were significantly higher ($p < 0.05$) than those in XPE mats (47 ± 41 ng g^{-1}). For both PBDEs and OPEs, XPE mats were the least contaminated (Fig. 1). It is hypothesized that the manufacturing technology for the four types of play mats were generally the same, and the different concentrations of PBDEs and OPEs were probably ascribed to different raw materials and/or additives used in the manufacturing processes (Chen, 2017; Ji, 2016; Su, 2016).

The compositional profiles of PBDEs and OPEs in each type of play mats are depicted individually to see if there is any difference. Compositional profiles of PBDEs are depicted only for PE and EVA mats (Fig. 2) as PBDEs were rarely detected in XPE and PVC mats. Profiles of PBDEs in play mats were quite similar to those in foam toys from China (Chen et al., 2009), characterized with low relative abundances of penta-BDE and high relative abundances of octa-, nona-, and deca-BDE.

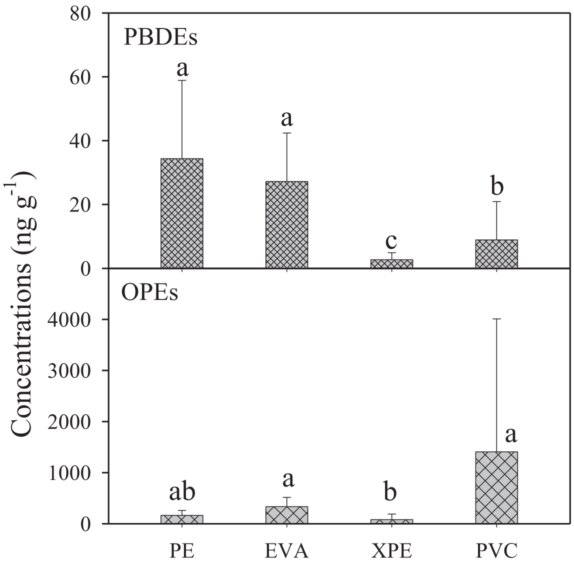

Fig. 1. Concentrations (average ± standard errors; ng g^{-1}) of PBDEs and OPEs in play mats of polyethylene (PE), ethylene–vinyl acetate copolymer (EVA), chemical crosslinked polyethylene (XPE), and polyvinyl chloride (PVC). Letters above each bar demonstrate the ANOVA results. Concentrations in different play mats that share different letters are significantly different from one another at $P < 0.05$.

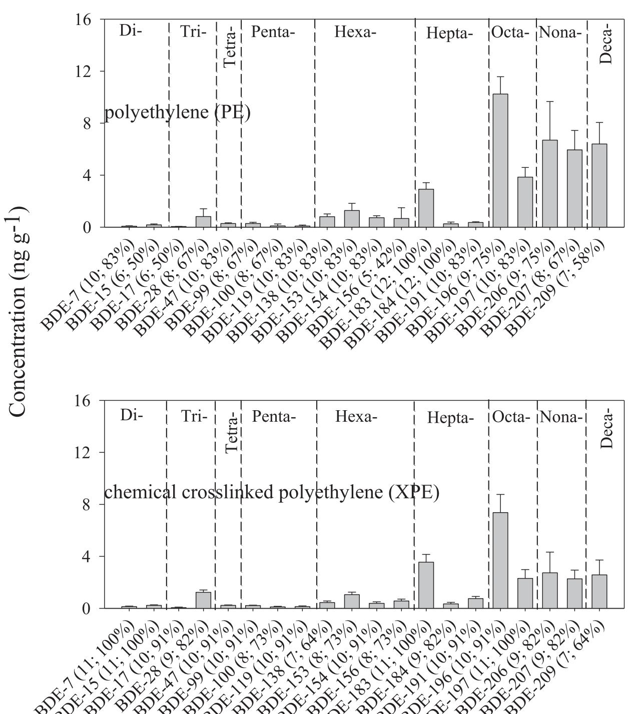

Fig. 2. Compositional profiles of PBDEs represented by concentrations (median ± standard error) of individual congener in polyethylene (PE) and ethylene–vinyl acetate copolymer (EVA) play mats. Number in the parenthesis means detection frequency.

In general, the PBDEs profiles in play mats were different from those in commercial mixtures. Commercial penta-BDE mixture is mainly composed of BDE-47 and BDE-99 (La Guardia et al., 2006). However, penta-BDE congeners accounted for a minor fraction of total PBDEs (0.13–21% and 0.51–11% in PE and EVA play mats, respectively). This is reasonable as penta-BDE was mainly used in PUF for furniture and upholstery (Chen et al., 2009), and that none of the play mats investigated in the present study was made of PUF. Deca-BDE commercial mixture contains mainly BDE-209 (≥97%) and trace amounts of octa-BDE (0–0.001%) and nona-BDE (0.3–3%) (Nilsson, 2018). The high abundances of octa- and nona-BDEs in play mats may have resulted from the debromination of BDE-209 (Chen et al., 2009, Nose et al., 2007, Söderström et al., 2004). A recent study demonstrated that BDE-209 in plastic casings was transformed to octa- and nona-BDE after thermal treatment (Li et al., 2018). The temperature used in manufacturing play mats was 220–240 °C (Chen 2017), quite similar to that (300 °C) of thermal treatment of plastic casings (Li et al., 2018). It should be noted that all the samples analyzed in the present study contained insufficient amounts of PBDEs to impart flame retardancy. These results indicated that PBDEs were not added during manufacturing. A plausible explanation is that recycled plastics (Ionas et al., 2014, Kajiwara et al., 2011) may have been used as raw materials to manufacture consumer products, e.g., PE and EVA play mats.

Similar to PBDEs, the amounts of OPEs in play mats were also inadequate to impart flame retardancy. Thus OPEs in play mats were not intentionally added during manufacturing. The compositional profiles of OPEs in the four types of play mats were different (Fig. 3), suggesting different magnitudes of contamination by raw materials. The compositions of OPEs in PE and EVA mats were similar (Fig. 3), with TCIPP being the most dominant congener. TCEP, TCIPP, and TDCIPP are important chlorinated additive flame retardants (van der Veen and de Boer, 2012). The levels of TCEP and TDCIPP were one order of magnitude lower than that of TCIPP. The low levels of chlorinated OPE compounds may have originated from the raw materials of play mats. Even if the raw materials of play mats contained high amounts of chlorinated OPEs, they could have undergone thermal decompositions as TCIPP decomposes at above 150 °C and TCEP rapidly decomposes above 220 °C (van der Veen and de Boer, 2012). The detection frequencies and concentrations of OPE compounds were low in XPE mats (Table S3). The highest median value is detected for TCIPP (Fig. 3). Relatively higher concentrations of EHDPP were found in PVC mats than the other types, consistent with the fact that EHDPP is used as a plasticizer in PVC polymers (van der Veen and de Boer, 2012). Additionally, non-chlorinated-OPEs are frequently used as plasticizers of polymeric materials (Araki et al., 2014), generally making up 1–30% of the product (Hartmann et al., 2004). Again, the levels of all non-chlorinated OPEs were far below this level. Therefore, non-chlorinated OPEs were probably not added as plasticizers in manufacturing. Remarkably high levels of EHDPP and TPhP were found in some PVC mats, consistent with the fact that EHDPP and TPHP are primarily used in PVC as plasticizers (Regnery et al., 2011). In summary, PBDEs and OPEs found in the play mats were most probably originated from raw materials for the consumer products. Other sources, such as contamination during the production process, packaging, storage, and transportation are also possible contributors.

3.3. Children's exposure and risk assessment

The daily exposures to PBDEs and OPEs from play mats for children at four age groups via dermal contact, inhalation, and hand-to-mouth ingestion as well as their combination are shown in Table 1 and depicted in Fig. 4. Generally, younger children (0.5–1 years) were subject to higher exposures than other groups. This is most likely due to their lower body weights and smaller body sizes. Exposures from the three pathways showed a decreasing sequence of dermal contact < inhalation < hand-to-mouth ingestion (Fig. 4).

The median daily exposures to PBDEs from play mats via dermal contact ranged from 1.4 to 1.7 pg (kg b.w.)$^{-1}$ day^{-1} for the four groups of children (Table 1), one order of magnitude lower than those from toys (30.5–43.3 pg (kg b.w.)$^{-1}$ day^{-1}) (Chen et al., 2009). The median daily exposures to OPEs via dermal contact were 24–29 pg (kg b.w.)$^{-1}$ day^{-1} (Table 1), 3–4 orders of magnitude lower than those (40,800–126,000 pg (kg b.w.)$^{-1}$ day^{-1}) from dermal contact with

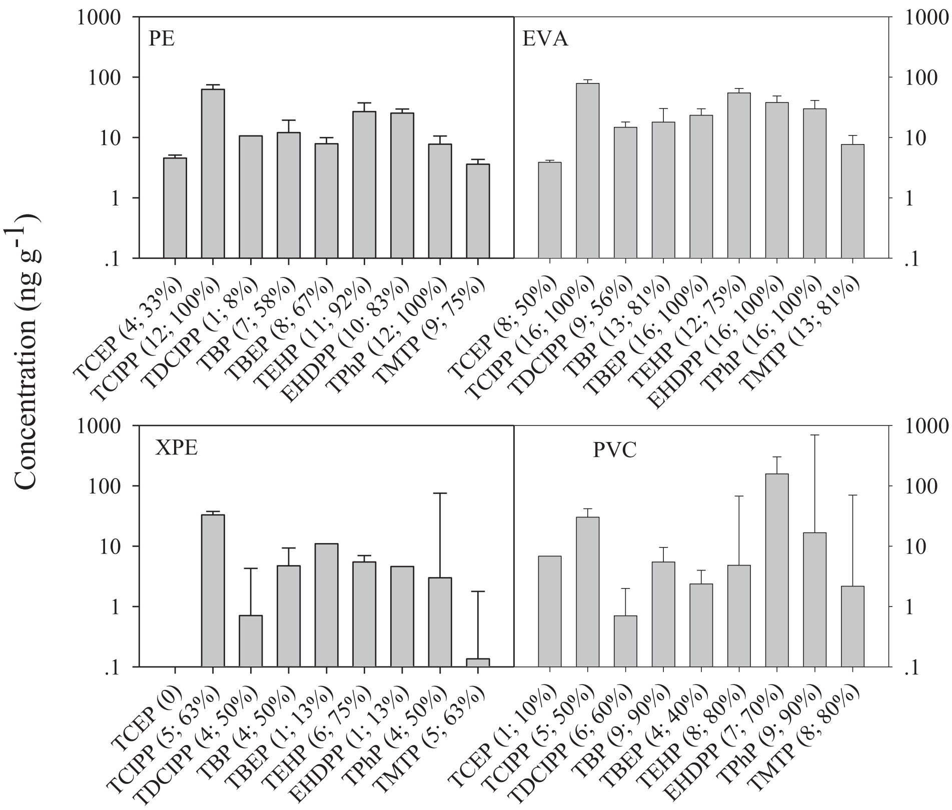

Fig. 3. Compositional profiles of OPEs represented by concentrations (median ± standard error) of individual congener in polyethylene (PE), ethylene–vinyl acetate copolymer (EVA), chemical crosslinked polyethylene (XPE), and polyvinyl chloride (PVC) play mats. The left plots share the left y-axis concentration scales, and the right plots follow the right y-axis scales.

dusts from the U.S. (Kim et al., 2019). In general, children's exposures to flame retardants via dermal contact were lower than those via inhalation (16–37 and 350–600 pg (kg b.w.)$^{-1}$ day^{-1} for PBDEs and OPEs, respectively). This is in contrast to the finding in a skin wipe study (Liu et al., 2017), which obtained much higher dermal exposure than inhalation.

The emission from play mats resulted in a median concentration of 19 pg m^{-3} for PBDEs, which was at the lower end of PBDE levels in indoor air of Guangzhou (0.30–11,000 pg m^{-3}) (Chen et al., 2008) and Hangzhou (0.30–5,700 pg m^{-3}) (Sun et al., 2016). The median daily exposures of total PBDEs via inhalation were 6.7–9.2 pg (kg b.w.)$^{-1}$ day^{-1} for the four groups of children (Table 1), one order of magnitude lower than those from toys (32.7–122 pg (kg b.w.)$^{-1}$ day^{-1}) (Chen et al., 2009), and two orders of magnitude lower than inhalation exposures estimated based on indoor air of Guangzhou (30–6640 pg (kg b.w.)$^{-1}$ day^{-1}) (Chen et al., 2009) and Hangzhou (2600 pg (kg b.w.)$^{-1}$ day^{-1}) (Sun et al., 2016). The median air concentration of OPEs (300 pg m^{-3}) resulted from the emission of play mats was far below those measured in in indoor air from Germany (3300–751,000 pg m^{-3}) (Zhou et al., 2017), Australia (7200–760,000 pg m^{-3}) (He et al., 2018), the U.S. childcare centers (32,000–92,000 pg m^{-3}) (Stubbings et al., 2018), and Beijing, China (1000–20,000 pg m^{-3}) (Cao et al., 2019). Inhalation exposures of OPEs (110–150 pg (kg b.w.)$^{-1}$ day^{-1}; Table 1) from play mats were much lower than those via indoor air from Australia (7000 pg (kg b.w.)$^{-1}$ day^{-1}) (He et al., 2018), Sweden (200–390,000 pg (kg b.w.)$^{-1}$ day^{-1}) (Marklund et al., 2005), and the U.S. childcare centers (14,000 pg (kg b.w.)$^{-1}$ day^{-1}) (Stubbings et al., 2018).

The above results suggested that children's inhalation exposures of PBDEs and OPEs associated with play mats accounted for a minor proportion of the daily inhalation exposure. Hand-to-mouth exposures were estimated only for children $<$ 3 years as they are more inclined to mouthing than those $>$ 3 years. The median hand-to-mouth exposure to PBDEs (11–26 pg (kg b.w.)$^{-1}$ day^{-1}; Table 1) from play mats were much lower than those from hard plastic toys (8916 and 782 pg (kg b.w.)$^{-1}$ day^{-1} for 3–18 months infants and 1.5–3 years toddlers, respectively) (Chen et al., 2009). In comparison to PBDEs, an increased exposure to OPEs from play mats were observed, with median exposure calculated to be 180–430 pg (kg b.w.)$^{-1}$ day^{-1} (Table 1).

The median total PBDEs exposures combining dermal absorption, inhalation, and hand-to-mouth ingestion were 16–37 pg (kg b.w.)$^{-1}$ day^{-1} for the four groups of children (Table 1). Exposures to PBDEs from play mats were one order of magnitude lower than the dietary exposures via consumption of fish (110–400 pg (kg b.w.)$^{-1}$ day^{-1}) from the Pearl River Delta and via inhalation (230–340 pg (kg b.w.)$^{-1}$ day^{-1}) (Meng et al., 2007). Children's daily exposures to PBDEs from play mats were 5–6 orders of magnitude lower than those via consumption of chicken eggs (520,000–1,400,000 pg (kg b.w.)$^{-1}$ day^{-1}) from an e-waste recycling area (Huang et al., 2018) and via consumption of breast milk (320,000 pg (kg b.w.)$^{-1}$ day^{-1}) (Abdallah and Harrad, 2014). The median daily exposures of OPEs ranged from 270 to 600 pg (kg b.w.)$^{-1}$ day^{-1} (Table 1), comparable to those via dust ingestion and dermal absorption (2150–5310 pg (kg b.w.)$^{-1}$ day^{-1}) (Sun et al., 2019), but three orders of magnitude lower than those via fish consumption (average 98,000 pg (kg b.w.)$^{-1}$ day^{-1}) from the Pearl River Delta (Liu et al., 2019). Clearly, children's exposures to PBDEs and OPEs from play mats were generally lower than those from other exposure sources.

The total exposure to PBDEs and OPEs from play mats were 3–6 orders of magnitude lower than the Reference Dose (RfD) (Table 1), depending on the target compounds. Based on the measured concentrations of PBDEs and OPEs in these play mats, the exposure risk assessment suggested no obvious health concern for children using the play mats under investigation. However, play mats might act as passive samplers and absorb flame retardants while used indoor, thus posing children under higher risks. Given the increasing production and usage of OPEs as flame retardants, efforts should be made to reduce children's exposure as much as possible. Further studies are needed to evaluate the migration of PBDEs and OPEs from various play mats under environmental conditions, to monitor these chemicals in household

Table 1
Children's exposure (pg (kg b.w.)$^{-1}$ day^{-1}) to selected PBDE and OPE compounds via dermal contact, inhalation, hand-to-mouth ingestion, and total exposure.

Age group	RfD	0.5–1 year			1–2 years			2–3 years			3–5 years		
		Mean	Median	95%	Mean	Median	95%	Mean	Median	95%	Mean	Median	95%
Dermal contact													
BDE-47	100 [a]	0.08	0.05	0.16	0.08	0.05	0.15	0.08	0.04	0.15	0.07	0.04	0.14
BDE-99	100[b]	0.07	0.05	0.17	0.07	0.04	0.16	0.06	0.04	0.16	0.06	0.04	0.14
BDE-209	7000[c]	1.1	0.48	2.60	1.0	0.45	2.47	0.98	0.43	2.35	0.91	0.40	2.2
Σ_{20}PBDE[e]		3.7	1.7	11	3.5	1.6	11	3.3	1.6	10	3.1	1.4	9.2
TCIPP	8000[d]	13	10	24	13	10	23	12	9.7	22	11.0	8.92	20
TPhP	7000[d]	150	1.4	386	140	1.3	367	130	1.3	349	120	1.2	320
OPEs[f]		210	29	389	200	27	370	190	26	352	170	24	330
Inhalation													
BDE-47	100	0.26	0.20	0.53	0.19	0.14	0.38	0.26	0.20	0.52	0.19	0.15	0.39
BDE-99	100	0.29	0.20	0.90	0.21	0.15	0.66	0.29	0.20	0.89	0.22	0.15	0.67
BDE-209	7000	5.1	2.3	13	3.7	1.7	9.7	5.0	2.3	13	3.8	1.7	9.9
Σ_{20}PBDE		15	9.2	43	11	6.7	32	15	9.1	43	11	6.8	32
TCIPP	8000	51	42	100	37	31	74	50	42	100	377	31	76
TPhP	7000	200	6.3	670	150	4.6	490	200	6.2	660	150	4.7	500
OPEs		350	150	730	250	110	530	344	145	720	260	110	540
Hand-to-mouth ingestion													
BDE-47	100	1.3	0.73	2.4	1.02	0.59	1.9	0.54	0.31	1.0			
BDE-99	100	1.1	0.71	2.6	0.84	0.57	2.1	0.45	0.30	1.1			
BDE-209	7000	16	7.1	39	13	5.7	31	7.0	3.0	17			
Σ_{20}PBDE		54	26	170	44	21	130	23	11	71			
TCIPP	8000	200	160	360	160	130	290	84	68	160			
TPhP	7000	2210	21	5770	1780	17	4660	950	8.9	3470			
OPEs		3080	430	5810	2480	346	4690	1320	180	2490			
Total (combination of dermal contact, inhalation, and hand-to-mouth ingestion)													
BDE-47	100	1.6	0.97	3.1	1.3	0.78	2.49	0.88	0.55	1.70	0.67	0.42	1.3
BDE-99	100	1.4	0.96	3.6	1.1	0.76	2.89	0.80	0.55	2.2	0.61	0.41	1.6
BDE-209	7000	22	9.86	55	18	7.8	44	13	5.7	32	9.8	4.4	24
Σ_{20}PBDE		73	37	220	59	29	180	42	22	120	32	16	94
TCIPP	8000	260	210	490	210	170	390	150	120	280	110	91	210
TPhP	7000	2550	29	6830	2070	23	5510	1280	16	3490	970	12	2650
OPEs		3630	600	6930	2930	480	5590	1850	360	3560	1410	270	2710

[a] Reference dose (RfD) value was cited from IRIS, U.S. EPA (2008a).
[b] Reference dose (RfD) value was cited from IRIS, U.S. EPA (2008b).
[c] Reference dose (RfD) value was cited from IRIS, U.S. EPA (2008c).
[d] Reference dose (RfD) values were calculated by Van den Eede et al. (2011).
[e] Σ_{20}PBDE is the sum of BDE-7, 15, 17, 28, 47, 99, 100, 119, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209.
[f] OPEs is the sum of TCEP, TCIPP, TDCIPP, TBP, TBEP, TEHP, EHDPP, TPhP, and TMTP.

products, especially children's products. Moreover, previously unrecognized flame retardants have been continuously identified, such as 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) (Guo et al., 2018), tri(2,4-di-t-butylphenyl) phosphate (TDTBPP) (Venier et al., 2018), and resorcinol bis(diphenyl phosphate) (RDP) (Wu et al., 2018), among others. There is a possibility that other flame retardants that are not included in this study might have been present in the play mats. Thus a wider screening of flame retardants is other need for future research.

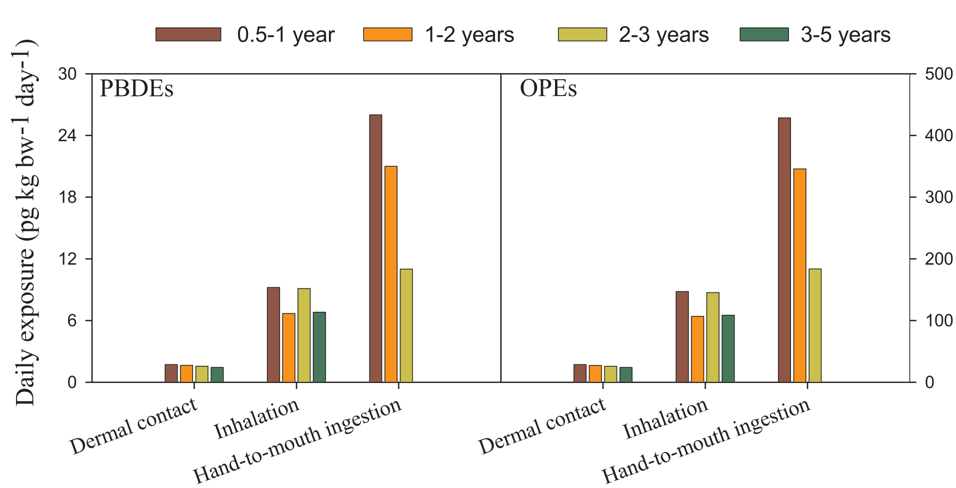

Fig. 4. Children's median daily exposure (pg (kg b.w.)$^{-1}$ day^{-1}) to PBDEs and OPEs from play mats via dermal contact, inhalation, and hand-to-mouth ingestion. The plot for PBDEs exposure follows the left y-axis concentration scales, and the plot for OPEs exposure follows the right y-axis scales.

4. Conclusions

The present study comprehensively determined the occurrences of PBDEs and OPEs in four types (PE, EVA, PVC, and XPE) of children's play mats from China. PBDEs and OPEs were frequently detected in all types of play mats, except for XPE mats, demonstrating the ubiquity of these chemicals. XPE mats contained the lowest concentrations of PBDEs and OPEs. The concentrations of PBDEs and OPEs in children's play mats were at the lower end of those from other exposure sources. Occurrences of PBDEs and OPEs in the four types of children's play mats from China were most probably resulted from raw material, e.g. recycled plastics, of the consumer products. The recycled content for the future products might differ from those for the nowadays products, probably resulting in different contamination. Children's combined exposures from play mats via dermal contact, inhalation, and hand-to-mouth ingestion did not suggest an obvious health concern with regard to PBDEs and OPEs. But the outcomes might be worse if cumulative exposure from other FRs containing household products are taken into consideration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The present study was financially supported by the National Natural Science Foundation of China (Nos. 21607057 and 21577142) and Guangdong Innovative and Enterpreneurial Research Team Program (No. 2016ZT06N258).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105348.

References

Abdallah, M.A.-E., Harrad, S., 2014. Polybrominated diphenyl ethers in UK human milk: implications for infant exposure and relationship to external exposure. Environ. Int. 63, 130–136.
Alaee, M., Arias, P., Sjödin, A., Bergman, Å., 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.
Andresen, J.A., Grundmann, A., Bester, K., 2004. Organophosphorus flame retardants and plasticisers in surface waters. Sci. Total Environ. 332, 155–166.
Araki, A., Saito, I., Kanazawa, A., Morimoto, K., Nakayama, K., Shibata, E., Tanaka, M., Takigawa, T., Yoshimura, T., Chikara, H., Saijo, Y., Kishi, R., 2014. Phosphorus flame retardants in indoor dust and their relation to asthma and allergies of inhabitants. Indoor Air 24, 3–15.
BfR, 2012. Introduction to the problems surrounding garment textiles, updated BfR opinion No. 041/2012, July 2012; http://www.bfr.bund.de/cm/349/introduction-to-the-problems-surroundinggarment-textiles.pdf (accessed October 2019).
Boor, B.E., Liang, Y., Crain, N.E., Järnström, H., Novoselac, A., Xu, Y., 2015. Identification of phthalate and alternative plasticizers, flame retardants, and unreacted isocyanates in infant crib mattress covers and foam. Environ. Sci. Technol. Lett. 2, 89–94.
Cao, D.-D., Lv, K., Gao, W., Fu, J., Wu, J., Fu, J.-J., Wang, Y.-W., Jiang, G.-B., 2019. Presence and human exposure assessment of organophosphate flame retardants (OPEs) in indoor dust and air in Beijing, China. Ecotox. Environ. Safe. 169, 383–391.
Carlsson, H., Nilsson, U., Becker, G., Östman, C., 1997. Organophosphate ester flame retardants and plasticizers in the indoor environment: analytical methodology and occurrence. Environ. Sci. Technol. 31, 2931–2936.
Chen, L.-G., Mai, B.-X., Xu, Z.-C., Peng, X.-C., Han, J.-L., Ran, Y., Sheng, G.-Y., Fu, J.-M., 2008. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. Atmos. Environ. 42, 78–86.
Chen, S.-J., Ma, Y.-J., Wang, J., Chen, D., Luo, X.-J., Mai, B.-X., 2009. Brominated flame retardants in children’s toys: concentration, composition, and children’s exposure and risk assessment. Environ. Sci. Technol. 43, 4200–4206.
Chen, W., 2017. A plastic floor mat. http://112.87.52.128:1522/TiffFile/PdfView/3A9CD64F663954A44651ED92FC4A5870B7FB6C82EC1373DD (accessed October 2019). The state intellectual property bureau of the People's Republic of China. China.
Covaci, A., Harrad, S., Abdallah, M.A.E., Ali, N., Law, R.J., Herzke, D., de Wit, C.A., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ. Int. 37, 532–556.
Cristale, J., Hurtado, A., Gómez-Canela, C., Lacorte, S., 2016. Occurrence and sources of brominated and organophosphorus flame retardants in dust from different indoor environments in Barcelona. Spain. Environ. Res. 149, 66–76.
Dishaw, L.V., Powers, C.M., Ryde, I.T., Roberts, S.C., Seidler, F.J., Slotkin, T.A., Stapleton, H.M., 2011. Is the PentaBDE replacement, tris(1,3-dichloro-2-propyl) phosphate (TDCPP), a developmental neurotoxicant? Studies in PC12 cells. Toxicol. Appl. Pharmacol. 256, 281–289.
Fu, L.-F., Du, B.-B., Wang, F., Lam, J.C.W., Zeng, L., Zeng, E.Y., 2017. Organophosphate triesters and diester degradation products in municipal sludge from wastewater treatment plants in China: spatial patterns and ecological implications. Environ. Sci. Technol. 51, 13614–13623.
Giulivo, M., Capri, E., Kalogianni, E., Milacic, R., Majone, B., Ferrari, F., Eljarrat, E., Barceló, D., 2017. Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins. Sci. Total Environ. 586, 782–791.
Guo, J., Stubbings, W.A., Romanak, K., Nguyen, L.V., Jantunen, L., Melymuk, L., Arrandale, V., Diamond, M.L., Venier, M., 2018. Alternative flame retardant, 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine, in an e-waste recycling facility and house dust in North America. Environ. Sci. Techonl. 52, 3599–3607.
Guzzonato, A., Puype, F., Harrad, S.J., 2017. Evidence of bad recycling practices: BFRs in children's toys and food-contact articles. Environ. Sci.: Process. Impacts 19, 956–963.
Harrad, S., Goosey, E., Desborough, J., Abdallah, M.A.-E., Roosens, L., Covaci, A., 2010. Dust from U.K. primary school classrooms and daycare centers: The significance of dust as a pathway of exposure of young U.K. children to brominated flame retardants and polychlorinated biphenyls. Environ. Sci. Technol. 44, 4198–4202.
Hartmann, P.C., Bürgi, D., Giger, W., 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere 57, 781–787.
He, C., Wang, X.-Y., Thai, P., Baduel, C., Gallen, C., Banks, A., Bainton, P., English, K., Mueller, J.F., 2018. Organophosphate and brominated flame retardants in Australian indoor environments: levels, sources, and preliminary assessment of human exposure. Environ. Pollut. 235, 670–679.
Hoffman, K., Butt, C.M., Chen, A., Limkakeng, A.T., Stapleton, H.M., 2015. High exposure to organophosphate flame retardants in infants: Associations with baby products. Environ. Sci. Technol. 49, 14554–14559.
Huang, C.-C., Zeng, Y.-H., Luo, X.-J., Tang, B., Liu, Y.-E., Ren, Z.-H., Mai, B.-X., 2018. Level changes and human dietary exposure assessment of halogenated flame retardant levels in free-range chicken eggs: a case study of a former e-waste recycling site, South China. Sci. Total Environ. 634, 509–515.
Ionas, A.C., Dirtu, A.C., Anthonissen, T., Neels, H., Covaci, A., 2014. Downsides of the recycling process: harmful organic chemicals in children's toys. Environ. Int. 65, 54–62.
IRIS (Integrated Risk Information System), U.S. EPA, 2008a. 2,2',4,4'-Tetrabromodiphenyl Ether (BDE-47). (CASRN 5436-43-1). In: Washington, D.U.E.P.a. (Ed.).
IRIS (Integrated Risk Information System), U.S. EPA, 2008b. 2,2',4,4',5-Pentabromodiphenyl Ether (BDE-99) (CASRN 60348-60-9). In: Washington, D.U.E.P.a. (Ed.).
IRIS (Integrated Risk Information System), U.S. EPA, 2008c. 2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl Ether (BDE-209). (CASRN 1163-19-5). In: Washington, D.U.E.P.a. (Ed.).
Ji, Y.-Q., 2016. Method for manufacturing floor mat. http://www.soopat.com/Patent/201610567784 (accessed October 2019). SooPAT. China.
Kajiwara, N., Noma, Y., Takigami, H., 2011. Brominated and organophosphate flame retardants in selected consumer products on the Japanese market in 2008. J. Hazard. Mater. 192, 1250–1259.
Kim, J.-W., Isobe, T., Muto, M., Tue, N.M., Katsura, K., Malarvannan, G., Sudaryanto, A., Chang, K.-H., Prudente, M., Viet, P.H., Takahashi, S., Tanabe, S., 2014. Organophosphorus flame retardants (PFRs) in human breast milk from several Asian countries. Chemosphere 116, 91–97.
Kim, U.-J., Wang, Y., Li, W., Kannan, K., 2019. Occurrence of and human exposure to organophosphate flame retardants/plasticizers in indoor air and dust from various microenvironments in the United States. Environ. Int. 125, 342–349.
La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used Penta-, Octa-, and Deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 40, 6247–6254.
Langer, S., Fredricsson, M., Weschler, C.J., Bekö, G., Strandberg, B., Remberger, M., Toftum, J., Clausen, G., 2016. Organophosphate esters in dust samples collected from Danish homes and daycare centers. Chemosphere 154, 559–566.
Li, T.-Y., Zhou, J.-F., Wu, C.-C., Bao, L.-J., Shi, L., Zeng, E.Y., 2018. Characteristics of polybrominated diphenyl ethers released from thermal treatment and open burning of e-waste. Environ. Sci. Technol. 52, 4650–4657.
Liu, L.-Y., He, K., Hites, R.A., Salamova, A., 2016. Hair and nails as noninvasive biomarkers of human exposure to brominated and organophosphate flame retardants. Environ. Sci. Technol. 50, 3065–3073.
Liu, L.-Y., Salamova, A., He, K., Hites, R.A., 2015. Analysis of polybrominated diphenyl ethers and emerging halogenated and organophosphate flame retardants in human hair and nails. J. Chromatogr. A 1406, 251–257.
Liu, X.-T., Yu, G., Cao, Z.-G., Wang, B., Huang, J., Deng, S.-B., Wang, Y.-J., Shen, H.-B., Peng, X., 2017. Estimation of human exposure to halogenated flame retardants through dermal adsorption by skin wipe. Chemosphere 168, 272–278.
Liu, Y.-E., Luo, X.-J., Huang, L.-Q., Zeng, Y.-H., Mai, B.-X., 2019. Organophosphorus flame retardants in fish from Rivers in the Pearl River Delta. South China. Sci. Total Environ. 663, 125–132.

Marklund, A., Andersson, B., Haglund, P., 2005. Organophosphorus flame retardants and plasticizers in air from various indoor environments. J. Environ. Monit. 7, 814–819.
Meng, X.-Z., Zeng, E.Y., Yu, L.-P., Guo, Y., Mai, B.-X., 2007. Assessment of human exposure to polybrominated diphenyl ethers in China via fish consumption and inhalation. Environ. Sci. Technol. 41, 4882–4887.
Ni, Y., Kumagai, K., Yanagisawa, Y., 2007. Measuring emissions of organophosphate flame retardants using a passive flux sampler. Atmos. Environ. 41, 3235–3240.
Nilsson, M.S.O.C., 2018. Decabromodiphenyl ether and other flame retardants in plastic waste destined for recycling.
Nose, K., Hashimoto, S., Takahashi, S., Noma, Y., Sakai, S.-I., 2007. Degradation pathways of decabromodiphenyl ether during hydrothermal treatment. Chemosphere 68, 120–125.
Regnery, J., Püttmann, W., Merz, C., Berthold, G., 2011. Occurrence and distribution of organophosphorus flame retardants and plasticizers in anthropogenically affected groundwater. J. Environ. Monit. 13, 347–354.
Ren, X.-H., Lee, Y.J., Han, H.J., Kim, I.S., 2008. Effect of tris-(2-chloroethyl)-phosphate (TCEP) at environmental concentration on the levels of cell cycle regulatory protein expression in primary cultured rabbit renal proximal tubule cells. Chemosphere 74, 84–88.
Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ. Sci. Technol. 38, 127–132.
Salamova, A., Hermanson, M.H., Hites, R.A., 2014. Organophosphate and halogenated flame retardants in atmospheric particles from a European Arctic site. Environ. Sci. Technol. 48, 6133–6140.
Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ. Sci. Technol. 43, 7490–7495.
Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., Webster, T.F., Blum, A., 2011. Identification of flame retardants in polyurethane foam collected from baby products. Environ. Sci. Technol. 45, 5323–5331.
Stubbings, W.A., Schreder, E.D., Thomas, M.B., Romanak, K., Venier, M., Salamova, A., 2018. Exposure to brominated and organophosphate ester flame retardants in U.S. childcare environments: effect of removal of flame-retarded nap mats on indoor levels. Environ. Pollut. 238, 1056–1068.
Su, J.-L., 2016. Production process of floor mat. http://www.soopat.com/Patent/201610689313 (accessed October 2019). SooPAT. China.
Sun, J.-Q., Wang, Q.-W., Zhuang, S.-L., Zhang, A.-P., 2016. Occurrence of polybrominated diphenyl ethers in indoor air and dust in Hangzhou, China: Level, role of electric appliances, and human exposure. Environ. Pollut. 218, 942–949.
Sun, Y., Liu, L.-Y., Sverko, E., Li, Y.-F., Li, H.-L., Huo, C.-Y., Ma, W.-L., Song, W.-W., Zhang, Z.-F., 2019. Organophosphate flame retardants in college dormitory dust of northern Chinese cities: Occurrence, human exposure and risk assessment. Sci. Total Environ. 665, 731–738.
Tilson, H.A., Veronesi, B., McLamb, R.L., Matthews, H.B., 1990. Acute exposure to tris(2-chloroethyl)phosphate produces hippocampal neuronal loss and impairs learning in rats. Toxicol. Appl. Pharmacol. 106, 254–269.
U.S. EPA, 2011. Exposure Factors Handbook, 2011 Edition (Final), (Washington, DC).
van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153.
Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. Environ. Int. 37, 454–461.
Venier, M., Stubbings, W.A., Guo, J., Romanak, K., Nguyen, L.V., Jantunen, L., Melymuk, L., Arrandale, V., Diamond, M.L., Hites, R.A., 2018. Tri(2,4-di- t-butylphenyl) phosphate: a previously unrecognized, abundant, ubiquitous pollutant in the built and natural environment. Environ. Sci. Techonl. 52, 12997–13003.
Washburn, S.T., Bingman, T.S., Braithwaite, S.K., Buck, R.C., Buxton, L.W., Clewell, H.J., Haroun, L.A., Kester, J.E., Rickard, R.W., Shipp, A.M., 2005. Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles. Environ. Sci. Technol. 39, 3904–3910.
Wei, G.-L., Li, D.-Q., Zhuo, M.-N., Liao, Y.-S., Xie, Z.-Y., Guo, T.-L., Li, J.-J., Zhang, S.-Y., Liang, Z.-Q., 2015. Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human exposure. Environ. Pollut. 196, 29–46.
WHO, 1998. Environmental Health Criteria 209: Flame Retardants: Tris(chloropropyl) Phosphate and Tris(2-chloroethyl) Phosphate. Switzerland, Geneva.
Wu, Y., Miller, G.Z., Gearhart, J., Romanak, K., Lopez-Avila, V., Venier, M., 2018. Children's car seats contain legacy and novel flame retardants. Environ. Sci. Technol. Lett. 6, 14–20.
Xue, J.-C., Liu, W.-B., Kannan, K., 2017. Bisphenols, benzophenones, and bisphenol a diglycidyl ethers in textiles and infant clothing. Environ. Sci. Technol. 51, 5279–5286.
Xue, J.-P., Zartarian, V., Moya, J., Freeman, N., Beamer, P., Black, K., Tulve, N., Shalat, S., 2007. A meta-analysis of children's hand-to-mouth frequency data for estimating nondietary ingestion exposure. Risk Anal. 27, 411–420.
Zhou, L.-L., Hiltscher, M., Gruber, D., Püttmann, W., 2017. Organophosphate flame retardants (OPFRs) in indoor and outdoor air in the Rhine/Main area, Germany: comparison of concentrations and distribution profiles in different microenvironments. Environ. Sci. Pollut. Res. 24, 10992–11005.