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Organophosphorus flame retardants and phthalate esters in indoor dust from different microenvironments: Bioaccessibility and risk assessment

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HIGHLIGHTS

- Indoor dust was collected from house, office, dorm, public microenvironments (PME).
- OPFRs/PAEs were 0.01–63.2/5.49–2161 μg g^{-1} with the lowest levels in dorm dust.
- Bioaccessibility was 8.18–54.5%/1.21–81.1% for OPFRs/PAEs.
- No compound pose risk higher than reference dose if considering bioaccessibility.

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ABSTRACT

Incidental ingestion of indoor dust is an important pathway for human exposure to organophosphorus flame retardants (OPFRs) and phthalate esters (PAEs). However, little is known about their bioaccessibility in indoor dust. In this study, indoor dust samples were collected from houses, offices, public microenvironments (PMEs), and university dorms, and physiologically based extraction test (PBET) was used to measure the bioaccessibility of OPFRs and PAEs in these dust samples. Total concentrations of OPFRs in dust samples ranged from 0.01 to 63.2 μg g^{-1}, with significantly lower concentrations in dorm dust (median = 0.30 μg g^{-1}) than those in houses (3.12), offices (5.94), and PMEs (11.6). Total PAEs ranged from 5.49 to 2161 μg g^{-1} with significantly lower concentrations in dorm dust (379 μg g^{-1}) than those in the other three types of dust (767, 515, and 731 μg g^{-1}). When subject to PBET, the bioaccessibility of OPFRs ranged from 8.18% (triphenyl phosphate) to 54.5% (Tris(2-chloroisopropyl) phosphate) for OPFRs, and from 1.21% (di-2-ethylhexyl phthalate, DEHP) to 81.1% (dimethyl phthalate) for PAEs. Estimated exposure doses for adults and infants to OPFRs via dust ingestion were much lower than the reference doses (RfD), but intake dose of DEHP for infants was higher than the RfD of 20 μg kg^{-1} d^{-1}. However, the DEHP intake dose did not exceed the RfD after incorporating bioaccessibility into risk assessment. Our data indicated the importance of considering contaminant bioaccessibility during risk assessment of indoor dust.

1. Introduction

Organophosphorus flame retardants (OPFRs) and phthalate esters (PAEs) were widely used as flame retardants and plasticizers in many household products, including upholstery materials, polyurethane foam (PUF) furniture, polyvinyl chloride (PVC) materials, and personal care products (Rudel et al., 2003; Van der Veen and de Boer, 2012; Brandsma et al., 2013). OPFRs are used as substitutes of polybrominated diphenyl ethers (PBDEs). The global market demand for OPFRs was reported to be 150,000 metric tons in 2010 (Ou, 2011). In China, the demands for OPFRs were expected to increase 15% annually due to its rapid economical development (Ou, 2011). In addition to OPFRs, the global production of plasticizers was ~3.5 million tons a year with more than 80% of

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plasticizers being PAEs (Kubwabo et al., 2013).

OPFRs and PAEs can be released into the environment through volatilization and abrasion during daily use of these household products, and they are frequently detected in indoor dust with high concentrations (Clausen et al., 2003; Stapleton et al., 2009; Takigami et al., 2009; Van den Eede et al., 2011). Information on PBDEs in indoor dust is substantial for many microenvironments, e.g., houses (Yu et al., 2012), offices (Cao et al., 2014a), or hotels (Cao et al., 2014b), while the data about occurrence and composition profiles of OPFRs and PAEs in indoor dust from various microenvironments are rather limited.

It has been indicated that indoor dust play a significant role in human exposure to OPFRs and PAEs due to incidental dust ingestion and high levels of OPFRs and PAEs in indoor dust (Mercier et al., 2011). This is especially important for young children, who have much higher frequency of hand-mouth behavior than adults. Mounting evidence showed that total concentrations of contaminants may overestimate the risk through ingestion (Ehlers and Luthy, 2003). Thus, accurate estimation of OPFR/PAE exposure through dust ingestion needs to measure their bioavailability, i.e., the fraction of OPFRs/PAEs which are absorbed into circulation system. In vivo test can be used to measure bioavailability (Rostami and Juhasz, 2011), but these approaches are ethically challenging, expensive and time consuming. Therefore, simple in vitro methods, which measure the fraction of contaminants that is mobilized in gastrointestinal (GI) solution and is potentially available for uptake into systemic circulation (i.e., bioaccessibility), have been developed (Rodriguez et al., 1999; Ruby et al., 2002; Van de Wiele et al., 2004). So far, limited studies have investigated the bioaccessibility of organic contaminants in indoor dust, including organochlorine pesticides (Wang et al., 2013a) and PBDEs (Yu et al., 2012). However, information about bioaccessibility of OPFRs and PAEs has rarely been reported.

Therefore, the objectives of this study were (1) to investigate the levels of OPFRs and PAEs in indoor dust collected from different microenvironments; (2) to measure bioaccessibility of OPFRs and PAEs in indoor dust using the physiologically based extraction test (PBET), which is one of the most used in vitro methods for organic contaminants (Rostami and Juhasz, 2011); and (3) to estimate the human health risks associated with indoor dust ingestion based on both total and bioaccessible OPFRs/PAEs.

2. Materials and methods

2.1. Chemicals and reagents

Four OPFRs and five PAEs were investigated, including tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and triphenyl phosphate (TPP) for OPFRs, and dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP) and di-2-ethylhexyl phthalate (DEHP) for PAEs. Since one of the main aims of this study is to assess the health risk on the basis of OPFR/PAE bioaccessibility, the selection of these target contaminants is mainly based on their toxicity. For example, the four OPFRs were demonstrated to be neurotoxic, potentially carcinogenic, and endocrine disrupting (e.g., reducing the human semen quality) (Abdallah and Covaci, 2014; Meeker and Stapleton, 2010). Meanwhile, the five PAEs in the current study have been classified by U.S. EPA as the priority pollutants due to their endocrine disrupting effects (Sun et al., 2015). The detailed physicochemical properties of all the OPFRs and PAEs are listed in supporting information as Table S1. Standards of the chemicals were purchased from Aladdin Industrial Corporation (Shanghai, China) and J&K Scientific (Shanghai, China) with purity > 98%. All solvents and chemicals were of HPLC or analytical grade. Stock solutions were prepared in methanol at concentrations of 100–1000 mg L^{-1} for each compound.

2.2. Indoor dust sampling

Indoor dust samples were collected between January 2014 and March 2015 from different microenvironments in Nanjing, China. The office (n = 12) and public microenvironments (PME, n = 7) (3 public laboratories, 1 classroom, 1 lobby, 1 hotel, and 1 supermarket) were collected from different districts in Nanjing. The dust samples were collected from air-conditioner filters (AC dust), which reflects both the indoor air quality and the properties of indoor dust. Therefore, dust samples from AC filters were collected to examine the potential health concerns for people who are working there. In addition, dust samples were collected from 6 houses in Nanjing, and 8 dorms at Nanjing University. Those samples were collected from surface of floor and furniture using a brush (surface dust), which was cleaned by water between samples to avoid cross contamination. Surface dust samples were collected from the houses and dorms since there was insufficient amount of dust on the AC filter. It is expected that young children are probably exposed more to surface dust since they often play on the floor at home while both children and adults are exposed to AC dust, which are suspended in the air.

All the samples were freeze-dried, and sieved through nylon sieve to collect particles less than 150 μm. The dust samples were then stored in aluminum foil at −20 °C until analysis. Total organic carbon (TOC) contents in dust were characterized by element analyzer (vario TOC select, Elementar, Germany) after carbonate carbon was removed by dissolving dust in 0.5 M HCl. The particle size of dust samples was measured by particle size analyzer (Malvern Instruments Ltd. USA) with wet method (dispersion in water).

2.3. Total concentrations of OPFRs and PAEs in indoor dust

Total concentrations of OPFRs and PAEs in dust were extracted based on Guo and Kannan (2011) with slight modifications. Before extraction, dust sample was spiked with deuterated tributyl phosphate (purity = 98–99%, Cambridge Isotope Laboratories, USA) as surrogate to monitor the extraction recovery. An aliquot of dust sample (~0.2 g) was extracted with 20 mL n-hexane in ultrasonic bath (SCOENTZ, SB-800 DTD, China) for 30 min three consecutive times. The extracts were collected after centrifugation at 3000 rpm for 5 min, and filtrated through anhydrous sodium sulfate for dehydration into 150 mL flask bottle. The combined extract was concentrated to near dryness by rotatory evaporator (IKA®RV10, Germany), and then reconstituted in 2 mL n-hexane, which was transferred to 2 mL amber vials through 0.45 mm PTFE filter (ANPEL, China) and stored at −20 °C until analysis. Triplicates were used for each dust sample, and procedural blank was also included.

2.4. Bioaccessibility of OPFRs and PAEs in indoor dust

Bioaccessibility of OPFRs and PAEs in dust samples were measured by PBET according to Ruby et al. (2002) and Tilston et al. (2011). Briefly, ~0.2 g dust sample was added into 20 mL gastric fluid at pH = 2.5, and the solution was shaken at 37 °C in an incubator (HZP-250, China) at 150 rpm. After 1 h, the solution was changed to intestinal fluid by adjusting pH to 7 and adding 0.035 g bile salts as well as 0.01 g pancreatin. Subtle changes of pH values were observed after incubation with values of 3.1 and 7.1 for gastric and intestinal solution. After shaking for 4 h at 37 °C at 150 rpm, the mixture was centrifuged at 3000 rpm for 5 min. An aliquot of 10 mL

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