Environment International 98 (2017) 113–119

Contents lists available at ScienceDirect

Environment International

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

Full length article

Occurrence of organophosphorus flame retardants on skin wipes: Insight into human exposure from dermal absorption

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ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form 20 October 2016
Accepted 20 October 2016
Available online 29 October 2016

Keywords:
Organophosphorus flame retardants
Skin wipes
Dermal absorption
Human exposure

ABSTRACT

This study surveyed occurrences and influencing factors of organophosphorus flame retardants (PFRs) on skin surface. Skin wipe samples from palms, back-of-hands and forearms of 30 adults were collected by using gauze pads soaked in isopropyl alcohol in Beijing, China. Tris(chloropropyl) phosphate isomers (∑TCPP), tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPHP) were the most abundant compounds with detection frequencies higher than 97%. ∑TCPP showed the highest mean level (4.6 μg/m^2), followed by TPHP (2.4 μg/m^2) and TCEP (1.6 μg/m^2). Levels on palms were slightly higher than on back-of-hands, and both were substantially higher than those on forearms. TCEP and ∑TCPP levels were strong reliable in three repeated measurements from 4 participants over a three month period (intraclass correlation of coefficient of 0.91 and 0.95, respectively), while TPHP levels were not. Washing with soap and water removed a large fraction of PFRs on hands with median reduction of 76, 72 and 67% for TCEP, ∑TCPP and TPHP, respectively. Paired dust samples, table surface wipe and hand wipe samples were collected from 17 offices (13 surface wipes and 22 hand wipes) in Beijing. Hand wipe TCEP, ∑TCPP and TPHP were neither correlated with dust samples nor with table surface wipe samples. Two methods were used for dermal exposure assessments. The estimated lower median total exposure from palms, back-of-hands and forearms by the relative absorption method were 0.6, 1.0, 0.3 ng/kg BW-d for TCEP, ∑TCPP and TPHP, respectively. These estimates were in the same range as those via dust ingestion for adults in Beijing, suggesting dermal absorption is likely a significant pathway of human PFR exposure.

1. Introduction

Phosphorus flame retardants (PFRs) emerging as substitute to polybrominated diphenyl ethers have been widely used in a range of products, including textiles, furniture, electronics, baby products, paints and plastics (Marklund et al., 2003; Kajiwara et al., 2011; Stapleton et al., 2011). PFRs can be released into the surrounding environment gradually from all those materials (Kemmlein et al., 2003). Hence, they have been ubiquitously measured in various matrices, including indoor air (Marklund et al., 2005; Yang et al., 2014), outdoor air (Salamova et al., 2014), indoor dust (Cao et al., 2014a, 2014b; Hoffman et al., 2015; Wu et al., 2016b), water (Bollmann et al., 2012) and sediment (Cao et al., 2012). In addition, occurrences of PFRs in human breast milk and their metabolisms in human urine indicate humans are widely exposed to those compounds (Sundkvist et al., 2010; Van den Eede et al., 2015), which may exert adverse health effects. Reproductive toxicity, embryo toxicity and neurotoxicity of tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP) and tris(1, 3-dichloro-2-propyl) phosphate (TDCIPP) were observed in laboratory animals (WHO, 1998). A study showed higher levels of TDCIPP in house dust may associate with higher hormone levels and lower semen quality in males (Meeker et al., 2013). Moreover, TCEP, TDCIPP, TCIPP and tris(2-butoxyethyl) phosphate (TBOEP) are suspected to be carcinogenic (WHO, 1998). Therefore, it is important to know how these ubiquitous chemicals enter into the human body.

Current understandings of human PFR exposure pathways have focused on dust ingestion (Wu et al., 2016a; Zheng et al., 2015; Fromme et al., 2014), inhalation (Yang et al., 2014; Cequier et al., 2014) and diet ingestion (Malarvannan et al., 2015; Ding et al., 2015). Dust ingestion appears to be one of the most significant contributors to PFR body burden (Meeker et al., 2013; Fromme et al., 2014; de Boer et al., 2016). Meanwhile, a few recent studies have raised dermal absorption as a potential significant pathway for PFR exposure. Hoffman et al. (2015) have reported urinary metabolites levels of TDCIPP and triphenyl phosphate (TPHP) were not associated with levels in house dust but with those in hand wipes, indicating hand to mouth or dermal absorption may be important exposure pathways. More recently, a

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http://dx.doi.org/10.1016/j.envint.2016.10.021
0160-4120/

study examined the exposure to TPHP through nail polish application suggests the primary exposure route of TPHP is dermal absorption (Mendelsohn et al., 2016). Furthermore, in vitro skin absorption studies (Abdallah et al., 2016; Hughes et al., 2001) revealed that TCEP, TCIPP and TDCIPP can be absorbed by human or mouse skin with a relatively high fraction. However, to date assessments of dermal exposure for PFRs are quite limited.

There were only two studies assessing PFR intakes via dermal absorption (Cequier et al., 2014; Abdallah et al., 2016) by using PFR levels in household dust. However, PFRs on the skin surface might be a consequence of contact with dust or FR-treated consumer products, deposition of particles and penetration of air from more than one microenvironment (Keller et al., 2014; Wu et al., 2016a). Wipe method is an effective removal procedure for direct assessment of dermal exposure accomplished by measuring concentrations of contaminants in the skin surface (USEPA, 1998). However, there is only one recent publication (Xu et al., 2016) examining the magnitude of PFR uptakes from dermal absorption by using this method. Furthermore, to date, no studies have examined the temporal variability, variation at different skin locations, and the influence of washing on skin PFRs. Such information is needed not only for better understanding the sources and characteristics of PFRs on the skin surface, but also for standardizing methods for skin wipes collection in the future (Stapleton et al., 2012).

Hence, the objectives of the this study are: (1) to explore levels and profiles of PFRs on skin surface, (2) to examine factors that may influence PFR levels on skin surface, and (3) to assess exposure of target PFRs via dermal absorption and to compare with that from other methods or via other pathways. This study fills the gap of the magnitude of PFR dermal exposure based on the skin surface levels and provides information for determining critical pathways for subsequent risk assessment of human PFR exposure.

2. Materials and methods

2.1. Participants

There were two groups of participants. One group (skin wipe sample group) was recruited from students or staffs in the School of Environment, Tsinghua University, and thirty-six (18 females and 18 males) individuals were selected. A second group (paired sample group, n = 22) was recruited to provide hand wipe sample and paired dust sample from their offices in Beijing. All participants were required not to wash hands and arms at least 1 h prior to sampling and not to do any chemical experiments in lab at least one week before sampling. Participants in the second group were required to stay in their office at least 5 h before sampling. Participants were also asked to fill out a simple questionnaire about age, gender, height, weight, activities before sampling, average daily working time with computer, last time to wash hands prior to sampling, and whether using any skincare products at the wipe parts (see Table S1 in supplementary material). All participants were required to give informed consent prior to providing samples and information.

2.2. Sample collection

Skin wipe samples were collected by one investigator in the laboratory from September to December 2015. In brief, sterile gauze pads (7.5 cm * 7.5 cm) were cleaned by an ultrasonic bath for 30 min with *n*-hexane/acetone (3/1, v/v), dried in a vacuum desiccator, and immersed in 4 mL of isopropyl alcohol (reagent grade) in a 60 mL cleaned (combusted at 450 °C for 6 h) brown glass jar. For each participant, the entire skin surface was wiped over two times using one surface of a gauze pad, and then wiped two additional times using the other side. Gauze pads were then put back into the same brown glass jar and spiked with two internal standards: triaryl phosphate (TAP) and triphenyl phosphate-d_{15} (TPHP-d_{15}) immediately and stored at −20 °C until analysis.

Thirty (15 males and 15 females) individuals were taken samples from their left and right palms, left and right backs-of-hands and left and right forearms. Wipes from left and right skin locations were stored and analyzed together, except that samples collected from left and right sides of six participants were analyzed separately. To examine the temporal variability, we took three repeated samples from 4 participants in three months. To investigate the effect of hand washing, another six participants (3 males and 3 females) were asked to take samples at one hand before-washing, and the other hand after-washing, and switched the next day. When washing, the participants were asked to use a hand sanitizer and rinse under flowing water at least 30 s. Field blanks were taken to examine potential background by soaking two gauze pads with ~8 mL isopropanol in a brown glass jar and then taking out for ~10 s and putting back into the jar. The surface area of sampled palms and back-of-hands was roughly estimated by drawing the hand shape in Cartesian graph papers. While for forearms, perimeter of each section of arms were measured by a fixed-width measurement tape and the total product of perimeter and width was taken as the surface area.

Paired samples were collected from March to May in 2016 from 17 offices in Beijing. Both palms and back-of-hands from 22 participants were taken by using the same procedures described before (in 5 offices, 2 participants in the same office were selected). After taken hand wipe samples, a commercial vacuum cleaner with a 25 mm nylon sampling sock (Guangzhou Qi Xin Filter Ltd., China) was used to vacuum floor dust in the main area of their offices. Surface wipe samples of some participants (n = 13) were taken by using soaking gauze pads wiped over the surface of main area of participants' tables. The sampled areas of table surface were measured by using tapes. Dust samples were then sieved to <50 μm through a stainless steel sieve in the laboratory and stored in 30 mL brown glass vials in −20 °C until analysis.

2.3. Sample analysis

A total of 10 PFRs triethyl phosphate (TEP), tri-*n*-propyl phosphate (TPP), tri-isobutyl phosphate (TIBP), tri-*n*-butyl phosphate (TNBP), tricresyl phosphate isomers (∑TMPP, mixture of 4 isomers), tris(chloropropyl) phosphate isomers (∑TCPP, mixture of 3 isomers), TBOEP, TCEP, TDCIPP, and TPHP were analyzed. Standards of all compounds were purchased from Chiron AS (Trondheim, Norway) except that standard of ∑TCPP was purchased from Pfaltz & Bauer (Waterbury, CT, USA). TAP (TCI Europe, Zwijndrecht, Belgium) was used as a surrogate standard for TEP, TPP, TIBP, TNBP, ∑TCEP, TCPP and TBOEP, while TPHP-d_{15} (Chiron AS, Trondheim, Norway) was used for TDCIPP, TPHP and ∑TMPP, respectively. Decachlorobiphenyl (Accustandard, CT, USA) was employed as a recovery standard for quantification of TAP and TPHP-d_{15}. All standards were dissolved in trimethylpentane (J.T. Baker, PA, USA).

The analytical method for wipe and dust samples was based on the one developed by Van den Eede et al. (2012). Gauze pads were firstly extracted with 30 mL *n*-hexane/acetone (3/1, v/v) in an ultrasonic bath for three times (10 min for each). About 50 mg dust was extracted by using ultrasonic with 2.5 mL *n*-hexane/acetone (3/1, v/v) for three times. The combined supernatant was then concentrated by rotary evaporators and/or nitrogen evaporation system to near dryness and re-solubilized in 1 mL of *n*-hexane. Clean-up process of extract was further performed on Florisil solid phase extraction (Supelclean ENVI-Florisil, 6 mL, 500-mg bed weight; Supelco). The cartridge was preconditioned with 8 mL ethyl acetate and 6 mL hexane in turn, then eluted with 10 mL *n*-hexane/dichloromethane (2:1, v/v) mixture followed by 10 mL ethyl acetate for wipe samples (for dust sample 10 mL hexane followed by 10 mL ethyl acetate). The second fraction was dried using a nitrogen concentration system and re-solubilized in 100 μL of a recovery standard and transferred to an auto sampler vial for gas chromatography–mass spectrometry (GC–MS). Information