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Detection and intake assessment of organophosphate flame retardants in house dust in Japanese dwellings

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HIGHLIGHTS

- We sampled dust from dwellings in which elementary school children were living.
- A high level of TBOEP was detected in Japanese dwellings.
- TBOEP concentration was related to several dwelling environments.
- TBOEP levels of intake assessment are well below the RfD values.

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ABSTRACT

The demand for phosphorus flame retardants (PFRs) has recently increased as an alternative to polybrominated diphenyl ether (PBDE). PFRs have been detected in house dust, but little is known about the concentrations of PFRs in private homes and the effects on human health. We measured the levels of 10 PFRs in indoor floor dust and upper surface dust from 128 Japanese dwellings of families with children in elementary school. The median (min–max) concentrations (μg/g) of PFRs were as follows: tris(2-butoxyethyl) phosphate (TBOEP), 30.88 (<0.61–936.65); tris(2-chloro-*iso*-propyl) phosphate (TCIPP), 0.74 (<0.56–392.52); and triphenyl phosphate (TPHP), 0.87 (<0.80–23.35). These values exceeded 50% detection rates, and the rates are median over the LOD in floor dust. The concentrations (μg/g) of TBOEP 26.55 (<0.61–1933.24), TCIPP 2.23 (<0.56–621.23), TPHP 3.13 (<0.80–27.47), tris(2-chloroethyl) phosphate (TCEP) 1.17 (<0.65–92.22), and tributyl phosphate (TNBP) 0.74 (<0.36–60.64) exceeded 50% detection rates in the upper surface dust. A significant positive correlation ($P < 0.05$) between the concentrations of TCIPP and TBOEP was shown in floor dust and upper surface dust ($n = 48$). Estimated median and 95th percentile daily intake was calculated for toddlers and elementary school children and was compared with reference dose values (RfD) from the literature. For TBOEP, the estimated 95th percentile intake from floor dust was 14% of RfD for toddlers and 4% for school children. The estimated intake from upper surface dust was somewhat lower. Estimated median intake of TBOEP and median intake for the other PFRs were less than 1% of the RfD. TBOEP, TCIPP and TPHP were the main PFRs in the dust. The median levels of PFRs are well below the RfD values.

1. Introduction

Phosphorus flame retardants (PFRs) are used as additives to flame retardants and plasticizers and are found in a variety of products. For example, tributyl phosphate (TNBP, CAS number 126-73-8), tris(2-chloroethyl) phosphate (TCEP, 115-96-8), tris(2-chloro-*iso*-propyl) phosphate (TCIPP, 6145-73-9), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP, 13674-87-8), and triphenyl phosphate (TPHP, 115-86-6) are used as flame retardants in polyurethane foam, thermoplastics, resins, polyvinyl chloride, synthetic rubbers, and textiles (Meeker and Stapleton, 2010). Trimethyl phosphate (TMP, 512-56-1) and triethyl phosphate (TEP, 78-40-0) are used as flame retardants in rigid urethane foam (Daihachi Chemical Industry Co, Ltd.,2013). TNBP, TPHP, and tricresyl phosphate (TMPP, 1330-78-5) are also used as lubricants, and tris(2-butoxyethyl) phosphate (TBOEP, 78-51-3) is often used in floor wax and plasticizers (WHO, 2000). Polybrominated diphenyl ethers

Abbreviations: LOD, limit of detection; PBDEs, polybrominated diphenyl ethers; PFRs, phosphorus flame retardants; PVC, polyvinyl chloride; RfD, reference dose; TBOEP, tris(2-butoxyethyl) phosphate; TCEP, tris(2-chloroethyl) phosphate; TCIPP, tris(2-chloro-*iso*-propyl) phosphate; TDCIPP, tris(1,3-dichloro-2-propyl) phosphate; TEP, triethyl phosphate; TEHP, tris(2-ethylhexyl) phosphate; TMP, trimethyl phosphate; TMPP, tricresyl phosphate; TNBP, tributyl phosphate; TPHP, triphenyl phosphate.

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(PBDEs) are some of the most extensively used flame retardants; Penta- and Octa-BDE were banned by the European Union in 2003, and their use has voluntarily decreased in the United States as well (van der Veen and de Boer, 2012) because of bioaccumulation (Covaci et al., 2007). In Japan, because PBDEs are being phased out, an increasing number of PFRs and alternative brominated flame retardants are being used (Kajiwara et al., 2011). TCEP, TCIPP, and TDCIPP are used as replacements for penta-BDE (Dodson et al., 2012). The presence of PFRs in indoor dust has been reported in Belgium (Van den Eede et al., 2011), Germany(Brommer et al., 2012), Romania(Dirtu et al., 2012), Spain (Garcia et al., 2007), Sweden (Bergh et al., 2011), the United States (Dodson et al., 2012), New Zealand (Ali et al., 2012a), Japan (Kanazawa et al., 2010), Pakistan (Ali et al., 2012b), and the Philippines (Kim et al., 2013). Concentrations of PFRs in indoor dust have been higher than concentrations of PBDEs in recent years (Ali et al., 2012b; Saito et al., 2007; Stapleton et al., 2012).

Only limited reports have been published on the effects of PFRs on human health. TCEP and TDCIPP are carcinogenic in animals, and TCIPP and TBOEP are possible carcinogens (WHO 1998, 2000). TCEP has toxic effects on fetal development in mice (Chapin et al., 1997). In animal experimental studies, TBOEP, TCEP, tris(2-ethylhexyl) phosphate (TEHP, 78-42-2), and TDCIPP caused mild irritation to the skin of rabbits (Leisewitz et al., 2000; WHO, 1991b; WHO, 1998; WHO, 2000). TNBP irritates the skin and eyes of humans (WHO, 1991a). One case clinical report described contact dermatitis from exposure to TPHP. The patients had a 6-month history of an itchy fissured psoriasiform dermatitis of both palms. Results of patch test, showed positive to TPHP (Camarasa and Serra-Baldrich, 1992). In epidemiological studies, TDCIPP showed a statistically significant negative association with free thyroxin T4 (Meeker and Stapleton, 2010). Free thyroxin T4 is one of the thyroid function indicator. Increases in TCIPP and TDCIPP concentrations were associated with an increase in the risk of atopic dermatitis, and increases in TNBP concentrations were associated with an increase in the risk of asthma and allergic rhinitis (Araki et al., 2013).

PFRs are known to adsorb to settled dust (Wensing et al., 2005). Over the past 10 years, there has been considerable interest in the exposure of vulnerable groups, such as infants, toddlers, and pregnant women, to PFRs to assess the impact on human health related with the indoor environment. Initially, interest in chemicals in indoor environments focused primarily on irritant and toxic properties of individual chemicals (Mercier et al., 2011; Mitchell et al., 2007) and reduce the identified human health risk of poor indoor environment particularly among children (Mercier et al., 2011). As a result, settled dust has been considered an exposure medium (Lioy et al., 2002; Mercier et al., 2011) particularly for infants and toddlers, who are at highest risk for exposure because of frequent hand-to-mouth activities. In addition, elementary school students are considered a high-risk group for exposure to house dust because their body weight is lower and they spend more time at home than adults. In recent years (Ali et al., 2012a; Brommer et al., 2012; Stapleton et al., 2009; Van den Eede et al., 2011), studies have shown that intake (both inhaled dust and eaten dust) to PFRs from dust is 2.5 (mean intake) to 4.0 (high intake) times higher for children than for adults.

Higher PFR concentrations have been detected in Japan than in any other country in previous studies (Araki et al., 2013; Kanazawa et al., 2010). However, these studies investigated only new (building age of 3 to 8 years) detached houses. Moreover, there might be differences in use of consumer products, which could be sources of PFRs, between houses with only adult inhabitants and families with young children.

Therefore, the aims of this study were to determine the concentrations of PFRs in indoor floor dust and upper surface dust in houses of families with children in elementary school and to estimate the intake of toddlers and children to PFRs via ingestion of dust in Japan.

2. Method

2.1. Participants and target

In this study, we focused on children in elementary school, because most Japanese children attend public school. Therefore, we could expect participation from wide social class.

This study was conducted in 2 phases: a baseline questionnaire in 2008 and a questionnaire, environmental measurements, and a building investigation survey in 2009 and 2010. Selection of the participants was previously reported (Ukawa et al. 2013). Briefly, the families of all 6393 schoolchildren from 12 public elementary schools in Sapporo were asked to participate in the study, and the families of 4408 children responded to the questionnaire (response rate of 69.0%). In total, 832 families (951 children) agreed to allow a home visit to conduct environmental measurements. In 2009 and 2010, we contacted the families of children who were still attending the same elementary school as in 2008, excluding those who did not provide information on the baseline questionnaire regarding the children's gender, grade, or presence of sick house syndrome. This selection procedure identified 128 families who allowed home visits for environmental measurements, dust collection, and completion of a questionnaire in October and November of 2009 or 2010 (Ait Bamai et al., 2014). We visited 128 homes but more than 128 allowed home visits. If participants permitted our visiting their homes, we were not able to adjust schedule in some cases by double-booking, because we collected the dust samples ourselves.

School buildings in which children were going were investigated by the questionnaire. Among 12 school, one school was excluded because of being a provisional school building.

2.2. Questionnaire

The investigators who visited each dwelling distributed and collected questionnaires for the parents to complete. The questionnaire included queries about the dwelling environment, such as the building structure, age of the building, years of residence, renovations, floor materials, carpet use, and ventilation. One question asked how often the living room floor was cleaned (times/week), and the answers were either (1) 4 times or more or (2) 3 times or less per week.

2.3. Environmental measurements

Indoor environmental measurements were performed in all 128 dwellings by well-trained investigators in a main living room where all children commonly spent most of their time. We observed the living room circumstances such as wall materials, floor materials and using electric devices. The Thermo Recorder TR-72U (T&D Corporation, Nagano, Japan) was used to monitor the room temperature and relative humidity in each house for 48 h.

Dust samples were collected by using a previously reported strategy (Kanazawa et al., 2010). Briefly, dust samples were categorized as either floor dust or upper surface dust. Samples of floor dust were collected from the floor surface (floor dust) and from objects within 35 cm above the floor by vacuuming of surface for 2 min per 1 m^2 floor area. Floor dust and upper surface dust were collected in the whole room because we needed enough dust samples to analyze PFRs concentrations by GC/MS. We vacuumed the whole floor except the furniture which is fixed or too heavy to move. Therefore, the square measure of sampling area was different with each home. Table 1 showed average and standard deviations. After vacuuming, sampling area was measured. Samples of upper surface dust were collected from objects more than 35 cm above the floor such as furniture, electrical devices, bay window, curtain rail and so on. The vacuum cleaners were with the same power used in this study, because quantity of the dust is affected by the power of the vacuum cleaner. The same type of hand-held vacuum cleaner (National HC-V15, Matsushita Electric Works, Ltd., Osaka, Japan)