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Organophosphate esters in dust samples collected from Danish homes and daycare centers

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HIGHLIGHTS

- Organophosphates were determined in dust from 497 homes and 151 daycare centers.
- Mass fractions in dust from daycare centers were larger than in dust from homes.
- Estimated exposures to organophosphates via dust ingestion were relatively low.
- The country-to-country distribution of organophosphates is more variable than that of phthalate esters.

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ABSTRACT

Organophosphates are used in a wide range of materials and consumer products and are ubiquitous in indoor environments. Certain organophosphates have been associated with various adverse health effects. The present paper reports mass fractions of organophosphates in dust samples collected from 500 bedrooms and 151 daycare centers of children living in Odense, Denmark. The identified compounds include: tris(isobutyl) phosphate (TIBP), tri-*n*-butyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenylphosphate (TPHP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate (TMPP). Both the number of organophosphates with median values above the limit of detection and the median values were higher for samples from daycare centers than for samples from homes. Organophosphates with median mass fractions above the limit of detection were: TCEP from homes (6.9 μg g^{-1}), and TCEP (16 μg g^{-1}), TCIPP (5.6 μg g^{-1}), TDCIPP (7.1 μg g^{-1}), TBOEP (26 μg g^{-1}), TPHP (2.0 μg g^{-1}) and EHDPP (2.1 μg g^{-1}) from daycare centers. When present, TBOEP was typically the most abundant of the identified OPs. The sum of the organophosphate dust mass fractions measured in this study was roughly in the mid-range of summed mass fractions reported for dust samples collected in other countries. On a global scale, the geographical distribution of organophosphates in indoor dust is quite variable, with higher concentrations in industrialized countries. This trend differs from that for phthalate esters, whose geographic distribution is more homogeneous. Exposure to organophosphates via dust ingestion is relatively low, although there is considerable uncertainly in this assessment.

1. Introduction

Semivolatile organic compounds (SVOC) are ubiquitous in indoor environments, and, depending on their chemical properties, can persist for a very long time (Weschler and Nazaroff, 2008; Shin

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et al., 2013). Indoor SVOCs commonly include organophosphate triesters. The use of the organophosphates is increasing because of their favorable properties as both flame retardants and plasticizers (Marklund et al., 2003). The halogenated organophosphates are mostly used as flame retardants while the non-halogenated compounds are generally used as plasticizers (Andresen et al., 2004). Organophosphorus flame retardants are found in a wide range of commercial products including textiles, rubber, polyurethane foam (PUF), antistatic formulations, cellulose, cotton, cutting oils, electronic equipment, glues, engineering thermoplastics, epoxy resins and phenolic resins (Marklund et al., 2005). Polyvinyl chloride (PVC) is an example of a product where phosphorus flame retardants also function as plasticizers (Marklund et al., 2003).

Organophosphates have been implicated in various adverse health effects, including skin irritation and contact dermatitis in humans, and neurological and carcinogenic effects in rats (WHO, 1991a,b, 1998; 2000). Araki et al. (2014) have recently found associations between organophosphates flame retardants and atopic dermatitis, asthma and allergic rhinitis. Organophosphates have also been associated with altered hormone levels and decreased semen quality in men (Meeker and Stapleton, 2010).

The widespread use of organophosphates in everyday products results in redistribution from their original source into other indoor compartments, including indoor air, airborne particles, settled dust and all exposed indoor surfaces (e.g. Marklund et al., 2005; Wensing et al., 2005). They were first reported in indoor airborne particles in 1980 (Weschler, 1980). Their concentrations have been found to be much higher indoors than outdoors, reflecting the much greater presence of their sources indoors compared to outdoors (Weschler, 1984; Staaf and Östman, 2005; Wensing et al., 2005). The mass fractions of various organophosphates in settled dust have been determined over the past 14 years in samples collected from homes, daycare centers and workplaces in various countries throughout the world (Brommer and Harrad, 2015; He et al., 2015; Hoffman et al., 2015; Luongo and Östman, 2015; Abdallah and Covaci, 2014; Araki et al., 2014; Cequier et al., 2014; Fan et al., 2014; Fromme et al., 2014; Shin et al., 2014; Tajima et al., 2014; Ali et al., 2013; Brommer et al., 2012; Kim et al., 2013; Dodson et al., 2012; Ali et al., 2012a,b; Bergh et al., 2011; Van den Eede et al., 2011; Dirtu et al., 2012; Kanazawa et al., 2010; Meeker and Stapleton, 2010; Stapleton et al., 2009; García et al., 2007; Wensing et al., 2005; Marklund et al., 2003; Nagorka and Ullrich, 2003; Kersten and Reich, 2003; Becker et al., 2002; Ingerowski et al., 2001). Human exposure to organophosphates is apparent from biomonitoring studies, which have detected various organophosphate metabolites in urine samples (e.g., Reemtsma et al., 2011; Fromme et al., 2014; Hoffman et al., 2014). A recent study found that levels of such metabolites in urine correlated with levels of organophosphates in dust, and that children's exposure to organophosphates can be related to levels found in their indoor environments (Cequier et al., 2015).

The aim of the present paper is threefold: to report the mass fractions of selected organophosphate esters (OPEs) measured in the dust samples collected from children's bedrooms (n = 500) and daycare centers (n = 151) as part of the IECH investigation; to examine potential correlations between levels of the individual organophosphates, both in the children's bedrooms and daycare facilities; and to compare the results with those reported in other studies to derive a sense of variations over geographic location and time. The information presented in this paper can be used to improve understanding of Danish children's exposure to organophosphate esters.

2. Material and methods

2.1. Study design

The Danish study "Indoor Environment and Children's Health (IECH)" has investigated the relationship between children's health and their indoor environments. The design of the IECH study and the methods used in the investigations have been described by Clausen et al. (2012). Questionnaires were sent to 17,486 families that had children between the ages of one and five. All children in the study lived on the Danish island of Fyn (482,310 inhabitants). The final database contained questionnaires from 11,082 children, *i.e.* the response rate was 63%. Using the information from the survey, 500 children between the ages of three and five and living in Odense (166,000 inhabitants) were selected for the case-base study: 200 "cases" with asthma/allergies and 300 randomly selected "bases", *i.e.* both healthy and sick children. All of the daycare facilities attended by these children were also included in the study (n = 151). Settled dust was collected from the children's bedrooms from non-floor surfaces such as shelves, ledges, and window sills as well as from horizontal non-floor surfaces in the daycare centers. Dust from floors was avoided, since it may be contaminated by direct contact with organophosphorus flame retardants or plasticizers present at the surfaces of flooring materials that contain these additives. The dust samples were subsequently analyzed for five phthalate esters and three polycyclic aromatic hydrocarbons (Langer et al., 2010) as well as for squalene and cholesterol (Weschler et al., 2011).

2.2. Dust collection

Dust was collected from non-floor surfaces in the children's bedrooms and daycares using ALK dust filters (ALK-Abelló A/S, Hørsholm, Denmark) mounted in a holder connected to a vacuum cleaner. Collection of dust from plastic surfaces and textiles was avoided. In 5% of the homes (randomly chosen) a field blank was obtained (filter was mounted in the holder but no sampling was performed).

2.3. Chemical analysis

Prior to sampling, the virgin filters were pre-conditioned at a temperature of 23 ± 1 °C and relative humidity of 50± 5%, weighed and assigned an ID number. The loaded filters or blanks were returned to the laboratory (shipped at ambient temperature) where they were conditioned, weighed, wrapped in aluminum foil and repacked in their original bag. The net dust mass on the loaded filters ranged from 43 to 1396 mg (average 198 mg; median 160 mg). Of the total number of more than 700 filters that were analyzed, 33 (~5%) were field blanks, and 42 were laboratory blanks.

The organic compounds in the dust were extracted using the procedure described by Rudel et al. (2003). Logistics and details of the chemical analysis are presented in the Supplementary Material.

The organophosphate esters evaluated in this study, in order of retention times, were: tris(isobutyl) phosphate (TIBP), tri-*n*-butyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloroisopropyl) (TDCIPP), tris(2-butoxyethyl) phosphate (TBOEP), triphenylphosphate (TPHP), 2-ethylhexyl-diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tris(methylphenyl) phosphate (TMPP). The compounds were named and abbreviated according to the nomenclature proposed by Bergman et al. (2012).

The original target compounds in these dust samples were phthalate esters and polycyclic aromatic hydrocarbons (Langer