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Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust

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ABSTRACT

A new and efficient analytical method was developed and validated for the analysis of organophosphorus flame retardants (OPFRs) in indoor dust samples. This method involves an extraction step by ultrasonication and vortex, followed by extract clean-up with Florisil solid-phase extraction cartridges and analysis of the purified extracts by gas chromatography-mass spectrometry (GC–MS). Method recoveries ranged between 76 and 127%, except for volatile OPFRs, such as triethyl phosphate (TEP) and tri-(*n*-propyl) phosphate (T*n*PP), which were partially lost during evaporation steps. The between day precision on spiked dust samples was <14% for individual OPFRs, except for TEP, tri-*iso*-butyl phosphate (T*i*BP) and tri (2-butoxyethyl) phosphate (TBEP). Method limit of quantifications (LOQ) ranged between 0.02 μg/g (T*n*PP and tris(1-chloro-2-propyl phosphate (TCPP)) and 0.50 μg/g (T*i*BP). The method was further applied for the analysis of indoor dust samples taken from Flemish homes and stores. T*i*BP, TBEP and TCPP were most abundant OPFR with median concentrations of 2.99, 2.03 and 1.38 μg/g in house dust and of 1.04, 3.61, and 2.94 μg/g in store dust, respectively. The concentration of all OPFRs was at least 20 to 30 times higher compared to polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Estimated exposure to OPFRs from dust ingestion ranged for individual OPFRs between <1 and 50 ng/kg body weight for adults and toddlers, respectively. The estimated body burdens were 1000 to 100 times below reference dose (RfD) values, except for the scenario with high dust ingestion and high concentrations of TBEP in toddlers, where intake was only 5 times below RfD. Exposure of non-working and working adults to OPFRs appeared to be similar, but in specific work environments, exposure to some OPFRs (e.g. TDCPP) was increased by a factor >5.

1. Introduction

The use of chemicals as additives (e.g. flame retardants) is a common approach to meet flammability standards for various materials (furniture, plastics, electronics equipment, textiles, etc.). Worldwide restrictions on the use of polybrominated diphenyl ethers (PBDEs) in new products have resulted in the increased use of alternate flame retardant (FR) chemicals, such as organophosphorus flame retardants (OPFRs) (USEPA, 2005; Stapleton et al., 2009). The annual consumption of OPFRs in EU (alkyl phosphates as plasticizers not included) increased from 84,000 tons in 2004 to 91,000 tons in 2006, of which 56% were chlorinated phosphates (EFRA, 2007).

OPFRs are used in a range of polymers depending on the type of side chain of the phosphate ester. Chlorinated alkyl phosphates (tris-2-chloroethyl phosphate: TCEP, tri(1-chloro-2-propyl) phosphate: TCPP, tris-1,3-dichloropropyl phosphate: TDCPP) are often applied in flexible and rigid polyurethane foams (EFRA, 2010a,b; Stapleton et al., 2009), while non-halogenated alkyl phosphates (triethyl phosphate: TEP, tri-*n*-butyl phosphate: T*n*BP, tri-*iso*-butyl phosphate: T*i*BP) are mostly used for their plasticizing properties in unsaturated polyester resins, cellulose acetate, polyvinylchloride, acrylonitrile-butadiene-styrene and synthetic rubber (Marklund et al., 2005). Triphenyl phosphate (TPP) and tricresyl (or tolyl) phosphate (TCP) are often used as flame retardant plasticizers in PVC, cellulosic polymers, thermoplastics and synthetic rubber (EFRA, 2010a,b). TPP is also used in polyurethane foams in various mixtures, such as AC073 from Supresta or Firemaster 550 from Chemtura. Other specific uses include the use of T*n*BP, TPP and TCP as lubricants in hydraulic fluids (Solbu et al., 2005). Tri (2-butoxyexthyl) phosphate (TBEP) is often used in floor wax and rubber stoppers (WHO, 2000).

Because OPFRs are not chemically bonded to the original material, they are slowly released in the environment by abrasion and volatilization (Marklund et al., 2003; Wensing et al., 2005). As a result of these processes and their growing consumption, they are widely distributed in both indoor and outdoor environment. Furthermore, some of these chemicals (e.g. chlorinated alkyl phosphates)

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have a low degradation potential and thus may be persistent (Meyer and Bester, 2004; Reemtsma et al., 2008). When released into (indoor) air by volatilization, OPFRs distribute between the gas phase and various organic films on surfaces and airborne particulate matter (Weschler and Nazaroff, 2008). When the emitting source is removed from the room, the organic film layers may act as secondary emitting sources for these chemicals (Weschler and Nazaroff, 2008).

OPFRs have been detected outdoors and indoors. Most outdoors reports are from surface water, where concentrations of TCPP and TBEP ranged from 100 to 350 ng/L, and from sediments, where concentrations of TCPP were up to 311 ng/g (Andresen et al., 2004; Stachel et al., 2005). However, the presence of OPFRs is generally higher in the indoor environment, with reported dust concentrations of TBEP ranging between 16 and 120 μg/g and air concentrations of TCPP between 5 and 330 ng/m³ (Marklund et al., 2003; Hartmann et al., 2004; Staaf and Östman, 2005). As people, and especially young children, spend most of their time indoors, such elevated dust and air concentrations may result in a significant exposure.

There is insufficient knowledge related to the toxicity of OPFRs and only few reports of adverse effects have been published. Experiments on laboratory animals showed a similar toxicity for the different compounds, e.g. interference with growth and liver toxicity on long term exposure (WHO, 1991a,b, 1998, 2000). T*n*BP and TCEP also showed neurotoxic properties after chronic exposure (WHO, 1991b, 1998), while chlorinated alkyl phosphates were suspected carcinogens with observed tumour growth in kidney and thyroid for TCEP, but also in brains, liver and testes for TDCPP (WHO, 1998). Reported or suspected side effects in humans include the Sick House Syndrome from T*n*BP (Kanazawa et al., 2010), contact dermatitis from TPP (Camarasa and Serra-Baldrich, 1992) and reduced thyroid hormone levels from TDCPP (Meeker and Stapleton, 2010). TPP was not only an inhibitor of the androgen receptor in *in vitro* experiments, but was also linked to a decline in sperm concentration in several patients (Fang et al., 2003; Meeker and Stapleton, 2010).

Most of the existing analytical protocols for OPFRs determination in environmental samples were validated for a relative low number of analytes or use rather complex analysis procedures (García et al., 2007; Quintana et al., 2008; Stapleton et al., 2009). In this study, we have therefore investigated analytical aspects for the determination of the most commercially important and most reported OPFRs in dust samples. We also determined the OPFR content of three standard reference materials (SRMs) for indoor dust (SRM 2583, 2584, and 2585), so that these materials could be used as an additional quality control step for future studies. Further, we estimated the human exposure through dust ingestion in Flanders, Belgium and compared their levels in dust with those of the brominated FRs, such as PBDEs, hexabromocyclodecane (HBCD) and tetrabromobisphenol-A (TBBPA). We also attempted to estimate the safety of the current exposure through reported data of experiments on laboratory animals (WHO, 1990, 1991a,b, 1998, 2000).

2. Materials and methods

2.1. Materials

Solvents used during analysis were all of analytical grade. Hexane was purchased from Acros Organics (Geel, Belgium). Acetone, dichloromethane (DCM), ethyl acetate (EtAc), *iso*-octane and methanol (MeOH) were purchased from Merck KGaA Chemicals (Darmstadt, Germany).

Standards of TEP, tri-*n*-propyl phosphate (T*n*PP), T*i*BP, T*n*BP, TPP, TCEP, TCP (mixture of 4 isomers), and TDCPP (mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway). Triamyl phosphate (TAP; internal standard 1) was purchased from TCI Europe (Zwijndrecht, Belgium). Labelled TPP-d15 (internal standard 2) and TBEP were purchased from Sigma Aldrich. TCPP (mixture of 3 isomers) were purchased from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards was >98%, except for TBEP (>94%). Indoor dust SRMs (2583, 2584 and 2585) were purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Florisil SPE cartridges (500 mg, 3 ml) were purchased from Supelco (Bellefonte, PA, USA).

Glass test tubes were cleaned by soaking for at least 12 h in an alkali solution (diluted RBS 35, pH 11–12) to hydrolyse any present OPFRs. After washing, they were rinsed with water and dried at 100 °C for at least 12 h. The tubes were rinsed with EtAc before use.

2.2. Sample collection

House dust samples were collected in frame of a previous study (Roosens et al., 2010) according to the following protocol. Dust samples ($n = 33$) were taken from individual houses or apartments in the Flemish region of Belgium by vacuuming 1 m² of carpeted floor or 4 m² of bare floor surface for 2 or 4 min, respectively of the kitchen, study, bedroom and living room area. Obtained dust samples were combined per house. Samples from electronics stores, mattress shops, pharmacies, a second-hand shop (for clothes, electronic equipment and furniture), a furniture shop, a carpenter workshop and an analytical laboratory were taken by vacuuming 2 m² of carpeted floor or 6 to 8 m² of bare floor surface for 4 and 8 min, respectively. All samples were collected with the same vacuum cleaner using nylon sampling socks which were mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie and stored separately in a polyethylene container. Before and after sampling different locations, the furniture attachment was cleaned thoroughly using water and soap and a hexane-impregnated disposable wipe. Dust samples were sieved with a 500 μm mesh prior to analysis.

2.3. Sample preparation

An accurately weighed amount of dust (75 mg) was spiked with 75 ng of both internal standards (equivalent to 1 μg/g dust). Samples were twice extracted by using 2 mL DCM per extraction and applying ultrasonication twice for 5 min and vortex for 1 min between each sonication period. After each extraction, the mixture was centrifuged at 2000 g, the supernatants combined afterwards, further evaporated until dryness and redissolved in 0.5 mL of Hex. Before fractionation, Florisil cartridges were pre-cleaned with 8 mL of MeOH and 3 mL of Hex. The extracts were quantitatively transferred to the cartridges by using 1.5 mL of Hex and afterwards a first fraction of 3 mL Hex which contained PBDEs was discarded. The OPFRs fraction was further collected by elution with 10 mL EtAc, evaporated until dryness and redissolved in 100 μL of *iso*-octane.

2.4. GC-EI-MS analysis

The analysis of OPFRs in the purified extracts was performed with an Agilent 6890 GC coupled to an Agilent 5973 MS operated in EI mode. The GC system was equipped with electronic pressure control and a programmable-temperature vaporizer (PTV). One μL of purified extract was injected on a HT-8 column (25 m × 0.22 mm × 0.25 μm) using cold splitless injection. The injection temperature was set at 90 °C, hold 0.03 min, ramp 12 °C/s to 290 °C. Injection was performed in pulsed pressure 14.3 psi until 1.5 min and purge flow to split vent of 50 mL/min after 1.25 min. The GC temperature program for the HT-8 column was 90 °C, hold 1.25 min, ramp 10 °C/min to 240 °C, ramp 20 °C/min to 310 °C, hold 16 min. The GC temperature program for the AT-5 column (20 m × 0.18 mm × 0.20 μm) was 90 °C, hold 1.25 min, ramp 10 °C/min to 310 °C, hold 8 min. Helium was used as a carrier gas with a flow rate of 1.0 mL/min.