



# Organophosphate esters flame retardants in the indoor environment



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## ABSTRACT

Concentrations of 13 organophosphate ester flame retardants (OPEs) were measured in air, dust and window wipes from 63 homes in Canada, the Czech Republic and the United States in the spring and summer of 2013 to look for abundances, differences among regions, and partitioning behavior. In general, we observed the highest concentrations for halogenated OPEs, particularly TCEP, TCIPP and TDCIPP, and also non-halogenated TPHP. Differences between regions strongly depended on the matrix. The concentrations of OPEs in dust were significantly higher in the US than in Canada (CAN) and Czech Republic (CZ). CZ had the highest concentrations in window film and CAN in air. ΣOPE concentrations were 2–3 and 1–2 orders of magnitude greater than ΣBFRs in air, and dust and window films, respectively. We found a significant relationship between the concentrations in dust and air, and between the concentrations in window film and air for OPEs with log  $K_{OA}$  values < 12, suggesting that equilibrium was reached for these compounds but not for those with log  $K_{OA}$  > 12. This hypothesis was confirmed by a large discrepancy between values predicted using a partitioning model and the measured values for OPEs with log  $K_{OA}$  values > 12.

## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are the most thoroughly studied class of flame retardants (FRs). They were widely used in numerous household products until the early 2000s when two of the commercial mixtures, Penta and OctaBDE, were withdrawn from the market in the US due to mounting evidence of adverse health effects and widespread environmental presence. This resulted in an increased use of alternative compounds, mostly either brominated compounds (e.g. 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), Bis(2-ethyl-1-hexyl) tetrabromophthalate (BEHTBP) or organophosphate esters (OPEs).

OPEs are phosphoric acid esters used as FRs, plasticizers and anti-foaming agents (Rauert and Harrad, 2015). Their application in products ranges from textiles, polyurethane foam (PUF) upholstered furniture, and electronics to construction materials (e.g., building insulation) and vehicles (Marklund et al., 2003; van der Veen and de Boer, 2012; Wei et al., 2015). While chlorinated and brominated OPEs see widespread use mostly as FRs, the non-halogenated OPEs are used also

as plasticizers, lubricants and pore size regulators (Andresen et al., 2004). Since OPEs are typically used as additive chemicals and are therefore not covalently bound to polymeric materials, they can easily migrate from products into the environment by means of volatilization, leaching and abrasion, and direct transfer to dust (Marklund et al., 2003; van der Veen and de Boer, 2012; Wei et al., 2015).

Due to their physical and chemical characteristics, OPEs are ubiquitous in various environmental compartments worldwide and have been detected in abiotic matrices such as sediment (Cao et al., 2012), surface and groundwater water (Regnery et al., 2010; Regnery et al., 2011; Venier et al., 2014), outdoor air including remote locations (Salamova et al., 2016; Sühling et al., 2016a), indoor air (Marklund et al., 2005; van der Veen and de Boer, 2012), and house dust (Dodson et al., 2012; Stapleton et al., 2009). They are also found in biota (van der Veen and de Boer, 2012) and human breast milk (Sundkvist et al., 2010), indicating that these compounds are bioavailable and might bioaccumulate (Greaves et al., 2016). Studies on the toxicity of OPEs are still limited but some OPEs have been reported to be mutagenic, carcinogenic, and neurotoxic, as well as potential developmental and

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reproductive toxins (Behl et al., 2015; Hendriks and Westerink, 2015; Schweizer et al., 2007; van der Veen and de Boer, 2012).

Due to its persistence, bioaccumulative potential and toxicity, Tris (2-chloroethyl) phosphate (TCEP) has been restricted from use in concentrations greater than 5 mg/kg in toys for children up to 3 years of age and for any toys intended for mouthing and has been designated as a substance of very high concern in the European Union (Toy Safety Directive, 2009/48/EC, European Chemicals Agency, 2015). As such, it is no longer produced in Europe (Green et al., 2008; Schreder et al., 2016; Sühling et al., 2016a). Some reports suggest that it has been replaced by other FRs, primarily Tris(1-chloro-2-propyl) phosphate (TCIPP). In 2001, this structurally similar and relatively cheap replacement for TCEP, represented approximately 80% of the chlorinated OPEs used in Europe (Leisewitz et al., 2001). In 2014 Canada prohibited new use of TCEP in products containing PUF intended for children under 3 years of age (Canada Gazette, 2014). TCEP was restricted for new uses in several US states starting in 2011 (Safer States) and is listed as a carcinogen under California's Proposition 65. TCIPP has been recommended for designation as "toxic" under the Canadian Environmental Protection Act (Environment and Climate Change Canada, 2016). The proposed risk management measures are limiting its use to < 0.1% in mattresses and upholstered furniture.

Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) appears to be used as a substitute for brominated FRs. TDCIPP is primarily used in foams in the automotive industry and to some extent also in upholstered furniture (Cooper et al., 2016). Tris(2,3-dibromopropyl) phosphate (TDBPP), a brominated analog for TDCIPP, was banned in children's sleepwear in the US in 1977 due to carcinogenicity concerns after mutagenic metabolites were detected in children's urine (Gold et al., 1978) and it is listed as a carcinogen in California's Proposition 65. TDCIPP is also listed as a carcinogen in California's Proposition 65 but has not been recommended for designation as "toxic" under the Canadian Environmental Protection Act (Environment and Climate Change Canada, 2016).

Triphenyl phosphate (TPHP), one of the most effective FRs used in polymers (van der Veen and de Boer, 2012), is used also in hydraulic fluids (Andresen et al., 2004). TPHP is a component in the Firemaster (FM) 550 mixture, introduced in 2004 as a replacement for the PentaBDE commercial mixture used in upholstered furniture. It is also used as a plasticizer in, for example, nail polish (Mendelsohn et al., 2016) and electronic components such as televisions and monitor screens (Kajiwara et al., 2011). EHDPP is mainly used as a flame retardant/plasticizer in flexible PVC (e.g., wire and cable insulators, connectors) and in certain food packaging in the US (Brooke et al., 2009).

In this study, we measured the concentrations of 13 OPEs - four halogenated (TCEP, TCIPP, TDCIPP and TDBPP) and nine non-halogenated (TPHP, EHDPP, TEHP, TNBP, o-TMPP, p-TMPP, TIPPP, TDMPP and TBPP) in air, dust and window film from homes in three different countries (Czech Republic, Canada and USA) during the spring and summer of 2013. These three matrices were chosen as the most relevant for human exposure, as well as being novel and convenient. The goals of this project were to evaluate the partitioning behavior of OPEs in the indoor environment, to compare within-house differences, and to examine regional differences between Central Europe and North America. Two companion papers reported on levels of brominated flame retardants (Venier et al., 2016) and perfluorinated alkyl substances (Karásková et al., 2016) in the same homes.

## 2. Experimental section

### 2.1. Sample collection

Air, dust and window film samples were collected from a total of 63 houses and apartments (20 homes each in Brno, Czech Republic and Bloomington, IN, US and 23 in Toronto, ON, Canada) during a sampling period of 28 days in May–August 2013. Samples from one room, usually

the bedroom, were collected in each home while a second room, usually the living room, was sampled in at least nine randomly chosen homes in each country. Participants were recruited as a "sample of convenience" among colleagues, friends, relatives and acquaintances.

Sampling involved deploying polyurethane foam (PUF) passive air samplers to estimate air concentrations, collecting settled floor dust into nylon socks by vacuuming, and collecting interior window films as representative of surface films on interior surfaces using Kimwipes. Details of sample collection can be found elsewhere (Venier et al., 2016) and only a brief description is provided here. Before sampling, all matrices (PUF disks, Kimwipes and nylon vacuum socks) were pre-cleaned in a Soxhlet extractor (8 h in acetone, then 8 h in toluene), dried and packed in aluminum foil and transported to the sites. Field blanks were collected by exposing pre-cleaned matrices during sample retrieval.

On day 1, floors were vacuumed and windows were cleaned with Kimwipes moistened with 2-propanol until no dirt was visible (Kimwipes were not saved at this time), PUF passive air samplers were deployed, and participants were asked not to vacuum rooms or wash the windows where the samplers were located until the end of the campaign. PUF disks were exposed to indoor air using a single-bowl in US and Canada or double-bowl in the Czech Republic (see Fig. S1) passive sampler housing for 28 days. Sampling rates for each passive air sampler configuration were calculated in a separate experiment by simultaneously deploying single- and double-bowl samplers along with active air samplers (Venier et al., 2016). More details on the calibration of the passive air samplers are reported in the Supporting Information. For this study, we used a sampling rate of 1.6 m<sup>3</sup>/day for the single-bowl sampler and 0.82 m<sup>3</sup>/day for the double-bowl sampler. Given the difficulty of calculating accurate and meaningful sampling rates, this approach seems reasonable.

On day 28, PUF discs were retrieved and window wipe samples were collected using a pre-cleaned Kimwipe moistened with 2-propanol (Kimwipes were saved at this time). Windows were wiped until no dirt was visible on the Kimwipe. The sampled area averaged at 0.32 m<sup>2</sup> for Canada, 0.93 m<sup>2</sup> for US, and 1.79 m<sup>2</sup> for the Czech Republic. Floor dust samples were collected using a pre-cleaned nylon sampling sock inserted into the tube of a conventional household vacuum cleaner, vacuuming the largest possible floor area and recording the area. After collection, all samples were wrapped in aluminum foil and sealed in plastic bags for transport to the laboratory. Samples were stored at –18 °C until extraction and analysis.

### 2.2. Target compounds and chemicals

The list of target compounds is reported in Table 1. The following OPEs standards were purchased from Wellington Laboratories (Guelph, ON, Canada): Tri-*n*-butylphosphate (TnBP), Tris(2-chloroethyl) phosphate (TCEP), Tris(1-chloro-2-propyl) phosphate (TCIPP), Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), Triphenyl phosphate (TPHP), 2-Ethylhexyl-diphenyl phosphate (EHDPP), Tris(2-ethylhexyl) phosphate (TEHP), Tri-*o*-tolyl phosphate (o-TMPP), Tri-*p*-tolyl phosphate (p-TMPP), Tris(2-isopropylphenyl) phosphate (TIPPP), and Tris(3,5-dimethylphenyl) phosphate (TDMPP). Tris(2,3-dibromopropyl) phosphate (TDBPP) was purchased from AccuStandard (New Haven, CT). Tris(4-*tert*-butylphenyl) phosphate (TBPP) was purchased from Sigma-Aldrich (St. Louis, MO). *d*<sub>12</sub>-Tris(2-chloroethyl) phosphate (*d*<sub>12</sub>-TCEP), <sup>13</sup>C<sub>18</sub>-triphenyl phosphate (MTPP) and <sup>13</sup>C<sub>12</sub>-BDE-77 were purchased from Wellington. The internal quantitation standards, *d*<sub>10</sub>-anthracene, *d*<sub>12</sub>-benz[*a*]anthracene, and *d*<sub>12</sub>-perylene, were obtained from Chem Service (West Chester, PA). All solvents were HPLC or Optima grade. Silica gel (100–200 mesh, 75–150 μm, Grade 644) and granular anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were purchased from Fisher Scientific (Pittsburgh, PA).

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