Environment International 112 (2018) 59–67

Contents lists available at ScienceDirect

Environment International

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

Presence of diphenyl phosphate and aryl-phosphate flame retardants in indoor dust from different microenvironments in Spain and the Netherlands and estimation of human exposure

Maria K. Björnsdotter[a], Encarnación Romera-García[a], Josep Borrull[b], Jacob de Boer[b], Soledad Rubio[a], Ana Ballesteros-Gómez[a,*]

[a] Department of Analytical Chemistry, Institute of Fine Chemistry and Nanochemistry, Marie Curie Building (Annex), Campus of Rabanales, University of Córdoba, 14071, Spain

[b] Vrije Universiteit Amsterdam, Environment and Health, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

ARTICLE INFO

Keywords:
Aryl-phosphate flame retardants
Indoor dust
Human exposure
Triphenyl phosphate
Diphenyl phosphate

ABSTRACT

Phosphate flame retardants (PFRs) are ubiquitous chemicals in the indoor environment. Diphenyl phosphate (DPHP) is a major metabolite and a common biomarker of aryl-PFRs. Since it is used as a chemical additive and it is a common impurity of aryl-PFRs as well as a degradation product, its presence in indoor dust as an additional source of exposure should not be easily ruled out. In this study, DPHP (and TPHP) are measured in indoor dust in samples collected in Spain and in the Netherlands (n = 80). Additionally, the presence of other emerging aryl-PFRs was monitored by target screening. TPHP and DPHP were present in all samples in the ranges 169–142,459 ng/g and 106–79,661 ng/g, respectively. DPHP concentrations were strongly correlated to the TPHP levels ($r = 0.90$, $p < 0.01$), suggesting that DPHP could be present as degradation product of TPHP or other aryl-PFRs. Estimated exposures for adults and toddlers in Spain to TPHP and DPHP via dust ingestion (country for which the number of samples was higher) were much lower than the estimated reference dose (US EPA) for TPHP. However, other routes of exposure may contribute to the overall internal exposure (diet, dermal contact with dust/consumer products and inhalation of indoor air). The estimated urinary DPHP levels for adults and toddlers in Spain (0.002–0.032 ng/mL) as a result of dust ingestion were low in comparison with the reported levels, indicating a low contribution of this source of contamination to the overall DPHP exposure. Other aryl-PFRs, namely cresyl diphenyl phosphate (CDP), resorcinol bis(diphenyl phosphate) (RDP), 2-ethylhexyl diphenyl phosphate (EDPHP), isodecyl diphenyl phosphate (IDP) and bisphenol A bis(diphenyl phosphate) (BDP), were all detected in indoor dust, however, with lower frequency.

1. Introduction

Due to their wide use in materials, such as furniture, electronics and textiles, flame retardants (FRs) are widespread in the environment. They are used to prevent ignition and to slow down the spread of an already initiated fire (EFRA, 2007). Concern has been raised considering their migration from materials as it affects the indoor air quality and being inhalation a route for human exposure (Kemmlein et al., 2003). The use of PBDEs as flame retardants has been common until they started to be banned or voluntarily phased-out in certain products, such as electrical and electronic equipment or polyurethane foam, due to their known toxicity, persistence and bioaccumulative properties (U.S. EPA, 2009). The European Union has banned the use of pentaBDE and octaBDE in 2004 (Directive 2002/96/EC) and the use of decaBDE in electric and electronic equipment in 2009 (European Court of Justice, 2008). This regulation has led to the introduction of alternatives, such as aryl-phosphate flame retardants (aryl-PFRs), onto the market. Studies have demonstrated an increase in the presence of alternative FRs in indoor dust, for which toxicity is still uncharacterized, in conjunction with the decrease of PBDE (Dodson et al., 2012; Tao et al., 2016; Cooper et al., 2016).

Triphenyl phosphate (TPHP; CAS no. 115-86-6) is an aryl-PFR mainly used as an additive in polymer mixtures used in electronic enclosure applications. The use of TPHP has resulted in environmental contamination due to its migration from materials (Kemmlein et al., 2003). TPHP has been reported in indoor dust collected from the floors of residences (< 2–1,798,000 ng/g) (Dodson et al., 2012; Garcia et al., 2007; Stapleton et al., 2009; Kanazawa et al., 2010; Bergh et al., 2011;

* Corresponding author.
E-mail address: a02bagoa@uco.es (A. Ballesteros-Gómez).

https://doi.org/10.1016/j.envint.2017.11.028
Received 28 September 2017; Received in revised form 24 November 2017; Accepted 29 November 2017

Van den Eede et al., 2011; Ali et al., 2012a; Ali et al., 2012b; Dirtu et al., 2012; Ali et al., 2013; Kim et al., 2013; Abdallah and Covaci, 2014; Araki et al., 2014; Brandsma et al., 2014; Cequier et al., 2014; Fan et al., 2014; Tajima et al., 2014; Brommer and Harrad, 2015; Hoffman et al., 2015; Mizouchi et al., 2015; Zheng et al., 2015; Ali et al., 2016; Canbaz et al., 2016; Cristale et al., 2016; Harrad et al., 2016; He et al., 2016; Wu et al., 2016; Kademoglou et al., 2017), in indoor dust from offices (11–50,000 ng/g) (Bergh et al., 2011; Abdallah and Covaci, 2014; Brommer and Harrad, 2015; Cristale et al., 2016; Harrad et al., 2016; He et al., 2016; Wu et al., 2016; Kademoglou et al., 2017) and in indoor dust from schools and daycare centers (10–90,000 ng/g) (Bergh et al., 2011; Cequier et al., 2014; Brommer and Harrad, 2015; Mizouchi et al., 2015; Cristale et al., 2016; Wu et al., 2016; Fromme et al., 2014). TPHP has also been reported in dust from cars (< 2–170,000 ng/g) (Ali et al., 2013; Abdallah and Covaci, 2014; Brandsma et al., 2014; Brommer and Harrad, 2015; Ali et al., 2016; Harrad et al., 2016), and from public microenvironments (PMEs) such as shops, restaurants and supermarkets (14–34,200 ng/g) (Van den Eede et al., 2011; Ali et al., 2012b; Abdallah and Covaci, 2014; Cristale et al., 2016; He et al., 2016). TPHP has also been reported in indoor air (0.19–5.7 ng/m^3) (Björklund et al., 2004; Hartmann et al., 2004), in outdoor air (0.003 ng/m^3) (Wolschke et al., 2016), sewage water influent (76–290 ng/L) and effluent (41–130 ng/L) and sewage sludge (52–320 ng/g dw) (Marklund et al., 2006), surface water (< LOD-10.3 ng/L) (Bollmann et al., 2012), sediment (5.6–253 ng/g) (Giulivo et al., 2016; Tan et al., 2016) and in fish (43–230 ng/g lw) (Giulivo et al., 2016; Matsukami et al., 2016). Furthermore, TPHP has been associated with airborne particles over the oceans indicating a potential for long-range atmospheric transport towards the polar regions (Möller et al., 2012).

The widespread occurrence of TPHP in the indoor- and outdoor environment has led to concern regarding human health and the environment. The human toxicity of TPHP is considered “low to high” according to a recent alternatives assessment report (U.S. EPA, 2014). Furthermore, PFRs including TPHP may be associated with altered hormone levels and decreased semen quality in men (Meeker and Stapleton, 2010). The aquatic toxicity is considered very high (Fish 96 h EC_{50} = 0.4 mg/L, fish 30-day LOEC = 0.037 mg/L) and TPHP may cause long-term adverse effects in the aquatic environment (U.S. EPA, 2014). The environmental persistence is considered low, although there is a moderate potential for bioaccumulation (U.S. EPA, 2014).

Human exposure to FRs as well as to other contaminants has been associated with inhalation and ingestion of contaminated indoor dust (Covaci et al., 2012). High levels of contaminants in indoor dust are posing a risk to human health, particularly vulnerable groups such as toddlers, which are especially exposed to contaminated dust when crawling and playing on the floor as well as when they put items in their mouth (World Health Organization (WHO), 2011).

As a major metabolite of aryl-PFRs, DPHP has been used as a biomarker for assessing exposure to TPHP in indoor dust and has been widely reported in urine in the range < 0.13–727 ng/mL (Hoffman et al., 2015; Cooper et al., 2011; Meeker et al., 2013; Van den Eede et al., 2013a; Hoffman et al., 2014; Van den Eede et al., 2015; Kosarac et al., 2016). However, the urinary levels of DPHP are not correlated to TPHP concentrations in indoor dust (r_S = 0.04 (Meeker et al., 2013); r_S = 0.15 (Hoffman et al., 2015)) indicating other exposure routes. A possible additional source could be the direct exposure to DPHP itself as it is used in other applications (e.g. DPHP is used as a catalyst in polymerization processeses$_{55,56}$ and as an additive in paints and coatings according to PubChem database) or direct exposure to DPHP via indoor dust ingestion as it may be present as an impurity and/or as a degradation product as a result of spontaneous or microbial hydrolysis of TPHP and/or of other aryl-PFRs. Furthermore, DPHP has been reported to be a metabolite of some other aryl-PFRs, such as 2-ethylhexyl diphenyl phosphate (EDPHP) (Nishimaki-Mogami et al., 1988; Ballesteros-Gomez et al., 2015a), resorcinol bis(diphenyl phosphate) (RDP) (Ballesteros-Gomez et al., 2015b) and *tert*-Butylphenyl diphenyl phosphate (BPDP) (Heitkamp et al., 1985). There is almost no data available about the presence of DPHP in the indoor environment, to the best of our knowledge only one study has reported levels of DPHP (75–190 ng/g) in 4 dust samples collected in Australia (Van den Eede et al., 2015).

In the present study, TPHP and DPHP levels were studied in indoor dust samples collected from households, offices, cars and public microenvironments in the Netherlands in June 2016 (n = 23) and in Spain in March and April 2017 (n = 57). The levels of TPHP and DPHP were compared between different microenvironments and between the two countries and the correlation between TPHP and DPHP levels was investigated. Human exposure to TPHP and DPHP via indoor dust ingestion was estimated using different exposure scenarios. It should be taken into account that this is only one of the major identified exposure routes to flame retardants, which include also the diet, dermal contact with dust/consumer products and inhalation of indoor air.

Furthermore, to gain knowledge about the presence of other aryl-PFRs in indoor dust, which could contribute to the formation of DPHP, the presence of other emerging aryl-PFRs were screened, namely cresyl diphenyl phosphate (CDP), RDP, EDPHP, isodecyl diphenyl phosphate (IDP) and bisphenol A bis(diphenyl phosphate) (BDP) by injection of authentic standards.

2. Materials and methods

2.1. Chemicals and reagents

Acetonitrile and methanol were acquired from VWR chemicals (Llinars del Vallès, Barcelona, Spain). Ammonium acetate was obtained from Sigma Aldrich (Zwijndrecht, the Netherlands). Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain). Standard reference material (SRM) 2585 (organic contaminants in house dust) was provided by the National Institute of Standards and Technology (NIST). TPHP, DPHP, TPHP-d_{15} and DPHP-d_{10} were obtained from Sigma Aldrich (Zwijndrecht, the Netherlands). Cresyl diphenyl phosphate (CDP), isodecyl diphenyl phosphate (IDP), 2-ethylhexyl diphenyl phosphate (EDPHP), resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) analytical standards were obtained from AccuStandard (New Haven, CT).

2.2. Sample collection

Sampling was performed using a filter (40 μm) mounted in a nozzle adapted to a vacuum cleaner and samples were not further sieved. Dust samples were collected from residences in the Netherlands in June 2016 from floors (n = 12) and from the surface of electrical equipment (n = 11) and in Spain in March and April 2017 from the floors of living rooms (n = 9), bedrooms (n = 9), offices (n = 4), surfaces of electrical equipment (n = 13), cars (n = 15) and public microenvironments (PMEs) (n = 7) (two electronic shops, two clothing shops, one sport clothing shop, one decoration shop and one cafeteria). Due to the limited amount of dust on top of electrical equipment, these samples were of approximately 20–50 mg.

2.3. Sample treatment and method validation

Approximately 50 mg dust (except for dust on top of electronic equipment, 20–50 mg) were accurately weighed in 15 mL glass tubes and spiked with IS (TPHP-d_{15} and DPHP-d_{10}, 0.1 μg each) prior to extraction. Salting-out extraction with acetonitrile was performed with 3 M aqueous ammonium acetate (NH_4Ac):acetonitrile (1:1 v/v) by vortex for 2 min followed by centrifugation at 3000 rpm for 5 min. After phase-separation, the acetonitrile layer was collected and transferred to a glass tube. The extraction was repeated 2 times and the