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Legacy and emerging organophosphorus flame retardants in car dust from Greece: Implications for human exposure

Christina Christia [a, b], Giulia Poma [a], Athanasios Besis [b], Constantini Samara [b], Adrian Covaci [a, *]

[a] Toxicological Center, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Antwerp, Belgium
[b] Environmental Pollution Control Laboratory, Aristotle University, 54124 Thessaloniki, Greece

HIGHLIGHTS

- Major PFRs were TCIPP and TDCIPP for EU and Asian cars and TCEP for US cars.
- Major ePFRs were V6 for EU cars and iDDPHP for Asian and US cars.
- No correlations between PFR concentrations and car interior characteristics.
- Intake was higher via dust ingestion than dermal absorption.
- PFR intakes via ingestion and dermal absorption were lower than RfDs.

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ABSTRACT

Organophosphorus flame retardants (PFRs) and emerging PFRs (ePFRs) are two groups of compounds used as replacements for brominated flame retardants (BFRs). They have already been detected in indoor dust (mainly in homes and offices). To date, few studies investigated the occurrence of FRs in car dust and the information of possible health risks is still limited. The present study reports on the investigation of the levels and profiles of eight target PFRs: tris(2-ethylhexyl) phosphate (TEHP), tris(2-chloroethyl) phosphate (TCEP), tris(2-butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPHP), tris(1-chloro-2-propyl) phosphate (TCIPP), tri cresyl phosphate (TCP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) and four target ePFRs; 2,2-bis(chloromethyl)propane-1,3-diyltetrakis(2-chloroethyl)bisphosphate (V6), isodecyl diphenyl phosphate (iDDPHP), resorcinol bis(diphenylphosphate) (RDP) and bisphenol A-bis(diphenyl phosphate) (BDP) in car dust from Greece. The samples were collected from the interior of 25 private cars in Thessaloniki, Greece, with different years of manufacture (1997–2015) and continents of origin. After ultrasonic extraction and Florisil fractionation, the PFR analysis was carried out by GC-EI/MS, whereas the ePFRs were analyzed by LC-MS/MS. Levels of Σ_8PFRs varied from 2000 to 190,000 ng g^{-1}, with mean and median concentrations of 20,000 and 11,500 ng g^{-1}, respectively. The concentrations of Σ_4ePFRs ranged from 44 to 8700 ng g^{-1}, with mean and median values at 1100 and 190 ng g^{-1}, respectively. Estimations of human exposure showed that toddlers are more exposed than adults to both PFRs and ePFRs. Yet, the intake via dust ingestion and dermal absorption was several orders of magnitude lower than the corresponding reference doses.

1. Introduction

Organophosphorus flame retardants (PFRs) are a class of organic compounds used as substitute of brominated flame retardants (BFRs) after the restrictions and phase-outs of the latter (Poma et al., 2017). Emerging organophosphorus flame retardants (ePFRs) are considered as the new generation of PFRs and include 2,2-bis(chloromethyl)-propane-1,3-diyltetrakis(2-chloroethyl) bisphosphate (V6), isodecyl diphenyl phosphate (iDDPHP), resorcinol bis(diphenylphosphate) (RDP), bisphenol A-bis (diphenyl phosphate) (BDP) (Ballesteros-Gomez et al., 2016a,b; 2014; Fang et al., 2013). Both groups of PFRs are applied to a wide range of

* Corresponding author.
E-mail address: adrian.covaci@uantwerpen.be (A. Covaci).

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products as flame retardants, plasticizers, stabilizers, lubricants, antifoaming agents etc. (Brandsma et al., 2014). As FRs, they are additive chemicals incorporated into the polymer mainly after the polymerization. They are not chemically bonded to the material, which facilitates their release from products to the environment, based on their physico-chemical properties (SFT, 2009). The detection of PFRs in air and indoor dust is the proof of this migration (Dodson et al., 2012; Eagle et al., 2012; Stapleton et al., 2008). Inhalation/ingestion of suspended dust particles are pathways of human exposure to organic contaminants in indoor environments (Dodson et al., 2012). The average time spent in a car has been estimated as 5.5% of the time spent indoors by humans (Mandalakis et al., 2008). However, despite the limited time spent in cars, concentrations of PFRs detected in car interiors are ten times higher than other indoor environments, such as homes and offices (Brommer et al., 2012). This may be due to the higher levels of being applied in the different polymers used in car interiors: polyurethane foam (PUF), used in car seats, acrylonitrile butadiene styrene (ABS) and propylene, plastic polymeric materials extensively applied in parts of instrument panels, electronic equipment and textiles in the automotive interior (Wei et al., 2015). Additionally, the high temperatures developed in car interiors could cause higher release of compounds from polymeric materials into the gas/particulate phase (Besis et al., 2017; Cetin and Odabasi, 2011; Schreder et al., 2016). In Mediterranean countries, such as Greece, cars are exposed to high temperatures and extreme sun radiation most of the year and thus we expect high release of PFRs.

The extent of human exposure to PFRs is of high scientific concern, due to their potential health risks of endocrine disruption, possible carcinogenicity, neurodevelopment disorders, hepatic and behavioral abnormalities (Ali et al., 2016). Specifically, the chlorinated PFRs, such as TDCIPP, TCIPP, TCEP and V6 have been characterized from moderate to high hazardous chemicals for carcinogenicity, genotoxicity, reproductive toxicity, developmental/neurodevelopmental toxicity, neurological toxicity and repeated dose toxicity in humans (EPA, 2015). Thus, a lot of effort has been done in order to understand how these compounds enter into the human body, with emphasis on the most vulnerable population groups, such as toddlers and infants (Mitchell et al., 2007). Among the possible pathways of PFR exposure, dust ingestion and diet intake are considered the dominant contributors to PFR body burden (de Boer et al., 2016; Yang et al., 2014; Poma et al., 2017; Malarvannan et al., 2015; Ding et al., 2015). Dermal absorption is an exposure pathway that has gained recent attention and several studies are currently focusing on the full understanding of its mechanism and development of alternative models (Liu et al., 2017; Pawar et al., 2016; Abdallah et al., 2016).

To our knowledge, this is the first study monitoring on the simultaneous presence of PFRs and ePFRs in dust samples of 25 private cars in Greece, reporting the concentration levels of eight PFRs (TEHP, TCEP, TBEP, TPHP, TCP, EHDPHP, TCIPP, TDCIPP) and 4 ePFRs (V6, iDDPHP, RDP, BDP). The aims of the study were: (1) to investigate the concentrations and profiles of target PFRs, (2) to report possible correlations between concentrations and car age or other characteristics, (3) to investigate the patterns of FRs among three continents of origin (Europe, Asia and U.S.A), (4) to compare the concentrations of target PFRs to those reported in the literature and (5) to estimate the human exposure to PFRs and ePFRs via dust ingestion and dermal absorption.

2. Materials and methods

2.1. Chemicals and reagents

Triamyl Phosphate (TAP) and the labelled TPHP-d_{15}, TDCIPP-d_{15}, TBEP-d_6 and TCEP-d_{12}, were used as internal standards (IS) for PFRs analysis. For analysis of ePFRs, TAP was also used as recovery standard (RS) and it was purchased from TCI Europe (Zwijndrecht, Belgium). The labelled ISs were custom synthesized (Dr. Vladimir Belov, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany) and had an isotopic purity above 98%. Chlorobiphenyl CB-207, used as RS for the PFRs analysis and was purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Standards of TCEP, TCP, TBEP TDCIPP, TEHP, EHDPHP, TCIPP (mixture of 2 isomers) and TPHP were purchased from Chiron AS (Trondheim, Norway). Standards of BDP, RDP, iDDPHP and V6 were purchased from Accustandard (New Heaven, CT, USA). Detailed information regarding the analytes is provided in Table S1.

Indoor dust standard reference material SRM 2585 was purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Polypropylene syringes were purchased by Sigma-Aldrich (St. Louis, Mo, USA). Florisil cartridges (500 mg, 3 mL) were purchased from Supelco (Bellefonte, PA, USA) and APS Bond Elut NH_2 (500 mg, 3 mL) cartridges were purchased from Agilent Technologies (Santa Clara, CA, USA). All solvents were chromatography grade: n-hexane (n-Hex) was purchased from Acros Organics (Belgium), ethyl acetate (EtAc), dichloromethane (DCM), iso-octane, toluene and acetonitrile (ACN) were purchased from Merck (Darmstadt, Germany).

2.2. Sampling

Dust samples were collected from the interior of private cars (n = 25) in Thessaloniki, Greece. The cars were sampled in parking areas of Aristotles University of Thessaloniki, one retailer of second-hand cars and commercial car washing spots, under sunlight. The continents of origin of cars were Europe (n = 13), Asia (n = 9) and U.S.A. (n = 3). The year of manufacture ranged from 1997 to 2015, with an average car age of 9 years old. Questionnaires were completed by the car owners who provided details concerning characteristics of the interior, engine type, and ventilation (see Supplementary Material, Table S2).

Car dust samples were collected using an 1800 W vacuum cleaner equipped with a clean paper bag per sample, replaced every time for a new sample, fitted in the interior of the device. Car interiors were sampled according to a modified version of the protocol reported by Harrad et al. (2008). Briefly, seats, dashboards and trunks were vacuum cleaned for 3 min. To avoid cross contamination, the furniture attachment, the tube, and the inner parts of the vacuum cleaner were cleaned thoroughly with ethanol after each sampling. After sampling, the paper bags were firmly closed, sealed in zip-lock plastic bags and carried to the laboratory where they were transferred to aluminum foil and stored at −20 °C. Prior to analysis, all dust samples were sieved through a 1000 μm mesh sieve and homogenized thoroughly.

2.3. Analytical procedure

2.3.1. PFRs analysis

The method used for the analysis of PFRs in dust samples was based on analytical methods described previously (Poma et al., 2017; Ionas et al., 2015; Van den Eede et al., 2012). Dust aliquots of 30 mg were weighted and spiked with 100 μL of IS. A mixture of IS (TAP, TBEP-d_6, TCEP-d_{12}, TDCIPP-d_{15}, and TPHP-d_{15}) in concentration of 500 pg μL^{-1} for each IS was used.

Samples were extracted using 2.5mLof n-Hex/acetone mixture (3:1, v/v) by a combination of vortexing and ultrasonication (twice 1 min vortex and 5min ultrasonication) repeated three times. After each extraction cycle, extracts were centrifuged at 3500 rpm for 5 min. Supernatants were collected and transferred into clean glass