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Sources and human exposure implications of concentrations of organophosphate flame retardants in dust from UK cars, classrooms, living rooms, and offices

Sandra Brommer, Stuart Harrad *

School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham B15 2TT, United Kingdom

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ABSTRACT

Concentrations of a number of organophosphate flame retardants (PFRs) were measured in floor dust collected from UK living rooms (n = 32), cars (n = 21), school and child daycare centre classrooms (n = 28), and offices (n = 61). While concentrations were overall broadly within the range of those reported previously for North America, Japan, and other European countries, median concentrations of TCIPP in all UK microenvironments exceeded those reported elsewhere in the world. Moreover, concentrations of TCIPP and TDCIPP in 2 UK car dust samples were – at 370 μg g^{-1} and 740 μg g^{-1} respectively – amongst the highest reported globally in indoor dust to date. Consistent with this, concentrations of TDCIPP in dust from UK cars exceed significantly those detected in the other microenvironments studied. Concentrations of EHDPP were shown for the first time to be significantly higher in classroom dust than in samples from other microenvironments. When compared to concentrations of PBDEs determined previously in the classroom dust samples; concentrations of all target PFRs exceeded substantially those of those PBDEs that are the principal constituents of the Penta- and Octa-BDE formulations. Moreover, while mass-based concentrations of BDE-209 exceeded those of most of our target PFRs, they still fell below those of TCIPP and EHDPP. In line with a previous observation in Sweden that indoor air contamination with TNBP was significantly lower in newer buildings; concentrations of TNBP in classroom dust were significantly higher in older compared to more recently-constructed schools. Consistent with the reported extensive use of TCIPP and TDCIPP in polyurethane foam, the highest concentrations of both TCIPP and TDCIPP in the classrooms studied, were observed in rooms containing the highest numbers of foam chairs (n = 31 and 18 respectively). Exposure to PFRs of both adults and young children via ingestion of indoor dust was estimated. While even our high-end exposure estimate for young children was ~100 times lower than one previously reported health-based limit (HBLV) value for TCIPP; the margin of safety was only 5-fold when compared to another HBLV for this contaminant.

1. Introduction

Recent restrictions within the EU on the use of polybrominated diphenyl ethers (PBDEs), without concomitant relaxation on fire retardancy regulations has led to an increased focus on alternative flame retardants. One such alternative are organophosphate flame retardants (PFRs), where in the US, the detection frequency of tris(1,3-dichloroisopropyl) phosphate (TDCIPP) in domestic sofas increased significantly from 24% detection in items purchased prior to 2005 to 52% in those bought post-2005 (Stapleton et al., 2012). PFRs have a wide range of uses. Along with TDCIPP, triphenyl phosphate (TPHP) and tris(2-chloroisopropyl) phosphate (TCIPP) have been used substantially to flame retard foam upholstery in cars, as well as in domestic and office applications. Moreover, non-chlorinated organophosphates like tri-n-butyl-phosphate (TNBP) are used mainly as plasticisers (Marklund et al., 2003). As PFRs are used as additive rather than reactive FRs, their emission from treated products is comparatively facile and their presence in indoor dust from countries such as Belgium, Germany, Japan, the Netherlands, Norway, Sweden, and the US has been reported (inter alia Van den Eede et al., 2011; Brommer et al., 2012; Kanazawa et al., 2010; Brandsma et al., 2014; Cequier et al., 2014; Bergh et al., 2011b; Dodson et al., 2012).

To date, studies of the adverse health effects of PFRs are scarce, thereby hampering complete understanding of their toxicity. The currently available data were reviewed recently (Van der Veen and de Boer, 2012) indicating that chlorinated alkyl phosphates are suspected carcinogens, with other effects also reported. These include: reduced thyroid hormone levels for TDCIPP (Meeker and Stapleton, 2010); contact dermatitis (Camarasa and Serra-Baldrich, 1992) and links with altered hormone levels and decreased semen quality for TPHP (Meeker and Stapleton, 2010); neurotoxicity for TDCIPP (Dishaw et al. 2011), tris(2-chloroethyl) phosphate (TCEP) (Umezu et al., 1998), and tri-cresylphosphate (TMPP) (Bolgar et al., 2008); haemolytic effects for 2-ethylhexyl diphenyl phosphate (EHDPP) (Jonsson and Nilsson, 2003); and increased risk of mucosal symptoms of sick housing

* Corresponding author.
E-mail address: S.J.Harrad@bham.ac.uk (S. Harrad).

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syndrome linked with higher indoor concentrations of TNBP (Kanazawa et al., 2010).

While the presence of brominated flame retardants (BFRs) such as PBDEs has been characterised extensively in indoor dust from a variety of UK microenvironments (Harrad et al., 2008, 2010), as yet no data exist on concentrations of PFRs in UK indoor dust. This study therefore determines concentrations of PFRs in samples of dust from UK cars, classrooms, living rooms, and offices. To our knowledge, our study represents the broadest survey to date of PFRs in dust from microenvironment categories relevant to human exposure, as well as being the largest survey of PFRs in offices. Our data are compared to values from other countries and used to derive estimates of exposure of UK adults and young children to PFRs via dust ingestion. These exposure estimates are compared with appropriate health-based limit values (HBLVs). To evaluate the level of UK indoor contamination with PFRs relative to that of PBDEs, we compare concentrations of PFRs with those of PBDEs detected in the same samples of classroom dust. Finally, we examine our data for relationships between putative sources and concentrations of PFRs in our dust samples.

2. Materials and methods

2.1. Sampling

Samples of settled dust were collected in 2011 and 2012 using previously reported methods (Harrad et al., 2008) from cars (n = 21), living rooms (n = 32), and offices (n = 61) from a variety of locations within the West Midlands conurbation in the UK. In brief, samples were collected by vacuuming a specified area of floor (1 m2 if carpeted, 4 m2 if bare floor) for a specified period of time (1 min if carpeted, 4 mins if bare floor). Dust was retained by a nylon "sock" (25 μm mesh size), inserted in the furniture attachment of the vacuum cleaner. In addition, we analysed archived samples of dust collected in 2007–08 from UK primary school and child daycare centre classrooms (n = 28) for which concentrations of other contaminants – including PBDEs – have been reported (Harrad et al., 2010). Following collection, samples were passed through a 500 μm mesh sieve prior to analysis.

2.2. Analysis

Based on their relative abundance in previous studies, the following PFRs were targeted: TDCIPP, TCIPP, TPHP, TNBP, EHDPP, TCEP, and TMPP. We originally targeted tris(2-butoxyethyl) phosphate (TBEOP) also. However, the comparatively high blank values we observed coupled with the highly variable concentrations we determined in initial evaluations of accuracy, which mirrored similar reports by other authors (Brandsma et al., 2013), meant that it was excluded from this study. Concentrations were determined via GC-MS in accordance with methods reported previously (Brommer et al., 2012). Briefly, dust samples (50 mg, accurately weighed), were treated with 100 ng each of d_{15}-TPHP and d_{27}-TNBP as internal (or surrogate) standards, and extracted via vortexing, sonication, and centrifugation with three successive aliquots of hexane:acetone (3:1 v/v, 2 mL). The combined extracts were reduced using a gentle stream of N_2 to incipient dryness and reconstituted with 1 mL hexane prior to elution through a pasteur pipette containing 1 g Florisil. Following initial elution with hexane (8 mL, fraction not analysed), PFRs were eluted with ethyl acetate (10 mL). This second fraction was reduced to incipent dryness under a stream of N_2 prior to reconstitution with 100 μL of 1 ng/μL triamylphosphate (TAP) in iso-octane as recovery determination (or syringe) standard. Final sample extracts were analysed via GC-EIMS using an Agilent 5975C MSD fitted with a DB-5 ms column (30 m, 0.25 mm id, 0.25 μm film thickness). The GC temperature programme was 90 °C, hold for 1.25 min, ramp 10 °C/min to 170 °C, ramp 5 °C/min to 240 °C, hold for 10 min, ramp 20 °C/min to 310 °C, hold for 10 min. The mass spectrometer was operated in selected ion electron ionisation mode, with Table SD-1 listing the ions monitored for each targeted compound.

Purchased standards of TCIPP, TDCIPP and TMPP contained different isomers. The commercial TCIPP mixture consists of 3 different isomers. As the third eluting isomer has a markedly lower response than the others, it can only be seen at higher concentrations. Due to this fact, it is common practice to report TCIPP levels as a sum of the 1st two eluting isomers only (referred to as TCIPP 1 and TCIPP 2) (Brandsma et al., 2013). This practice is adopted in this study. Where elevated concentrations of TCIPP were present, TCIPP 3 was used as an additional quality control step to confirm the elevated TCIPP concentration in the sample but this isomer is not reported. The commercial TDCIPP mixture consists of 2 different isomers with both reported. Hence reported TDCIPP concentrations in this study are the sum of both isomers. Similarly, four different peaks are distinguishable (referred to as TMPP 1, 2, 3, and 4) in the commercial TMPP mixture when analysed via GC. TMPP concentrations in this study are therefore reported as the sum of these 4 peaks.

2.3. QA/QC

One aliquot of SRM2585 (NIST, organics in dust) was analysed with every batch of 10 dust samples. As the UK samples were analysed as part of a larger study, overall 56 aliquots of SRM2585 were analysed. Table SD-2 illustrates the high reproducibility of our method with relative standard deviations ranging between 6.4% and 14% for individual PFRs. Neither certified nor indicative values for our target PFRs are provided by NIST. However, Table SD-2 compares our data with the average $\pm\sigma_n$ values reported for SRM2585 in a recent report on an interlaboratory trial of PFR analysis in environmental samples (Brandsma et al., 2013). The good agreement between our reported concentrations and those reported in the interlaboratory trial are evidence of the accuracy of our data.

At least one blank was run with every sample batch (thus every 6th sample was a blank). Overall, as this UK study was part of a larger project analysing PFRs in dust, a total of 107 blanks were run. A blank sample consisted of pre-baked Na_2SO_4 treated as sampled dust. In addition, field blanks were collected. These consisted of pre-baked Na_2SO_4, taken to the sampling location, spread on aluminium foil and vacuumed as a normal sample. Acceptable blank concentrations were deemed those where the concentration of the target analyte was less than 5% of the lowest concentration in that batch. Where the analyte concentration in the blank fell between 5% and 20% of the concentration in samples from that batch, concentrations were corrected accordingly via subtraction of the blank concentration. If blank concentrations exceeded 20% of those in samples from the same batch, all samples in that batch were discarded and reanalysed. Concentrations of TNBP, EHDPP, TDCIPP and TMPP were below detection limits in all blank samples analysed. In contrast, low levels of TCEP (median = 0.023 μg g^{-1}), TCIPP (median = 0.03 μg g^{-1}), and TPHP (median 0.006 μg g^{-1}) were detected in a small proportion of blanks. Where appropriate, correction for these blank levels was conducted.

3. Results and discussion

3.1. Concentrations of PFRs in UK indoor dust

A statistical summary of the concentrations of PFRs in all samples analysed in this study is provided as Table 1, alongside data from other studies elsewhere in the world. Concentrations of PFRs in individual samples analysed in this study are provided as Table SD-3. PFRs were detected in all samples, with TCIPP relatively abundant in all microenvironments, with EHDPP, TDCIPP, and TPHP also featuring strongly in one or more microenvironments. In general, concentrations in this study are broadly similar in magnitude (i.e. μg g^{-1} levels) to those reported elsewhere in the world, with some differences in the relative abundance