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Concentrations of organophosphate flame retardants in dust from cars, homes, and offices: An international comparison

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ABSTRACT

Concentrations of a number of organophosphate flame retardants (PFRs) were measured in floor dust collected from living rooms in Australia (n = 42), Canada (n = 14), Germany (n = 22), and Kazakhstan (n = 9); cars from Australia (n = 39) and Germany (n = 19); and offices from Germany (n = 25) and Kazahkstan (n = 8). PFR concentrations in these samples were compared with each other and with previously reported data for PFRs in dust from similar microenvironments in the UK. Our data reveal significant between-country differences in both absolute concentrations and the relative abundance of specific PFRs in each of the microenvironments studied. Most notably, concentrations of TCIPP in UK living room dust (median = 21 μg g^{-1}) exceeded significantly ($p < 0.05$) those in all other countries studied here; a substantial number of car dust samples contained elevated concentrations of TDCIPP, and German samples generally contained lower levels of PFRs in all microenvironments studied. In addition, PFRs were determined in dust samples collected from living room couches in both Australia (n = 41) and the UK (n = 10). The elevated concentrations of TCIPP in UK living room dust are likely attributable to the favoured use of this PFR in UK couch foam. This is indicated by concentrations of TCIPP in UK couch dust (median = 610 μg g^{-1}) exceeding significantly those in Australian couch dust (median = 2.9 μg g^{-1}). Moreover, concentrations of TCIPP in UK couch dust originating from couches 15 years old or less, display a marked relationship with the age of the couch, with concentrations in such samples increasing significantly ($p < 0.01$) with couch age.

1. Introduction

Recent restrictions worldwide on the use of polybrominated diphenyl ethers (PBDEs), have led to increased use of alternative flame retardants, such as organophosphate flame retardants (PFRs). As PFRs are used as additive flame retardants (FRs), their transfer from products in which they are used into the environment is relatively facile, and their presence in indoor dust has been reported in a number of studies [1–6,14,15,17,19,20,24,26,27,29,30]. We reported recently on concentrations of PFRs in samples of floor dust from UK cars, school classrooms, homes, and offices [11].

The currently available data on the adverse health effects of PFRs were reviewed recently [31]. In summary, chlorinated alkyl phosphates such as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloro-2-propyl)phosphate (TDCIPP) are suspected carcinogens, with other effects such as reduced thyroid hormone levels [25], contact dermatitis [12], and neurotoxicity [16] also reported for TDCIPP. For the non-chlorinated PFRs, reported impacts include links with altered hormone levels and decreased semen quality for triphenyl phosphate (TPHP) [25]; neurotoxicity for tri-cresylphosphate (TMPP) [7]; haemolytic effects for 2-ethylhexyl diphenyl phosphate (EHDPP) [22]; and increased risk of mucosal symptoms of sick housing syndrome linked with higher indoor concentrations of tri-*n*-butyl phosphate (TNBP) [23].

While our UK study found no significant relationships between PFR concentrations in dust from cars, classrooms, homes, and

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offices and the presence of putative PFR sources in such UK microenvironments [11]; the same study did highlight elevated concentrations of TCIPP in house dust and suggested that this was likely attributable to extensive use of TCIPP in couch foam, as reported in the US [28]. This study explores this further, by comparing concentrations of TCIPP in Australian couch dust and from living rooms in which the couch was located; hypothesising that significantly elevated concentrations of TCIPP in couch compared to floor dust, combined with significant positive correlation between the two groups, would indicate couches to be a significant source. Moreover, while our earlier UK study [11] highlighted possible international differences in the absolute concentrations and relative abundance of individual PFRs in indoor dust; disparities between the sampling and analytical methodology employed by the various laboratories conducting studies in different countries, introduces some uncertainty. As a result, this study employs identical dust collection and analytical procedures to evaluate differences in concentrations of PFRs in samples of indoor dust taken from a variety of microenvironment categories in each of the following countries: Australia, Canada, Germany, and Kazakhstan. Concentrations reported in these samples are compared with those reported previously for the UK. To the best of our knowledge, these data are the first reported for Kazahkstan.

2. Materials and methods

2.1. Sampling

Samples of settled dust were collected at various points over the period 2011 to 2012 (except for Kazahkstani samples that were collected in 2009) using previously reported methods [21]. Samples were collected from: cars in Australia (n = 39) and Germany (n = 19), living rooms in Australia (n = 42), Canada (n = 14), Germany (n = 22), and Kazahkstan (n = 9); as well as offices from Germany (n = 25) and Kazahkstan (n = 8). We also collected couch dust samples from Australia (n = 41) and the UK (n = 10). Australian samples were collected predominantly from Brisbane and Sydney, Canadian from Toronto, German from several different cities, Kazahkstani from Almaty and Astana, while UK samples were obtained in the Birmingham area. For offices and living rooms, samples were obtained by vacuuming a set area of floor (1 m^2 if carpeted, 4 m^2 if bare floor) for a set duration (1 min if carpeted, 4 min if bare floor). For cars, the seats and the dashboard area were sampled for 2 min, with couch dust collected by vacuuming the areas in contact with the sitter for 2 min. Dust was retained within a nylon "sock" (25 μm mesh size), placed in the vacuum cleaner furniture attachment. Following collection, samples were passed through a 500 μm mesh sieve prior to analysis.

2.2. Analysis

Consistent with our previous study of PFRs in UK indoor dust, we measured concentrations of the following PFRs: TDCIPP, TCIPP, TPHP, TNBP, EHDPP, TCEP, and TMPP. An exception to this was for 12, 6, and 10 samples of German car, living room, and office dust respectively, for which data have been reported previously [10] but in which EHDPP was not measured. Concentrations were determined via GC-MS in accordance with methods reported previously [10,11]. 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 near 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-5ms 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. While the commercial TCIPP mixture consists of 3 different isomers, the third eluting isomer has a markedly lower response than the others, and can only be seen at higher concentrations. Thus we report TCIPP levels here as a sum of the 1st two eluting isomers only (referred to as TCIPP 1 and TCIPP 2) [8,11]. Likewise, consistent with our UK study [11], concentrations of TDCIPP and TMPP in this study are reported as the sum of both and all four isomers respectively.

2.3. QA/QC

One aliquot of SRM2585 (NIST, organics in dust) was analysed with every batch of 10 dust samples. As the samples reported here are part of a larger PhD study, a total of 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 reported by NIST. Nonetheless, Table SD-2 compares our data with the average$\pm\sigma_n$ (consensus) values obtained for SRM2585 in an interlaboratory trial of PFR analysis in environmental samples [8]. The good agreement between our reported concentrations and those reported in the interlaboratory trial is evidence that our data are consistent with those published by other researchers.

One blank (comprising pre-baked Na_2SO_4 treated as a dust sample) was analysed with every sample batch (thus every 6th sample was a blank), and a total of 107 blanks were analysed. Field blanks were also collected. These consisted of pre-baked Na_2SO_4, taken to the sampling location, spread on aluminium foil and vacuumed as a normal sample – i.e. 50 mg of Na_2SO_4 was analysed as a surrogate for dust. Concentrations in a batch of samples were not corrected for those detected in blanks where the concentration of the target PFR in the blank from the same batch was less than 5% of the lowest concentration in that batch. Where the PFR concentration in the blank was 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, (expressed as ng PFR per g Na_2SO_4 "dust") 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.