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► To cite this version:

Chang He, Xianyu Wang, Phong Thai, Christine Baduel, Christie Gallen, et al.. Organophosphate and brominated flame retardants in Australian indoor environments: Levels, sources, and preliminary assessment of human exposure. *Environmental Pollution*, 2018, 235, pp.670 - 679. 10.1016/j.envpol.2017.12.017 . hal-01744765

HAL Id: hal-01744765

<https://hal.science/hal-01744765v1>

Submitted on 26 Sep 2024

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He, Chang, Wang, Xianyu, [Thai, Phong](#), Baduel, Christine, Gallen, Christie, Banks, Andrew, Bainton, Paul, English, Karin, & Mueller, Jochen (2018)

Organophosphate and brominated flame retardants in Australian indoor environments: Levels, sources, and preliminary assessment of human exposure.

Environmental Pollution, 235, pp. 670-679.

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<https://doi.org/10.1016/j.envpol.2017.12.017>

Organophosphate and brominated flame retardants in Australian indoor environments: Levels, sources, and preliminary assessment of human exposure

Chang He, Xianyu Wang, Phong Thai, Christine Baduel, Christie Gallen, Andrew Banks, Paul Bainton, Karin English, & Jochen F. Mueller

Concentrations of nine organophosphate flame retardants (OPFRs) and eight polybrominated diphenyl ethers (PBDEs) were measured in samples of indoor dust (n = 85) and air (n = 45) from Australian houses, offices, hotels, and transportation (buses, trains, and aircraft). All target compounds were detected in indoor dust and air samples. Median P9OPFRs concentrations were 40 mg/g in dust and 44 ng/m³ in indoor air, while median P8PBDEs concentrations were 2.1 mg/g and 0.049 ng/m³.

Concentrations of FRs were higher in rooms that contained carpet, air conditioners, and various electronic items. Estimated daily intakes in adults are 14000 pg/kg body weight/day and 330 pg/kg body weight/day for P9OPFRs and P8PBDEs, respectively. Our results suggest that for the volatile FRs such as tris(2-chloroethyl) phosphate (TCEP) and TCIPP, inhalation is expected to be the more important intake pathway compared to dust ingestion and dermal contact.

1. Introduction

Flame retardants (FRs) have been widely used as additives for several decades to meet fire safety standards for consumer products. Before 2004, polybrominated diphenyl ethers (PBDEs) were the most common FRs in commercial and household products (Ma et al., 2013). Owing to the increasing concerns about their persistence, bioaccumulation, and toxicity, restrictions were implemented worldwide (Tao et al., 2017). The commercial Penta- and Octa-BDE mixtures of PBDEs, were banned in Europe (in 1998) and North America (in 2004), followed by a ban on Deca-BDE in Europe and several states of the USA (in 2008) (Alaee et al., 2003; Kemmlein et al., 2009). PBDEs have not been manufactured in Australia, and the import of penta-BDE and octa-BDE to Australia was ceased in 2005 (NICNAS, 2007; Toms et al., 2008).

The phase-out of PBDEs has led to an increase in the production and use of alternative FRs over the past few years, including organophosphate flame retardants (OPFRs) (van der Veen and de Boer, 2012; Butt et al., 2014). In 2006, the global consumption volume of OPFRs was 465,000 tons (van der Veen and de Boer, 2012) and was projected to expand by 4.6% per year until 2018 to reach a volume of 2.8 million tons (ICL, 2015). Similar to PBDEs, OPFRs have also been detected in air, dust, wastewater, human serum, and breast milk in recent years (Abdallah and Covaci, 2014; Kim et al., 2014; Shoeib et al., 2014; Cequier et al., 2015a; O'Brien et al., 2015; Li et al., 2017). OPFRs may also have adverse effects on the environment and human health. In experimental studies, OPFRs have been observed to disrupt normal endocrine and reproductive functions and nervous system development and are also suspected carcinogens (World Health Organization, 1991a, b; 1998; van der Veen and de Boer, 2012). Although data are scarce, human epidemiological studies suggest that OPFR exposure is associated with human hormone levels and semen quality parameters (Stapleton et al., 2009; Meeker and Stapleton, 2010; Meeker et al., 2013). Thus, it is important to assess their potential risks on environment and human health.

There is therefore considerable interest in how FRs are released from sources, enter environmental compartments, and their ability to accumulate in biota including humans. Moreover, a recent study showed that FRs were detected in a broad range of consumer products including foam, mattress, and electrical equipment in Australia (Gallen et al., 2014). Treated products therefore represent significant reservoirs of FRs, so they are the focus of attention for source identification (Abbasi et al., 2015). Their main pathways of release include volatilization or abrasion during the use of treated products (Kemmlein et al., 2003; Webster et al., 2009; Johnson et al., 2010). Following their release, like other semi-volatile organic compounds, FRs can distribute throughout the indoor environment through repeated partitioning to dust and surfaces followed by volatilization (Weschler and Nazaroff, 2008; Mitro et al., 2016). Human intake of FRs in the indoor environment occurs through dust ingestion, dermal contact, and inhalation (Fromme et al., 2009), and these chemicals or their metabolites have been detected in human specimens (Butt et al., 2014; Cequier et al., 2015b; Van den Eede et al., 2015).

In this study, we investigated the level, sources, and human exposure to FRs, including nine highly produced OPFRs (tri-n-butyl phosphate [TNBP], tris(2-chloroethyl) phosphate [TCEP], tris(2-chloroisopropyl) phosphate [TCIPP], tri(1,3-dichloroisopropyl)phosphate [TDCIPP], tris(2-butoxyethyl) phosphate [TBOEP], triphenyl phosphate [TPHP], 2-ethylhexyl diphenyl phosphate [EHDPP], tris(2-ethylhexyl) phosphate [TEHP], and tris(methylphenyl) phosphate [TMPP]) and eight PBDE congeners (28, 47, 99, 100, 153, 154, 183, and 209) (Table 1) for which limited data were available in Australia (Toms et al., 2009a; Harrad et al., 2016). The objectives of this study were (1) to understand the levels and distribution of OPFRs and PBDEs in Australian indoor environment including private houses, offices, hotels, and transportation; (2) to investigate the contamination profile and composition and attempt to elucidate the sources of FRs in microenvironments,

especially the influence from indoor products; and (3) to assess the intake of FRs from indoor environments through dust ingestion, dermal contact, and air inhalation in Australian adults and toddlers.

Table 1

2. Materials and methods

2.1. Sampling protocols

Dust and air samples were collected in Brisbane and Canberra, Australia (Fig. S1), from January to March 2015. Dust samples were collected from 85 indoor settings including 40 private houses, 27 offices spaces, 15 public transportation (buses, trains, and aircraft), and 3 hotels. Air samples were collected from 16 houses and 29 offices, where matched dust-air samples were available in 16 houses and 24 offices. During dust sampling, the presence of polymer, foam, and textile products that were accessible in the sampling sites were recorded. A product that presented in >5% rooms was set as a category to assess their contributions to FR concentrations. For this project, all the samples have been collected with ethics approval from the University of Queensland (approval number: 2015000153).

Settled dust was collected using a clean nylon sampling sock that was inserted into the entry hose of a vacuum cleaner (Bosch). Samples were collected by vacuuming for approximately 15 min over the surfaces in the living areas of the home (bedroom, living room, etc) and of the office. The sampling sock was sealed in a zip lock bag and stored at room temperature once they arrived at the laboratory. The dust samples were sieved using a pre-cleaned 1 mm mesh sieve to remove larger particles and to ensure the homogeneity of the sample.

Air samples were collected by a polyurethane foam–glass fiber filter (PUF-GFF) passive air sampler (PAS) adopted from the design of Harner et al. (2004) (Fig. S2). PUF and GFF were pre-cleaned by the accelerated solvent extraction (ASE) method using 73 mL n-hexane and acetone mixture (50:50, v:v). For individual sample, a PUF disk was inserted into a metal housing covered by a GFF. This feature allows that both airborne particulates and volatile chemicals are collected. Samplers were placed for between 48 and 101 days in each room that was sampled. The different deposit days was caused by the inconvenience of the house owners or office workers. These results were later corrected by sampling rates to eliminate the effect of different numbers of sampling days (Fig. S3).

After retrieval, PUF and GFF were stored separately at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2. Analytical methods

The analytical procedure including method validation used for the analysis of OPFRs and BDEs is described in detail in He et al. (2017). Samples were extracted by the ASE method and purified using a two-step solid-phase extraction purification method. Briefly, PUF and GFF samples were analyzed separately, and ~ 0.1 g of dust samples were used for analysis. Air or dust samples were spiked with internal standards (1 ng 13C12-PBDE mixture, 30 ng 13C12-BDE 209, 10 ng each of TCIPP-d18, TPHP-d15, and TNBP-d27), and extracted by the ASE method. Samples were separated into two fractions on a silica gel and alumina cartridge, eluting first with 42 mL of n-hexane and DCM mixture (50:50, v:v) and then with 24 mL of ethyl acetate. For air samples, two fractions were then concentrated and combined. For dust samples, a further clean-up step was needed. A

Strata™ FL-PR cartridge was used for the first fraction and an Envi-Carb cartridge for the second fraction. The two fractions were then combined. The combined fractions for both air and dust samples were finally concentrated to near dryness under a gentle stream of nitrogen and made up in 50 µL of instrument standards (200 pg/µL 13C12-BDE 77 in isoctane).

The analysis of OPFRs and PBDEs (except for BDE 209) was performed using a TSQ Quantum GC (Thermo Fisher Scientific) system coupled with triple quadrupole mass spectrometer Quantum (QqQ) and a TRACE GC Ultra equipped with a TriPlus autosampler. BDE 209 was analyzed on a Shimadzu QP2010 gas chromatography mass spectrometer (GC-2010 coupled with a GCMS QP-2010). Details are given in the Supporting Information (SI).

2.3. Derivation of concentration in air

Air concentrations were calculated based on the study by Rauert et al. (2016). In general, concentrations in air for targeted chemicals are derived from passive samplers by dividing the amount of chemical collected on the sampler (e.g., pg/sampler) by an effective air sampling volume (V_{eff} , m³), as OPFRs and PBDEs have been shown to maintain linear-phase sampling in PUFs at a rate of about 4.0 m³/day and 3.5 m³/day, respectively, for deployment periods of a few months (Harner et al., 2006; Shoeib et al., 2014; Liu et al., 2016).

These V_{eff} values were confirmed by a further validation test, which is provided in the SI. So the V_{eff} can be simply estimated as the linear-phase sampling rate multiplied by the number of sampling days.

2.4. Quality assurance and quality control

Field blank samples were collected during sample collection. For dust samples, field blanks samples were prepared by introducing pre-cleaned ~5 g of Na₂SO₄ into sampling socks on site, and they were then treated as all other dust samples collected on different sites. As for the dust samples, field blank samples containing Na₂SO₄ were sieved before extraction. For passive air samples, field blank samples were prepared by placing clean PUF and GFF into metal housings, for X min. The field blank sample was extracted and analyzed in each batch of samples, and the average blank value for each analyte was subtracted from each sample mass.

The limits of detection (LODs) were defined as the average procedural blank concentrations plus three times their standard deviations (SDs), and limits of quantifications (LOQs) were defined as average blank concentrations plus ten times their SD, which were 0.20–1000 ng/g for dust and 0.00080–0.29 ng/m³ for air samples. LOQs for individual chemicals are given in the SI (Table S3). The recoveries of internal standards ranged from 78% to 130% with a relative SD (RSD) below 20% in most cases, except for TCIPP where the RSD was 27%. A pooled QC sample was included in each dust batch to ensure the reproducibility of the analytical method. Ten duplicates of dust samples and 5 duplicates of air samples were collected and analyzed in different batches. The RSDs of individual concentrations in QC and duplicate samples were less than 30%.

2.5. Statistical analysis

Statistical analyses were performed by using SPSS 23 (Chicago, USA) software package for Windows. The Student t-test was performed to compare the concentrations and profiles of FRs in different microenvironments and also the influences from different consumer products. Bivariate correlations (Spearman correlation coefficients) were used to investigate the correlation between chemicals and to

describe the relationships between the products (presence and/or amount of item in the indoor environment) and FR concentrations.

The Spearman rank correlation analysis was performed to assess the correlations between dust and air concentrations. Statistical significance was set at $p < .05$. Concentrations of target compounds were assumed to be LOQ/2 when they were lower than the LOQ.

Human intakes of FRs from inhalation, dust ingestion, and dermal contact with dust were estimated separately. Daily intakes through inhalation were estimated according to equation (1) (Harrad et al., 2004).

$$(1) \text{Intake } (\mu\text{g}/\text{kg}/\text{day}) = [(C_w F_w) + (C_h F_h) + (C_t F_t) + (C_o F_o)] \times RR / (BW \times 1000)$$

where $C_w/h/t/o$ is the Σ FR concentration in workplace/home/transport/outdoor air, respectively, (ng/m^3); $F_w/h/t/o$ is the respective fraction of day spent at workplace/home/transport/outdoor; RR is the respiration rate ($20 \text{ m}^3/\text{d}$ for adults, and $4.5 \text{ m}^3/\text{d}$ for toddlers (EPA, 1997)); and BW is the body weight (kg); the value 1000 is used to convert ng to μg .

Daily intakes through dust ingestion were estimated according to equation (2) (Tajima et al., 2014).

$$(2) \text{Intake } (\mu\text{g}/\text{kg}/\text{day}) = C_{\text{dust}} \times \text{DIG} / (BW \times 1000)$$

where C_{dust} is the dust concentration for each FR, DIG is the estimated dust ingestion rate (mg/day), and 1000 is used to convert mg to g.

Daily intakes through dermal contact with dust were estimated according to equation (3). (Johnson-Restrepo and Kannan, 2009).

$$(3) \text{Intake } (\mu\text{g}/\text{kg}/\text{day}) = C_{\text{dust}} \times \text{BSA} \times \text{SAS} \times \text{AF} \times F_w/h/t/o / (BW \times 1000)$$

where BSA is the body surface area (cm^2/day); SAS is the soil adhered to skin (mg/cm^2); and AF is the fraction of chemicals absorbed in the skin.

3. Results and discussions

3.1. Concentrations and patterns of OPFRs and PBDEs in indoor dust samples

Concentration for Σ 9OPFRs in the dust samples ranged from 7.4 to 880 $\mu\text{g}/\text{g}$ (median, 40 $\mu\text{g}/\text{g}$) (shown as Table S3 and Fig. 1). TCEP, TCIPP, TBOEP, TPHP, EHDPP, and TMPP were more frequently detected (DFs >95%) than other OPFRs (TNBP, TDCIPP, and TEHP). The compounds with the highest concentration in dust from all the microenvironments combined were TBOEP and TCIPP, which accounted for 37% and 18% of Σ 9OPFRs on average, respectively. The predominance of TBOEP and TCIPP suggests a greater use of these chemicals in consumer products in Australia. We found a median concentration of 15 $\mu\text{g}/\text{g}$ for TBOEP in the dust samples from Australia, which is similar to what has been reported in studies from the Netherlands (Brandsma et al., 2014) and Sweden (Bergh et al., 2011). TBOEP is used as a plasticizer in rubber and plastics and as a polisher in floor-finishing products (up to 0.5%–8%) (Marklund et al., 2003; Kajiwara et al., 2011; Brandsma et al., 2014), which might be an important source in indoor environments. The median concentrations of TCIPP in indoor environments range from 0.57 to 26 $\mu\text{g}/\text{g}$, which exceeded the concentrations reported from the USA (Stapleton et al., 2009) but is comparable to the data from Asian (Araki et al., 2014; Tajima et al., 2014; He et al., 2015), and European countries (Garcia et al., 2007; Dirtu et al., 2012). Overall, alkyl OPFRs (TNBP, TBOEP, and TEHP) predominated in Australian dust, accounting for ~50% of the Σ 9OPFRs, which was followed by

chlorinated OPFRs (TCIPP, TDCIPP, and TCEP, ~36%) and aryl OPFRs (TPHP, TMPP, and EHDPP, ~15%). This contamination profile was similar to that in Romanian (Dirtu et al., 2012) and Spanish (Garcia et al., 2007) indoor dust and also is consistent with the profile in Australian wastewater (O'Brien et al., 2015). In contrast, chlorinated OPFRs were found to predominate the OPFR profiles reported for dust samples collected from Saudi Arabia (Ali et al., 2016). Such country-specific patterns of OPFR profiles in the indoor microenvironment could be explained by different patterns of usage as FRs and/or as plasticizers, by the time of usage (recent/past application), as well as by the sampling method (Garcia et al., 2007; Dirtu et al., 2012; Ali et al., 2014, 2016).

Fig. 1

Concentrations of Σ 8PBDEs ranged from 0.42–18 $\mu\text{g/g}$. BDE 209 was the most frequently detected, as it was quantifiable in all samples. BDE 47, 99, 100, 153, and 183 were detected in most samples (>70%), while BDE 28 and 154 were detected only in less than 50% samples (Table S3). Concentrations for Σ 8PBDEs were 0.091–300 $\mu\text{g/g}$ (median of 2.1 $\mu\text{g/g}$) in Australian indoor dust. Σ 8PBDE concentration was lower than that in studies conducted in the UK (Tao et al., 2016) and the USA (Johnson et al., 2013) but higher than that in Germany (Fromme et al., 2009; Brommer et al., 2012) and Kuwaiti (Ali et al., 2013). This result was consistent with our previous study in 2005 of 5 house dust (0.087–0.73 $\mu\text{g/g}$) and 3 office dust (0.58–3.1 $\mu\text{g/g}$) samples (Toms et al., 2009a). This indicates the constant release of BDEs from legacy sources and products. BDE 209 predominated in dust, contributing to 86%, 81%, 97%, and 88% of Σ 8PBDEs in samples from homes, offices, transportation, and hotels, respectively. This predominance of BDE 209 was similar to other countries in Europe and Asia but different when compared to studies conducted in North America where greater use of penta-BDE led to a greater contribution from BDE 47 and 99 (Fromme et al., 2009; Toms et al., 2009a; Zhu et al., 2015; Tao et al., 2016).

The highest FR concentrations were found in the dust collected from public transport vehicles (buses/trains/planes) (median of 190 and 8.1 $\mu\text{g/g}$ for Σ 9OPFRs and Σ 8PBDEs, respectively). Compared with the transportation, significantly lower concentrations of Σ 9OPFR were found in samples from houses (median 33 $\mu\text{g/g}$) and offices (median 32 $\mu\text{g/g}$). Likewise for PBDEs, lower concentrations of Σ 8PBDEs were found in samples from houses (median 2.1 $\mu\text{g/g}$) and offices (median 2.1 $\mu\text{g/g}$) compared to transportation, although the finding was not significant. In some other studies, higher levels of OPFRs were also reported in dust from transportation (e.g., bus and aircraft) compared to house or office dust (Brommer et al., 2012; Ali et al., 2013, 2016; Abdallah and Covaci, 2014). The highest level of fire safety is required for materials used for public transportation (ACC., 2017). The applications of FRs in public transportation include in polypropylene polymers and acrylonitrile butadiene styrene used in instrument panels, and also in textiles, PUFs, and electronics (Brommer et al., 2012; Ali et al., 2013, 2016; Abdallah and Covaci, 2014).

Among the 15 transportation dust samples, 5 were collected from aircraft cabins, 5 were collected from trains, and the other 5 were from buses. For Σ 9OPFRs and Σ 8PBDEs, similar concentrations were found in aircraft and trains, while concentrations were lower in buses. However, significantly higher ($P < .001$) concentrations of TNBP and TMPP were found in aircraft dust. Both TMPP and TNBP were used in plastics and rubbers (Wei et al., 2015), which are commonly used in aircraft. It also should be noted that TMPP is one of the most frequently used aircraft turbine engine oils (De Nola et al., 2008), and TNBP is also used as hydraulic oil in aircraft (Solbu et al., 2011). More research is needed to assess the potential release of TMPP and TNBP from oil.

To visualize the different sources of FRs in different microenvironments, the composition of FRs between these environments was assessed (Fig. 2). Although alkyl phosphate (including TBOEP) predominated in all the indoor environments, the contribution of aryl phosphates in transportation (36%) was significantly higher ($P < .05$) than those in offices (12%), houses (15%), and hotels (5.6%). The aryl phosphate EHDPP, which is

added in PVC (polyvinylchloride) (van der Veen and de Boer, 2012), appeared to drive this trend, as it accounted for 27%, 2.1%, 9.7%, and 4.3% of Σ OPFR in transportation, houses, offices, and hotels, respectively.

Fig. 2

To investigate the possible common sources of OPFRs and PBDEs, the Spearman rank correlation analysis was used to assess relationships between each chemical/group. The correlation was not investigated in hotel dust owing to the limited number of samples collected. Detailed information of these relationships is given in Table S5. A strong and significant correlation ($r = 0.721$, $P < .01$) between Σ OPFR and Σ 8PBDE concentrations was found in transportation dust. Strong correlations ($r > 0.79$, $P < .001$) were found among BDE 47, BDE 99, BDE 100, BDE 153, and BDE 154, which were all present in penta-BDE commercial products. In addition, all these penta-BDEs were moderately correlated with TCEP ($r > 0.45$, $P < .001$) and weakly correlated ($0.232 < r < 0.435$, $P < .032$) with TPHP, TBOEP, EHDPP, and BDE 209. Some OPFRs such as TPHP and TDCIPP have been reported as the replacement for penta-BDE for decades (Dodson et al., 2012). The similar distribution of penta-BDEs and these OPFRs in indoor dust is likely due to this trend in FR usage. The ratio of Σ 8PBDE/ Σ 9OPFR concentrations in dust can also be used to assess the replacement for PBDEs. In the USA, the value changed from 0.26 in 2006 to 0.19 in 2011, suggesting the gradually decreasing levels in the environment (Dodson et al., 2012). While in Europe, the values were 0.017 in homes and 0.011 in offices in 2010, when penta-BDE and octa-BDE have been banned for more than a decade (Brommer et al., 2012). In this study, the values were 0.064 in homes and 0.066 in offices. These ratios indicated the relatively high concentration and great usage of OPFRs in Australia. We cannot describe the phase-out process of PBDEs here owing to the lack of previous data in Australia, but these values could be used to track the changes of FR composition if we continue to investigate FR concentrations in air and/or dust overtime.

3.2. Concentrations and patterns of OPFRs and PBDEs in indoor air

Concentrations of Σ 9OPFRs were 7.2–760 ng/m³, with a median of 44 ng/m³, in Australian indoor air (Fig. 3). Our results are slightly higher than those in a study conducted in South America, where PASs were also applied to collect outdoor air (Rauert et al., 2016). TDCIPP and TMPP were only detected in ~60% of air samples, while the other OPFRs were detected in >98% of samples. In contrast to dust samples, 90% of the Σ 9OPFR concentration was attributable to chlorinated OPFRs, followed by alkyl OPFRs (9%) and aryl OPFRs (1%). TCIPP was the predominant OPFRs, with a median concentration of 16 ng/m³ and 48 ng/m³ in house and office air, respectively. This pattern is similar to studies on active air sampling (Yang et al., 2014; Zhou et al., 2017). The high presence of chlorinated OPFRs could be attributed to their use as plasticizers and FRs in a number of flexible and rigid PUFs (Marklund et al., 2003; Solbu et al., 2007; Stapleton et al., 2009) and also to their stability in the environment (van der Veen and de Boer, 2012). More volatile chemicals such as TNBP showed higher detection frequencies and higher concentrations in air, while the less volatile TBOEP and TMPP were less frequently detected in air samples. This is likely attributable to their relatively higher vapour pressures and lower KOA values (Tao et al., 2016).

Σ 8PBDEs concentration ranged from 0.014–0.56 ng/m³, with a median of 0.049 ng/m³. BDE 209 was the congener most frequently detected in air samples (96% detection frequency). Lower brominated diphenyl ethers were also frequently detected, but hexa- and hepta-BDEs were infrequently detected. The high detection frequency of BDE 209 and lower congeners is likely due to the widespread presence of BDE-209 in indoor environments and the higher vapour pressure of lower brominated diphenyl ethers (English et al., 2016). The high detection frequency of BDE 209 and lower congeners is likely due to the widespread presence of BDE-209 in indoor environments and the higher vapour pressure of lower brominated diphenyl ethers (English et al., 2016). The lower detection frequencies for hexa- and hepta-BDEs were possibly due to the lower sampling rates of PUF disk for high molecular congeners (Melymuk et al., 2011). Concentrations for Σ 8PBDEs were 0.010–4.4 ng/m³ (median, 0.049 ng/m³). The median concentrations were lower than those observed in studies from the USA (Bennett et al., 2015), Europe (Fromme et al., 2009; Vorkamp et al., 2011; Thuresson et al., 2012), and China (Ding et al., 2016) but comparable to a previous study in Australia in 2009

(Toms et al., 2009a). BDE 209 predominated in house and office air, contributing to 76% and 41% of $\Sigma 8$ PBDEs, respectively. The predominance of BDE-209 matched our previous study (Toms et al., 2009a).

Concentrations of OPFRs in air were generally greater in offices than in houses. In offices and houses, median concentrations of $\Sigma 9$ OPFRs were 56 and 23 ng/m³, respectively. By contrast, $\Sigma 8$ PBDEs concentrations were fairly similar between offices and houses, at 0.045 and 0.061 ng/m³, respectively. However, concentrations of penta-PBDE congeners, BDE 28 ($P = .02$), 47 ($P = .01$), 99 ($P = .04$), and 100 ($P = .03$) were significantly higher in office air than house air. We also assessed the relative contribution of individual FR congeners to total concentrations in offices versus homes. A relatively high contribution (37%) of BDE 47 was found in office air compared to houses (2%), suggesting that penta-BDE sources are more important in offices than homes.

Similar to dust, significant correlations ($P < .001$) were found between the following PBDE congeners: BDE 28, 47, 99, and 100 (Table S6). In addition, significant correlations were found between TDCIPP and TCEP ($r = 0.472$, $P < .01$). Correlations of BDE 153 and 154 were not assessed owing to their low detection frequencies.

3.3. Relationships between indoor dust and air

In 40 rooms (16 houses and 24 offices), we collected matched dust and air samples in the same area. Correlations between dust and air samples for individual FR concentrations were explored.

A strong correlation ($r = 0.665$, $P < .005$) was found in house samples for $\Sigma 9$ OPFRs. In addition, significant correlations between concentrations of chemicals in air and dust were observed in all houses and offices ($P < .05$) for the more volatile chemicals including TCEP ($r = 0.490$, $P < .01$), TCIPP ($r = 0.507$, $P < .01$), TDCIPP ($r = 0.585$, $P < .01$), TBOEP ($r = 0.329$, $P = .04$), BDE 99 ($r = 0.530$, $P < .01$), and BDE 100 ($r = 0.550$, $P < .01$) (Fig. 4).

Fig. 4

The ratio between dust and air concentration for a given chemical ($C_{\text{dust}}/C_{\text{air}}$) was used to assess the distribution between dust and air (Harrad et al., 2009; Tao et al., 2016). In this study, median values of the ratio in homes and offices were linearly associated with KOA values for most of the studied FRs (shown in Fig. S4), suggesting a thermodynamic equilibrium existed between air and dust concentrations of FRs. Similar relationships were reported by Cequier et al. (2014) for OPFRs and PBDEs in Norwegian homes and classrooms. The authors concluded that knowledge of concentrations of FRs in either air or dust permits prediction of their levels in the other phase, given the KOA of the compound in question (Cequier et al., 2014). However, in both office and house samples, TBOEP concentrations in dust were higher than would be expected, given the relatively low concentrations measured in air. This could be explained by the short half-time of TBOEP in air (3 h for photodegradation) (Wei et al., 2015). Regnery and Püttmann (2010) showed rapid degradation of TBOEP by sunlight. Marklund et al. (2005) also found an extremely high dust concentration of TBOEP coupled with low atmospheric concentrations in a Swedish prison.

3.4. Relationship between concentrations and indoor products

Indoor products that were present in >5% of sampled microenvironment and target chemicals that were detected in >50% of the analyzed samples were selected to assess the relationship. Owing to the differences in FR concentrations in house and offices as observed in the previous section, we investigated the house and office data separately in this section. The associations between chemicals in house dust/air and consumer products are shown in Fig. 5 and SI (Tables S7–S10).

Fig. 4

Significantly higher concentrations of TDCIPP ($P < .001$, medians of 0.93 and 0.26 $\mu\text{g/g}$ in carpeted and uncarpeted houses, respectively) and TCIPP ($P = .03$, medians of 7.1 and 1.5 $\mu\text{g/g}$ in carpeted and uncarpeted houses, respectively) were found in dust collected from carpeted houses. Higher mean concentrations of TDCIPP and TCIPP were also found in carpeted dwellings in Japan (Tajima et al., 2014; Araki et al., 2014). In houses with air conditioner, BDE 209 concentrations (median, 2.2 ng/m^3) were found to be significantly ($P < .01$) higher compared to houses without air conditioners (median, 0.76 ng/m^3). Sun et al. (2016) claimed that BDE 209 could be released from the air conditioner based on the fact that a higher concentration of BDE 209 in dust collected from the inside of air conditioners was found in China. In addition, dust concentration of TBOEP ($P = .01$) was higher in houses with lamps in the sampling area, and air concentration of EHDPP was higher in houses with microwaves in the sampling area. No differences in FR concentrations were observed based on the presence of TVs in the sampling area.

In the workplace, the presence of microwaves was associated with higher levels of TCEP ($P = .05$ in dust, $P = .02$ in air), TBOEP ($P = .02$ in air), BDE 47 ($P = .01$ in air), and BDE 209 ($P = .03$ in air). Laptops were also associated with greater TCEP concentrations in air ($P = .01$). Moreover, TCEP ($P = .01$) and TDCIPP ($P = .01$) concentrations in air were higher in offices with printers. FRs concentrations may be higher in media collected from offices because of the greater quantity of FR sources in these microenvironments, including electronic appliances (computers, printers, etc.) and FR-treated textiles and furniture.

Although we found some associations between FRs concentrations and specific products, further studies need to be undertaken to confirm such statements. Indeed, associations do not mean causality, so it is not possible to strongly conclude that a given chemical can be released from a particular product because of (1) the complexity and multiple sources of FRs in indoor microenvironments, (2) differences in behavior (such as degradation and air-dust partition) of individual FRs in environmental matrices as a result of their specific physical properties, (3) variations in the FR content of products of the same type, and (4) the limitations of the study design and statistical methods, in particular the small sample size and multiple statistical tests.

3.5. Human exposure assessments to OPFRs and PBDEs

Human intakes of FRs through inhalation, dust ingestion, and dermal contact with dust were separately estimated based on equations (1)–(3) (Harrad et al., 2004; Johnson-Restrepo and Kannan, 2009; Tajima et al., 2014). Total intakes for toddlers were also estimated. More attention should be given to toddlers owing to their frequent hand–mouth contact and “mouthing” toys and other objects in contact with floors (Jones-Otazo et al., 2005; Toms et al., 2009c).

We assume that transportation has the same air concentration of FRs as offices, and concentration in outdoor air is considered as 0. The fraction of total indoor time was $88\% \pm 6\%$. Participants spent $54\% \pm 12\%$ of their time in homes. Participants stayed inside the workplace for $29\% \pm 10\%$ of the time. The fraction of total outdoor time was $4\% \pm 4\%$. Transportation time accounted for $7.1\% \pm 3.4\%$ (Lee et al., 2000). Sleeping hours

for Australian adults was 7.3 (Jessica Manousakis, 2015). For toddlers, we assumed that they spent 90% of time in private houses (Toms et al., 2009b). According to Australian Health survey in 2012, the average of body weight was 78.5 for adults (18–64 years) and 76.7 for seniors (65 + years). The median of weight for children was 12.5 kg. DIG is 41 mg/day for infants and 2.5 mg/day for adults (Tajima et al., 2014). BSA is 4615 cm²/day for adults and 2564 cm²/day for toddlers, SAS is 0.096 mg/cm² and AF is 0.03 (Johnson-Restrepo and Kannan, 2009). The estimated daily intakes (EDIs) of FRs through different pathways are listed in Table 2.

Table 2

The EDIs of Σ 9OPFRs and Σ 8PBDEs for adults were 14000 pg/kg body weight (bw)/day and 330 pg/kg bw/day, respectively. Human EDIs of Σ 9OPFRs through indoor dust (ingestion and dermal contact) were 5900 pg/kg bw/day, while for inhalation, it was 7900 pg/kg bw/day. The greater contribution through inhalation was attributable to TCIPP owing to its high concentration in indoor air. The EDIs of Σ 8PBDEs were 10 pg/kg bw/day, 64 pg/kg bw/day, and 250 pg/kg bw/day through inhalation, dust ingestion, and dust contact, respectively. Higher EDIs were estimated for toddlers, at 84000 pg/kg bw/day for Σ 9OPFRs and 4300 μ g/kg bw/day for Σ 8PBDEs. For toddlers, dust ingestion had a higher contribution to total EDIs than inhalation for most FRs, except for TNBP. For adults, the relative contribution of inhalation versus ingestion varied. For volatile FRs such as TNBP, TCEP, TCIPP, and BDE 28, inhalation was the greatest contributor to total EDI. By contrast, dust ingestion was a more important route for less volatile FRs.

Reference doses (RfDs) for individual FR are listed in Table 2. Median EDIs were well under (at least <5% of the RfD) the RfD for both adults and toddlers. However, under the worst case scenario (based on P 95 concentrations) of TBOEP exposure, the EDI was 26% of the RfD value for toddlers. Although the EDIs of most of the FRs studied in this study were under their RfDs, the risk of exposure of humans, especially toddlers, to FRs may still be a concern, considering additional intake from other sources including food ingestion.

4. Conclusion

Σ 9OPFRs concentration was at least 10 times higher than Σ 8PBDEs concentration in both dust and air samples collected in Australian indoor environments. TBOEP was the predominant FR in dust samples, while TCIPP predominated in air samples. The highest concentration of target FRs was found in dust that collected from transport, especially in aircraft and trains. This is probably because of a higher level of fire safety requirement for materials used for public transportation. Higher concentrations of particular FRs were found in rooms with carpet, air conditioners, computers, and printers. Human exposure results suggested that median intakes for individual FR were less than 5% of reference doses. Inhalation is a more important intake pathway for the volatile FRs including TCEP and TCIPP.

Acknowledgement

This work was financially supported by the Australian Government Department of the Environment and Energy and the University of Queensland (C02183). The authors would like to thank the owners of private houses and workers of offices who participated in this research. The authors also thank Dr. Daniel Drage for his experimental guidance, Dr. Michael Gallen and Dr. Laurence Hearn for their instrumental support, and the anonymous reviewers for their critical comments that helped to improve the quality of our paper. Mr. Chang He is supported by an International Postgraduate Research Scholarship granted by the Australian Government and a University of Queensland Centennial Scholarship granted by UQ. Prof. Jochen Mueller is funded by an Australian Research Council Future Fellowship (FF120100546). Dr. Phong K. Thai is funded by a QUT VC Research Fellowship. Dr. Christine Baduel is funded by the French National Research Agency (ANR-16-ACHN-0026). Ms. Karin English is funded by an Australian Government Research Training Program Scholarship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at

<https://doi.org/10.1016/j.envpol.2017.12.017>

References

- Abbasi, G., Buser, A.M., Soehl, A., Murray, M.W., Diamond, M.L., 2015. Stocks and flows of PBDEs in products from use to waste in the US and Canada from 1970 to 2020. *Environ. Sci. Technol.* 49, 1521e1528.
- Abdallah, M.A.-E., Covaci, A., 2014. Organophosphate flame retardants in indoor dust from Egypt: implications for human exposure. *Environ. Sci. Technol.* 48, 4782e4789.
- ACC, 2017. Transportation: Fire Safety Requirements for Transportation. <https://flameretardants.americanchemistry.com/Fire-Safety-Requirements-for-Transportation/>. <https://flameretardants.americanchemistry.com/Fire-Safety-Requirements-for-Transportation/>.
- Alaee, M., Arias, P., Sjödin, A., Bergman, Å., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* 29, 683e689.
- Ali, N., Ali, L., Mehdi, T., Dirtu, A.C., Al-Shammari, F., Neels, H., Covaci, A., 2013. Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: implication for human exposure via dust ingestion. *Environ. Int.* 55, 62e70.
- Ali, N., Eqani, S.A.M.A.S., Ismail, I.M.I., Malarvannan, G., Kadi, M.W., Albar, H.M.S., Rehan, M., Covaci, A., 2016. Brominated and organophosphate flame retardants in indoor dust of Jeddah, Kingdom of Saudi Arabia: implications for human exposure. *Sci. Total Environ.* 569, 269e277.
- Ali, N., Mehdi, T., Malik, R.N., Eqani, S.A., Kamal, A., Dirtu, A.C., Neels, H., Covaci, A., 2014. Levels and profile of several classes of organic contaminants in matched indoor dust and serum samples from occupational settings of Pakistan. *Environ. Pollut.* 193, 269e276.
- Araki, A., Saito, I., Kanazawa, A., Morimoto, K., Nakayama, K., Shibata, E., Tanaka, M., Takigawa, T., Yoshimura, T., Chikara, H., 2014. Phosphorus flame retardants in indoor dust and their relation to asthma and allergies of inhabitants. *Indoor Air* 24, 3e15.
- Bennett, D.H., Moran, R., Wu, X., Tulse, N., Clifton, M., Colón, M., Weathers, W., Sjödin, A., Jones, R., Hertz-Picciotto, I., 2015. Polybrominated diphenyl ether (PBDE) concentrations and resulting exposure in homes in California: relationships

among passive air, surface wipe and dust concentrations, and

temporal variability. *Indoor Air* 25, 220e229.

Bergh, C., Torgrip, R., Emenius, G., Östman, C., 2011. Organophosphate and phthalate

esters in air and settled dust in a multi-location indoor study. *Indoor Air* 21,

67e76.

Brandtsma, S.H., de Boer, J., van Velzen, M.J.M., Leonards, P.E.G., 2014. Organophosphorus

flame retardants (PFRs) and plasticizers in house and car dust and

the influence of electronic equipment. *Chemosphere* 116, 3e9.

Brommer, S., Harrad, S., Van den Eede, N., Covaci, A., 2012. Concentrations of

organophosphate esters and brominated flame retardants in German indoor

dust samples. *J. Environ. Monit.* 14, 2482e2487.

Butt, C.M., Congleton, J., Hoffman, K., Fang, M., Stapleton, H.M., 2014. Metabolites of

organophosphate flame retardants and 2-ethylhexyl tetrabromobenzoate in

urine from paired mothers and toddlers. *Environ. Sci. Technol.* 48,

10432e10438.

Cequier, E., Ionas, A.C., Covaci, A., Marcé, R.M., Becher, G., Thomsen, C., 2014.

Occurrence of a broad range of legacy and emerging flame retardants in indoor

environments in Norway. *Environ. Sci. Technol.* 48, 6827e6835.

Cequier, E., Marcé, R.M., Becher, G., Thomsen, C., 2015a. Comparing human exposure

to emerging and legacy flame retardants from the indoor environment and diet

with concentrations measured in serum. *Environ. Int.* 74, 54e59.

Cequier, E., Sakhi, A.K., Marcé, R.M., Becher, G., Thomsen, C., 2015b. Human exposure

pathways to organophosphate triesters in a biomonitoring study of

mother-child pairs. *Environ. Int.* 75, 159e165.

De Nola, G., Kibby, J., Mazurek, W., 2008. Determination of ortho-cresyl phosphate isomers of tricresyl phosphate used in aircraft turbine engine oils by gas

chromatography and mass spectrometry. *J. Chromatogr. A* 1200, 211e216.

Ding, N., Wang, T., Chen, S.-J., Yu, M., Zhu, Z.-C., Tian, M., Luo, X.-J., Mai, B.-X., 2016.

Brominated flame retardants (BFRs) in indoor and outdoor air in a community

in Guangzhou, a megacity of southern China. *Environ. Pollut.* 212, 457e463.

Dirtu, A.C., Ali, N., Van den Eede, N., Neels, H., Covaci, A., 2012. Country specific

comparison for profile of chlorinated, brominated and phosphate organic

contaminants in indoor dust. Case study for Eastern Romania, 2010. *Environ.*

Int. 49, 1e8.

Dodson, R.E., Perovich, L.J., Covaci, A., Van den Eede, N., Ionas, A.C., Dirtu, A.C., Brody, J.G., Rudel, R.A., 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. *Environ. Sci. Technol.* 46, 13056e13066.

English, K., Toms, L.-M.L., Gallen, C., Mueller, J.F., 2016. BDE-209 in the Australian environment: desktop review. *J. Hazard Mater.* 320, 194e203.

EPA, U., 2017. Integrated Risk Information System. Accessed in Feb. <http://www.epa.gov/iris>.

Fromme, H., K€orner, W., Shahin, N., Wanner, A., Albrecht, M., Boehmer, S., Parlar, H., Mayer, R., Liebl, B., Bolte, G., 2009. Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany. *Environ. Int.* 35, 1125e1135.

Gallen, C., Banks, A., Brandsma, S., Baduel, C., Thai, P., Eaglesham, G., Heffernan, A., Leonards, P., Bainton, P., Mueller, J.F., 2014. Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci. Total Environ.* 491, 255e265.

Garcia, M., Rodriguez, I., Cela, R., 2007. Microwave-assisted extraction of organophosphate flame retardants and plasticizers from indoor dust samples.

J. Chromatogr. A 1152, 280e286.

Harner, T., Shoeib, M., Diamond, M., Ikonou, M., Stern, G., 2006. Passive sampler derived air concentrations of PBDEs along an urban-rural transect: spatial and temporal trends. *Chemosphere* 64, 262e267.

Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B., 2004. Using passive air samplers to assess Urban-Rural trends for persistent organic pollutants. 1.

Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* 38, 4474e4483.

Harrad, S., Abdallah, M.A.-E., Covaci, A., 2009. Causes of variability in concentrations and diastereomer patterns of hexabromocyclododecanes in indoor dust. *Environ. Int.* 35, 573e579.

Harrad, S., Brommer, S., Mueller, J.F., 2016. Concentrations of organophosphate flame retardants in dust from cars, homes, and offices: an international comparison.

Emerg. Contam. 2, 66e72.

Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C., Baker, R., 2004. Preliminary assessment of U.K. Human dietary and inhalation exposure to polybrominated diphenyl ethers. Environ. Sci. Technol. 38, 2345e2350.

Hartmann, P.C., Bürgi, D., Giger, W., 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere 57, 781e787.

He, C.-T., Zheng, J., Qiao, L., Chen, S.-J., Yang, J.-Z., Yuan, J.-G., Yang, Z.-Y., Mai, B.-X., 2015. Occurrence of organophosphorus flame retardants in indoor dust in multiple microenvironments of southern China and implications for human exposure. Chemosphere 133, 47e52.

He, C., Wang, X., Thai, P., Mueller, J.F., Gallen, C., Li, Y., Baduel, C., 2017. Development and validation of a multi-residue method for the analysis of brominated and organophosphate flame retardants in indoor dust. Talanta 164, 503e510.

ICL, 2015. Worldwide flame retardants market to reach 2.8 million tonnes in 2018. Addit. Polym. 2015, 11.

Jessica Manousakis, 2015. The Sleep Habits of an Australian Adult Population: a Report on the 2015 Online Sleep Survey from the Sleep Health Foundation.

Monash University. http://www.sleephealthfoundation.org.au/pdfs/sleepweek/SHF%20Sleep%20Survey%20Report_2015_final.pdf. http://www.sleephealthfoundation.org.au/pdfs/sleep-week/SHF%20Sleep%20Survey%20Report_2015_final.pdf.

sleephealthfoundation.org.au/pdfs/sleep-week/SHF%20Sleep%20Survey%20Report_2015_final.pdf.

Johnson-Restrepo, B., Kannan, K., 2009. An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. Chemosphere 76, 542e548.

Chemosphere 76, 542e548.

Johnson, P.I., Stapleton, H.M., Mukherjee, B., Hauser, R., Meeker, J.D., 2013. Associations between brominated flame retardants in house dust and hormone levels in men. Sci. Total Environ. 445, 177e184.

Johnson, P.I., Stapleton, H.M., Sjodin, A., Meeker, J.D., 2010. Relationships between polybrominated diphenyl ether concentrations in house dust and serum. Environ. Sci. Technol. 44, 5627e5632.

Jones-Otazo, H.A., Clarke, J.P., Diamond, M.L., Archbold, J.A., Ferguson, G., Harner, T., Richardson, G.M., Ryan, J.J., Wilford, B., 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to

PBDEs. *Environ. Sci. Technol.* 39, 5121e5130.

Kajiwara, N., Noma, Y., Takigami, H., 2011. Brominated and organophosphate flame retardants in selected consumer products on the Japanese market in 2008.

J. Hazard Mater. 192, 1250e1259.

Kemmlin, S., Hahn, O., Jann, O., 2003. Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials.

Atmos. Environ. 37, 5485e5493.

Kemmlin, S., Herzke, D., Law, R.J., 2009. Brominated flame retardants in the European chemicals policy of REACH regulation and determination in materials.

J. Chromatogr. A 1216, 320e333.

Kim, J.-W., Isobe, T., Muto, M., Tue, N.M., Katsura, K., Malarvannan Sudaryanto, A., Chang, K.-H., Prudente, M., Viet, P.H., Takahashi, S., Tanabe, S.,

2014. Organophosphorus flame retardants (PFRs) in human breast milk from several Asian countries. *Chemosphere* 116, 91e97.

Lee, K., Yang, W., Bofinger, N.D., 2000. Impact of microenvironmental nitrogen dioxide concentrations on personal exposures in Australia. *J. Air Waste Manag. Assoc.* 50, 1739e1744.

Li, P., Jin, J., Wang, Y., Hu, J., Xu, M., Sun, Y., Ma, Y., 2017. Concentrations of organophosphorus, polybromobenzene, and polybrominated diphenyl ether flame retardants in human serum, and relationships between concentrations and donor ages. *Chemosphere* 171, 654e660.

Melymuk, Lisa, Robson, Matthew, Helm, Paul A., Diamond, Miriam L., 2009. Evaluation of passive air sampler calibrations: Selection of sampling rates and implications for the measurement of persistent organic pollutants in air. *Environ. Int.* 35, 688e693.

Liu, R., Lin, Y., Liu, R., Hu, F., Ruan, T., Jiang, G., 2016. Evaluation of two passive samplers for the analysis of organophosphate esters in the ambient air. *Talanta* 147, 69e75.

Ma, Y., Salamova, A., Venier, M., Hites, R.A., 2013. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. *Environ. Sci. Technol.* 47, 11457e11464.

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere*

53, 1137e1146.

Marklund, A., Andersson, B., Haglund, P., 2005. Organophosphorus flame retardants and plasticizers in air from various indoor environments. *J. Environ. Monit.* 7, 814e819.

Meeker, J.D., Cooper, E.M., Stapleton, H.M., Hauser, R., 2013. Exploratory analysis of urinary metabolites of phosphorus-containing flame retardants in relation to markers of male reproductive health. *Endocr. Disruptors* 1, e26306.

Meeker, J.D., Stapleton, H.M., 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. *Environ. Health Perspect.* 118, 318e323.

Mitro, S.D., Dodson, R.E., Singla, V., Adamkiewicz, G., Elmi, A.F., Tilly, M.K., Zota, A.R., 2016. Consumer product chemicals in indoor dust: a quantitative meta-analysis of U.S. Studies. *Environ. Sci. Technol.* 50, 10661e10672.

NICNAS, 2007. In: Australian Government, D.o.H.a.A. (Ed.), *Interim Public Health Risk Assessment of Certain PBDE Congeners*.

O'Brien, J.W., Thai, P.K., Brandsma, S.H., Leonards, P.E., Ort, C., Mueller, J.F., 2015. Wastewater analysis of Census day samples to investigate per capita input of organophosphorus flame retardants and plasticizers into wastewater. *Chemosphere* 138, 328e334.

Rauert, C., Harner, T., Schuster, J.K., Quinto, K., Fillmann, G., Castillo, L.E., Fentanes, O., Ibarra, M.V., Miglioranza, K.S.B., Rivadeneira, I.M., Pozo, K., Puerta, A.P., Zuluaga, B.H.A., 2016. Towards a regional passive air sampling network and strategy for new POPs in the GRULAC region: perspectives from the GAPS Network and first results for organophosphorus flame retardants. *Sci. Total Environ.* 573, 1294e1302.

Regnery, J., Püttmann, W., 2010. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. *Water Res.* 44, 4097e4104.

Rudel, R.A., Camann, D.E., Spengler, J.D., Korn, L.R., Brody, J.G., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrinedisrupting compounds in indoor air and dust. *Environ. Sci. Technol.* 37, 4543e4553.

Saito, I., Onuki, A., Seto, H., 2007. Indoor organophosphate and polybrominated

flame retardants in Tokyo. *Indoor Air* 17, 28e36.

Shoeib, M., Ahrens, L., Jantunen, L., Harner, T., 2014. Concentrations in air of organobromine, organochlorine and organophosphate flame retardants in Toronto, Canada. *Atmos. Environ.* 99, 140e147.

Solbu, K., Daae, H.L., Olsen, R., Thorud, S., Ellingsen, D.G., Lindgren, T., Bakke, B., Lundanes, E., Molander, P., 2011. Organophosphates in aircraft cabin and cockpit airdmethod development and measurements of contaminants. *J. Environ. Monit.* 13, 1393e1403.

Solbu, K., Thorud, S., Hersson, M., Øvrebø, S., Ellingsen, D., Lundanes, E., Molander, P., 2007. Determination of airborne trialkyl and triaryl organophosphates originating from hydraulic fluids by gas chromatographyemass spectrometry: development of methodology for combined aerosol and vapor sampling. *J. Chromatogr. A* 1161, 275e283.

SRC, 2017. PHYSPROP Database. Syracuse Research Corporation. <https://www.srcinc.com/>.

Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants Sun, J., Wang, Q., Zhuang, S., Zhang, A., 2016. Occurrence of polybrominated diphenyl ethers in indoor air and dust in Hangzhou, China: level, role of electric appliances, and human exposure. *Environ. Pollut.* 218, 942e949.

Tajima, S., Araki, A., Kawai, T., Tsuboi, T., Bamai, Y.A., Yoshioka, E., Kanazawa, A., Cong, S., Kishi, R., 2014. Detection and intake assessment of organophosphate flame retardants in house dust in Japanese dwellings. *Sci. Total Environ.* 478, 190e199.

Tao, F., Abdallah, M.A.-E., Ashworth, D.C., Douglas, P., Toledano, M.B., Harrad, S., 2017. Emerging and legacy flame retardants in UK human milk and food suggest slow response to restrictions on use of PBDEs and HBCDD. *Environ. Int.* 105, 95e104.

Tao, F., Abdallah, M.A.-E., Harrad, S., 2016. Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants? *Environ. Sci. Technol.* 50, 13052e13061.

Thuresson, K., Björklund, J.A., de Wit, C.A., 2012. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm

microenvironments 1: levels and profiles. *Sci. Total Environ.* 414, 713e721.

Toms, L.-M.L., Bartkow, M.E., Symons, R., Paepke, O., Mueller, J.F., 2009a. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. *Chemosphere* 76, 173e178.

Toms, L.-M.L., Hearn, L., Kennedy, K., Harden, F., Bartkow, M., Temme, C., Mueller, J.F., 2009b. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. *Environ. Int.* 35, 864e869.

Toms, L.-M.L., Mortimer, M., Symons, R.K., Paepke, O., Mueller, J.F., 2008. Polybrominated diphenyl ethers (PBDEs) in sediment by salinity and land-use type from Australia. *Environ. Int.* 34, 58e66.

Toms, L.-M.L., Sjödin, A., Harden, F., Hobson, P., Jones, R., Edenfield, E., Mueller, J.F., 2009c. Serum polybrominated diphenyl ether (PBDE) levels are higher in children (2-5 years of age) than in infants and adults. *Environ. Health Perspect.* 117, 1461.

Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. *Environ. Int.* 37, 454e461.

Van den Eede, N., Heffernan, A.L., Aylward, L.L., Hobson, P., Neels, H., Mueller, J.F., Covaci, A., 2015. Age as a determinant of phosphate flame retardant exposure of the Australian population and identification of novel urinary PFR metabolites. *Environ. Int.* 74, 1e8.

van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* 88, 1119e1153.

Vorkamp, K., Thomsen, M., Frederiksen, M., Pedersen, M., Knudsen, L.E., 2011. Polybrominated diphenyl ethers (PBDEs) in the indoor environment and associations with prenatal exposure. *Environ. Int.* 37, 1e10.

Webster, T.F., Harrad, S., Millette, J.R., Holbrook, R.D., Davis, J.M., Stapleton, H.M., Allen, J.G., McClean, M.D., Ibarra, C., Abdallah, M.A.-E., 2009. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. *Environ. Sci. Technol.* 43, 3067e3072.

Wei, G.-L., Li, D.-Q., Zhuo, M.-N., Liao, Y.-S., Xie, Z.-Y., Guo, T.-L., Li, J.-J., Zhang, S.-Y., Liang, Z.-Q., 2015. Organophosphorus flame retardants and plasticizers: sources, occurrence, toxicity and human exposure. *Environ. Pollut.* 196, 29e46.

Weschler, C.J., Nazaroff, W.W., 2008. Semivolatile organic compounds in indoor environments. *Atmos. Environ.* 42, 9018e9040.

World Health Organization, 1991a. Environmental Health Criteria 111, Triphenyl Phosphate. Geneva, Switzerland.

World Health Organization, 1991b. Tributyl Phosphate. Environmental Health Criteria 112. Geneva, Switzerland.

World Health Organization, 1998. Flame Retardants: tris(chloropropyl) phosphate and tris (2-chloroethyl) phosphate. *Environ. Health Criteria* 209.

World Health Organization, 2000. Tris (2-butoxyethyl) Phosphate, Tris (2-ethylhexyl) Phosphate and Tetrakis (Hydroxymethyl) Phosphonium Salts.

Yang, F., Ding, J., Huang, W., Xie, W., Liu, W., 2014. Particle size-specific distributions and preliminary exposure assessments of organophosphate flame retardants in office air particulate matter. *Environ. Sci. Technol.* 48, 63e70.

Zhou, L., Hiltcher, M., Gruber, D., Püttmann, W., 2017. Organophosphate flame retardants (OPFRs) in indoor and outdoor air in the Rhine/Main area, Germany: comparison of concentrations and distribution profiles in different microenvironments. *Environ. Sci. Pollut. Res.* 24, 10992e11005.

Zhu, N.-Z., Liu, L.-Y., Ma, W.-L., Li, W.-L., Song, W.-W., Qi, H., Li, Y.-F., 2015. Polybrominated diphenyl ethers (PBDEs) in the indoor dust in China: levels, spatial distribution and human exposure. *Ecotoxicol. Environ. Saf.* 111, 1e8.

Table 1
Information of targeted flame retardants and related physico-chemical properties (at 25 °C) (SRC, 2017).

Chemicals	Abbreviation	CAS number	Vapour pressure (mm Hg)	Water solubility (mg/L)	Log K _{ow}
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	3.9×10^{-4}	7.0×10^3	1.44
Tris(2-chloroisopropyl) phosphate	TCIPP	13674-84-5	5.64×10^{-5}	1.2×10^3	2.59
Tris(1,3-dichloroisopropyl) phosphate	TDCIPP	13674-87-8	2.85×10^{-7}	7.0	3.65
Tri-n-butyl phosphate	TNBP	126-73-8	3.5×10^{-3}	2.8×10^2	4.00
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	6.1×10^{-7}	6.00×10^{-1}	9.49
Tris(2-butoxyethyl) phosphate	TBOEP	78-51-3	1.2×10^{-6}	1.1×10^3	3.75
Triphenyl phosphate	TPHP	115-85-6	4.7×10^{-7}	1.9	4.59
tris(2-methylphenyl) phosphate	TMPP	78-30-8	2.0×10^{-5}	N.A.	N.A.
2-ethylhexyl diphenyl phosphate	EHDPP	1241-94-7	3.3×10^{-5}	1.9	5.73
2,4,4'-tribromodiphenyl ether	BDE 28	41318-75-6	2.19×10^{-3}	7.0×10^{-1}	5.53
2,2',4,4'-tetrabromodiphenyl ether	BDE 47	5436-43-1	1.85×10^{-4}	1.5×10^{-2}	6.11
2,2',4,4',5-pentabromodiphenyl ether	BDE 99	60348-60-9	1.76×10^{-5}	9.4×10^{-3}	6.61
2,2',4,4',6-pentabromodiphenyl ether	BDE 100	189084-64-8	2.85×10^{-5}	4.0×10^{-2}	6.51
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE 153	68531-49-2	2.09×10^{-6}	8.7×10^{-4}	7.13
2,2',4,4',5,6'-hexabromodiphenyl ether	BDE 154	207122-15-4	3.80×10^{-6}	8.7×10^{-4}	7.39
2,2',3,4,4',5,6'-heptabromodiphenyl ether	BDE 183	207122-16-5	4.68×10^{-7}	1.5×10^{-3}	7.14
2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether	BDE 209	1163-19-5	5.42×10^{-11}	1.3×10^{-8}	9.97

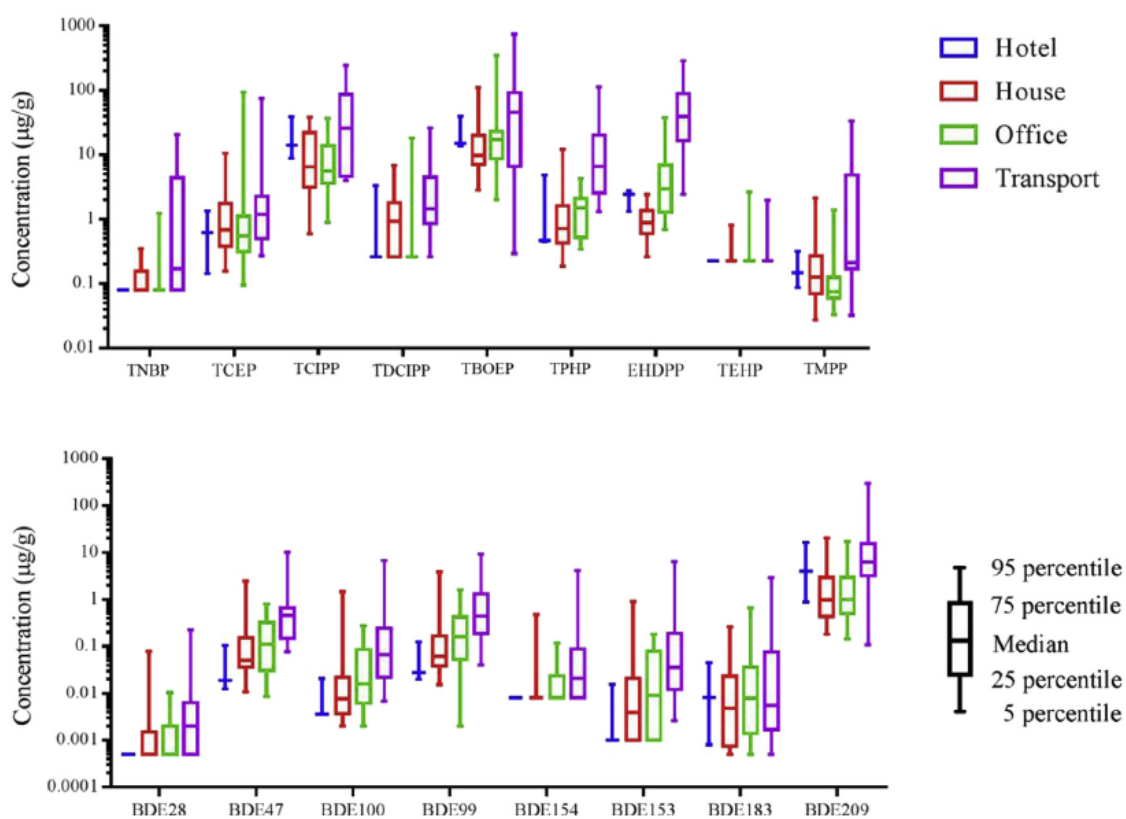


Fig. 1. Dust concentrations ($\mu\text{g/g}$) of targetted OPFRs and PBDEs in different microenvironments in Australia.

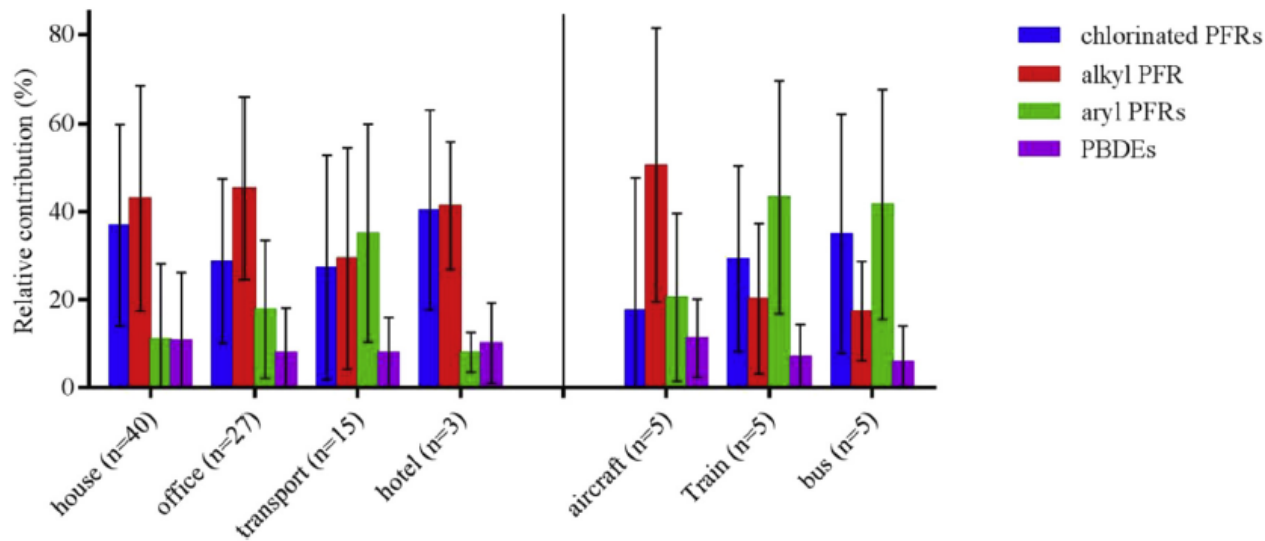


Fig. 2. Contribution (%) of individual OPFRs and PBDEs in different indoor environments.

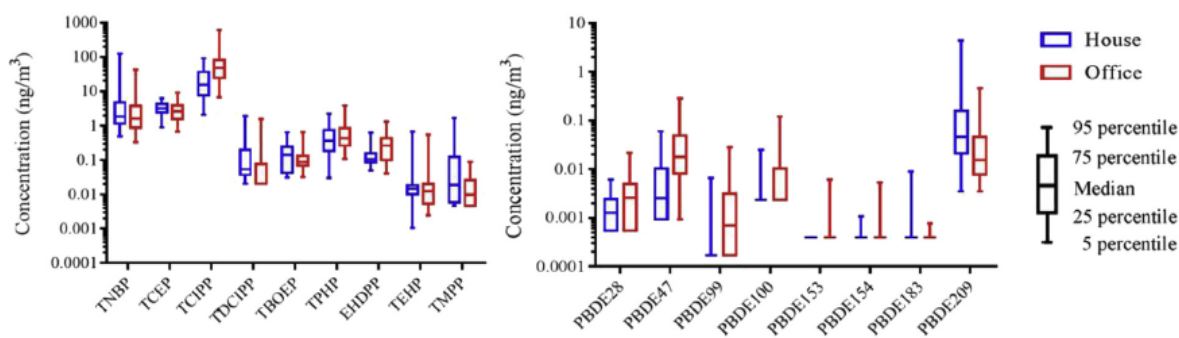


Fig. 3. Atmospheric concentrations (ng/m^3) of targeted OPFRs and PBDEs in Australian houses and offices.

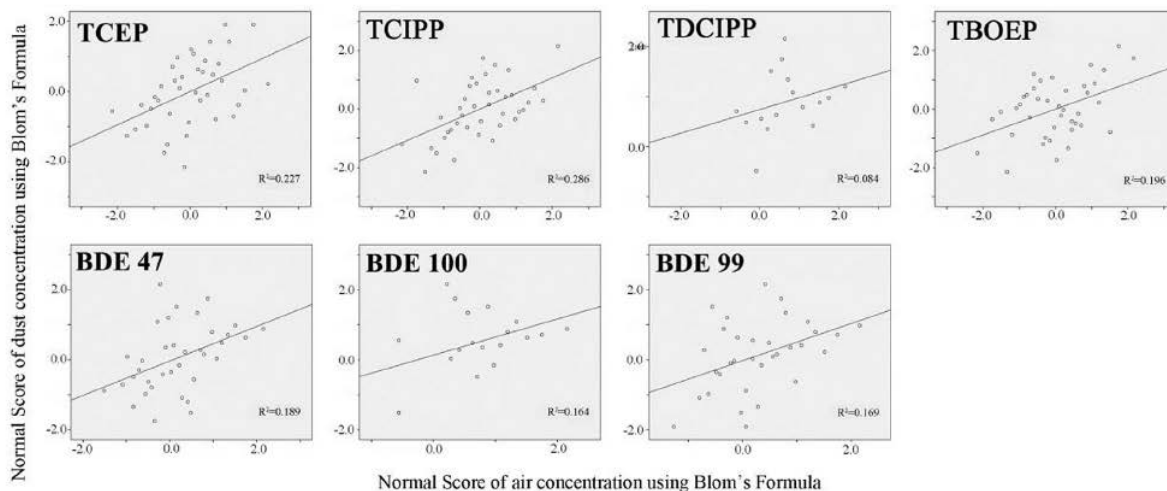


Fig. 4. Correlations of flame retardant concentrations in matched air and dust samples, Blom's formula is defined as $(r-3/8)/(w+1/4)$, where r is the rank and w is the sum of case weights.

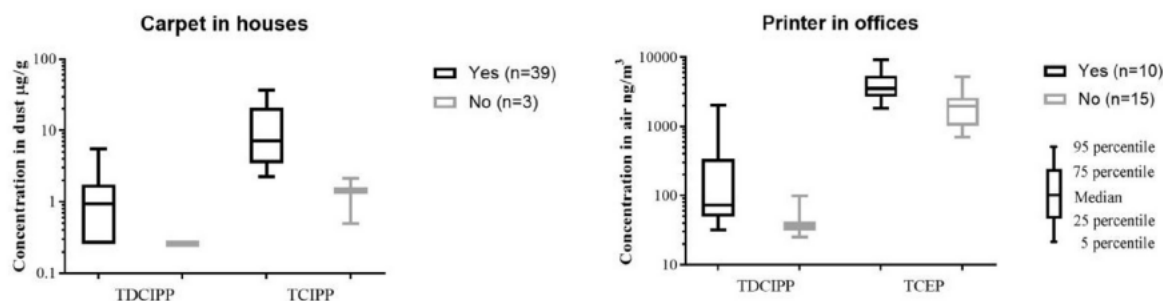


Fig. 5. Relationships between FR concentration and some major products in indoor environment.

Table 2

Human intake of OPFRs and PBDEs through different pathways in an Australian population (pg/kg body weight/day).

	Inhalation	Dust ingestion	Dust contact	Sum			RfD value
	Median	Median	Median	Median	5th%ile	95th%ile	
Adults							
TNBP	400	3.0	13	410	110	25000	2.4×10^{6a}
TCEP	680	23	100	800	200	3600	2.2×10^{6a}
TCIPP	6600	280	1200	8000	1100	89000	8.0×10^{6a}
TDCIPP	11	22	110	150	51	1500	1.5×10^{6a}
TBOEP	28	580	2400	3000	620	19000	1.5×10^{6a}
TPHP	90	59	220	370	72	2200	7.0×10^{6a}
EHDPP	39	210	700	950	140	3500	6.0×10^{5c}
TEHP	3.1	7.4	34	45	40	370	2.9×10^{6c}
TMPP	3.4	3.7	17	25	7.6	570	1.3×10^{6a}
Σ OPFRs	7900	1200	4700	14000	2300	140000	
BDE28	0.42	0.022	0.094	0.53	0.21	8.7	—
BDE47	2.0	4.2	16	22	4.2	270	1.0×10^{5b}
BDE99	0.67	5.0	19	25	3.4	430	1.0×10^{6b}
BDE100	0.088	0.61	2.3	3.0	0.48	110	1.0×10^{6b}
BDE153	0.092	0.33	1.2	1.6	0.30	79	2.0×10^{5b}
BDE154	0.092	0.31	1.4	1.8	1.5	66	2.0×10^{5b}
BDE183	0.092	0.21	1.0	1.3	0.19	39	—
BDE209	6.9	53	210	270	52	4100	7.0×10^{6b}
Σ PBDEs	10	64	250	330	62	5100	
Toddlers							
TNBP	610	260	43	910	470	42000	2.4×10^{6a}
TCEP	1100	2300	350	3700	1000	31000	2.2×10^{6a}
TCIPP	5100	22000	3400	30000	6200	170000	8.0×10^{6a}
TDCIPP	18	3100	490	3600	1000	25000	1.5×10^{6a}
TBOEP	47	32000	5600	38000	13000	400000	1.5×10^{6a}
TPHP	120	2400	390	2900	770	26000	7.0×10^{6a}
EHDPP	34	2900	470	3400	1200	9000	6.0×10^{5c}
TEHP	4.8	740	120	870	870	2800	2.9×10^{6c}
TMPP	6.0	420	65	490	130	6300	1.3×10^{6a}
Σ OPFRs	7000	66000	11000	84000	24000	710000	
BDE28	0.42	1.7	0.26	2.3	2.1	170	—
BDE47	0.84	170	29	200	74	5800	1.0×10^{5b}
BDE99	0.87	200	35	240	68	11000	1.0×10^{6b}
BDE100	0.056	25	4.1	29	7.7	2500	1.0×10^{6b}
BDE153	0.13	13	2.0	15	4.0	1400	2.0×10^{5b}
BDE154	0.13	26	4.3	31	31	1800	2.0×10^{5b}
BDE183	0.13	16	3.1	19	2.0	430	—
BDE209	14	3300	500	3800	930	61000	7.0×10^{6b}
Σ PBDEs	16	3700	580	4300	1100	84000	

^a Van den Eede et al. (2011).

^b EPA (2017).

^c Estimated based on the no observed adverse effect level (NOAEL) values (World Health Organization, 2000; Rudel et al., 2003; Hartmann et al., 2004; Saito et al., 2007).