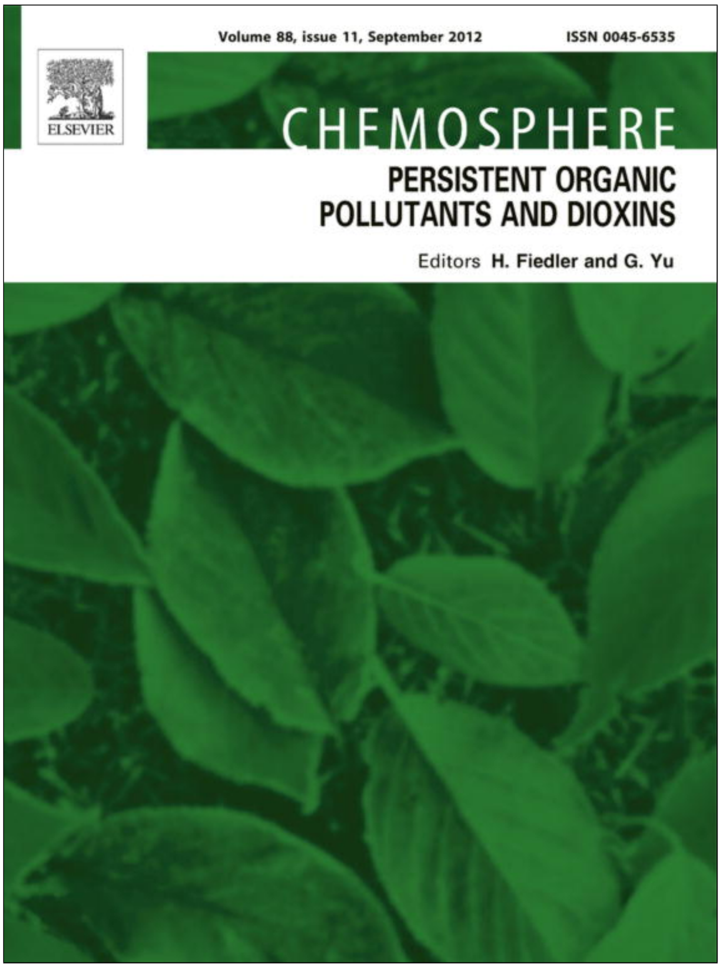

Chemosphere 88 (2012) 1276–1282

Contents lists available at SciVerse ScienceDirect

Chemosphere

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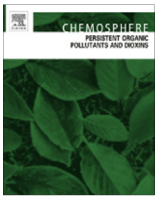

Occurrence of alternative flame retardants in indoor dust from New Zealand: Indoor sources and human exposure assessment

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ARTICLE INFO

Article history:
Received 8 November 2011
Received in revised form 23 March 2012
Accepted 31 March 2012
Available online 30 April 2012

Keywords:
Organophosphate flame retardants (OPFRs)
Novel brominated flame retardants (NBFRs)
Human exposure
Indoor dust
New Zealand

ABSTRACT

Due to worldwide restrictions on polybrominated diphenyl ethers (PBDEs), the demand for alternative flame retardants (AFRs), such as organophosphate flame retardants (OPFRs), novel brominated FRs (NBFRs) and hexabromocyclododecanes (HBCDs), has recently increased. Little is known about human exposure to NBFRs and OPFRs and that their levels in dust have been scarcely evaluated worldwide. To increase the knowledge regarding these chemicals, we measured concentrations of five major NBFRs, ten OPFRs and three HBCD isomers in indoor dust from New Zealand homes. Dust samples were taken from living room floors ($n = 34$) and from mattresses of the same houses ($n = 16$). Concentrations (ng g^{-1}) of NBFRs were: 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) (<2–175), decabromodiphenyl ethane (DBDPE) (<5–1430), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) (<2–2285) and bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH) (<2–640). For OPFRs, concentrations (ng g^{-1}) ranged between: tri-ethyl-phosphate (TEP) (<10–235), tri-*n*-butyl-phosphate (T*n*BP) (<20–7545), tris-(2-chloroethyl)-phosphate (TCEP) (<20–7605), tris-(1-chloro-2-propyl) phosphate (TCPP) (20–7615), tri-(2-butoxyethyl)-phosphate (TBEP) (50–27325), tris-(2,3-dichloropropyl)-phosphate (TDCPP) (20–16560), tri-phenyl-phosphate (TPhP) (20–35190), and tri-cresyl-phosphate (TCP) (<50–3760). HBCD concentrations fell in the range <2–4100 ng g^{-1}. BTBPE, DBDPE, TBPH, TBEP, and T*n*BP showed significant positive correlation ($p < 0.05$) between their concentrations in mattresses and the corresponding floor dust ($n = 16$). These data were used to derive a range of plausible exposure scenarios. Although the estimated exposure is well below the corresponding reference doses (RfDs), caution is needed given the likely future increase in use of these FRs and the currently unknown contribution to human exposure by other pathways such as inhalation and diet.

1. Introduction

To meet fire regulations, flame retardants (FRs) are commonly used in consumer products (furniture, plastics, electronics equipment, textiles, etc.). The most extensively used FRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBP-A) (Alaee et al., 2003). However, these FRs are environmentally ubiquitous with PBDEs and HBCDs being also bioaccumulative (Law et al., 2003; Covaci et al., 2006). These properties have led to the ban on the use of Penta- and Octa-BDE mixtures in different countries (EU, 2003; Renner, 2004) and recently these mixtures were listed under the Stockholm Convention on Persistent Organic Pollutants (http://chm.pops.int/default.aspx). The use of Deca-BDE in electrical and electronic appliances has also been banned recently in the EU (ECJ, 2008). Moreover, HBCDs remain in widespread use in thermal insulation building materials, upholstery textiles, and electronics (Covaci et al., 2006). Recently, HBCD has been under active consideration for listing under the Stockholm Convention (Marvin et al., 2011).

These restrictions and bans have resulted in an increased demand for AFRs to meet flammability standards, such as "novel" brominated flame retardants (NBFRs) and organophosphate flame retardants (OPFRs). For example, 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) is produced by the Great Lakes Chemical Corporation as a replacement to Octa-BDE and is used as an additive FR in thermoplastics, ABS polymer systems, HIPS and polycarbonate coatings (WHO/IPCS, 1997; Hoh et al., 2005). Decabromodiphenylethane (DBDPE), a replacement to Deca BDE

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0045-6535/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.03.100

(Albemarle Corporation) is mainly used as an additive in thermoplastics, ABS, polypropylene and textiles (WHO/IPCS, 1997; Kierkegaard et al., 2004, 2009). A FR mixture, Firemaster® 550 (FM® 550), containing two NBFRs, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH) (4:1, *w*/*w*), has been marketed since 2003 by Chemtura as a replacement for Penta-BDE in polyurethane foam applications (Stapleton et al., 2008; Chemtura, 2006). Another class of chemicals for which demand is expected to increase as they replace restricted FRs, consists of halogenated as well as non-halogenated OPFRs. They are used to impart flame retardancy in plastics, electronics and fabrics, as well as plasticizers and additives in hydraulic fluids (WHO, 1990, 1991, 1998, 2000; Marklund et al., 2003; Hartmann et al., 2004).

In view of this increasing use of such AFRs, recent studies have reported the presence of NBFRs in several indoor matrices like air, dust and furniture foam (Harrad et al., 2008a; Stapleton et al., 2008, 2009; Zhu et al., 2008; Ali et al., 2011a,c; Covaci et al., 2011), as well as in biota, e.g. porpoise blubber (Lam et al., 2009). The presence of OPFRs in indoor dust samples at the $\mu g\ g^{-1}$ level (i.e. comparable to or exceeding concentrations of restricted FRs) has also been documented (Marklund et al., 2003; Stapleton et al., 2009; Bergh et al., 2010; Kanazawa et al., 2010; Ali et al., 2011c; Van de Eede et al., 2011) and in indoor air at the $ng\ m^{-3}$ level (Hartmann et al., 2004; Staaf and Östman, 2005; Saito et al., 2007; Bergh et al., 2010). Concerns regarding the impact of exposure to such contaminated air and dust are exacerbated by reports that certain OPFRs possess possible carcinogenic, neurotoxic and endocrine disrupting properties which might be associated with male fertility (Hudec et al., 1981; WHO, 1998; Fang et al., 2003; Meeker and Stapleton, 2010; Aulette and Hogan, 1981).

Even though such AFRs have never have been manufactured nor imported directly into New Zealand; we have documented previously the presence of PBDEs in indoor dust from New Zealand homes, which were also not manufactured or imported directly, but assumed to arise via the presence in imported electronic and electrical items (Harrad et al., 2008b). As a consequence, the present study focused on reporting concentrations of NBFRs ($n = 5$), OPFRs ($n = 10$) and HBCDs in indoor dust samples collected in 2008 from New Zealand (floor $n = 34$; mattress $n = 16$). This study is part of a research project focussing on evaluating concentrations of POPs in indoor dust from New Zealand and the relationship with concentrations in human milk. The focus of the present paper stems from the previous observation that indoor dust ingestion could constitute a major exposure pathway to PBDEs for New Zealanders (Harrad and Porter, 2007). The objectives of the present study are thus: (i) to measure concentrations of AFRs in indoor dust from selected New Zealand homes; (ii) to estimate exposure to AFRs of toddlers and adults via dust ingestion and to compare these estimates with those reported for other countries; (iii) by comparing with concentrations of PBDEs that were measured in the same samples, to evaluate the evidence that AFRs are replacing PBDEs; (iv) and to compare their levels in floor dust with those in mattress dust as this may provide insights into the sources of these chemicals and the relative influence of the two sample categories on human exposure.

2. Experiment methodology

2.1. Reagent, materials and solutions

Standards of BTBPE, DBDPE, hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), TBB, TBPH and HBCD isomers were purchased from Wellington Laboratories (Canada), while standards of tri-ethyl-phosphate (TEP), tri-*n*-propyl-phosphate (T*n*PP), tri-iso-butyl-phosphate (T*i*BP), tri-*n*-butyl-phosphate (T*n*BP), tri-phenyl-phosphate (TPhP), tris-(2-chloroethyl)-phosphate (TCEP), tri-cresyl-phosphate (TCP) (mixture of 4 isomers) and tris-(2,3-dichloropropyl)-phosphate (TDCPP) (mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway). Tri-(2-butoxyethyl)-phosphate (TBEP) was purchased from Sigma Aldrich, while tris-(2-chloroisopropyl)-phosphate (TCPP) (mixture of 3 isomers) were purchased from Pfaltz & Bauer (Waterbury, CT, USA). The purity of analytical standards for OPFRs was >98%, except for TBEP (>94%). 3,3′,4,4′-Tetrabromodiphenyl ether (BDE 77) and 2,2′,3,3′,4,4′-Hexabromodiphenyl ether (BDE 128) (AccuStandard Inc., USA), $^{13}C_{12}$-Decabromodiphenyl ether ($^{13}C_{12}$-BDE 209) and $^{13}C_{12}$-HBCD ($^{13}C_{12}$-α-, β-, γ-HBCD isomers) (Wellington Laboratories), Tri-amyl-phosphate (TAP) (TCI Europe, Zwijndrecht, Belgium) and Tri-phenyl-phosphate-d_{15} (TPP-d_{15}) (Sigma) were used as internal standards. Dichloromethane (DCM), and acetone (Ace), *iso*-octane and toluene were purchased from Merck (Darmstadt, Germany), while *n*-Hexane (Hex) was purchased from Acros Organics (Geel, Belgium). All solvents used were of analytical grade. Concentrated sulphuric acid (98%) (H_2SO_4) and silica gel were purchased from Merck. Empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3 mL Supelclean™ ENVI™- Florisil® cartridges were purchased from Supelco (Bellefonte, PA, USA). Silica gel was washed with Hex and activated overnight at 160 °C. Prior to each experiment, silica was heated for 2 h at 160 °C for activation. Acid impregnated silica (44%, *w*/*w*) was prepared by adding dropwise with continuous stirring 22 mL concentrated sulphuric acid (98%) to 50 g silica. All glassware was soaked for 12 h in an alkali solution (diluted RBS T 105, pH 11–12) to degrade any remaining FRs. After washing, glassware was rinsed with water and dried overnight at 105 °C. Prior to use, glassware was rinsed with Hex.

2.2. Sampling, sample preparation and instrumentation

Indoor dust samples ($n = 50$) were collected from different homes in selected rural and urban areas of New Zealand (Wellington, Wairarapa, Christchurch, and North Canterbury). Samples were taken from living room floors ($n = 34$) and from mattresses ($n = 16$). Sampling details are similar to those presented in Harrad et al. (2008a,b). More specifically, house dust samples were collected by the fieldworkers, using their own vacuum cleaner (Nilfisk *Sprint Plus* 1600 W vacuum cleaner) and following a specific protocol for floor and mattress dust. For floor dust, 1 m^2 in case of wall to wall carpet or rugs and 4 m^2 in case of bare floors were vacuumed evenly and thoroughly for exactly 2 min or 4 min in case of bare floors. For sampling of mattresses, duvets, blankets or sheets were removed from the bed, but undersheets or mattress covers were left on. The whole area of the mattress was vacuumed evenly and thoroughly for 2 min.

The sample extraction and purification method was described in detail elsewhere (Van de Eede et al., 2012). Briefly, an accurately weighed aliquot of dust (typically 75 mg) was spiked with internal standards and extracted by ultrasonication and vortex with Hex:Ace (3:1, *v*/*v*). Florisil was used to obtain two fractions; a 1st fraction was eluted with 8 mL Hex and a 2nd fraction with 10 mL ethyl acetate. All NBFRs, except TBPH, were present in the 1st fraction, while HBCDs, TBPH and OPFRs were present in the 2nd fraction. After concentration, the 1st fraction was further cleaned on acid silica and analytes were eluted with 10 mL Hex:DCM (1:1, *v*/*v*). After evaporation to dryness, each fraction was resolubilised in 100 μL of *iso*-octane prior GC–MS analysis. NBFRs were analysed by gas chromatography (GC) coupled to mass spectrometry (MS) operated in electron capture negative ionisation (ECNI) mode, OPFRs by GC/MS in electron impact (EI) mode and determination of $\sum$HBCDs and separation of α-, β-, and γ-HBCD was achieved using a dual pump Agilent 1100 Series liquid chromatograph coupled to an Agilent 6410 triple quadrupole MS system operated in the electrospray negative ionisation mode. Instrumental details are given elsewhere (Van de Eede et al., 2012). Quantification and confirmation ions of OPFRs, NBFRs, and corresponding ISs are given in Table S-1.

2.3. Quantification and quality assurance

Concentrations in laboratory blanks ($n = 6$) and in SRM 2585 organics in indoor dust standard reference materials from NIST ($n = 6$) were determined in parallel with the dust samples to assess the influence of any possible contamination during sample preparation and instrumental analysis and to evaluate method accuracy. If present and consistent (relative standard deviation <15%) in the blanks, levels of target analytes were blank-subtracted. The values detected in this study of NBFRs and OPFRs in SRM 2585 were in good agreement (deviation <15%) with published values (Ali et al., 2011b; Van de Eede et al., 2011; Bergh et al., 2012) (Table S-2).

2.4. Statistical analysis

Descriptive analysis was performed using Minitab 15. Outliers were identified by using box plots. Non-detects were replaced by $f \times$ LOQ, where f is the fraction of samples above LOQ. The Ryan-Joiner normality test revealed that some FRs did not display a normal distribution ($p < 0.05$) and therefore data were log transformed before statistical analysis. To study correlations between the levels of FRs measured in the 16 homes where both floor and mattress dust samples were collected, a Spearman rank-order correlation coefficient was calculated. An unpaired t test was applied to test for differences in the FR levels between all floor ($n = 34$) and mattress ($n = 16$) dust samples; while a paired t test was performed to study differences between FR levels in matched floor ($n = 16$) and mattress ($n = 16$) dust samples.

3. Results and discussion

3.1. Concentrations of AFRs

While HCDBCO and T*n*PP were not detected in any of the dust samples, all other OPFRs, NBFRs and HBCDs occurred in dust samples with different detection frequencies (Table S-3). To our knowledge, this is the first report on AFRs in dust from New Zealand indoor microenvironments. For all analytes very high standard deviation (Table S-3) was observed which indicates substantial inter-household variation in concentrations.

In general, levels of NBFRs were low in New Zealand dust compared to the few other countries for which dust levels of these compounds have been reported (Table 1), with DBDPE and TBPH being measured at one order of magnitude higher concentrations than BTBPE and TBB. Concentrations of BTBPE and DBDPE in floor and mattress dust in this study were similar to those reported in Pakistan, Sweden and UK homes dust, but lower than those reported in Chinese homes, Indian commercial and e-waste sites, UK schools, Belgian offices and US homes (Harrad et al., 2008a,b; Stapleton et al., 2008; Wang et al., 2010; Ali et al., 2011a,c; Devanathan et al., 2011).

Levels of TBB and TBPH in the present study were in line with Belgian and Pakistan house dust, but lower than those reported in Belgian office, US house dust and UK school dust (Ali et al., 2011a,c; Stapleton et al., 2008). These low concentrations of both TBB and TBPH may imply limited use of FM® 550 in polyurethane-containing foam consumer products in New Zealand. The TBPH:TBB ratio in FM® 550 is 1:4 (Chemtura, 2006), and it is therefore interesting to note that similar to reports in Belgian homes and offices, UK schools, and US homes; higher TBPH:TBB ratios were observed in dust samples examined in this study (Stapleton et al., 2008; Ali et al., 2011a). This may indicate: the existence of additional sources of TBPH, (e.g. TBPH has been used as a plasticizer in PVC and neoprene (Anderson et al., 2006), compound-specific differences in behaviour in the indoor environment, or more facile degradation of TBB relative to TBPH (Davis and Stapleton, 2009).

Similar to NBFRs, levels of OPFRs in dust in the present study were lower than or in line with those reported in other countries (Table 2). TEP was more frequently detected in mattress dust (50%) compared to floor dust (29%). Yet, this may be of minor significance, because spiked control dust samples showed a recovery of 31% with a variability of 66% for TEP. Mattresses may constitute a source, since TEP is sometimes used as an additive together with halogenated OPFRs in polyurethane foams (Eastman chemical b.v.). Because of highly variable blank values for T*i*BP, its concentrations are not reported here. Similar to other countries, except Japanese homes and Swedish day care centres where concentrations were higher (Bergh et al., 2010; Kanazawa et al., 2010), concentrations of T*n*BP were sub $\mu g\, g^{-1}$ dust (Marklund et al., 2003; García et al., 2007; Van de Eede et al., 2011; Ali et al., 2011c). TPhP was detected at concentrations similar to those in Belgian house dust (Van de Eede et al., 2011), but at lower levels than in house dust from Japan, Spain, Sweden and the US (García et al., 2007; Stapleton et al., 2009; Bergh et al., 2010; Kanazawa et al., 2010).

Based on a comparison of their concentrations in dust, the use of TCEP and TCPP appears lower in New Zealand compared to Belgium, Japan, Spain and Sweden (García et al., 2007; Bergh et al., 2010; Kanazawa et al., 2010; Van de Eede et al., 2011). This may be due to the use of other FRs in furniture in New Zealand. TDCPP was detected at markedly lower concentrations than in Japanese, Swedish and US dust samples (Stapleton et al., 2009; Bergh et al., 2010; Kanazawa et al., 2010). The more frequent use of TDCPP in soft furniture foams in the US (Stapleton et al., 2009) and possibly also in Sweden and Japan, might explain this observation. Concentrations of TCP are comparable to the low levels present in Belgian dust samples, the low concentrations probably due to its infrequent use as a FR and/or less facile release from consumer products because of its low vapour pressure compared to other OPFRs. The use of TBEP in floor wax and PVC floor coverings (Saito et al., 2007), may explain why its concentrations are significantly higher in floor as opposed to mattress dust. As shown in Table 3, concentrations of HBCDs in this study were in the same range as those reported elsewhere (Abdallah et al., 2008a,b; Roosens et al., 2009). The lower concentrations of OPFRs and BFRs in this study may suggest a lower use of AFRs in New Zealand. However, the small number of New Zealand homes studied means that the values reported here may not be representative of the exposure of the New Zealand population overall.

3.2. Correlations and differences in absolute concentrations and patterns between floor and mattress dust

For mattress ($n = 16$) and the corresponding floor ($n = 16$) dust samples, concentrations of T*n*BP ($p = 0.003$; $r = 0.68$), TBEP ($p = 0.019$; $r = 0.52$), TPhP ($p = 0.001$; $r = 0.71$), BTBPE ($p = 0.000$; $r = 0.88$), and TBB ($p = 0.046$; $r = 0.39$) showed positive correlations suggesting common sources of emission in floor and mattress dust. No such correlation was observed for other analytes, suggesting more diverse emission sources. The outcome of these correlation analyses is supported by the results of our conduct of a paired t test that evaluated differences between concentrations in the same mattress and floor dust pairs. This showed levels of T*n*BP, TPhP, TCP, BTBPE, and TBB to be statistically indistinguishable ($p > 0.05$) between floor and mattress dust from the same homes.

Table 1
Comparison of median concentrations of NBFRs reported in indoor dust (ng g^{-1} dust).

Country	NBFRs	BTBPE	TBB	TBPH	DBDPE	Reference
New Zealand (F)	Homes ($n = 34$)	2	2	12	23	Present study
New Zealand (M)	Homes ($n = 16$)	1	3	1	9	Present study
Belgium	Homes ($n = 39$)	2	1	13	153	Ali et al. (2011a)
Belgium	Offices ($n = 6$)	19	7	64	721	Ali et al. (2011a)
Sweden	Homes ($n = 5$)	4.8[a]	n.m.	n.m.	47[a]	Karlsson et al. (2007)
UK	Homes ($n = 30$)	5	n.m.	n.m.	24	Harrad et al. (2008a)
UK	Offices ($n = 18$)	<dl	n.m.	n.m.	99	Harrad et al. (2008a)
UK	Schools ($n = 36$)	9	25	96	98	Ali et al. (2011a)
China	Homes ($n = 27$)	6.47	n.m	n.m	2733	Wang et al. (2010)
India[b]	Residential	48	n.m	n.m	15	
	E-waste	65 000	n.m	n.m	120	
	Commercial	220	n.m	n.m	67	
Pakistan	Homes ($n = 31$)	2.7	0.03	3.5	12	Ali et al. (2011c)
USA	Homes ($n = 37$)	30	133	142	201	Stapleton et al. (2008)

'n.m.' – not measured; '<dl' – below detection limit; 'F' – floor; 'M' – mattress.

[a] Arithmetic mean values.

[b] $n = 35$.

Table 2
Comparison of median concentrations of OPFRs studied in indoor dust (μg g^{-1} dust).

Country	Sample size	TnBP	TCEP	TCPP	TBEP	TPhP	TDCPP	TCP	Reference
New Zealand (F)	Homes ($n = 34$)	0.08	0.11	0.35	4.02	0.6	0.23	0.12	Present study
New Zealand (M)	Homes ($n = 16$)	0.07	0.04	0.25	1.55	0.24	0.11	0.16	Present study
Belgium	Homes ($n = 33$)	0.13	0.23	1.38	2.03	0.5	0.36	0.24	Van de Eede et al. (2011)
USA	Homes ($n = 50$)	n.a.	n.a.	0.57	n.a.	7.36	1.89	n.a.	Stapleton et al. (2009)
Spain	Homes ($n = 8$)	0.23	0.5	3.8	9.4	1.9	0.12	n.a.	García et al. (2007)
Japan	Homes ($n = 41$)	1.4	7.5	18.7	1570	5.4	4	n.a.	Kanazawa et al. (2010)
Belgium	Shops ($n = 15$)	0.21	0.59	2.94	3.61	1.97	0.76	0.2	Van de Eede et al. (2011)
Sweden	Public places ($n = 15$)	0.4	1.4	2.4	31	3.1	1.1	n.a.	Marklund et al. (2003)
Sweden	Homes ($n = 10$)	0.3	2.1	1.6	4	1.2	10	n.a.	Bergh et al. (2010)
	Day care centres ($n = 10$)	1.2	30	3.1	1600	1.9	9.1	n.a.	
	Work places ($n = 10$)	0.2	6.7	19	87	5.3	17	n.a.	
Pakistan	Homes ($n = 31$)	0.014	n.a.	n.a.	0.03	0.08	n.a.	n.a.	Ali et al. (2011c)

'n.a.' – not available.

Table 3
Comparison of concentrations of individual HBCD isomers and $\sum$HBCDs in indoor dust (ng g^{-1} dust).

Country	Analytes	Median	Mean ± SD	Range	Reference
New Zealand ($n = 50$)	$\sum$HBCDs	190	460 ± 730	20–4100	Present study
	α-HBCD	99	200 ± 320	3–1790	
	β-HBCD	12	37 ± 60	3–270	
	γ-HBCD	96	225 ± 470	8–3020	
Belgium ($n = 16$)	$\sum$HBCDs	114	160 ± 170	33–760	Roosens et al. (2009)
	α-HBCD	69	93 ± 107	22–480	
	β-HBCD	14	19 ± 19	4–87	
	γ-HBCD	31	48 ± 50	7–190	
United Kingdom ($n = 45$)	$\sum$HBCDs	1300	8300 ± 26 000	140–140 000	Abdallah et al. (2008a)
	α-HBCD	380	3200 ± 11000	22–66 000	
	β-HBCD	93	1,000 ± 3900	9–26 000	
	γ-HBCD	670	4200 ± 13 000	70–75 000	
United Kingdom ($n = 31$)	$\sum$HBCDs	730	6000 ± 20 000	140–110 000	Abdallah et al. (2008b)
	α-HBCD	170	2800 ± 12 000	22–66 000	
	β-HBCD	66	470 ± 1500	9–7800	
	γ-HBCD	440	2800 ± 7700	70–37 000	
Canada ($n = 8$)	$\sum$HBCDs	640	670 ± 390	64–1300	Abdallah et al. (2008b)
	α-HBCD	300	340 ± 210	25–670	
	β-HBCD	72	70 ± 42	6–130	
	γ-HBCD	230	260 ± 15	34–470	
United States ($n = 13$)	$\sum$HBCDs	390	810 ± 1100	110–4000	Abdallah et al. (2008b)
	α-HBCD	80	260 ± 460	17–1800	
	β-HBCD	28	56 ± 79	6–300	
	γ-HBCD	300	490 ± 580	79–2000	

In contrast, concentrations of all other FRs monitored differed significantly between mattress and floor dust.

Additionally, an unpaired t test was applied to study if the levels of FRs in mattress dust ($n = 16$) differed significantly from those in floor dust ($n = 34$). Differences in the levels of BTBPE, TBB, TPhP, T*n*BP, TCPP and TCP were not statistically significant ($p > 0.05$) for floor and mattress dust, which might indicate uniform occurrence, similar sources and behaviour of these chemicals in indoor environments. In contrast, differences in the levels of TBPH, DBDPE, TEP, TCEP, TBEP, TDCPP and HBCDs were significant ($p < 0.05$), suggesting different sources of these chemicals in floor and mattress dust. The existence of different sources to mattress and floor dust is plausible. For example, TDCPP is mostly associated with its application in polyurethane foams for upholstery and mattresses, while TCEP is now more often used in polyester resins and PVC materials, which may have been used for the floor covering. Likewise TBEP is typically associated with the use of floor polish used on wooden floors or PVC floor coverings (WHO, 2000; Marklund et al., 2003).

The profile for both types of dust was similar and dominated by OPFRs (TBEP, TCPP, TDCPP, TPhP) which combined constituted more than 90% of the total AFRs present (Fig. 1). The occurrence of OPFRs at higher levels than other AFRs might be due to their wider range of consumer applications. TPhP is used inter alia as a flame retarding plasticizer in PVC, cellulosic polymers, thermoplastics, synthetic rubber and as an additive in lacquers and paints (Marklund et al., 2003; EFRA, 2010b), while TCPP is used in polyurethane foams, which are used for upholstery and thermal insulation (EFRA, 2010a). As shown in Fig. 1, NBFRs contributed <1% of the total FR burden measured in both floor and mattress dust. FM® 550 was present in 18 floor and 7 mattress dust samples, as identified by the simultaneous detection of TBB, TBPH and TPhP in these samples.

3.3. Correlation between concentrations of AFRs and PBDEs

Correlations between the levels of PBDEs and their corresponding replacement AFRs were investigated for both floor and mattress dust. Levels of TBB, TBPH and TPhP were compared with the levels of major Penta-BDE congeners 47 and 99. Levels of BTBPE were compared with levels of major Octa-BDE congeners 183 and 197, and levels of DBDPE were compared with the levels of BDE 209. Significant correlations (Table S-4) were found for TBPH with BDE 47 and BDE 99, and BTBPE with BDE 197 levels in mattress dust. In a similar vein;, in floor dust levels of TBB exhibited significant association with BDE 47, and those of BTBPE with BDE 183 and BDE 197. Despite restrictions on the use of Penta-BDE, concentrations of PBDEs associated with this formulation remain higher than those of TBB and TBPH (Table 2). This may be due to the relative recent (2003) introduction of FM® 550 in the consumer market and the slower turnover of consumer products in residences, where older products may still emit Penta-BDEs. Another possibility is that NBFRs have been introduced only recently, are emitted slowly and thus may not yet have reached their maximum indoor levels, while indoor Penta-BDE levels would diminish only when the sources have been removed.

Conversely, levels of TPhP exceed those of Penta-BDE congener in our dust samples; this might be due a wider range of applications for TPhP in consumer products (Marklund et al., 2003; EFRA, 2010b). Although TBB, TBPH and TPhP are all components in FM® 550, only TBB and TBPH showed a significant correlation between each other in both floor dust ($p = 0.038$; $r = 0.308$) and mattress dust ($p = 0.036$; $r = 0.462$). This suggests similar sources and behaviour for these two contaminants in indoor microenvironments. By comparison, no significant correlation was observed between TBPH and TPhP concentrations in both floor and mattress dust ($p > 0.05$) indicating that other applications than FM® 550 may exist for TPhP (Anderson et al., 2006; EFRA, 2010b). Alternatively, the fact that TBB showed significant correlation with TPhP ($p = 0.020$; $r = 0.353$) in floor dust but not in mattress dust, might indicate different environmental behaviour pattern of TPhP or simply the use in different applications.

3.4. Exposure assessment via dust ingestion

As indoor dust ingestion has been identified as an important source of exposure to PBDEs (Jones-Otazo et al., 2005); we hypothesised that it would constitute a similarly important source of exposure to AFRs. In order to make a preliminary evaluation of human exposure to AFRs via indoor dust ingestion, we assumed 100% absorption of intake in line with other studies (Jones-Otazo et al., 2005). We assumed average adult and toddler dust ingestion figures of 20 and 50 mg d^{-1}, and high dust ingestion figures for adults and toddlers of 50 and 200 mg d^{-1} respectively (Jones-Otazo et al., 2005). Various plausible low-end, "typical" and high-end dust ingestion exposure scenarios for homes and mattress dust were estimated by combining the data for floor and mattress dust samples and using 5th percentile, median and 95th percentile concentrations in the combined floor and mattress dust data, respectively. We assumed 70 kg body weight (bw) for adults and 12 kg bw for toddlers.

Table 4 shows that typical high end exposure estimates (i.e. using median concentrations and assuming a high dust ingestion rate), for adults ranged between <0.1 and 2.17 ng kg^{-1} bw d^{-1} for different individual OPFRs,<0.01 and 0.01 ng kg^{-1} bw d^{-1} for different individual NBFRs and 0.13 ng kg^{-1} bw d^{-1} for $\sum$HBCDs.

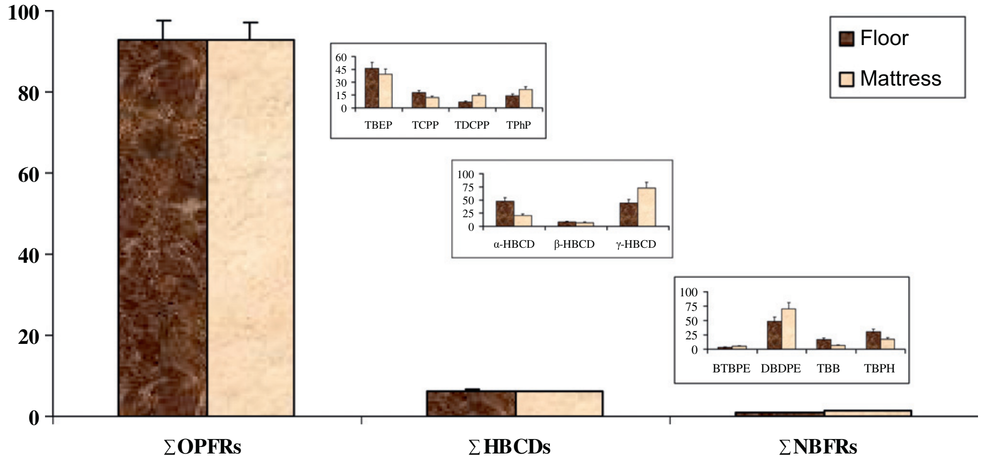

Fig. 1. Profiles of HBCDs, NBFRs and OPFRs in floor and mattress dust.

Table 4

Assessment of human exposure to AFRs via dust ingestion, using mean and high dust intake rates for adults and toddlers. All values are in ng kg^{-1} bw d^{-1}. We have assumed 100% absorption of intake dust (Jones-Otazo et al., 2005). Exposure assessment for OPFRs and NBFRs in toddlers and adults using mean and high dust intake rates, i.e., 20 mg d^{-1} (mean intake) and 50 mg d^{-1} (high intake) for adults, and 50 mg d^{-1} (mean intake) and 200 mg d^{-1} (high intake) for toddlers. For OPFRs, reference doses (RfDs) values (ng kg^{-1} bw d^{-1}) were calculated by dividing chronic NOAEL by a factor of 1000, while for NBFRs and HBCDs RfD values were used from Hardy et al. (2008) and European Chemicals Bureau (2007), respectively.

		Adult						Toddler					
Analytes	RfD values	Mean dust ingestion[a]			High dust ingestion[b]			Mean dust ingestion[a]			High dust ingestion[b]		
	ng kg^{-1} bw d^{-1}	5th%ile	Median	95th%ile	5th%ile	Median	95th%ile	5th%ile	Median	95th%ile	5th%ile	Median	95th%ile
TnBP	24,000	0.01	0.02	0.18	0.01	0.05	0.46	0.08	0.31	2.66	0.32	1.23	10.7
TCEP	22,000	0.01	0.02	0.12	0.01	0.06	0.29	0.08	0.34	1.71	0.33	1.36	6.83
TCPP	80,000	0.01	0.09	0.68	0.05	0.23	1.70	0.20	1.37	9.95	0.79	5.48	39.8
TBEP	15,000	0.18	0.87	2.49	0.46	2.17	6.23	2.66	12.7	36.4	10.6	50.6	145
TPhP	70,000	0.01	0.10	0.40	0.01	0.26	1.00	0.08	1.50	5.82	0.33	5.99	23.3
TDCPP	15,000	0.01	0.05	0.45	0.01	0.13	1.10	0.08	0.73	6.43	0.33	2.93	25.7
TCP	13,000	0.01	0.04	0.12	0.03	0.09	0.31	0.17	0.54	1.82	0.68	2.17	7.27
BTBPE	243000	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.05	0.01	0.01	0.20
TBB	20000	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.05	0.02	0.04	0.20
TBPH	20000	<0.01	<0.01	0.02	<0.01	0.01	0.04	<0.01	0.05	0.26	0.01	0.19	1.02
DBDPE	333333	<0.01	<0.01	0.02	<0.01	0.01	0.06	0.02	0.04	0.34	0.06	0.16	1.35
$\sum$HBCDs	200	0.01	0.05	0.50	0.02	0.13	1.26	0.13	0.78	7.32	0.53	3.13	29.3

[a] Mean dust ingestion rate for adults = 20 mg d^{-1}; for toddlers = 50 mg d^{-1}.

[b] High dust ingestion rate for adults = 50 mg d^{-1}; for toddlers = 200 mg d^{-1}.

Similarly, for toddlers, high end exposure estimates fell between 0.05 and 50.6 ng kg^{-1} bw d^{-1} for OPFRs, 0.01 and 0.19 ng kg^{-1} bw d^{-1} for NBFRs and were 3.13 ng kg^{-1} bw d^{-1} for $\sum$HBCDs. It is important to note that the small number of dust samples analysed, and uncertainties in our assumed dust ingestion rates, means that our exposure estimates are indicative only; and that larger studies and sounder data on dust ingestion rates may lead to very different estimates. Furthermore, the analysis of floor and mattress dust does not provide the complete picture for human exposure. Floor dust is generally a better indicator for the exposure of toddlers, than for adults. The analysis of hand wipe samples or surface dust samples would provide additional insights. Exposure values for both toddlers and adults were several orders of magnitude lower than their corresponding reference dose (RfD) values (Table 4). Reference doses (RfDs) values (ng kg^{-1} bw d^{-1}) for OPFRs were calculated by dividing chronic NOAELs by a safety factor of 1000, while for NBFRs, RfD values were used from Hardy et al. (2008). While this is reassuringly welcome, it is noted that these RfD values are based on relatively old toxicological studies. It is therefore possible that new toxicological data on such compounds may reduce the margin of safety. Moreover, while the acute toxicity of NBFRs is low (Harju et al., 2008), little is known about their chronic toxicity, as well as those of the OPFRs. It is also important to bear in mind that the use of these AFRs are likely to rise substantially given the recent restrictions on other FRs like PBDEs and that this will lead to concomitant increases in human exposure.

4. Concluding remarks

The present study is the first to report contamination by AFRs in the indoor environment of New Zealand and adds to the limited data already reported for other countries. In general, concentrations of AFRs in this study were similar or lower than those reported in Belgian, Japanese, Spanish, UK and US indoor dust, and are consistent with the presently modest use of these chemicals. The lower concentrations of OPFRs in this study than reported elsewhere may suggest lower use of AFRs in New Zealand. However, this is based on a small sample of New Zealand homes which may not be representative of the exposure of the New Zealand population overall. Despite this, this study adds to the growing weight of evidence for environmental contamination by AFRs and provides evidence that both adults and young children are exposed to these chemicals via ingestion of indoor dust. Against this backdrop, there is a clear need for further investigations into the origins of such contamination in indoor environments and into the human health implications arising from exposure to AFRs.

Acknowledgements

A.C. acknowledges a postdoctoral fellowship from the Research Scientific Foundation of Flanders (FWOs). N.A. and N.V.d.E. thank the University of Antwerp (UA) for financially supporting their Ph.D. studies. A.C.D. acknowledges financial support from FWO and a GOA Project at the UA. This study was partly funded by the Massey University Research Fund (10/0073).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.03.100.

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