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

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Novel brominated flame retardants (NBFRs)
Human exposure
Indoor dust
New Zealand

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).

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 (TnP) (<20–7545), tri-(2-chloroethyl)-phosphate (TCEP) (<20–7605), tris-(1-chloro-2-propyl) phosphate (TCP) (20–7615), tri-(2-butoxyethyl)-phosphate (TBP) (50–27325), tri-(2,3-dichloropropyl)-phosphate (TCP) (<50–3760), tri-phenyl-phosphate (TPh) (20–35190), and tri-cresyl-phosphate (TCP) (<50–3760). HBCD concentrations fell in the range <2–4100 ng g⁻¹. BTBPE, DBDPE, TBPH, TBP, and TnBP 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.

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applications (Stapleton et al., 2008; Chemtura, 2006). Another class
of OPFRs has also been documented (Marklund et al., 2003; Stapleton
and Tri-phenyl-phosphate-d15 (TPP-d15) (Sigma) were used as
internal standards. Dichloromethane (DCM), and acetone (Ace),
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%) (H2SO4) and silica gel
were purchased from Merck. Empty polypropylene filtration tubes
(3 mL) SPE cartridges and 500 mg/3 mL Supelclean™ ENV™ Florisil
10 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/v) was prepared by
adding dropwise with continuous stirring 22 mL concentrated sul-
phuric 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 col-
lected by the fieldworkers, using their own vacuum cleaner (Nilfisk
Sprint Plus 1600 W vacuum cleaner) and following a specific pro-
ocol for floor and mattress dust. For floor dust, 1 m2 in case of wall
carpet or rugs and 4 m2 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-
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 \( \alpha \), \( \beta \)- and \( \gamma \)-HBCDs was achieved using a
dual pump Agilent 1100 Series liquid chromatograph

2. Experiment methodology

2.1. Reagent, materials and solutions

Standards of BTBPE, DBOPE, hexachlorocyclopentadienyl-dib-
romyclooctane (HCDBCO), TBB, TBPH and HBCD isomers were
purchased from Wellington Laboratories (Canada), while standards of
tri-ethyl-phosphate (TEP), tri-n-propyl-phosphate (TnPP),
tri-iso-butyl-phosphate (TiBP), tri-n-butyl-phosphate (TnBP), tri-
phenyl-phosphate (TPHP), tri-(2-chloroethyl)-phosphate (TCEP),
tri-cresyl-phosphate (TCP) (mixture of 4 isomers) and tri-(2,3-
dichloropropyl)-phosphate (TDCP) (mixture of 2 isomers) were
purchased from Chiron AS (Trondheim, Norway). Tri-(2-butoxy-
yl)-phosphate (TBP) was purchased from Sigma Aldrich, while tri-
(2-chloroisopropyl)-phosphate (TCP) (mixture of 3 isomers) were
purchased from Pfaltz & Bauer (Waterbury, CT, USA). The purity of
analytical standards for OPFRs was >98%, except for TBP (>94%).
3,3,4,4'-Tetrabromodiphenyl ether (BDE 77) and 2,2,3,3',4,4'-Hexabromodiphenyl ether (BDE 128) (AccucStandard
Inc., USA), 13C12-Decabromodiphenyl ether (13C12-BDE 209)
and 13C12-HBCD (13C12-\( \alpha \)-, \( \beta \)-, \( \gamma \)-HBCD isomers) (Wellington Laboratories),
Tri-amyI-phosphate (TAP) (TCI Europe, Zwijndrecht, Belgium)
and Tri-phenyl-phosphate-d15 (TAPP-d15) (Sigma) were used as
internal standards. Dichloromethane (DCM), and acetone (Ace),

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phuric 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.

Even though such AFRs have never been manufactured nor
imported directly into New Zealand; we have documented previ-
ously 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 pres-
cent 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 Zea-
landers (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

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and dried overnight at 105 °C. Prior to use, glassware was rinsed
with Hex.
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 Is 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 / 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 HCBDCO and TnPBP 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 intra-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 TBBH 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 TBBH 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 TBBH 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. TBBH 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 TBPB, 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 TnBP were sub μg 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 TCP appears lower in New Zealand compared to Belgium, Japan, Spain and Sweden (García et al., 2007; Bergh et al., 2010; Kanazawa et al., 2010). 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 TBP 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 TDCPP and TCPP appear lower in New Zealand compared to Belgium, Japan, Sweden and the US (García et al., 2007; Bergh et al., 2010; Kanazawa et al., 2010). 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 TnPBP (p = 0.003; r = 0.68), TBBH (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 TnBP, TPhP, TCP, BTBPE, and TBB to be statistically indistinguishable (p > 0.05) between floor and mattress dust from the same homes.
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, TnBP, TCP 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 TBBP, DBDPE, TEP, TCEP, TBPB, 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 TBPB is typically associated with the use of floor polish used on wooden floors or PVC floor coverings \((\text{WHO, 2000; Marklund et al., 2003)}\).

The profile for both types of dust was similar and dominated by OPFRs \((\text{TBPB, TCP, TDCPP, TPhP})\) which combined constituted more than 90% of the total AFRs present \((\text{Fig. 1)}\). 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 \((\text{Marklund et al., 2003; EFRA, 2010b)}\), while TCP is used in polyurethane foams, which are used for upholstery and thermal insulation \((\text{EFRA, 2010a)}\). As shown in \text{Fig. 1}, NBFRs contributed <1% of the total FR burden measured in both floor and mattress dust. FM\textsuperscript{e} 550 was present in 18 floor and 7 mattress dust samples, as identified by the simultaneous detection of TBB, TBPB 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, TBPB 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 (\text{Table S-4}) were found for TBPB with BDE 47 and BDE 99, and BTBPE with BDE 197 levels in mattress dust. In a similar vein, in floor dust levels of TBPB 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 (\text{Table 2}). This may be due to the relative recent (2003) introduction of FM\textsuperscript{e} 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 TBPB exceed those of Penta-BDE congeners in our dust samples: this might be due to a wider range of applications for TPhP in consumer products \((\text{Marklund et al., 2003; EFRA, 2010b)}\). Although TBB, TBPB and TPhP are all components in FM\textsuperscript{e} 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\textsuperscript{e} 550 may exist for TPhP \((\text{Anderson et al., 2006; EFRA, 2010b)}\). 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 \((\text{Jones-Otazo et al., 2005)}\); 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 \((\text{Jones-Otazo et al., 2005)}\). We assumed 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 \((\text{Jones-Otazo et al., 2005)}\). 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 \((\text{bw})\) for adults and 12 kg bw for toddlers.

\text{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 0.01 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 \(\sum\text{HBCDs}\).
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. 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.

**Table 4**

<table>
<thead>
<tr>
<th>Analytes</th>
<th>RfD values (\text{ng kg}^{-1} \text{ bw d}^{-1})</th>
<th>Adult Mean dust ingestion(^a)</th>
<th>High dust ingestion(^b)</th>
<th>Toddler Mean dust ingestion(^a)</th>
<th>High dust ingestion(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TnBP</td>
<td>24,000</td>
<td>0.01 0.02 0.18</td>
<td>0.01 0.05 0.46</td>
<td>0.08 0.31 2.66</td>
<td>0.32 1.23 10.7</td>
</tr>
<tr>
<td>TCEP</td>
<td>22,000</td>
<td>0.01 0.02 0.12</td>
<td>0.01 0.06 0.29</td>
<td>0.08 0.34 1.71</td>
<td>0.33 1.36 6.83</td>
</tr>
<tr>
<td>TCP</td>
<td>80,000</td>
<td>0.01 0.08 0.68</td>
<td>0.05 0.23 1.70</td>
<td>0.20 1.37 9.95</td>
<td>0.79 5.48 39.8</td>
</tr>
<tr>
<td>TBBP</td>
<td>15,000</td>
<td>0.18 0.87 2.49</td>
<td>0.46 2.17 6.23</td>
<td>2.66 12.7 36.4</td>
<td>10.6 50.6 145</td>
</tr>
<tr>
<td>TPPh</td>
<td>70,000</td>
<td>0.01 0.10 0.40</td>
<td>0.01 0.26 1.00</td>
<td>0.08 1.50 5.82</td>
<td>0.33 5.99 23.3</td>
</tr>
<tr>
<td>TDCPP</td>
<td>15,000</td>
<td>0.01 0.05 0.45</td>
<td>0.01 0.13 1.10</td>
<td>0.08 0.73 6.43</td>
<td>0.33 2.93 25.7</td>
</tr>
<tr>
<td>TCP</td>
<td>13,000</td>
<td>0.01 0.04 0.12</td>
<td>0.03 0.09 0.31</td>
<td>0.17 0.54 1.82</td>
<td>0.68 2.17 7.27</td>
</tr>
<tr>
<td>BTBPE</td>
<td>241000</td>
<td>&lt;0.01 &lt;0.01 &lt;0.01</td>
<td>&lt;0.01 &lt;0.01 0.01</td>
<td>&lt;0.01 &lt;0.01 0.05</td>
<td>0.01 0.01 0.20</td>
</tr>
<tr>
<td>TBB</td>
<td>20000</td>
<td>&lt;0.01 &lt;0.01 &lt;0.01</td>
<td>&lt;0.01 &lt;0.01 0.01</td>
<td>&lt;0.01 &lt;0.01 0.05</td>
<td>0.01 0.01 0.05</td>
</tr>
<tr>
<td>TBPH</td>
<td>20000</td>
<td>&lt;0.01 &lt;0.01 &lt;0.01</td>
<td>&lt;0.01 &lt;0.01 0.01</td>
<td>&lt;0.01 &lt;0.01 0.05</td>
<td>0.01 0.01 0.20</td>
</tr>
<tr>
<td>DBDPE</td>
<td>333,333</td>
<td>&lt;0.01 &lt;0.01 &lt;0.01</td>
<td>&lt;0.01 &lt;0.01 0.01</td>
<td>&lt;0.01 &lt;0.01 0.05</td>
<td>0.01 0.01 0.20</td>
</tr>
<tr>
<td>(\sum)HBCDs</td>
<td>20000</td>
<td>0.01 0.05 0.50</td>
<td>0.02 0.13 1.26</td>
<td>0.13 0.78 7.32</td>
<td>0.53 3.13 29.3</td>
</tr>
</tbody>
</table>

\(^a\) 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 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.

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**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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