ASSESSMENT OF HUMAN EXPOSURE TO ALTERNATIVE FLAME RETARDANTS IN NEW ZEALAND VIA INDOOR DUST INGESTION

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Introduction

To meet fire regulations, flame retardants (FRs) are commonly used in consumer products (furniture, electronic and electrical equipment, textiles, etc). The most used FRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBP-A)[1]. Studies have shown that these FRs are ubiquitous and persistent in the environment, because they can enter the environment during their production, and because of the use and disposal of products within which they are incorporated[2-4]. Strict restrictions and bans on the use of certain commercial PBDE formulations have resulted in increased demand for alternative flame retardants, such as organophosphate compounds (OPs) and novel brominated flame retardants (NBFRs). Recent studies have already shown that these alternative FRs can accumulate in the environment[5-8]. Moreover, production and use of OPs surpasses that of PBDEs Europe and North America[8]. Recent studies have shown that concentrations of alternative FRs in indoor dust are of the same order of magnitude as or exceed those of PBDEs[8]. In the present study, we investigate the presence of alternative FRs (see acronyms in Table 1) in indoor dust samples from New Zealand and the implications for human exposure.

Materials and Methods

Sampling and sample preparation Indoor dust samples (n = 50) were collected using vacuum cleaner and nylon dust bag from rural and urban homes across New Zealand [9]. Samples were taken from living room floors (n = 34), and from mattresses (n = 16). The sample extraction and purification method is described in detail elsewhere[10]. Briefly, an accurately weighed aliquot (typically 75 mg) was spiked with internal standards (ISs) (BDE 77 (15 ng), BDE 128 (15 ng), $^{13}C_{12}$-BDE 209 (75 ng), TAP (75 ng) and TPP-d_{15} (75 ng)) and extracted by ultrasonication with 2 mL (3×) of *n*-hexane: acetone (3:1, v/v). Prior to clean up, the extract was evaporated to incipient dryness under a gentle nitrogen stream, prior to resolubilisation in 1 mL of *n*-hexane, and fractionation on Florisil cartridges (500 mg/3 mL, Supelco). The 1st fraction was collected with 8 mL *n*-hexane and the 2nd with 10 mL ethyl acetate. All NBFRs, except TBPH, were present in the 1st fraction, while TBPH and OPs were present in the 2nd fraction. The 1st fraction was concentrated to approximately 1 mL under a gentle nitrogen stream before purification on 1 g 44% acid silica cartridges, eluted with 10 mL *n*-hexane: DCM (1:1 *v/v*). The purified 1st fraction and the 2nd fraction were dried separately under a gentle stream of nitrogen before resolubilisation in 100 µL of *iso*-octane, ready for GC-MS analysis.

Instrumentation Details about the instrumental methods employed can be found elsewhere[10]. Briefly, the analysis of OPs was performed with an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electron impact (EI) mode using a HT-8 column (25 m×0.22 mm×0.25 µm). While, the analysis of NBFRs was performed using a 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI) equipped with DB-5 column (15 m × 0.25 mm × 0.10 µm). Quantification and identification ions for OPs, NBFRs and the corresponding IS are shown in Table 1.

QA/QC Levels of selected FRs in laboratory blanks (n = 6) and indoor dust standard reference materials (SRMs) from the National Institute of Standards & Technology (SRM 2584 n = 3 and SRM 2585, n = 3) were analyzed in parallel with the dust samples to evaluate method accuracy and to assess the influence of any possible contamination during sample preparation and analysis. Levels of target analytes were blank-corrected. The observed levels of NBFRs and OPs in SRM 2584 and SRM 2585 were very similar to published values[6,8].

Table 1. Nomenclature, acronyms, identification and quantification ions (bold values), and respective internal standard (IS) of OPs and NBFRs.

Compound	**Acronyms**	Identification - **Quantification Ions**	**Internal Standard (IS)**
Tri-ethyl-phosphate	TEP	**155**	TAP
Tri-*n*-propyl-phosphate	T*n*PP	**183**	TAP
Tri-*iso*-butyl-phosphate	T*i*BP	155, **211**	TAP
Tri-*n*-butyl-phosphate	T*n*BP	155, **211**	TAP
Tris-(2-chloroethyl)-phosphate	TCEP	251, **249**	TAP
Tris-(2-chloroisopropyl-)phosphate	TCPP	279, **277**	TAP
Tri-(2-butoxyethyl)-phosphate	TBEP	199, **299**	TAP
Tris-(2,3-dichloropropyl)-phosphate	TDCPP	379, **381**	TPP-dl5
Tri-phenyl-phosphate	TPP	325, **326**	TPP-dl5
Tri-tolyl-phosphate	TTP	367, **368**	TPP- dl5
Tri-amyl-phosphate (IS)	TAP	169, **239**	
Tri-phenyl-phosphate-d15 (IS)	TPP-d15	339, **341**	
1,2-*bis*(2,4,6-tribromophenoxy)ethane	BTBPE	81, **79**	BDE 128
Decabromodiphenylethane	DBDPE	81, **79**	^{13}C-BDE 209
Hexachlorocyclopentadienyl-Dibromocyclooctane	HCDBCO	79, **310**	BDE 77
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	TBB	359, **357**	BDE 77
bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	TBPH	515, **384**	BDE 128
3,3',4,4'-Tetrabromodiphenyl ether (IS)	BDE 77	81, **79**	
2,2',3,3',4,4'-Hexabromodiphenyl ether (IS)	BDE 128	81, **79**	
^{13}C - Decabromodiphenyl ether (IS)	^{13}C-BDE 209	497, **495**	

Results and Discussion:

Concentrations of FRs Five NBFRs and ten OPs were quantified in the house dust from New Zealand. The median, 5th and 95th percentile (%ile) concentrations of NBFRs and OPs are presented in Table 2. In general, concentrations of target alternative FRs in this study were similar or lower than those reported elsewhere[6,8,11-14]. The lower concentrations of OPs in this study may suggest a lower use of alternative FRs in New Zealand. However, this based on a very small and selected sample of New Zealand homes which is likely not representative of the exposure of the New Zealand population overall.

Correlation between floor and mattress dust All OPs and NBFRs except HCDBCO and TnPP were detected in the dust samples with different detection frequencies. Concentrations of T*i*BP concentrations were unduly influenced by irreproducible blank values and are therefore not reported. A Ryan-Joiner test combined with visual inspection revealed the concentration data to be log-normally distributed. Hence further statistical analysis was conducted on log-transformed data. Two-sample T-test was applied to study correlation between (n = 16) mattress and their respective (n = 16) floor dust samples. For the 16 homes where both floor and mattress dust samples were available, concentrations of TEP, T*n*BP, TPhP, TCP,TCPP, BTBPE, TBB and DBDPE showed a significant positive correlation ($p<0.05$). This suggests common sources for these compounds in these two categories of sample. Similar correlations were not observed for TCEP, TBEP, TDCPP and TBPH ($p>0.05$), implying different sources for these FRs in floor and mattress dust.

Exposure assessment via dust ingestion In order to make a preliminary evaluation of the exposure via dust ingestion to alternative FRs, we assumed 100% absorption of intake similar to other studies[15]. 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[15]. Low-end, "typical" and high-end dust ingestion exposure scenarios for floor and mattress dust were estimated by combining the data and using 5th %ile, median and 95th %ile concentrations in the dust samples. Exposure assessment was calculated in ng kg^{-1} bw d^{-1}, assuming 70 kg bw for adults and 20 kg bw for toddlers. Different exposure scenarios using median, 5th percentile and 95th percentile concentrations were calculated using mean and high dust ingestion figures (Table 2).

Table 2. Assessment of human exposure to alternative FRs 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-Otzao et al., 2005).

Analytes	Concentrations (ng g^{-1} dust) [a]			Adult Mean dust ingestion [b]			Adult High dust ingestion [c]			Toddler Mean dust ingestion [b]			Toddler High dust ingestion [c]		
	Median	5th %ile	95th %ile	Median	5th %ile	95th %ile	Median	5th %ile	95th %ile	Median	5th %ile	95th %ile	Median	5th %ile	95th %ile
TEP	5.0	5.0	13	<0.01	<0.001	0.01	<0.01	<0.01	0.01	0.01	0.01	0.05	0.05	0.05	0.13
TnBP	75	5.0	650	0.02	<0.001	0.19	0.05	<0.01	0.47	0.19	0.01	1.63	0.75	0.05	6.50
TCEP	85	22	410	0.02	0.01	0.12	0.06	0.02	0.29	0.21	0.05	1.03	0.85	0.22	4.10
TCPP	350	120	2420	0.10	0.04	0.69	0.25	0.09	1.73	0.87	0.31	6.06	3.50	1.20	24.20
TBEP	3040	680	7770	0.87	0.19	2.22	2.17	0.49	5.55	7.59	1.71	19.43	30.40	6.80	77.70
TPP	520	20	1560	0.15	0.01	0.45	0.37	0.01	1.11	1.29	0.05	3.90	5.20	0.20	15.6
TDCPP	150	10	770	0.04	<0.001	0.22	0.11	0.01	0.55	0.37	0.03	1.92	1.50	0.10	7.70
TCP	120	25	380	0.03	0.01	0.11	0.09	0.02	0.27	0.30	0.06	0.95	1.20	0.25	3.80
BTBPE	1.0	1.0	12.5	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.00	<0.01	0.03	0.01	0.01	0.12
TBB	2.0	1.0	13	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	0.03	0.02	0.01	0.13
TBPH	12	1.0	55	<0.01	<0.01	0.02	0.01	<0.01	0.04	0.03	<0.01	0.14	0.12	0.01	0.55
DBDPE	11	2.5	65	<0.01	<0.01	0.02	0.01	<0.01	0.05	0.03	0.01	0.16	0.11	0.25	0.65

[a] Concentrations (ng g^{-1} dust)calculated using Excel 2003

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

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

Typical high end exposure, using median concentrations, estimates for adults ranged between <0.1 – 2.2 ng kg^{-1} bw d^{-1} for OPs and <0.01 - 0.01 ng kg^{-1} bw d^{-1} for NBFRs. By comparison, for toddlers, typical high end exposure fell between 0.05 – 30.4 ng kg^{-1} bw d^{-1} for OPs and 0.01 - 0.12 ng kg^{-1} bw d^{-1} for NBFRs. Exposure values for both toddlers and adults were several orders of magnitude lower than their corresponding reference dose (RfD) values. The used RfD values for NBFRs are: BTBPE = 243,000 ng kg^{-1} bw d^{-1}, DBDPE = 333,333 ng kg^{-1} bw d^{-1}, TBB = 20,000 ng kg^{-1} bw d^{-1}, TBPH = 20,000 ng kg^{-1} bw d^{-1} described elsewhere[16]. For OPs, RfD values were calculated using reported chronic NOAEL or NOEL values divided by a safety factor of 1,000 as described by the USEPA. For OPs, RfD values[8] are: TnBP = 24000 ng kg^{-1} bw d^{-1}, TCEP = 22000 ng kg^{-1} bw d^{-1}, TCPP = 80000 ng kg^{-1} bw d^{-1}, TBEP = 15000 ng kg^{-1} bw d^{-1}, TPP = 70000 ng kg^{-1} bw d^{-1}, TDCPP = 15000 ng kg^{-1} bw d^{-1} and TCP = 13000 ng kg^{-1} bw d^{-1}. These RfD values have been established on the basis of relatively old toxicological studies with a lack of robust or recent data and therefore the health impacts of these exposures cannot be fully evaluated at the moment. Despite the fact that this preliminary assessment for human exposure to alternative FRs in New Zealand is significantly below the RfD values, one should keep in mind that the use of these alternative FRs is likely to rise substantially given the recent restrictions on other FRs like PBDEs. Also, the knowledge of the human toxicology of these compounds is currently incomplete. Hence, the presence of alternative FRs in our microenvironments demands thorough toxicological studies, which may lead to a revision of these RfD values.

In summary, the observed levels of alternative FRs in this study are consistent with their presently modest use. However, caution is needed, given the likely future increase in use of these FRs, and the currently unknown contribution to human exposure received via inhalation and diet. Finally, while this study demonstrates the presence of alternative FRs in indoor environments, studies are required to elucidate their specific sources in individual microenvironments.

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