

LEVELS OF ORGANOHALOGENATED FLAME RETARDANTS IN FLOOR AND AIR CONDITIONER FILTER DUST FROM JEDDAH, KINGDOM OF SAUDI ARABIA

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Introduction

Organohalogenated flame retardants (HFRs) constitute a diverse group of compounds used to prevent and minimize fire hazards¹. They have a wide range of applications in consumer products and building materials, including thermal insulation boards, printed circuit boards, housing for electric and electronic equipment, furniture foams and fabrics etc. to delay combustion and meet fire safety standards¹. Many HFRs are additive rather than chemically bonded to the product matrix and thus migrate into the environment leading to exposure of humans through various pathways such as ingestion, inhalation, and dermal contact with household dust, among other sources²⁻⁵. This exposure is of concern due to the potential health risks, such as endocrine disruption, neurodevelopmental and behavioral outcomes, hepatic abnormalities and possibly cancer⁶⁻¹⁰. Such evidences have contributed to list polybrominated biphenyl ethers (PBDEs) formulations (Penta-, Octa-BDE) under the Stockholm Convention list of persistent organic pollutants (POPs), while use of Deca-BDE is subjected to restrictions^{11,12}. In literature, house dust is referred as an “indoor pollution archive” and occurrence of different classes of HFRs in indoor dust has been well documented in literature¹³. Indoor dust has been associated with human exposure to various organic contaminants and risk posed to human health by indoor contaminants particularly to the most vulnerable groups, such as toddlers and pregnant women is of great concern^{7,14}. People spend more time inside the home/office, while indoor they are continuously exposed to these chemicals and indoor dust samples could be a source for these chemicals. No information is available about the occurrence and dynamics of HFRs in the indoor environment of Kingdom of Saudi Arabia (KSA). Therefore, reporting these chemicals in indoor media from the country is a highly necessary.

The aims of the present study were: (i) to evaluate the levels and profiles of HFRs in indoor dust from two microenvironments of Jeddah, (ii) to establish potential sources of targeted organic contaminants in the studied areas, (iii) to evaluate the evidence that alternative flame retardants are replacing PBDEs, (iv) to estimate exposure to these chemicals for toddlers and adults *via* dust ingestion.

The following HFRs were analyzed in the study:

(i) PBDEs: (47, 99, 100, 153, 154, 183, 209).

(ii) Emerging new brominated/chlorinated flame retardants: (i) 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), (ii) 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), (iii) Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), (iv) Decabromodiphenylethane (DBDPE), (v) Dechlorane plus (DP).

(iii) Organophosphate flame retardants (chlorinated) (PFRs): (i) Tris-(2-chloroethyl)-phosphate (TCEP), (ii) Tris-(1,3-dichloro-isopropyl)-phosphate (TDCPP), (iii) Tris-(1-chloro-2-propyl)-phosphate (TCPP).

Material and methods

Sampling and sample preparation. Paired indoor dust samples (floor N=15; AC filter N=15) were collected from Jeddah, KSA. For floor dust, vacuum cleaner bags were collected from volunteer houses. While, AC filters were cleaned with brush to collect dust samples. To avoid cross contamination brush from the respective houses were used after pre-cleaning. Each sample was sieved through 250 μ m mesh to achieve homogenized sample. Sample extraction and purification method is described in detail elsewhere¹⁵. Briefly, an accurately weighed aliquot of dust (typically 50 mg) was spiked with internal standards and extracted by ultrasonication and vortexed with hexane: acetone (3:1, v/v). Florisil was used for fractionation; a 1st fraction was eluted with 8 mL hexane and a 2nd fraction with 10 mL ethyl acetate. PBDEs, DP and new brominated flame retardants (NBFRs), except TBPH, were present in the 1st fraction, while PFRs and TBPH were present in the 2nd fraction. First fraction was further cleaned on acid

silica and analytes were eluted with 10 mL hexane: dichloromethane (1:1, v/v). After evaporation to dryness, each fraction was resolubilized in 100 μ L of iso-octane prior to analysis.

Instrumentation. Details about the instrumental analysis are given elsewhere¹⁵. Briefly, the analysis of NBFRs and PBDEs was performed by 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI). A DB-5 column (15 m \times 0.25 mm \times 0.10 μ m) was used for separation and the MS was employed in selected ion monitoring (SIM) mode. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 $^{\circ}$ C, respectively. The analysis of PFRs was performed by GC-MS in electron ionization (EI) mode. A HT-8 column (25 m \times 0.22 mm \times 0.25 μ m) was used and the MS was operated in SIM mode with two characteristic ions acquired for each compound. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 $^{\circ}$ C, respectively. The values of selected HFRs in SRM 2585 and 2584 were in agreement (RSD < 15%) with published values¹⁶.

Results and discussion

HFRs in dust samples: PFRs were the major HFRs in dust with following order of significance TDCPP>TCPP>TCEP in both floor and AC filter dust. For both types of dust, levels of NBFRs were in similar range to the levels of PBDEs. BDE 209 and Penta-BDE congeners (-47 and -99) were the principal contributor in PBDE profile. DBDPE was the dominant NBFR, while TBB and TBPH, principal component of FM-550 (a replacement for Penta-BDE), were the other major NBFRs. BTBPE and DP were the minor contributors in the HFRs profile in both floor and AC filter dust.

The higher levels of PFRs in floor dust compared to PBDEs and NBFRs are similar to those reported in the literature¹⁶⁻²⁰. This shows wider application of PFRs in polymers and higher use as a replacement to the regulated PBDEs. In comparison to literature data, the median concentrations of PBDEs, TBB, TBPH and BTBPE in this study were comparable to the levels reported in house dust from Australia²¹, Belgium, Kuwait¹⁶ and Romania¹⁷, but were lower than those from USA²², UK²² and Canada²³. DBDPE median levels were lesser than Chinese²⁴ household dust though higher than those of other countries. Based on a comparison of their concentrations in dust, the usage of TCEP and TCPP appears low in KSA compared to Belgium¹⁹, Japan¹⁸, Spain²⁵, and Sweden²⁶, but is in line with Kuwait¹⁶. TDCPP was detected at markedly lower concentrations than in Belgian¹⁹, Japanese¹⁸, Swedish²⁶ and USA²⁰ dust samples, however was comparable to Kuwaiti house dust¹⁶. The profile of HFRs in KSA and Kuwait house dust was quite similar for TCEP, BDE 209, and DBDPE were the major contributor from the respective group (Figure 1). This shows the connection between the extent of indoor contamination and socio-economic status.

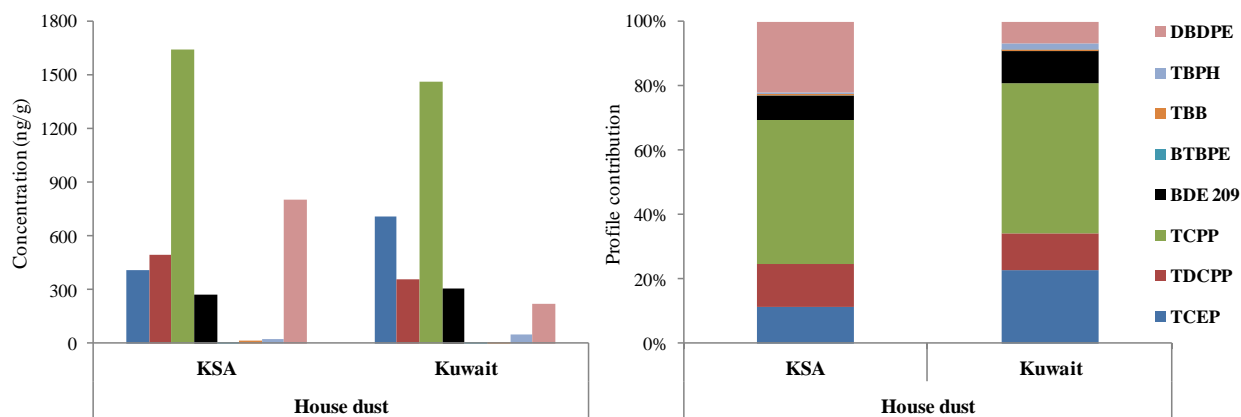


Figure 1 Comparison of selected HFRs levels and profile between KSA and Kuwait house dust.

To the best of our knowledge, few studies have reported occurrence of PBDEs in AC filter dust, but this is a very first study reporting NBFRs and PFRs in AC filter dust, which makes these findings very important. Computed Spearman rank-order correlation coefficient between floor and AC filter dust showed significantly positive

correlation for TCEP, TBB, DP and PBDE congeners ($p < 0.05$), suggesting common sources of emission for these two types of dust. No such correlation ($p > 0.05$) was observed for other analytes, suggesting more diverse emission sources or different environmental fates for these compounds in studied microenvironments.

The differences in the levels of HFRs in indoor dust from various countries could be attributed to the country's fire safety regulations, which are generally more stringent in North America and UK. Another hypothesis might be the different timing for the replacement of PBDEs in various countries. Neither the use of HFRs in consumer products is regulated, nor they are produced in KSA. Most of the furniture and electronics stuff in KSA is imported and the occurrence of HFRs is assumed to arise *via* the presence in imported furniture and electronic stuff.

Table 1 Descriptive data (mean, standard deviation, median, and range) of studied HFRs analytes measured in floor and AC filter dust samples.

Analyte	LOQs	House floor dust			AC filter dust		
		Detection (%)	Mean±SD	Median (Range)	Detection (%)	Mean±SD	Median (Range)
TCEP	20	100	560±515	410 (125-1650)	100	2650±4500	820 (120-16500)
TDCPP	20	100	1770±2500	500 (150-8700)	100	14300±18000	7800 (1000-61234)
TCPP	20	100	1600±1150	1650 (200-3700)	100	3300±3600	2000 (200-11500)
BDE 47	2	100	125±370	27 (3-1450)	100	1150±2450	50 (4-9050)
BDE 100	2	87	35±100	5 (LOQ-450)	94	420±850	10 (LOQ-2800)
BDE 99	2	100	220±670	35 (5-2650)	100	2000±3600	45 (5-10550)
BDE 154	3	53	20±50	3 (LOQ-210)	44	150±250	1.5 (LOQ-850)
BDE 153	3	60	25±80	4 (LOQ-310)	56	200±425	4 (LOQ-1600)
BDE 183	4	73	4±2	4 (LOQ-8)	38	7±9	2 (LOQ-35)
BDE 209	10	100	450±440	275 (25-1670)	100	250±200	170 (60-800)
ΣPBDEs		100	880±1300	350 (50-5300)	100	4100±7300	350 (100-23500)
DP	1	100	5±5	3 (1-16)	100	7±10	3 (2-38)
BTBPE	2	93	6±4.5	5 (LOQ-18)	75	6±8	4 (LOQ-33)
TBB	2	93	45±70	16 (LOQ-250)	100	450±1350	25 (10-5500)
TBPH	2	100	50±80	25 (LOQ-330)	100	13±13	10 (2-55)
DBDPE	10	100	850±450	800 (110-1650)	100	670±300	650 (250-1200)

Exposure assessment via dust ingestion

In order to make a preliminary evaluation of the exposure *via* dust ingestion to HFRs, we combined the data of floor and AC filter dust. In absence of bioavailability data for selected HFRs, for consistency we assumed 100% absorption of contaminants from ingested dust and average dust intake of 20 and 50 mg/day, and high dust ingestion figures of 50 and 200 mg/day for adults and toddlers, respectively. We assumed an average body weight (bw) of 70 kg for adults and 12 kg for toddlers.

Different exposure scenarios were calculated using 5th percentile (low end exposure), median, and 95th percentile (high end exposure) concentrations. For both groups, the estimated exposure levels (Table 2) for most HFRs were several orders of magnitude lower than their reference dose (RfD). However, high end exposures of Penta-BDE congeners for toddlers was even higher than the corresponding RfD. These findings are in agreement with the recent studies where ingestion of indoor dust is suggested as significant exposure pathway to HFRs^{7,14,27}. Together with other exposure pathways i.e., indoor and outdoor air or food is a matter of concern for the chronic exposure to these HFRs. However, due to the small number of samples analyzed in the study, it should be stressed that the range of exposure estimates is only an indication of the likely range for toddlers and adults within the population. The substantial inter-individual variation in exposure depends on the time spent in indoor and the quantity of the dust ingested.

Table 2 Assessment of human exposure to HFRs *via* dust ingestion, all values are provided in ng/kg bw/day.

Analyte	RfD values	Toddlers						Adults					
		Median		Low end exposure		High end exposure		Median		Low end exposure		High end exposure	
		High	Mean	High	Mean	High	Mean	High	Mean	High	Mean	High	Mean
TCEP	22,000	10	2	2.5	0.5	135	35	0.3	0.1	0.1	0	6	2.5
TDCPP	15,000	50	12	4.5	1.5	670	170	2	1	0.2	0.1	30	12
TCPP	80,000	30	7	3.5	1	155	40	1.5	0.5	0.1	0.1	7	3
BDE 47	100	0.6	0.1	0.1	0	55	15	0	0	0	0	2.5	1
BDE 100	100	0.1	0	0	0	25	6	0	0	0	0	1.5	0.5
BDE 99	100	0.6	0.2	0.1	0	125	30	0	0	0	0	5.5	2.5
BDE 209	7,000	4	1	1.1	0.5	15	4	0.2	0.1	0	0	0.6	0.2
DP		0.1	0	0	0	0.5	0.1	0	0	0	0	0	0
BTBPE	243,000	0.1	0	0	0	0.5	0.1	0	0	0	0	0	0
TBB	20,000	0.5	0.1	0.1	0	8	2	0	0	0	0	0.5	0.1
TBPH	20,000	0.2	0.1	0	0	1	0.5	0	0	0	0	0	0
DBDPE	333,333	12	3	4	1	22	6	0.5	0.2	0.2	0.1	1	0.5

Acknowledgements

Nadeem Ali acknowledges Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, KSA for financial support. We are grateful to all of the volunteers who participated in the study.

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