PROBABILISTIC HEALTH RISK ASSESSMENT FOR INGESTION OF POLYBROMINATED DIPHENYL ETHERS BOUND TO HOUSE DUST

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated hydrocarbons, that have been used as flame retardant chemicals for a long time. They may be released to the environment via volatilization, abrasion and dissolution from PBDE-containing products, recycling of electronic wastes, burning of residential waste dump, and steel production processes [1,2]. Production of certain PBDEs has been banned in Europe and the US [3,4]. The commercial penta [5] and octa-BDE mixtures [6] were added to Stockholm Convention list of persistent organic pollutants in 2008, commercial deca-BDE was added in 2016 [7]. Because of their persistence and lipophilicity [8], that result in bioaccumulation in the environment and the food chain, exposure to PBDEs are of utmost importance. Animal and *in vitro* studies show thyroid disorders, reproductive health effects, and neurobehavioral and developmental anomalies are some of the associated health effects [9]. PBDEs are classified as semi-volatile organic compounds (SVOCs), which may be more persistent indoors because of their partitioning to particle phase and lower degradation rates compared to those in ambient air [10]. PBDEs are found to be mainly associated with indoor particles and pose considerable exposure and health risks to humans. In this context, dust-bound PBDE concentrations in homes, schools and Cafe/Bar/Restaurants (C/B/R) were measured, and used to estimate population health risk levels in Izmir, Turkey.

Materials and methods

House dust and samples were collected from schools, homes, and C/B/R in Izmir, Turkey, the third populous city in Turkey with about 4 million inhabitants. Dust samples were sieved with 500 μm sieve. About 0.5 g of the samples were transferred to the extraction vials (40 mL, amber glass) and spiked with surrogate compounds. 25 ng of BDE-77 and BDE-181 were spiked for analytical recovery of extraction, clean-up, and analysis processes. Extraction was conducted with 20 mL of acetone:hexane (Ace:Hxn; 1:1, v:v) mixture using ultrasonic bath (Elmasonic, 37 kHz) after overnight soaking. After waiting for the settling of suspended particles, upper solvent phase was taken into clean amber vials. Ace:Hxn mixture (20 mL) was added to the extraction vials and extraction was repeated to gain residual target analytes. After the settling period of secondary extraction, solvent phase was combined with first solvent phase, and concentrated to ≈2 mL using rotary evaporator for clean-up stage.

Si based solid phase extraction (SPE) cartridges (Agilent Bond Elute Mega BE, Si 5g) were used for clean-up. SPE cartridges were preconditioned and cleaned with 20 mL acetone. Concentrated samples were added to the SPE cartridges and eluted (Phase 1) dropwise with 30 mL hexane and acetone (30 mL, Phase 2). Phase 1 and 2 were combined and concentrated to 2-3 mL with rotary evaporator. Solvent was exchanged to isooctane with triplicate addition of 3 mL isooctane. Finally, samples were concentrated to 1 mL and 25 ng of 1,2,3,4,5,6-Hexachlorocyclohexane (epsilon-BHC) was spiked as a volumetric standard. Thermo Scientific gas chromatography-mass spectroscopy (GC-MS, Trace-ISQ) was used in negative chemical ionization mode for PBDE analysis. Oven program was started with the 1 min hold time at 90 ˚C, increased to 315 ˚C with the rate of 20 ˚C/min, and hold temperature for 6 min. While ions 79 and 81 were used for quantification of BDE-28, -47, -77, -99, -100, -153, -154, -181; 486.5 and 488.5 were used for the quantification of BDE-209. Internal standard (epsilon-BHC) was quantified using ions 253 and 257. Calibration curves of all targeted compounds were determined to be linear (R^2>99%).

A probabilistic exposure assessment for PBDEs was conducted for accidental ingestion of settled dust. Average daily dose (ADD) was estimated considering chronic-toxic health effects using Equation 1. All measured house-dust PBDE concentrations were fitted a probability distribution using Crystal Ball software (n=10000 trial, Oracle Inc.). Probability distribution of accidental ingestion rate was taken from the Exposure Factors Handbook[11]. Exposure frequency was assumed to be 350 day/yr. Lifetime was assumed to be 75 years. Chronic-toxic health risk (CTR) was estimated based on Reference Dose (RfD, IRIS database [12]) of individual PBDEs by using Equation 2. A combined probability distribution of females and males body weights was used for simulation of ADD[13]. Exposure duration was assumed to be equal to averaging time for CTR and replaced with 30 years for carcinogenic risk (CR).

$$ADD=(C\times IR\times EF\times ED\times CF)/(BW\times AT) \quad (1)$$

$$HQ=(ADD)/(RfD) \quad (2)$$

where, ADD: average daily dose (mg/kg-day), C: concentration (ng/g), IR: ingestion rate (mg/day); EF: exposure frequency (day/yr); ED: exposure duration (yr); CF: conversion factor (1×10^{-9}); BW: body weight (kg); AT: averaging time (yr); RfD: reference dose (mg/kg-day); HQ: hazard quotient (unitless).

Lifetime ADD (LADD) was also estimated for BDE-209 to determine the associated carcinogenic risk levels (CR) [14]. Exposure duration was assumed to be 30 years to obtain LADD (Eq. 3) [13]. Slope factor was obtained from the IRIS database [12] to estimate CR (Eq. 4).

$$LADD=(C\times IR\times EF\times ED\times CF)/(BW\times LT) \quad (3)$$

$$CR=LADD\times SF \quad (4)$$

Results and discussion

House-dust PBDE concentrations in Izmir are shown in Figure 1. The median concentrations of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209 were determined to be 0.41, 1.54, 0.19, 3.91, 0.44, 15.0, 0.77, and 1346 ng/g, respectively. The median Σ_8BDE concentration was 1368 ng/g. BDE-209 was determined to be the dominant congener in the house dust. The median Σ_8BDE concentrations was 1704 ng/g in schools, 1526 ng/g in homes, and 806 ng/g in C/B/R. The highest PBDE concentrations were determined to be in schools, followed by homes and C/B/R. Home median Σ_8BDE concentration in this study (1526 ng/g) is similar to that reported by Pasecnaja et al. (1567 ng/g) [15]. Coincidentally, BDE-209 concentrations in both of these studies are equal at 1510 ng/g. While the median value for schools (classrooms) of Izmir (1704 ng/g) is higher than the levels reported by Young et al. [16] (248 ng/g) and by Adeyi et al. [17] (31.1 ng/g), it is lower than that of Irish nursery and nursing schools (4355 ng/g) and schools (8110 ng/g) [18]. Since factors such as source density, building age and type, distance to industrial areas are very variable for indoor environments of different studies, the concentration and congener profile of indoor POPs (especially fire retardants) vary more compared to the atmospheric levels.

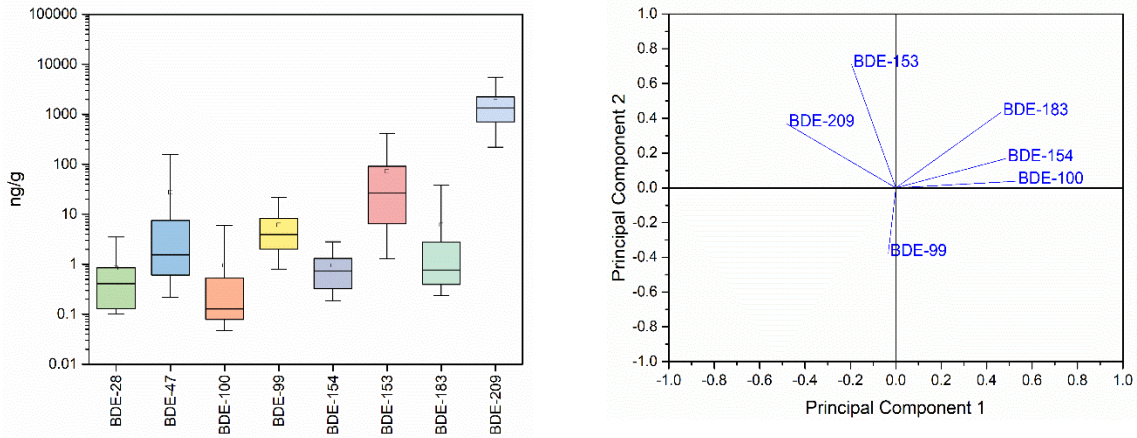

Figure 1. (a) House-dust PBDE concentrations and (b) the loading plot of their PCA analysis.

In this study, the concentrations of BDE congeners (except for BDE-209) at home and school were determined to be 16 and 25 ng/g, respectively. In a study conducted in male and female dormitories[19], the concentrations of BDE congeners (except BDE-209) were reported as 28.2 and 9.41 ng/g, close to those measured in this study. Our results, in agreement with the literature, show that higher PBDE levels occur in schools compared to houses and C/B/R. Children's exposure to contamination bound to house dust is of importance because they spend more time on the ground along with hand-to-mouth activity with decreasing age compared to the adults. For these reasons, it is critical to develop strategies to reduce indoor PBDE concentrations in schools. PBDEs tend to be on organic surfaces, especially those with high octanol-air partition coefficients. In turn, the accumulation of PBDEs on house dust with adsorption increases with increasing particle age indoors [20]. Consequently, the prolongation of periods in between cleaning events, and the presence flooring, such as carpets, that allow dust accumulation would result in relatively higher indoor PBDE levels. Principle component analysis (PCA) loading plot (Figure 1b) shows the segregation of PBDE congeners, grouped as (i) BDE-99, (ii) BDE-153 and BDE-209, and (iii) BDE-100, BDE-154, and BDE-183, implying that dust-bound PBDEs were originated from three different sources.

Table 1. House-dust PBDE concentrations (ng/g)

Sampling Site	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣBDE	Ref
School*	0,55	91.2	0.63	11.4	1.03	126	13.3	2149	2393	
School **	0.38	131	0.48	11.4	1.02	53.0	6.82	1679	1704	
Home *	1.01	15.7	0.81	3.39	0.91	20.1	4.85	1998	2039	This study
Home **	0.37	1.36	0.16	3.15	0.44	11.0	0.78	1510	1526	
C/B/R*	0.41	1.68	1.05	2.83	0.27	14.4	0.54	1013	1032	
C/B/R**	0.41	0.81	0.11	2.05	0.27	2.25	0.34	794	806	
Home **	2.13	13.8	4.48	16.6	3.92	4.6	11.0	1510	1567	[15]
School **	3.98	60.9	27.2	12.7	9.18	18.3	19.5	95.8	248	[16]
Office**	8.10	48.8	21	129	5.31	19.5	51.6	381	628	[16]
Male Dormitory**	1.94	3.90	4.92	4.99	-	11.1	1.39	-	28.2	[19]
Female Dormitory**	0.32	1.30	0.54	-	-	3.70	3.55	-	9.41	[19]
Printing Center**	1.17	10	8.87	7.95	1.55	305	2.79	-	337	[19]
Nursery and nursing school**	180	340	370	270	240	220	230	<0.04	4355	[21]
Office**	140	140	240	350	40	90	130	110	2095	[21]
School**	2.1	-	7.60	2.82	9.98	2.17	19.4	4.14	31.1	[17]
Home **	0.67	34.1	66.8	40.4	17	3.71	40.2	8.68	227	[17]
Home **	0.24	2.55	0.92	3.07	0.46	0.57	5.91	128	141	[22]
Home**	-	7.6	-	13	-	-	1	13000	13021	[18]
School**	-	5	-	5.10	-	-	<0.83	8100	8110	[18]

*Average

**Median

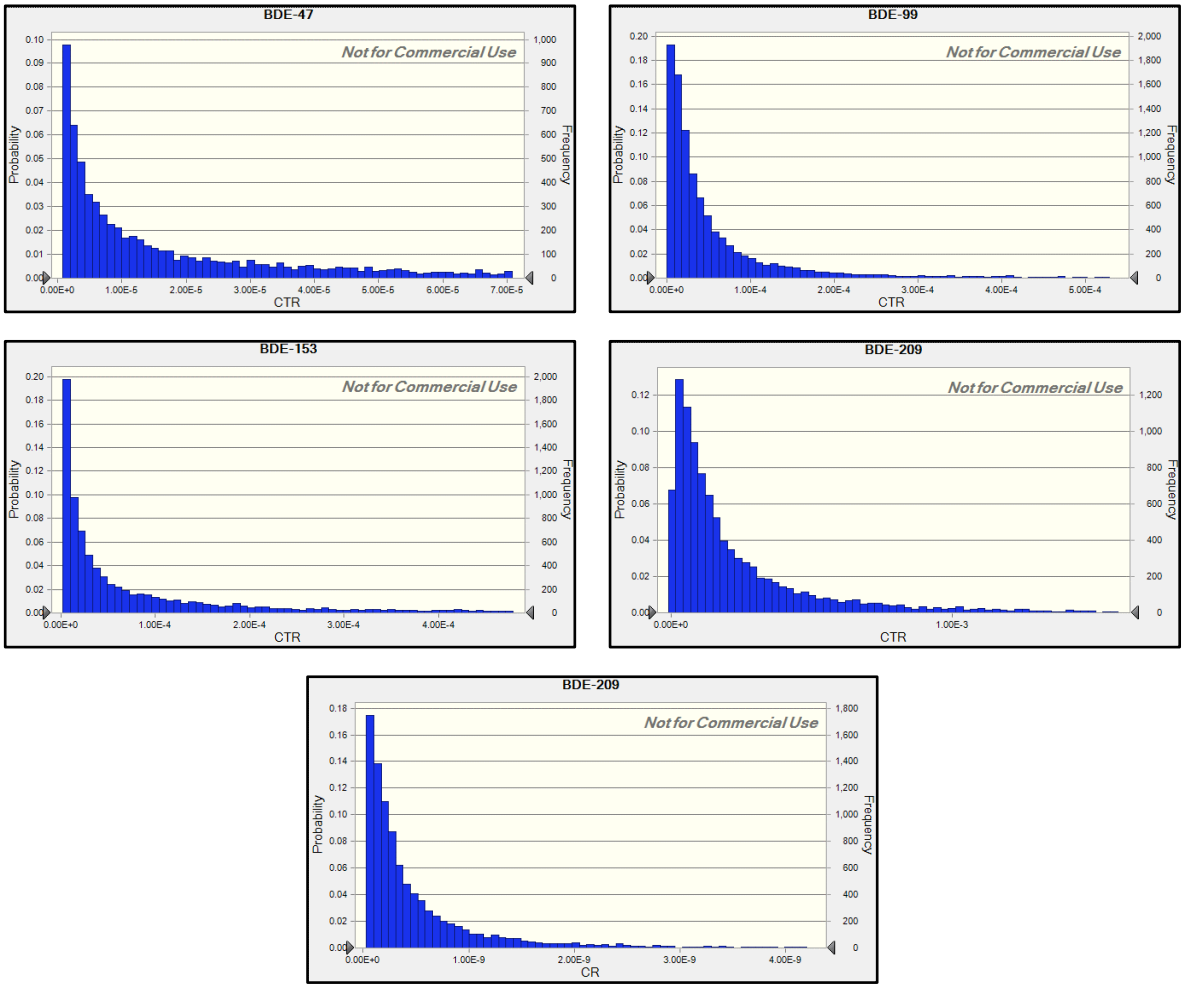

Figure 2. The distributions of CTR and CR levels due to the accidental ingestion of house-dust PBDEs

The median ADD levels of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209 were estimated to be 2.51×10^{-10}, 1.85×10^{-9}, 2.82×10^{-9}, 1.89×10^{-10}, 8.15×10^{-9}, 3.53×10^{-10}, 8.36×10^{-10}, and 9.26×10^{-7} mg/kg-day, respectively, while the median value of the LADD of BDE-209 was estimated to be 3.70×10^{-7} mg/kg-day. ADD of BDE-209 was significantly higher than those of the other congeners due to the higher indoor concentrations. Probability distributions of the CTR levels of accidental ingestion of house-dust BDE-47, BDE-99, BDE-153, and BDE-209 are shown in Figure 2. The median CTR levels of BDE-47, BDE-99, BDE-153, and BDE-209, due to the accidental ingestion of house dust, were estimated to be 1.85×10^{-5}, 2.82×10^{-5}, 4.07×10^{-5}, and 1.32×10^{-4}, respectively, and were lower than the threshold of '1' even at the maximum level. The maximum values of CTR for BDE-47, BDE-99, BDE-153, and BDE-209 were estimated to be 2.22×10^{-1}, 6.21×10^{-3}, 6.22×10^{-1}, and 1.04×10^{-2}, respectively. Estimated distribution of CR for BDE-209 is also shown in Figure 2. The median and maximum value of the CR was 2.59×10^{-10} and $2.04\times10^{-8,}$ respectively, all of which being lower than the acceptable risk level of 10^{-6}. As a conclusion, although limited by the simplifying assumptions made in exposure-risk modeling and a relatively small sample size, CTR and CR associated with accidental ingestion of house dust are not considerable. A further detailed simulation, however, is needed for confirmation.

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