HOUSE DUST PBDE LEVELS AND ESTIMATED GAS PHASE CONCENTRATIONS IN SCHOOLS

Edebali Ö[1], Genisoglu M.[1], Sofuoglu A.[2], Turgut C.[3], Sofuoglu S.C.[1]

[1]Izmir Institute of Technology, Dept. of Environmental Engineering, Izmir, Turkey, 35430, ozgeedebali@iyte.edu.tr; [2]Izmir Institute of Technology, Dept. of Chemical Engineering, Izmir, Turkey, 35430; [3]Aydın Adnan Menderes University, Dept. of Plant Protection, Aydin, Turkey, 09970

Introduction

Polybrominated diphenyl ethers (PBDEs) were extensively used in electronic devices, paints, textiles, automobiles, commercial and household goods until their ban in commercial production. Despite the ban, they are found in both of the gas and particle phases in air due to their resistance to degradation and accumulation on organic surfaces[1]. Globally, PBDEs have been commercially produced with main formulations of Penta-BDE, Octa-BDE, and Deca-BDE. While the commercial Penta-BDE mixtures were widely used in electronic equipment such as fax machines, computers, and televisions, commercial Deca-BDE mixtures have been used in a production of fabrics, building materials, polypropylene drapery. As a result, PBDEs have become one of the most exposed chemical groups in our daily life[2].

Gas phase, particulate matter and house dust PBDE levels, and their partitioning among them in indoor environments, where we spend most of our time, are important in terms of estimating associated health effects. Schools are one of the most important places of PBDE exposure for children[3]. Children having higher inhalation rate/body weight ratio and accidental dust ingestion rate result in higher health risks than that for adults[4]. Σ_8PBDE concentrations were determined to range from 11 to 2163 ng/g with the average level of 600 ng/g in schools in Australia, which were higher than those in homes[3]. A previous study that we conducted in a computer technical service in Izmir, Turkey, house-dust average PBDE concentrations were measured to be 4.69; 17.8; 18.1; 5.79; 71.0; 2.62; 23.5 and 1802 ng/g for BDE-28, -47, -99, -100, -153, -183 and -209, respectively[5]. While there are no reports of indoor PBDE levels for schools in Turkey, median house-dust BDE-28, -47, -99, -100, -153, -154, -183, and -209 levels in homes and offices in Istanbul were determined to be 0.12, 61.8, 34.1, 2.37, 26.2, 0.12, 20.9, and 574 ng/g, respectively[6].

Measurement of the indoor environmental pollution levels in schools is important to ensure healthy learning indoor environments for children, and for public health mitigation efforts. Occurrence of higher doses due to children's higher inhalation rate/body weight ratio and accidental dust ingestion rates compared to adults for the same contamination levels fortifies this importance because of the potential risks associated with legacy organic compounds such as PBDEs. While the legacy-flame-retardant-rich old materials are strong sources that determine the indoor levels, level of urbanization and industrialization, and abundance of organic materials are some of the other affecting variables. In this context, the purpose of this study is to explore the effect of urbanization level on house-dust PBDE levels in schools of Izmir, Turkey.

Materials and methods

Sampling

House dust samples were collected in 21 schools (7 urban, 7 semi-urban, 7 rural) in Izmir, Turkey, in October 2019-February 2020. House dust samples were collected from a random classroom in each school along with outdoor settled dust sample from ground surfaces where children spend time during breaks.

House dust samples were collected by a vacuum cleaner (BEKO, BKS 1295 C) with a HEPA filter (up to 99.97% efficient to 0.3 microns). HEPA filters were pre-cleaned by acetone: hexane (Ace:Hxn; 1:1, v:v) before sampling. Sampling was carried out for 5 minutes to cover classroom floor of roughly 4 m^2. The HEPA filter and dust accumulated in dustbin of the machine were wrapped in pre-burned aluminum foil and placed in zip-lock bags. Outdoor settled dust samples were collected by brushing onto a pre-burned patch of aluminum foil. Samples were stored at -20 ˚C until the extraction.

Sample processing and analysis

Dust samples were sieved with a 500-µm sieve to eliminate the rough particles and undesired pieces such as hair, pebbles, paper and pencil scraps. Approximately 0.5 gram of dust was weighted and transferred to a pre-cleaned 40 mL, amber glass vial for extraction, spiked with 25 ng of BDE-77 and BDE-181 for analytical recovery determination. 20 mL of Ace:Hxn; 1:1, v:v mixture was added into the vial, closed with a Teflon (PTFE)-lined cap, and placed in the dark for preventing photodegradation overnight. After the overnight soaking, samples were

extracted in an ultrasonic bath using 37 kHz ultrasonic frequency for 15 minutes. Following concentration, a single-step clean-up procedure was applied using Si-based solid phase extraction (SPE) cartridges (Agilent Bond Elute Mega BE, Si 5g) and vacuum manifold. Samples were transferred to into GC vials after another concentration and solvent exchange (to isooctane), and analyzed by gas chromatography-mass spectroscopy (GC-MS, Thermo Scientific Trace-ISQ) equipped with a DB-5MS (30 m x 0.25 mm x 0.10 μm) capillary column, in Negative Chemical Ionization (NCI) mode. The targeted compounds were BDE-28, -47, -99, -100, -153, -154, -183, and -209.

Modelling gas phase concentrations

Gas phase PBDE concentrations were estimated using the house-dust concentrations (Eq 1). K_{oa} values of targeted PBDEs were taken from the EPI Suite[7]. f_{om_dust} and ρ_{dust} values were assumed to be 0.2 and 2 g/cm^3, respectively[8]. Coefficient of Determination (R^2) of the simple linear regression between experimental and modeled concentrations using this equation were determined to be 0.86[8-9].

$$Cg = \frac{\rho dust \times Xdust}{fom\_dust \times Koa} \quad \text{Eq 1}$$

where, X_{dust} (pg/g): dust PBDE concentration; Cg (pg/m^3): gas phase PBDE concentration; f_{om_dust}: organic matter fraction of dust; Koa: octanol-air partition coefficient; ρ_{dust} density of dust (g/cm^3).

Results and discussions

The average Σ_8BDE concentrations of pooled house dust samples (n=21) were determined to be 2393 ng/g in İzmir. BDE-209 was the dominant BDE congener with a mass fraction of 89.8 % followed by BDE-153 and BDE-47 with 5.26 and 3.81 %, respectively, while it was <1 % for the remaining congeners. The average BDE-28, -47, -99, -100, -153, -154, -183 and -209 concentrations of indoor dusts were determined 0.55; 91.2; 11.4; 0.63; 126; 1.03; 13.3 and 2149 ng/g, respectively. Descriptive statistics of pooled samples are shown in Table 1. BDE-209 was detected in all house dust samples with a range of 435 – 8079 ng/g and a median concentration of 1679 ng/g, showed a right-skewed distribution. BDE-99, -100, -153, and -183 were the other highly detected (≥10/21) congeners.

Table 1. Descriptive statistics of pooled indoor dust PBDE concentrations (ng/g)

BDEs	n	Mean	SD	CV	Min	Median	Max
BDE-28	6	0.55	0.59	1.06	0.07	0.38	1.60
BDE-47	5	91.2	81.4	0.89	1.60	131	174
BDE-99	14	11.4	6.20	0.55	1.47	11.4	22.4
BDE-100	10	0.63	0.56	0.89	0.12	0.48	1.83
BDE-153	19	126	166	1.32	1.30	52.9	650
BDE-154	8	1.03	0.32	0.31	0.58	1.02	1.50
BDE-183	13	13.3	16.1	1.21	0.10	6.82	41.5
BDE-209	21	2149	1760	0.82	435	1679	8079

Figure 1 and 2 shows variation in the concentrations according to urbanization. BDE-209 dominated the ΣBDE concentrations of rural samples with a fraction of 92.3 %. While the fraction of BDE-153 was 6.80 % in rural samples, other BDE congeners were <1 %. All of the three groups were dominated by the heavier congeners while BDE-47 was on par in the urban schools. Figure 2 also shows that BDE-209, as the dominating congener, was at much higher concentrations compared to the outdoors settled dust.

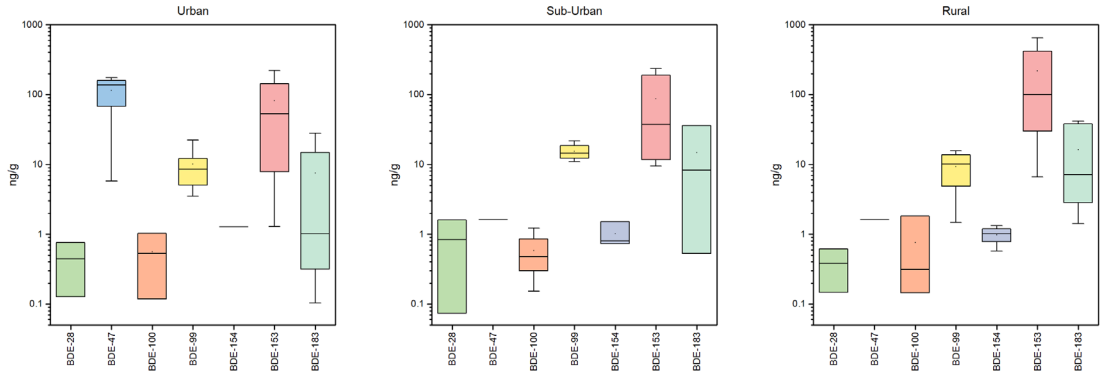

Figure 1. House dust BDE (without BDE-209) concentrations for the three urbanization groups.

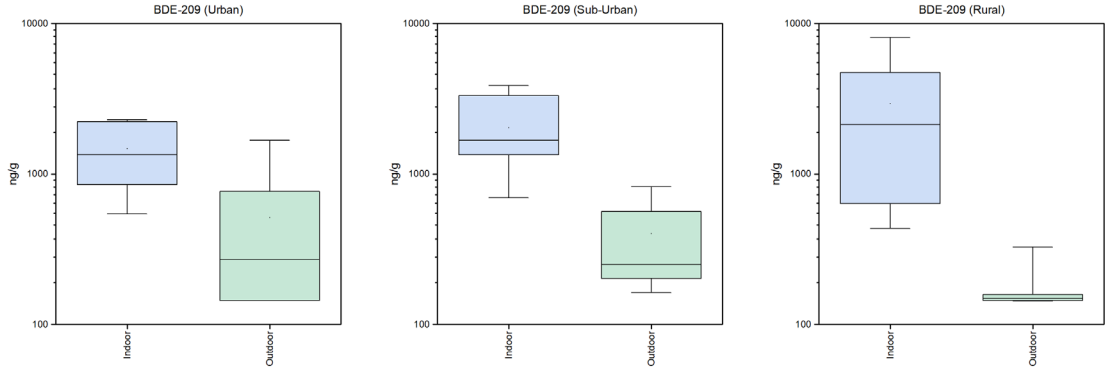

Figure 2. Urbanization level dependent BDE-209 concentrations of indoor and outdoor settled dust samples from schools in Izmir.

The average concentrations of BDE-28, -99, -100, -153, -154, -183 and -209 were determined to be 0.84, 15.5, 0.58, 86.7, 1.01, 14.9, and 2026 ng/g, respectively, in suburban schools. The concentrations of these BDE congeners were between 0.07-1.60, 11.0-21.9, 0.15-1.22, 9.45-237, 0,73-1,50, 0,53-35,8, and 695-3878 ng/g, respectively. The highest indoor settled dust PBDE concentrations were determined to be in two Technical Vocational High Schools (TVHS), which might be due to the abundance of the electric equipment in laboratories. Indoor settled dust BDE-209 concentrations in TVHS A and TVHS B were determined to be 3878 and 3313 ng/g, respectively.

The average indoor-settled dust associated BDE-28, -47, 100, -99, -154, -153, -183, and -209 concentrations in urban schools were determined to be 0.44, 114, 10.0, 0.56, 81.6, 1.28, 7.54, and 1476 ng/g, respectively. BDE-209 was dominated the total targeted BDE concentrations with fraction of 87.3 %. Concentration fractions of BDE-47 and BDE-153 were determined to be 6.71 % and 4.82 %, respectively. The other targeted BDE concentration fractions were <1 % of the BDE concentrations. BDE-47 was detected in 4 of 7 urban schools while its detection frequency was 0 and 1 for suburban and rural schools. The highest BDE-47 was measured in an urban school (174 ng/g).

The reason for BDE-209 being the dominant congener in all samples might be the higher production volume before their ban and its affinity to organic matter. Concentration profile of house-dust PBDE was similar to our previous study in a computer technical service[5]. While the BDE-47 concentrations in the samples taken from the urban area are similar to the levels measured in homes and offices in Istanbul[6], other PBDE congeners were observed at higher levels in Istanbul that those of this study.

BDE-28, -99 and -153 concentrations in house dust samples taken from 10 schools in Lagos city (urban area), Nigeria[2], are at similar levels with those measured in this study. The average BDE-209 concentration in Izmir was determined to be four times higher than that in primary schools in Brisbane, Australia[3]. House dust PBDE concentrations measured in Korea[10] (24 schools in industrial, urban and semi-urban areas) and BDE-28 and -154 concentrations in urban daycare centers and primary schools in England[8] are also at similar levels with this study, whereas BDE-99 and -209 measured in England[11] are approximately 3 times higher than the those in this study.

In conclusion, considerably high indoor BDE-209 levels were determined in school house dust. Organic surfaces acts as a sink for PBDEs due to the high octanol-air partitioning coefficient. So, higher-MW BDE concentrations might be related to their sorption to house dust and length of time between cleaning along with effectiveness of cleaning. Also, age of the buildings and presence of many cable lines and the devices (smart board and projector connections) they are connected to might be the other contributing factors for detection even in rural schools. Cleanliness might be the main factor that determine the difference in house-dust BDE concentrations between urban and suburban/rural schools as urban schools were observed to be more careful about their cleanliness. The other anticipated factor that affect PBDE levels is the industrial activity around the city, as PBDE concentrations increased towards the North. Measurement of relatively high house-dust PBDE concentrations indicate that students, teachers, and staffs might be exposed to significant levels of PBDE.

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